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Author
Song, Yang

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INTERFACIAL FUNCTIONALIZATION AND ENGINEERING OF
NANOPARTICLES

A dissertation submitted in partial satisfaction
of the requirements for the degree of

DOCTOR OF PHILOSOPHY

in

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by

Yang Song

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The Dissertation of Yang Song
is approved:

Professor Shaowei Chen, Chair

Professor Ilan Benjamin

Professor Yat Li

Tyrus Miller
Vice Provost and Dean of Graduate Studies
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INTERFACIAL FUNCTIONALIZATION AND ENGINEERING OF NANOPARTICLES

Yang Song

ABSTRACT

The intense research interest in nanoscience and nanotechnology is largely fueled by the unique properties of nanoscale materials. In this dissertation, the research efforts are focused on surface functionalization and interfacial engineering of functional nanoparticles in the preparation of patchy nanoparticles (e.g., Janus nanoparticles and Neapolitan nanoparticles) such that the nanoparticle structures and properties may be manipulated to an unprecedented level of sophistication.

Experimentally, Janus nanoparticles were prepared by an interfacial engineering method where one hemisphere of the originally hydrophobic nanoparticles was replaced with hydrophilic ligands at the air|liquid or solid|liquid interface. The amphiphilic surface characters of the Janus nanoparticles were verified by contact angle measurements, as compared to those of the bulk-exchange counterparts where the two types of ligands were distributed rather homogeneously on the nanoparticle surface.

In a further study, a mercapto derivative of diacetylene was used as the hydrophilic ligands to prepare Janus nanoparticles by using hydrophobic hexanethiolate-protected gold nanoparticles as the starting materials. Exposure to UV irradiation led to effective covalent cross-linking between the diacetylene moieties of neighboring ligands and hence marked enhancement of the structural integrity of the
Janus nanoparticles, which was attributable to the impeded surface diffusion of the thiol ligands on the nanoparticle surface, as manifested in fluorescence measurements of aged nanoparticles.

More complicated bimetallic AgAu Janus nanoparticles were prepared by interfacial galvanic exchange reactions of a Langmuir-Blodgett monolayer of 1-hexanethiolate-passivated silver nanoparticles on a glass slide with gold(I)-mercaptopropanediol complex in a water/ethanol solution. The resulting nanoparticles exhibited an asymmetrical distribution not only of the organic capping ligands on the nanoparticle surface but also of the metal elements in the nanoparticle cores, in contrast to the bulk-exchange counterparts where these distributions were homogeneous within the nanoparticles, as manifested in contact angle, UV–vis, XPS, and TEM measurements. More interestingly, the electrocatalytic performance of the Janus nanoparticles was markedly better than the bulk-exchange ones, suggesting that the segregated distribution of the polar ligands from the apolar ones might further facilitate charge transfer from Ag to Au in the nanoparticle cores, leading to additional improvement of the adsorption and reduction of oxygen.

This interfacial protocol was then adopted to prepare trimetallic Ag@AuPt Neapolitan nanoparticles by two sequential galvanic exchange reactions of 1-hexanethiolate-capped silver nanoparticles with gold(I)-thiomalic acid and platinum(II)-hexanethiolate complexes. As both reactions were confined to an interface, the Au and Pt elements were situated on two opposite poles of the original Ag nanoparticles, which was clearly manifested in elemental mapping of the
nanoparticles, and consistent with the damping and red-shift of the nanoparticle surface plasmon resonance.

As nanoscale analogs to conventional amphiphilic molecules, the resulting Janus nanoparticles were found to form oil-in-water micelle-like or water-in-oil reverse micelle-like superparticulate structures depending on the solvent media. These unique characteristics were exploited for the effective transfer of diverse guest nanoparticles between organic and water phase. The transfer of hydrophobic nanoparticles from organic to water media or water-soluble nanoparticles to the organic phase was evidenced by TEM, DLS, UV-Vis, and PL measurements. In particular, line scans based on EDS analysis showed that the vesicle-like structures consisted of multiple layers of the Janus nanoparticles, which encapsulated the guest nanoparticles in the cores. The results highlight the unique effectiveness of using Janus nanoparticles in the formation of functional nanocomposites.

Part of the dissertation research was also devoted to graphene quantum dots (GQDs)-supported platinum (Pt/G) nanoparticles and their electrocatalytic activity in oxygen reduction reaction. These Pt/G nanocomposites were prepared by a hydrothermal procedure at controlled temperatures. Spectroscopic measurements based on FTIR, Raman and XPS confirmed the formation of various oxygenated structural defects on GQDs and the variation of their concentrations with the hydrothermal conditions. Interestingly, electrocatalytic activity of GQD/Pt composites exhibited a volcano-shaped variation with the GQD structural defects, with the best identified as the samples prepared at 160 °C for 6 h where the mass
activity was found to meet the DOE target for 2015. This remarkable performance was accounted for by the deliberate manipulation of the adsorption of oxygen and reaction intermediates on platinum by the GQD structural defects through partial charge transfer. The strategy presented herein may offer a new paradigm in the design and engineering of nanoparticle catalysts for fuel cell electrochemistry.

In addition, studies were also carried out to study intervalence charge transfer between ferrocenyl moieties bonded on carbon nanoparticle surfaces by diazonium reaction. Electrochemical studies exhibited two pairs of voltammetric waves with a difference of their formal potentials at about 78 mV, suggesting nanoparticle-mediated intraparticle charge delocalization at mixed valence as a result of the strong core–ligand covalent bonds and the conductive sp² carbon matrix of the graphitic cores. Consistent behaviors were observed in near-infrared measurements, indicating that the particles behaved analogously to a Class I/II mixed-valence compound.
DEDICATION

Dedicated

To

My Grandparents
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Chapter 5: Yang Song, Shaowei Chen, "Trimetallic Ag@AuPt Neapolitan Nanoparticles", *Nanoscale*, 2013, 5, 7284.


Chapter 1

Introduction
1.1 Background

Work in the nanotechnology field began as early as 1959. Nowadays, a tremendous upsurge of interest in the properties of nanoparticles and possible applications in a wide variety of areas leads to rapid development during the past decade in biochemistry, physical chemistry and engineering. Nanoparticles (NPs), which range in size from 1 to 100 nm, are attractive multifunctional materials due to their unique size, chemical and physical properties. As physicist Richard Feynman stated that “There is plenty of room at the bottom”, the theoretical capability of building things with atomic precision inspired technological innovations to manipulate properties of nanomaterials, which make them promising candidates as fundamental building blocks for novel electronic devices and circuitries. Nanomaterials exhibit unique and tunable properties that are non-existent in their bulk counterparts as a direct result of quantum confinement phenomena in optical, magnetic and electronic properties.\(^1,2\)

The synthesis and processing techniques for the preparation of high quality monodispersed nanocrystals of different semiconducting and metallic materials, fullerenes of varying properties, single and multi-wall carbon nanotubes, as well as polymeric dendrimers, and other nanophase systems are now rather well established. However, the applications of as-prepared nanoparticles are largely limited by either lack of surface properties or undesired interactions with host media, substrates and/or other individual species such as molecules and other particles. One of the beneficial consequences of functionalizing nanoparticles is that the properties can be controlled
in a predictable manner to fit the specific applications.\textsuperscript{3-8} The processes used to generate, manipulate and deploy functionalized nanoparticles provide new exciting possibilities for the development of new multifunctional tools for catalytic, biomedical and nanotechnological applications.

Within this context, the principal objectives of this dissertation are to develop effective protocols to functionalize nanoparticles and to examine their effects on their properties. Specifically, patchy nanoparticles with asymmetric surface chemical and metallic structures are used as the illustrating examples in this work.

1.2 Janus Nanoparticles

Typical nanoparticles are in spherical shape with isotropically arranged surface chemical ligands to minimize interfacial tension energy. However anisotropic particles show advantages on controlling molecular recognition and self-assembling processes, which have been proposed/proved by theoretical\textsuperscript{9,10} and experimental studies.\textsuperscript{8,11-13} Therefore, the synthesis of anisotropic nanoparticles are an intriguing and challenging aspect in current materials science.

A complementary approach towards the synthesis of anisotropic nanoparticles is the preparation of particles with diversely functionalized hemispheres. Among these, of particular interest is the creation of amphiphilic nanoparticles that exhibit hydrophobic characters on one side and hydrophilic on the other, akin to the dual-faced Roman god, Janus (hence, Janus nanoparticles, as suggested by de Gennes).\textsuperscript{14,15} These particles represent a unique nanoscale analogue to conventional surfactant molecules, and thus, may be exploited in the formation of functional superstructures
by virtue of self-assembly.\textsuperscript{16} Such supraparticular assemblies\textsuperscript{17,18} will not be accessible with homogeneously functionalized building blocks,\textsuperscript{19} and thus, offer a novel paradigm to the rational design and preparation of functional ensembles.

Yet, most prior research has been focused on (sub)micron-sized Janus particles based on polymeric materials. Several effective routes have been reported towards the synthesis of these biphasic particles.\textsuperscript{20,21} For instance, microfluidic flow systems have been used to prepare amphiphilic particles by the polymerization of the Janus droplets formed within the microfluidic channels.\textsuperscript{18,20} Submicron-sized Janus particles were also prepared by biphasic electrified jetting of two polymer precursors.\textsuperscript{21} In another report, Suzuki and Kawaguchi demonstrated that Janus particles could be produced by sputtering gold onto the top face of a polymer bead array upon which further functionalization on the gold surface might be achieved.\textsuperscript{22} Additionally, Paunov and Cayre reported the fabrication of Janus particles by the replication of particle monolayers at liquid surfaces by using a gel trapping technique.\textsuperscript{23}

For bare colloids, research into Janus particles has mostly focused on bi-compartmental structures. A typical synthetic procedure involves partial masking of the surfaces of the particles prior to selective engineering and functionalization of the exposed particle surfaces.\textsuperscript{24-29} These include surface coating by vapor deposition of metal thin films/particles,\textsuperscript{22,30-33} spin-coating of a photoresistant layer and metal evaporation,\textsuperscript{34} electrostatic deposition,\textsuperscript{35,36} layer-by-layer self-assembly,\textsuperscript{17,37} polymer self-assembly,\textsuperscript{38,39} surface-initiated free-radical polymerization,\textsuperscript{40,41} photo-
polymerization in a microfluidic channel\textsuperscript{42,43} the Pickering emulsion method\textsuperscript{44} biphasic electrified jetting\textsuperscript{21,45} protonation–deprotonation cycling\textsuperscript{46} in situ click chemistry\textsuperscript{47} and chemical modification\textsuperscript{48}.

It should be noted that, in these earlier studies, the typical particle sizes range from a few hundred nanometers to a few micrometers. Several review articles have emerged that are primarily focused on the synthesis and/or self-assembly of polymeric and oxide colloidal Janus particles\textsuperscript{24-26,49,50} and the design and fabrication of other patchy and multi-compartmental structures\textsuperscript{27-29,51} However, reports on the synthesis of nanometer-sized Janus particles are actually rather scarce\textsuperscript{48} In fact, the majority of nanometer-sized Janus particles refer to bifunctional heterodimers that consist of two different materials segregated in the particle cores, forming snowman or dumbbell-like nanostructures\textsuperscript{52,53} whereas only a limited number of studies are focused on Janus nanoparticles with two types of organic capping ligands segregated on the two hemispheres of the nanoparticles. In addition, for (sub)micron-sized Janus particles, the structural asymmetry may be directly visualized with the aid of a conventional electron microscope. Yet, for much smaller, nanometer-sized Janus particles, verification of the amphiphilic structures has become much more challenging, where typical characterization tools include two-dimensional NOSEY NMR spectroscopy\textsuperscript{54} photoluminescence\textsuperscript{55} and EDS elemental mapping\textsuperscript{56,57}.

Therefore, herein, we will describe the preparation and characterization of Janus and Neapolitan nanoparticles by interfacial functionalization and engineering method. Further investigation of their electrochemical and catalytic properties will be
carried out.

1.3 Carbon Nanoparticles

Carbon is one of the most abundant elements in nature. Carbon nanoparticles represent a unique class of carbon-based nanomaterials. Analogous to their well-known cousins as fullerenes and carbon nanotubes, carbon nanoparticles exhibit interesting optical and electronic properties that may be exploited for diverse applications such as optoelectronics, chemical sensing, biological labeling, and etc.\textsuperscript{58,59}

Typically, carbon nanoparticles are prepared by laser ablation.\textsuperscript{60-62} Recently we reported an effective synthetic protocol for the preparation of carbon nanoparticles from the combustion soot of natural gas.\textsuperscript{63} After thermal refluxing in acid, the obtained carbon nanoparticles become water-soluble with average particle size of ca. 5 nm in diameter. The particles exhibit apparent photoluminescence, suggesting that the nanoparticles behave as indirect bandgap materials and the surface trap states are responsible for the photoluminescence properties.

It has been rather well-known that carbon surfaces were covered with a variety of oxygen-containing groups such as carboxylic acid and quinone moieties.\textsuperscript{63} The drastic effects of hydrothermal treatment on photoluminescent efficiency of carbon nanoparticles have been reported.\textsuperscript{64} Acid–base titration has also been applied to identify and quantify several oxygenated functional groups.\textsuperscript{65} Specifically, the oxygenated species such as carboxyl groups, cyclic anhydrides, lactones, and hydroxyl groups of phenolic character are differentiated and quantified by
neutralization with NaHCO₃, Na₂CO₃, and NaOH, respectively, by taking advantage of the large discrepancy of their acidity (pKₐ). Chemical labeling has also been employed to confirm the presence of ortho- and para-quinone moieties on the nanoparticle surface by using o-phenylenediamine as the molecular probe, as manifested in electrochemical and spectroscopic measurements. More importantly, surface functional groups provide active sites for (electro)chemical grafting of diazonium derivatives to the carbon substrate via a strong covalent C–C bond. Such a unique interfacial bonding interaction may be exploited to initiate intraparticle electronic coupling between particle-bound functional moieties, as the carbon nanoparticles exhibit a graphitic core with an sp² carbon network that serves as a conducting medium.

1.4 Intervalance Charge Transfer

Electron transfer through molecular backbones has been extensively studied in a more fundamental level, which occurs in donor-bridge-acceptor molecules. The localized metal centers with mixed valence states serve as a donor or acceptor, where the molecular backbone connecting the metal centers serve as a bridge. Although the application of a bias between the molecular junctions differentiates it from the intramolecular charge transfer, they do share common features and are complementary approaches to understand electron transfer in molecular scale.

Typically, the intramolecular electron transfer is observed in ligand bridged dinuclear organometallic compounds |M_I(L)_n|(BL)|M_{II}(L)_n|, where M’s are metal centers having mixed valence states, BL is conjugated molecular bridge and L is
terminal ligands. When the compound is $+1$ charged, $M_I$ and $M_{II}$ will have mixed charge states $|M_I^+M_{II}^0\rangle$ or $|M_I^0M_{II}^+\rangle$. Electron oscillation will occur between the two metal centers, resulting in remarkable optical absorption typically in the near-infrared region, the parameter that may reveal important information about energy barrier involved in such electron transfer. Hush proposed a model based on the Marcus theory that correlates the optical absorption frequency ($\nu$), reorganizational energy within the inner sphere ($\lambda_i$) and outer sphere ($\lambda_o$) and electronic coupling coefficient $H_{ab}$. Robin and Day proposed criteria to classify the intramolecular charge transfer by the degree of charge delocalization or the interaction extent ($\alpha$) between the donor and acceptor, which is strongly dependent upon the structure of molecular bridge.\textsuperscript{66}

Typically, there are three classes of such mixed valence compounds. In the first class, the two metal centers are far apart or their interaction is spin forbidden or symmetrical and thus $\alpha$ is close to 0; the compounds with $\alpha = 0.707$ are defined as class III; When $\alpha$ is between 0 and 0.707 the compounds is classified as class II.

Ferrocene has been widely used as a metal center in intervalence charge transfer systems due to its fast reaction dynamics and reversibility and stability. Theoretically, ferrocene based dinuclear intervalence charge transfer molecules have been investigated extensively, where molecular bridges include saturated C-C single bonds, multiple conjugated C=C double bonds, multiple C≡C triple bonds, aromatic rings and the mixture of some of them. The electronic coupling of ferrocene centers and further the effectiveness of intervalence charge transfer have been investigated.

Experimental investigation for ferrocene-based molecules has made
significant progress at the same time. In the case of biferrocene, with the overlap of the $\pi$ and $\pi^*$ orbitals of the two ferrocene molecules, strong intervalence charge transfer results in two pairs of voltammetric waves corresponding to two sequential reversible one-electron redox reactions of the iron metal centers. The potential spacing between the two Voltammetric waves signifies the coupling strength between the two metal centers. This model is further investigated by introducing substituents adjacent to the connection of the two ferrocene, which results in conformational changes of the biferrocene molecules. It is demonstrated that the steric hindrance of the trans conformation of the molecule skews the conformation of the molecules and reduces the overlap of the $\pi$ and $\pi^*$ orbitals, thus the coupling strength of the two metal centers become weaker. In addition, through-bond charge transfer will be the primary pathway when the two ferrocene moieties are connected through conjugated bonds. For instance, biferrocene conjugates through polyenes $\text{Fc(CH=CH)}_n\text{Fc}$ ($n = 1$ to 6) have been synthesized and the coupling strength between those ferrocene is investigated systematically in the mixed-valence states. It is revealed that the potential spacing of the voltammetric waves decreases from 170 mV for $n = 1$ to 100 mV for $n = 3$ and the two voltammetric waves are barely resolved when $n$ is greater than 3. The electronic coupling over a distance of up to 6 conjugated double bonds decays exponentially, in a good agreement with theoretical calculations. More complicated molecular structures have been synthesized and factors such as solvents and temperature that may modify the intervalence charge transfer have also been attempted. However, most of the intervalence charge transfer studies are currently
based on organometallic complexes. In 1968, Hush predicted that metal centers could have effective coupling at the metal electrode/electrolyte interface through extensively conjugated bonding between the metal electrode and the metal centers.\textsuperscript{73} Until recently, intervalence charge transfer has been successfully realized experimentally through the synthesis of Ru=carbene double bonds at the ruthenium bulk electrode surface and ruthenium nanoparticles,\textsuperscript{74,75} where the metal core of the nanoparticle serves as the electron/hole conductor. Such intervalence charge transfer has offered novel perspectives for further diversifying the electronic and optical properties of nanoparticles and their application in molecular electronics as chemical sensors and so on. However, such research is still very limited.

Charge delocalization through conjugated Ru-ligand linkage on ruthenium nanoparticles was well investigated to unravel the charge transfer mechanism in our lab.\textsuperscript{74-80} This dissertation illustrates a new pathway of electronic communication via C(sp\textsuperscript{2})–C(sp\textsuperscript{2}) interfacial bonding between carbon nanoparticle and surface functionalized ferrocenyl moieties at mixed valence, leading towards the manipulation of the chemical and physical properties of carbon nanoparticles.\textsuperscript{81}

1.5 Electrochemical Energy Conversion

One of the grand challenges facing the scientific community at present is the energy crisis that several natural resources of fossil-fuel are predicted to be exhausted within a single human lifespan.\textsuperscript{82} The use of fossil fuels has exacerbated the atmospheric carbon dioxide content, which is considered to be a root cause of global warming.\textsuperscript{83} Human activity, primarily due to burning of fossil fuels in the last
hundred years, has pushed atmospheric CO$_2$ levels to about 380 ppm.$^{84,85}$ While the global warming theory has its opponents, the exhaustible nature of fossil fuels such as petroleum products, natural gas, coal etc., is irrefutable.$^{82}$ Fortunately, there is a growing awareness regarding the necessity of clean, safe, and secure energy sources to ensure energy security for the exponentially growing human population as recently pointed out by the U.S. Department of Energy (DOE) report.$^{86}$ Given this circumstance, there has been increasing research and development activity in various renewable energy sources, in particular electrochemical energy storage and conversion devices such as fuel cells and batteries.$^{85}$

Electrochemistry is a special discipline that deals with the interplay of electrical energy and chemical energy. Fuel cells are electrochemical energy conversion devices that convert chemical energy stored in fuels directly into electrical energy. Proton exchange membrane (PEM) and alkaline anion exchange membrane (AAEM) fuel cells are two of the most studied fuel cells that operate at low temperatures (below 100°C).

A typical PEM fuel cell include two electronically conducting electrodes, an anode and a cathode, which are separated by a solid ionomer membrane that designed to conduct protons while being impermeable to gases such as oxygen or hydrogen. Fuels such as compressed gaseous hydrogen are fed to the anode to yield protons and electrons by electro-oxidation reaction, as depicted in Scheme 1.1(a). Protons are then transported across the membrane to the cathode under the influence of the so-called electrochemical potential gradient. Electrons are transported across the external
circuit to the cathode. Protons and electrons recombine at the cathode and involve in oxygen reduction reaction to water. The anodic oxidation and the cathodic reduction reactions are as shown below:

**Anode:** \( H_2 \rightarrow 2H^+ + 2e^- \) \( E^0 = 0.00 \) V vs. SHE \hspace{1cm} (1.1)

**Cathode:** \( \frac{1}{2}O_2 + 2H^+ + 2e^- \rightarrow H_2O \) \( E^0 = 1.23 \) V vs. SHE \hspace{1cm} (1.2)

SHE represents the Standard Hydrogen Electrode. The involvement of protons in the above reactions causes PEM fuel cells to operate under acidic conditions. While the above reactions exemplify the half-cell reactions, the overall cell reaction \( (E_{Cell} = E_{Cathode} - E_{Anode}) \) is the spontaneous conversion of hydrogen and oxygen to water, heat and electricity.

**Overall:** \( H_2 + \frac{1}{2}O_2 \rightarrow H_2O \) \( E_{Cell} = 1.23 \) V \hspace{1cm} (1.3)

The enthalpy associated with reaction (1.3) is \( \Delta H^o = -286 \) kJ mol\(^{-1}\) at 25°C and atmospheric pressure. This basically implies that all energy is dissipated as heat in a spontaneous chemical combustion reaction. The standard Gibbs free energy change is \( \Delta G^o = -237 \) kJ mol\(^{-1}\). Given \( \Delta G^o = \Delta H^o - T\Delta S^o \), it can be calculated that \( T\Delta S^o = -49 \) kJ mol\(^{-1}\). However, if \( H_2 \) and \( O_2 \) are physically separated and subjected to discharge in a fuel cell configuration the external circuit constitutes a load resistance. Here the energy corresponding to the term \( T\Delta S^o = -49 \) kJ mol\(^{-1}\) is inevitably liberated as thermal energy, whereas \( \Delta G^o = -237 \) kJ mol\(^{-1}\) is theoretically converted into electrical energy. So this \( \Delta G \) term is identified as the maximum useful work done.\(^87\) The combination of anode, cathode and the ionomer membrane is called
the Membrane Electrode Assembly (MEA). State-of-the-art anode and cathode catalysts for PEM fuel cells consist of platinum or platinum alloy nanoparticles supported on high surface area carbon supports. Ionomer membranes are solid polymers that are permeable to either anions or cations. In PEM fuel cells, sulfonated tetrafluoroethylene based ionomer membranes (Nafion®) are used as a proton conductor.

AAEM fuel cells are alkaline counterparts of the PEM fuel cell systems as schematically shown in Scheme 1.1(b). The primary difference is the chemical composition and function of alkaline ionomer membrane used between the electrodes. In AAEM fuel cells, anion exchange membrane with quaternary ammonium anion exchange groups that transport hydroxide anions from cathode to anode are used. Involvement of hydroxide anions causes the cell to operate under alkaline conditions. The anodic oxidation of hydrogen and cathodic reduction of oxygen take place under alkaline conditions as shown below:

\[
\text{Anode: } H_2 + 2OH^- \rightarrow 2H_2O + 2e^- \quad E^0 = -0.828 \text{ V vs. SHE} \quad (1.4)
\]

\[
\text{Cathode: } \frac{1}{2}O_2 + H_2O + 2e^- \rightarrow 2OH^- \quad E^0 = 0.401 \text{ V vs. SHE} \quad (1.5)
\]

The overall cell reaction in alkaline fuel cell is the conversion of hydrogen and oxygen to heat, water and electricity.
Scheme 1.1 Schematic illustrations of (a) PEM and (b) AAEM fuel cells.
Overall: $H_2 + \frac{1}{2}O_2 \rightarrow H_2O \quad E_{\text{Cell}} = 1.23 \text{ V}$ \hspace{1cm} (1.6)

In comparison to their acidic counterparts, AAEM fuel cells open the possibility of using inexpensive non-noble electrocatalysts based on (i) supported noble/non-noble metal clusters, and (ii) metal-organic and inorganic complexes due to alkaline media. At high pH, attack of the ionomer membrane by peroxide radicals is suppressed, allowing the use of hydrocarbon backbone membranes and avoiding expensive fluorinated polymers. More importantly, AAEM fuel cells allow wider choices of fuel feed such as ethanol, xylitol, oxalic acid, formic acid, gasoline, ammonia etc., apart from hydrogen and methanol used in acidic environments due to enhanced C-C bond cleavage possibilities in alkaline media.

Comparing to thermodynamically reversible and minimal overpotential loss of hydrogen oxidation reaction at the anode during fuel cell operation, the oxygen reduction reaction (ORR) is irreversible and exhibits significant kinetic barriers. ORR involves various reaction intermediates and multiple electron transfer as illustrated in Scheme 1.2 in acidic and alkaline media. For example, in alkaline media, ORR may proceed to the $4e$ product either via the direct ($k_1$) or series ($k_2+k_3$) path. These two pathways represent efficient $4e$ reduction of $O_2$ to $OH^-$. However, an inefficient $2e$ pathway ($k_5$) leads to the intermediate peroxide anion as the stable product. The analogous case of ORR in acidic media is also shown in Scheme 1.2.

Rotating ring-disk electrode (RRDE) technique has been extensively used to investigate the kinetics of ORR,\textsuperscript{87} as shown in Scheme 1.3. This technique involves
Scheme 1.2 Summary of Oxygen Reduction Reaction in acidic and alkaline medium.

**Acidic Medium**

**Direct:** \( O_2 + 4H^+ + 4e \rightarrow 2H_2O \quad E^0 = 1.23V \)

**Series:** \( O_2 + 2H^+ + 2e \rightarrow H_2O_2 \quad E^0 = 0.695V \)
\( H_2O_2 + 2H^+ + 2e \rightarrow 2H_2O \quad E^0 = 1.763V \)

\[
\begin{align*}
O_{2,aq} & \rightarrow O_{2,ads} & & k_1(4e) \\
& \Leftrightarrow H_2O_2,ads & & k_2(2e) \\
& \rightarrow H_2O & & k_4(2e) \\
& \downarrow k_3 & & k_5 \\
H_2O_2 & & & \\
\end{align*}
\]

**Basic Medium**

**Direct:** \( O_2 + 4H_2O + 4e \rightarrow 4OH \quad E^0 = 0.401V \)

**Series:** \( O_2 + H_2O + 2e \rightarrow HO_2^- + OH^- \quad E^0 = -0.065V \)
\( HO_2^- + H_2O + 2e \rightarrow 3OH^- \quad E^0 = 0.867V \)

\[
\begin{align*}
O_{2,aq} & \rightarrow O_{2,ads} & & k_1(4e) \\
& \Leftrightarrow HO_2^- & & k_2(2e) \\
& \rightarrow H_2O & & k_4(2e) \\
& \downarrow k_3 & & k_5 \\
HO_2^- & & & \\
\end{align*}
\]
Scheme 1.3 Schematic of Rotating Ring-Disk Electrode
the convective transport of dissolved molecular oxygen from the bulk to the electrode surface prior to diffusive transport within the diffusion layer to the catalyst site. This technique allows the detection of stable reaction intermediates generated at the disk during ORR by potential control of the ring electrode. RRDE typically consists of a glassy carbon disk electrode around which a gold ring electrode is concentrically placed. Oxygen reduction reaction (ORR) is carried out at the catalyst deposited on the disk. The electrode is immersed into the O₂ saturated electrolyte and physically rotated to draw molecular O₂ to the electrode surface. Oxygen reduction takes place at the disk and any stable intermediate formed during ORR is detected at the ring electrode, which is potentiostatically controlled at a suitable potential. Current regions obtained from RRDE experiments can be divided into two regions, namely the kinetically- and diffusion-limited regions. In the kinetically controlled region, the ORR process is limited by the electron transfer kinetics. In the diffusion-limited region, the ORR process is limited by the mass transport of dissolved O₂ to the electrode surface. The total disk current ($I_D$) can then be written as the sum of the reciprocals of the kinetic current ($I_k$) and diffusion limited current ($I_d$) values shown below:

$$\frac{1}{I_D} = \frac{1}{I_k} + \frac{1}{I_d}$$  \hspace{1cm} (1.7)

Kinetic current can then be extracted from the total current density using the following equation:

$$I_k = \frac{(I_d \cdot I_D)}{(I_d - I_D)}$$  \hspace{1cm} (1.8)
Limiting current is characterized by the Levich equation as a function of rotation rate as shown below:

\[ I_d = B\omega^{1/2} \]  

(1.9)

The Levich constant ‘B’ is typically used to extract the number of electrons \((n)\) transferred during ORR based on the equation below:

\[ B = 0.62nAFD_O^{2/3}v^{-1/6}C_O \]  

(1.10)

where \(F\) is the Faradaic constant (96500 C/mol), \(v\) is the kinematic viscosity of the aqueous electrolyte (1.26×10^{-6} mol/cm^3), \(D_O\) and \(C_O\) are the diffusion coefficient (1.93×10^{-5} cm^2/s) and solubility (1.26×10^{-6} mol/cm^3) of O_2, and A is the geometric surface area of the electrode. The ring current is due to stable reaction intermediates that are generated during ORR at the disk electrode. Only a certain fraction of the intermediate generated at the disk is detected at the ring due to geometric limitations such as the disk-ring design and the spacing between them. This necessitates the use of a parameter called the collection efficiency \((N)\), which is 37\% for all works in this dissertation. Using the ring current and the collection efficiency values, the number of electron transfer \((n)\) can be quantified as shown below:

\[ n = 4 \cdot \frac{I_D}{I_D + I_R/N} \]  

(1.11)

Fuel cell commercialization is seriously impeded by the poor performance of cathodic catalysts in ORR. Under electrochemical conditions, most non-noble metal electrodes undergo passivation, implying that the surface is covered with a thin layer of oxide film. This oxide film prevents the chemisorption of molecular O_2, which is a
prerequisite for efficient ORR process. This leads to the use of Pt-based electrocatalysts materials for fundamental studies as well as fuel cell applications. However, the sluggish kinetics of ORR decreases the thermal efficiency by as much as 30–40% even with the use of state-of-the-art Pt catalysts. The Pt catalysts are usually dispersed as fine particles on carbon black (Pt/C) to reduce Pt loading and to enhance surface accessibility. To further improve the ORR activity, substantial efforts have been devoted to the manipulation of the composition and morphology of Pt-based catalysts, such as Pt-monolayer catalysts, Pt–M (M = Fe, Co, Ni, Pd, etc.) alloy catalysts, and shape-controlled nanocrystals.

Recently, chemical functionalization of noble metal surfaces with specific molecules/ions to improve electrocatalytic performance has received increasing attention. Of these, aryl-stabilized metal nanoparticles through M–C covalent bonds have received great interest. It is well known that in a polysubstituted benzene molecule there exist rather apparent electronic interactions between the substituent moieties. For example, the acidity of para-substituted benzoic acid increases with increasing electronegativity of the para substituents. A systematic study was carried out to examine the effects of phenyl para-substituent groups on the ORR activity of aryl-stabilized Pt nanoparticles. The results indicate that the ORR activity of the resulting Pt nanoparticles increases with the substituents in the order of \(-\text{CH}_3 < -\text{F} < -\text{Cl} < -\text{OCF}_3 < -\text{CF}_3\), which is in line with the increase of their electron-withdrawing capability, according to the corresponding Hammet substituent constants (\(\sigma\)). The enhanced ORR activity may be rationalized by the weakening of
oxygen adsorption on Pt.\textsuperscript{6}

On the other hand, cost, scarcity and scientific curiosity have been pushing researchers to search for non-Pt based electrocatalysts for ORR. Ag-based catalysts have been examined as a substitute of Pt because of their obviously low costs and specially, high stability in alkaline media of AAE fuel cell; yet, typically a large amount of silver is required because of its relatively low catalytic activity. In recent years, a number of strategies have been proposed and employed to improve the ORR activity of Ag nanoparticles that typically involve manipulation of the elemental composition, size, and surface atomic arrangements of the nanoparticle catalysts. One strategy is alloying Ag with other metal as alloy catalysts show significantly enhanced ORR activity as compared with pure Ag.\textsuperscript{103,104} Lately, another effective strategy has emerged, whereby the nanoparticle electrocatalytic performance may be further enhanced by deliberate chemical functionalization with specific molecules/ions, as a result of the manipulation of the energy of the nanoparticle d electrons and hence the interactions with adsorbed oxygen.\textsuperscript{6,98}

In this dissertation, Ag-based electrocatalysts will be further investigated to unravel the role of surface chemical/metallic components in ORR catalytic activity as compared with monometallic Ag nanoparticles. In additional, the role of interaction between supporting materials and metal particles in electrocatalytic activity is also discussed.

1.6 Dissertation Outline

The dissertation research described herein primarily focuses on surface
functionalization and engineering of nanosized particles, where the surface structure of nanoparticles plays significant roles in manipulating the catalytic and optical properties of nanoparticles. Thereafter, the functionalized nanoparticles will be investigated extensively by spectroscopic techniques such as UV-vis, photoluminescence, $^1$H nuclear magnetic resonance (NMR), FT-infrared and X-ray photoelectron spectroscopy (XPS) and electrochemical techniques like cyclic voltammetry (CV), and differential pulse voltammetry (DPV). The electrocatalytic activities of functionalized nanoparticles will be determined by rotating ring-disk electrode RRDE technique.

Within the context of surface functionalization and engineering of nanoparticles, the rest of the dissertation consists of the following chapters:

In chapter 2, experimental details such as the chemicals used, the methods of nanoparticles synthesis, procedures for the functionalization and manipulation of nanoparticles and characterization of properties will be included.

In chapter 3, covalent cross-link of surface ligands on Janus nanoparticle will be reported, where the amphiphilic surface characters of the Janus nanoparticles will be verified by contact angle measurements, comparing to bulk-exchange counterparts. In addition, spectroscopy measurements will provide evidence of enhanced structural stability of Janus nanoparticles from surface ligand cross-linking.

In chapter 4, the interfacial engineering method will combine with galvanic replacement reaction to prepare AgAu bimetallic Janus nanoparticles. Furthermore, high electrocatalytic activity of AgAu bimetallic Janus nanoparticles as ORR
catalysts in alkaline media will be examined by electrochemical methods.

In chapter 5, Ag@AuPt trimetallic Neapolitan nanoparticles will be synthesized by a two-step interfacial galvanic replacement method. The separated surface domains of Ag, Au and Pt will be illustrated by spectroscopy methods and EDS elemental mapping technique.

In chapter 6, the multilayered vesicle structure formed by Janus nanoparticles will be characterized by electronic microscopy methods. More importantly, the capability of Janus nanoparticles as versatile phase transfer reagents will be illustrated.

In chapter 7, graphene quantum dot (GQD) supported Pt nanoparticles will be prepared as ORR electrocatalysts. The role of defects of GQD and interaction between supporting materials and Pt nanoparticles will be determined by spectroscopy, electronic microscopy, and electrochemical methods.

In chapter 8, ferrocene functionalized carbon nanoparticle will be synthesized. Intervalance charge transfer of ferrocene moieties via carbon nanoparticle will be investigated by spectroscopy and electrochemical methods.
1.7 Reference


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Chapter 2

Experimental Section
2.1 Chemicals Required

Hydrogen tetrachloroauric acid (H\textsubscript{Au}Cl\textsubscript{4} \cdot xH\textsubscript{2}O) were synthesized by dissolving ultra-high purity gold (99.999%, Johnson Matthey) in freshly prepared aqua regia followed by crystallization. Silver nitrate (AgNO\textsubscript{3}, Fisher Scientific), Tetraoctyl-ammonium bromide (Alfa Aesar, 98%), hexanethiol (C\textsubscript{6}SH, Acros, 96%), L-glutathione (GSH, Aldrich, 98%), 3-mercapto propane-1,2-diol (MPD, Aldrich, 95%), 1-octyne (HC8, 97%, Sigma-Aldrich), 4-trifluoromethylaniline (NH\textsubscript{2}PhCF\textsubscript{3}, ≥97%, Sigma-Aldrich), superhydride (LiB(C\textsubscript{2}H\textsubscript{5})\textsubscript{3}H, 1 M in THF, ACROS), sodium citrate (≥99%, Sigma-Aldrich), sodium borohydride (NaBH\textsubscript{4}, Acros, 99 %), toluene (Acros, 99%), sodium hydroxide (NaOH, ACROS), ethanol (Fischer, 100 %), methanol (Fischer, 99 %), dichloromethane (CH\textsubscript{2}Cl\textsubscript{2}, Fischer, 99.9 %), tetrahydrofuran (THF, Acros, 99%), hexane (98%, Fischer), chloroform (98%, Acros), deuterated tetrahydrofuran (THF-d\textsubscript{4}, Acros, 99.5%), deuterated chloroform (CDCl\textsubscript{3}, Acros, 99.5%) were all used as received.

Scheme 1.1. Synthetic Procedure of DAT

Ferrocenylaniline were synthesized and characterized according to literatures.\textsuperscript{1,2} 3,5-octadiyne-1-ol-8-thiol (DAT) ligand was synthesized in three-step
procedure as illustrated in Scheme 1.1: (1) bromination of 3,5-dioctadiyn-1,8-diol, (2) synthesis of 8-Bromo-3,5-dioctadiyn-1-ol, and (3) Synthesis of 8-Thioacetate-3,5-dioctadiyn-1-ol. Water was supplied by a Barnstead Nanopure water system (18.3 MΩ cm). The Au\(^{\text{I}}\)MPD complex was prepared by mixing a stoichiometric amount of HAuCl\(_4\) and MPD in methanol, which was a white precipitate as a result of the reduction of Au\(^{\text{III}}\) to Au\(^{\text{I}}\) by the thiol moieties. The precipitate was collected by centrifugation and washed extensively with methanol.\(^1\) Similarly, the Au\(^{\text{I}}\)TMA complex was prepared by mixing a stoichiometric amount of HAuCl\(_4\) and TMA in acetone, of which the product was soluble in water with a concentration of 1 mM.\(^1\) The Pt\(^{\text{II}}\)C\(_6\) complex was prepared by mixing a PtCl\(_2\) aqueous solution with hexanethiol in chloroform. The formation of Pt\(^{\text{II}}\)C\(_6\) was signified by the color appearance in the chloroform phase whereas the water phase became colorless. The chloroform phase was collected, dried and further washed with methanol to remove excessive thiol, affording Pt\(^{\text{II}}\)C\(_6\) that was soluble in acetone.

2.2 Particle Synthesis

2.2.1 Alkyl-thiolate Gold Nanoparticles

The alkyl thiolate gold nanoparticles are synthesized by using the Brust protocol.\(^2\) HAuCl\(_4\) is dissolved in water and subsequently transferred to the toluene phase by a phase transfer reagent tetraoctyl ammonium chloride by vigorous stirring of the solution. The color of the toluene phase becomes orange and the color of the water phase changes from yellow to colorless, which indicates the completion of
phase transfer. Alkanethiol (RSH) is then added into the toluene phase that is separated and purified from mixture. The solution is then kept in an ice bath for 1 hour followed by the addition of freshly prepared NaBH₄. Upon addition of NaBH₄ the solution turns to dark brown within few seconds indicating the formation of nanoparticles. The solution is allowed to run overnight followed by washing with copious amount of water and methanol to get rid of the excess thiol ligands. The particles were then fractionated by using a binary solvent-nonsolvent mixture of toluene and ethanol and the fraction with average core diameter of 2.0 nm was used for the present study. This was followed by thermal annealing in toluene at 110 °C for 8 hours in an oil bath to reduce the core size dispersity.

2.2.2. Alkyl-thiolate Silver Nanoparticles

Similar method was applied to prepare alkyl-thiolate silver nanoparticles. Briefly, 0.1 mmol of AgNO₃ was first dissolved into 1 mL of Nanopure water, into which was added 0.3 mmol of alkanethiol in 10 mL of tetrahydrofuran (THF) under magnetic stirring. The solution changed from clear to cloudy, indicating the formation of Ag-thiolate complex. A freshly prepared ice-cold NaBH₄ solution (0.3 mmol in 2 mL of ethanol) was added dropwise into the solution, leading to the appearance of a dark-brown color, which signified the formation of silver nanoparticles. The reaction mixture was stirred for 8 h before the nanoparticles were extracted by toluene and washed by Nanopure water. The solvents were then removed by a rotary evaporator, and the remaining solids were washed with a copious amount of methanol to remove impurities and excessive ligands.
Water-soluble AgGSH nanoparticles were synthesized by adopting a literature method. Briefly, 0.25 mmol (42.4 mg) of AgNO₃ was dissolved in 50 mL of water, into which was added 1 mmol (307 mg) of GSH. A cloudy white liquid was produced, due to the formation of a silver thiolate suspension, into which was then added a 10 ml aqueous solution of 0.2 M NaBH₄ (2.0 mmol) in a dropwise fashion under magnetic stirring. The color of the solution immediately changed from cloudy white to slightly yellow and then to dark brown after about 15 min. The reaction mixture was concentrated to a volume of ca. 5 mL in a rotary evaporator at room temperature, and AgGSH nanoparticles were precipitated by adding ~20 mL of methanol into the solution. The precipitates were washed with methanol several times to remove excessive glutathione ligands and other unreacted materials. The purified AgGSH nanoparticles were soluble in water with an average core size of ca. 1.5 nm.

2.2.3 Carbon nanoparticles (CNPs).

The preparation of carbon nanoparticles has been detailed previously. Briefly, carbon soot was collected on the inside wall of a glass beaker by placing the beaker upside-down above the flame of a natural gas burner. Typically 100 mg of the soot was then refluxed in 10 mL of 5 M HNO₃ for 12 h. When cooled down to room temperature, the brownish yellow supernatant after centrifugation was neutralized by Na₂CO₃, and then dialyzed against Nanopure water through a dialysis membrane for 3 days, affording purified carbon nanoparticles which exhibited an average core diameter of 4.8 ± 0.6 nm with well-defined graphitic crystalline lattices, as determined by high-resolution transmission electron microscopic measurements.
2.2.4 Graphene Quantum Dots (GQDs).

GQDs were prepared by following a literature procedure. In brief, 1.00 g of carbon fibers was added into a mixture of concentrated H$_2$SO$_4$ (60 mL) and HNO$_3$ (20 mL). The solution was sonicated for 2 h and stirred for 24 h at 120 °C. The mixture was then cooled and diluted with Nanopure water (800 mL) with the pH adjusted to about 8 by Na$_2$CO$_3$. The solution was then dialyzed in a dialysis bag (cutoff molecular weight 2000 Da) for 3 d, affording purified GQDs. These GQDs were then used as supporting substrates for platinum nanoparticles, as detailed below.

2.2.5 GQD-Supported Platinum Nanoparticles (Pt/GQD).

In a typical reaction, PtCl$_2$ (6.65 mg, 0.025 mmol) was dissolved in 1 mL of hydrochloric acid under heating. The solution was then added into a 15 mL aqueous solution with 20 mg of GQDs prepared above under magnetic stirring. The pH was adjusted to 10 by NaOH, and the mixture was transferred to Teflon-lined autoclave and hydrothermally treated at 140, 160, 180, and 200 °C for 3, 6, or 12 h, respectively. Black precipitates appeared in the flask as a result of thermolytic reduction of Pt(II) and GQDs to form GQDs-supported platinum nanoparticles (at 20wt% of Pt). The precipitates were collected, washed extensively with Nanopure water and ethanol, and dried in a vacuum oven at room temperature for 12 h. The resulting nanoparticles were denoted as Pt/G-temperature-time. For instance, Pt/G-140-6h referred to the sample prepared at 140 °C for 6 h.  


2.3 Patchy Nanoparticles

Langmuir-based methods have been adopted as an effective way for the production of Janus nanoparticles that exhibit hydrophobic characters on one side and hydrophilic on the other. Recently, we developed two effective strategies based on interfacial engineering for the preparation of Janus nanoparticles. The first method is depicted in Scheme 2.2 (A). Briefly, $n$-hexanethiolate-capped gold nanoparticles (AuC6, average core diameter 5 nm, as determined by TEM measurements) were used as the starting materials. Experimentally, the amphiphilicity was rendered to the AuC6 nanoparticles by subjecting them to ligand exchange reactions with, for example, hydrophilic 3-mercaptopropane-1,2-diol (MPD, HSCH(OH)CH₂OH) at the air|water interface at a sufficiently high surface pressure by mechanical compression. The Janus nanoparticles were used in Chapter 6 as phase transfer reagents.

In the second approach, Scheme 2.2 (B), a monolayer of AuC6 nanoparticles was first deposited onto a substrate surface by the Langmuir-Blodgett technique at a sufficiently high surface pressure, where ligand intercalation between adjacent nanoparticles occurred. The sample was then immersed into an aqueous solution of hydrophilic ligands, such as 3,5-octadiyne-1-ol-8-thiol (DAT) ligands, where the ligand exchange reactions were limited to the top face of the nanoparticles, leading to the formation of Janus nanoparticles. Janus particles prepared by this method were employed in Chapter 3. With this experimental setup, the exchange dynamics might also be readily assessed by contact angle measurements.
2.3.1 Bimetallic AgAu Janus Nanoparticles

AgAu bimetallic Janus nanoparticles were prepared by interfacial galvanic exchange reactions of AgC6 nanoparticles with Au\textsuperscript{I}MPD complex. The procedure is similar to that used previously in the preparation of monometallic Janus nanoparticles (as depicted in Scheme 2.2 B). In brief, the AgC6 nanoparticle monolayer was formed on air\textbackslash water interface in a LB trough, which was then transferred onto a clean glass slide surface by the up-stroke deposition method. Then the glass slides were immersed into an acetone solution of the Au\textsuperscript{I}MPD complex solution for the galvanic exchange reactions of the AgC6 particles with the Au\textsuperscript{I}MPD complex. The reaction took place only at the top face of the particles that was in direct contact with the water/methanol phase, leading to the generation of Janus nanoparticles. At varied immersion time intervals, the glass slide was taken out of the Au\textsuperscript{I}MPD solution, gently rinsed with copious amounts of methanol and water to remove excessive Au\textsuperscript{I}MPD, displaced silver ion, and hexanethiolate ligands, dried in a gentle stream of ultrahigh-purity nitrogen, and then subject to contact angle measurements (see below) before being collected into a vial by THF. At least four batches of particle samples were prepared and collected under identical conditions so that there were enough materials for further analyses. The resulting Janus particles were found to be soluble in chloroform and THF.

As a control measurement, galvanic exchange reactions of the AgC6 nanoparticles with Au\textsuperscript{I}MPD were also carried out by mixing a calculated amount of AgC6 nanoparticles and Au\textsuperscript{I}MPD ligands in THF and were stirred for varied periods
of time. The solution was then dried under reduced pressure with a rotary evaporator, and excessive ligands were removed by extensive rinsing with methanol. The resulting particles were denoted as bulk-exchange particles and, similar to the Janus nanoparticles, were also soluble in chloroform and THF.

2.3.2 Ag@AuPt Neapolitan Nanoparticles

The trimetallic Neapolitan nanoparticles were prepared by combining two methods above to two-step interfacial galvanic replacement reactions of AgC6 nanoparticles with Au\textsuperscript{I}TMA and Pt\textsuperscript{II}C6 complexes. The first step was similar to that used to prepare bimetallic AgAu Janus nanoparticles that was detailed previously.\textsuperscript{11} In brief, the AgC6 nanoparticle monolayer was formed on air|water interface in a LB trough. At this point, a calculated amount of the Au\textsuperscript{I}TMA aqueous solution was injected into the water subphase, where the first interfacial galvanic exchange reactions occurred leading to the formation of AgC6–AuTMA bimetallic Janus nanoparticles. The nanoparticle monolayers were then transferred onto a clean glass slide surface by the up-stroke deposition method so that the hydrophobic side with the hexanethiolate ligands was exposed. Then the glass slides were immersed into an acetone solution of the Pt\textsuperscript{II}C6 complex for the second interfacial galvanic replacement reaction (this procedure was used previously in the preparation of another type of Janus nanoparticles\textsuperscript{10}), which took place at the hexanethiolate face of the particles that was in direct contact with the acetone solution, resulting in the generation of trimetallic Neapolitan nanoparticles. Then, the glass slides with Neapolitan nanoparticle monolayers were gently rinsed with copious amounts of acetone and
dried in a gentle stream of ultrahigh-purity nitrogen before being collected into a
glass vial by THF. At least four batches of particle samples were prepared and
collected under identical conditions so that there were enough materials for further
analyses. The resulting Neapolitan particles were found to be soluble in chloroform
and THF.

As a control measurement, galvanic replacement reactions of the AgC6
nanoparticles with Au\textsuperscript{I}TMA and Pt\textsuperscript{II}C6 complexes were also carried out by mixing a
calculated amount of AgC6 nanoparticles with Au\textsuperscript{I}TMA and Pt\textsuperscript{II}C6 complexes in
THF under magnetic stirring for 8 h. The solution was then dried under reduced
pressure with a rotary evaporator, and excessive ligands were removed by extensive
rinsing with methanol. The resulting particles were denoted as bulk-exchange
particles and, similar to the Neapolitan nanoparticles, were soluble in chloroform and
THF.

2.3.3 Phase transfer by Janus nanoparticles.

Phase transfers facilitated by Janus nanoparticles were tested for both CH\textsubscript{2}Cl\textsubscript{2}
to water and water to CH\textsubscript{2}Cl\textsubscript{2}. In the test of transfer CH\textsubscript{2}Cl\textsubscript{2} to water, 0.05 mg AuC6-
MPD Janus nanoparticles in 300 µL of CH\textsubscript{2}Cl\textsubscript{2} was added to 5 mL of water in a 7 mL
glass vial, corresponding to an oil/water (o/w) ratio of 0.06:1. The vial was then
subject to mechanical agitation with a Fisher Vortex Genie 2 at approximately 3200
rpm for 10 min, after which the solution was allow to settle down for at least 1 h. The
transfer of water to CH\textsubscript{2}Cl\textsubscript{2} was tested in a similar fashion. Briefly, 300 µL of water
was mixed with 5 mL CH\textsubscript{2}Cl\textsubscript{2} solution of 0.05 mg AuC6-MPD Janus Nanoparticles in
a glass vial (o/w ratio 1:0.06), which was then subject to mechanical agitation for 10 min followed by 1 h settlement. As controls, AuC6 nanoparticles were used instead of AuC6-MPD Janus nanoparticles and the rest of the procedure was identical.

For nanoparticle transfer test, the procedure was identical as well except that hydrophobic nanoparticles (AgC6 nanoparticles or C60, 0.05 mg) were dispersed in 300 µL of CH₂Cl₂ and added to 0.05 mg of AuC6-MPD Janus nanoparticles in 5 mL of water or hydrophilic nanoparticles (AgGSH nanoparticles or CNPs, 0.05 mg) were dispersed in 300 µL of water and added to 0.05 mg AuC6-MPD Janus nanoparticles in 5 mL of CH₂Cl₂.

2.4 Electrochemistry

Voltammetric measurements were carried out with a CHI 440 or CHI 710 electrochemical workstation. A polycrystalline gold disk (sealed in a glass tubing) or glassy carbon electrode was used as the working electrode. An Ag/AgCl wire and a Pt coil were used as the (quasi)reference and counter electrodes, respectively. The gold electrode was first polished with alumina slurries of 0.05 mm and then cleansed by sonication in 0.1 M HNO₃, H₂SO₄ and Nanopure water successively. Prior to data collection, the electrolyte solution was deaerated by bubbling ultrahigh-purity N₂ for at least 20 min and blanketed with a nitrogen atmosphere during the entire experimental procedure. A UV light source (370 nm, 18 W) was may applied for voltammograms, if needed.

For electrocatalytic activity study of nanoparticle catalysts, the electrochemical setup consists of a CHI710 electrochemical workstation with a Pt foil
counter electrode and a reversible hydrogen electrode (RHE) at room temperature. The working electrode was a rotating ring-disk electrode (RRDE, AFE7R9GCAU from Pine Instrument Co.) with a glassy carbon disk (GC, diameter 5.61 mm) and a gold ring. The collection efficiency (N) was determined to be 37.3% by RRDE measurements in 5 mM K₄Fe(CN)₆⁺ 0.1 M Sr(NO₃)₂, which is consistent with the manufacturer’s value of 37 %. The RRDE was prepared according to a procedure proposed by Gloagen et al. In a typical experiment, 500 µg of the AgC6 or the bimetallic (Janus or bulk-exchange) nanoparticles were mixed with 2 mg of XC-72 carbon black (mass ratio of metal: C = 1: 4) in toluene with 3 µL of a Nafion 117 solution (5 wt. %) and dispersed under sonication. A measured volume (ca. 10 µL) of this catalyst ink was then transferred via a syringe onto the freshly polished glassy carbon disk. The solvent was evaporated at room temperature yielding a catalytic loading of 15 µg with ca. 3 µg of metals (20 wt.%).

Prior to electrochemical tests of oxygen reduction, the catalyst films on the glassy-carbon electrode surface were electrochemically pretreated in a nitrogen-saturated electrolyte (0.1 M HClO₄ or 0.1 M NaOH) by rapid potential cycling at 200 mV/s in a desired electrochemical potential window until a steady voltammogram was observed. The electrocatalytic activity for oxygen reduction was then evaluated in an O₂-saturated electrolyte solution. The solution ohmic drop (i.e., IR drop) was electronically compensated.
2.5 Instruments

2.5.1 Langmuir Films

The monolayer was formed on Langmuir-Blodgett trough NIMA 61ID. The particle monolayer was then compressed to a desired surface pressure where the interparticle edge-to-edge separation was maintained at a value smaller than twice the extended ligand chain length such that the interfacial mobility of the particles was impeded.

2.5.2 Contact Angle

Contact angles were measured with a Tantec CAM-PLUS contact angle meter. For the bulk-exchange nanoparticles, the contact angles were measured with their monolayers deposited onto a clean glass slide surface by the Langmuir–Blodgett method at the same surface pressures where Janus nanoparticles were prepared. For self-assembled monolayers of hexanethiol, DAT, and their mixture, the samples were prepared by immersing a clean Au thin film on a glass slide into an ethanolic solution (1 mM) of the respective thiol for about 24 h. For each sample, at least eight independent measurements were carried out for statistical analyses.

2.5.3 Spectroscopy

UV-visible spectroscopic measurements were carried out with a UNICAM ATI UV4 spectrometer, whereas fluorescence properties were performed with a PTI Fluorescence Spectrometer. FTIR measurements were carried out with a Perkin-Elmer FTIR spectrometer (Spectrum One) where the samples were prepared by
compressing the materials of interest into a KBr pellet. The spectral resolution was 4 cm\(^{-1}\). NMR spectroscopy of the sample was done in Varian Unity-500+ spectrometer. To determine the nanoparticle size aggregates, dynamic light scattering (DLS) measurements were carried out with a Dynapro Temperature Controlled Microsampler. The results were reported in terms of %mass. X-ray photoelectron (XPS) spectra were recorded with a PHI 5400/XPS instrument equipped with an Al K\(\alpha\) source operated at 350 W and 10\(^9\)Torr. Silicon wafers were sputtered by argon ions to remove carbon from the background and used as substrates.

**2.5.4 Microscopy**

The morphology and sizes of the nanoparticles were characterized by transmission electron microscopic studies (TEM, Philips CM300 at 300 kV). The samples were prepared by casting a drop of particles solution (cone. ~ 1 mg/ml) onto a 400 mesh carbon only grid. The particle core diameter was then estimated by using Image J analysis of the TEM micrographs. Typically, at least 200 nanoparticles were measured to obtain a size histogram. Energy-dispersive X-ray spectroscopy studies (EDS) were carried by using a Philips CM200/FEG transmission electron microscope for element maps.
2.6 Reference


Chapter 3

Enhanced Stability of Janus Nanoparticles by
Covalent Cross-Linking of Surface Ligands

3.1 Introduction

Nanoparticles have attracted increasing attention because of their potential application as novel building blocks for the fabrication of next-generation optical/electronic devices. This is attributed to their unique material properties that are vastly different from those of their constituent atoms or bulk forms. Yet, to exploit these unprecedented material properties, it becomes critically important to search for additional material design parameters beyond the conventional variables of size and shape. Toward this end, preparation of amphiphilic Janus nanoparticles has represented an attractive route. Actually, it was Casagrande and co-workers who first created the term “Janus beads” to denote partial hydrophobic modification of commercial glass spheres. Janus particles refer to a class of nanoparticle materials that exhibit hydrophobic characters on one side and hydrophilic characters on the other, akin to the Roman god, Janus. Because of their asymmetrical surface chemistry, the nanoparticles behave analogously to conventional surfactant molecules and thus may be exploited in the formation of functional superstructures by virtue of controlled self-assembly.

Previously, we developed two effective approaches based on interfacial engineering for the preparation of nanosized Janus particles. In both routes, alkanethiolate-protected gold nanoparticles were used as the starting materials. In the first method, a particle monolayer was formed at the air|water interface by the Langmuir method. At sufficiently high surface pressures, intercalation of the protecting ligands between neighboring particles occurred, leading to impeded
interfacial mobility of the nanoparticles. At this point, injection of a calculated amount of hydrophilic thiol derivatives (e.g., 1,2-mercaptopropanediol, MPD) into the water subphase led to ligand-exchange reactions that were confined to the bottom face of the nanoparticles and, hence, to the production of Janus nanoparticles. In the second method, the nanoparticle monolayer was first transferred onto a glass slide by the Langmuir–Blodgett (LB) method and then was immersed into a water (or ethanolic) solution containing the hydrophilic thiol ligands (e.g., 2-(2-mercaptopethoxy)ethanol, MEA). As the nanoparticles were tightly arranged on the substrate surface, ligand-exchange reactions were limited to the top side of the nanoparticles, resulting in asymmetrical functionalization of the nanoparticles. The amphiphilic nature of these nanoparticles was then examined by contact angle, adhesion force microscopy, nuclear Overhauser enhancement spectroscopy (NOESY) NMR, and other spectroscopic measurements, and the particles were found to form stable superstructures in appropriate solvent media, similarly to conventional surfactant molecules, as manifested in dynamic light scattering, transmission electron microscopy, and atomic force microscopy studies.  

The asymmetrical surface chemistry has also been exploited for further chemical functionalization, as demonstrated by the preparation of Au-TiO$_2$ heterodimers that serve as an effective photocatalyst for the oxidation of methanol to formaldehyde.  

However, it has been well-known that thiol molecules exhibit rather apparent lateral diffusion on gold surfaces even at ambient temperature, which might be driven entropically, as manifested in the diminishment of domain segregation between thiol
ligands with different functional moieties.\textsuperscript{11,12} In fact, the Janus nanoparticles prepared above appeared to lose the amphiphilic characters after an extended period of time in solution, with the final structure similar to that of the particles that underwent ligand-exchange reactions in a solution (rather than at an interface) with the same hydrophilic ligands (the so-called bulk-exchange particles).\textsuperscript{8} This indicates that a rather homogeneous mixing was reached eventually between the hydrophobic and hydrophilic ligands on the Janus nanoparticle surface, most probably as a consequence of ligand lateral diffusion on the nanoparticle surface (additional contribution may arise from ligand hopping between particles\textsuperscript{12}). Such an observation presents a great challenge in the further functionalization and utilization of the Janus nanoparticles. Thus, it becomes imperative to develop effective protocols to enhance the structural integrity of the Janus nanoparticles, one of which is to covalently cross-link the nanoparticle surface ligands. This is the primary motivation of the present study.

Herein, using the protocols that we developed earlier,\textsuperscript{7-10} we prepared Janus nanoparticles with 1-hexanethiolates on the hydrophobic side and with 3,5-octadiyne-1-ol-8-thiol (DAT) as the hydrophilic ligands, where photopolymerization of the diacetylene moieties was exploited for covalent cross-linking between the surface ligands and, hence, for enhanced structural stability of the Janus nanoparticles. It has been demonstrated that polymerization of diacetylene derivatives has to abide by topochemical principles.\textsuperscript{13-15} In fact, effective photopolymerization has been observed with mercapto derivatives of diacetylene self-assembled on gold surfaces, regardless
of the vertical position of the diacetylene moieties within the molecular backbones.\textsuperscript{16} On gold nanoparticle surfaces, apparent photopolymerization also occurs; yet, the polydiacetylene phase (or the degree of polymerization) has been found to depend critically on the particle core size as well as on the exact location of the diacetylene moieties within the ligand structures, most probably because of the nanoscale curvatures of the metal cores and the resulting diminishment of ligand-packing density along the radial direction.\textsuperscript{17}

In the present study, we demonstrated that the diacetylene moieties on the Janus nanoparticles could also be effectively photopolymerized and that the extent of polymerization was markedly greater than that observed with the bulk-exchange counterparts at similar diacetylene surface concentration, leading to marked enhancement of the Janus nanoparticle structural integrity.

\textbf{3.2 Results and Discussion}

To confirm the amphiphilic character of the resulting Janus nanoparticles, the contact angle of the nanoparticle monolayers was monitored at different immersion time intervals (step ii). The result is depicted in Figure 3.1. It can be seen that prior to the immersion of the nanoparticle monolayers into the DAT solution (i.e., at $t = 0$ h), the contact angle of the AuC6 nanoparticle film was $63.4^\circ \pm 0.8^\circ$, and it decreased slightly to $62.2^\circ \pm 0.7^\circ$ after one hour of exchange reactions. Further immersion led to a more rapid decrease of the contact angle, and at $t = 4$ h, it dropped drastically to $53.6^\circ \pm 1.2^\circ$. Yet, it remained statistically invariant thereafter ($52.8^\circ \pm 1.4^\circ$ at 8.5 h). The observed evolution of the contact angle of the nanoparticle LB monolayers with
immersion time might be accounted for by the nanocrystalline morphology of the nanoparticles, where ligand place exchange reactions on alkanethiolate-protected gold nanoparticles presumably start with the surface defect sites (e.g., edges and vertices) and then propagate to the terrace sites.\textsuperscript{18-20} That is, the small decrease of contact angle within the first hour is likely a consequence of the initial phase of exchange reactions involving surface defects, whereas the more significant drop of contact angles at 4 h arises from the incorporation of hydrophilic DAT ligands onto the more populous terrace sites on the particle surface. The almost constant contact angle after 4 h seems to suggest that the exchange reaction has reached an equilibrium. Similar behaviors were observed previously with 2-(2-mercaptoethoxy)ethanol (MEA) as the hydrophilic ligands.\textsuperscript{8}

The contact angles of the self-assembled monolayers of C6SH and DAT on flat gold thin film surfaces were 62.8° ± 0.9° and 52.6° ± 1.0°, respectively (Table 3.1). These are very consistent with those observed with the original AuC6 nanoparticles ($t = 0$ h) and the Janus nanoparticles ($t = 8.5$ h) as depicted in Figure 3.1, again supporting the notion that the top face of the nanoparticle monolayers indeed underwent effective ligand-exchange reactions. In addition, experimentally, we observed no loss of nanoparticles into the ethanol solution during the entire experimental procedure, which implies that not all the original hydrophobic ligands (hexanethiolates) were replaced by the hydrophilic DAT ligands. This may be
Figure 3.1. Contact angles of a Langmuir-Blodgett monolayer of AuC6 nanoparticles after being immersed in 1 mM DAT in ethanol at room temperature for different periods of time.
Table 3.1. DAT Coverage on the Nanoparticle Surface and Contact Angles of Janus and BE Nanoparticles and of Self-Assembled

<table>
<thead>
<tr>
<th>Sample</th>
<th>DAT Coverage (%)</th>
<th>Contact Angle</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>AuC6/Janus nanoparticles</strong></td>
<td>51.86&lt;sup&gt;a&lt;/sup&gt;</td>
<td>63.4° ± 0.8° (0h) 52.8° ± 1.4° (8.5 h)</td>
</tr>
<tr>
<td><strong>BE-1 nanoparticles</strong></td>
<td>24.40</td>
<td>60.1°±1.0°</td>
</tr>
<tr>
<td><strong>BE-2 nanoparticles</strong></td>
<td>57.20</td>
<td>58.0°±0.9°</td>
</tr>
<tr>
<td><strong>BE-3 nanoparticles</strong></td>
<td>73.21</td>
<td>55.3°±1.4°</td>
</tr>
<tr>
<td><strong>C6 SAM</strong></td>
<td></td>
<td>62.8°±0.9°</td>
</tr>
<tr>
<td><strong>DAT SAM</strong></td>
<td></td>
<td>52.6°±1.0°</td>
</tr>
<tr>
<td><strong>C6-DAT (1:1) mixed SAM</strong></td>
<td></td>
<td>57.3°±1.3°</td>
</tr>
</tbody>
</table>

<sup>a</sup> Obtained from the samples collected after 8.5 h of exchange reactions (Figure 3.1).

Ascribed to the inaccessibility of the bottom face of the nanoparticles by the DAT ligands because of ligand intercalation, which impeded interfacial mobility of the nanoparticles on the substrate surface and, hence, led to the formation of asymmetrically functionalized nanoparticles.<sup>8</sup>

Further control experiments were carried out with the BE nanoparticles. As manifested previously, the DAT ligands were anticipated to be incorporated rather homogeneously onto the particle surface during bulk-exchange reactions, and thus, the contact angles of the BE particle monolayers should be in the intermediate range between those observed with Janus nanoparticles and those of the original AuC6 nanoparticles and decreased with increasing DAT coverage. In fact, the contact angles were 60.1° ± 1.0°, 58.0° ± 0.9°, and 55.3° ± 1.4° for the LB monolayers of BE-1, BE-2, and BE-3 nanoparticles, respectively (Table 3.1). Notably, for BE-2 that
exhibited a DAT coverage of 57.20%, the contact angle was similar to that observed with a mixed self-assembled monolayer (SAM) of C6SH and DAT (molar ratio 1:1) on a gold film surface, 57.3° ± 1.3°, indeed suggestive of a homogeneous mixing of the ligands on the BE nanoparticle surfaces.

The amphiphilic structure of the Janus nanoparticles was further manifested in the formation of stable nanoparticle superstructures in selected solvent media, as examined by dynamic light scattering (DLS) measurements, in comparison with the bulk-exchange counterparts. lists the size of the aggregates of the Janus and BE nanoparticles in different solvents. It can be seen that the Janus nanoparticles formed stable aggregates when dispersed in THF, with the average radius of the aggregates at 327.0 nm. With the addition of an equal amount of water into the THF solution, the size of the aggregates increased to 404.0 nm; when THF was removed from the solution by nitrogen bubbling, the aggregates shrank somewhat to 312.0 nm. These observations suggest that stable aggregates of Janus nanoparticles were formed in these three solvent media of different polarity, most likely because of the amphiphilic character of the nanoparticle surface that rendered it energetically favorable for the nanoparticles to form (reverse-)micelle-like superstructures.

Table 3.2. Average Size of Particle Aggregates in Different Solvents by DLS Measurements

<table>
<thead>
<tr>
<th>Solvent</th>
<th>Janus particles (nm)</th>
<th>BE-1 particles (nm)</th>
<th>BE-2 particles (nm)</th>
<th>BE-3 particles (nm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>THF</td>
<td>327.0</td>
<td>8.4</td>
<td>98.0</td>
<td>95.4</td>
</tr>
<tr>
<td>THF/H2O (50: 50)</td>
<td>404.0</td>
<td>58.7</td>
<td>6.8</td>
<td>47.4</td>
</tr>
<tr>
<td>H2O</td>
<td>312.0</td>
<td>105.0</td>
<td>115.0</td>
<td>96.1</td>
</tr>
</tbody>
</table>
The behaviors were drastically different with the BE nanoparticles. When dispersed in THF, BE-1 nanoparticles exhibited a very low degree of aggregation with the average radius of the aggregates at 8.4 nm (the physical diameter of the nanoparticles, gold core plus two fully extended ligands, is about 6.5 nm), most probably because the low concentration of DAT on the nanoparticle surface rendered the particles soluble in relatively apolar organic solvents, whereas for BE-2 and BE-3 nanoparticles that exhibited a higher concentration of DAT on the nanoparticle surface, the aggregates were much larger at 98.0 and 95.4 nm, respectively. However, in a THF/water mixture (1:1 v: v), the BE-2 nanoparticles behaved as individual nanoparticles with the measured size of 6.8 nm, whereas BE-1 and BE-3 nanoparticles were found to form aggregates of 58.7 and 47.4 nm, respectively. This seems to suggest that the polarity of the mixed solvent media was compatible with that of the BE-2 nanoparticles that featured a mixed monolayer of approximately 1:1 ratio between the hydrophobic and the hydrophilic ligands. In pure water, however, the three BE nanoparticles formed aggregates with sizes all close to 100 nm.

One can see that in any of the solvent media under study, the Janus nanoparticles were able to form much larger stable aggregates, and the size of the aggregates only fluctuated slightly with the polarity of the solvents. This is, again, most probably attributable to the amphiphilic nature of the particles that rendered it energetically favorable to arrange the particles in response to the solvent media, analogously to conventional surfactant molecules that have been found to form micelles or reverse-micelles depending on the solvent polarity. Such responsive
Figure 3.2. UV-vis spectra of (A) BE-1, (B) BE-2, (C) BE-3, and (D) Janus nanoparticles before (black) and after (red) UV exposure. The particle concentrations were all ca. 0.5 mg/mL in THF. The absorption spectrum of monomeric DAT in THF was also included (blue curve in panel C).
arrangements of the nanoparticles cannot be achieved with bulk-exchange nanoparticles where the hydrophilic and hydrophobic ligands were mixed rather homogeneously on the entire nanoparticle surface.

The incorporation of the DAT ligands onto the nanoparticle surface rendered the nanoparticles photoactive. Yet, because of the drastic difference in the way the DAT ligands were distributed on the Janus and BE nanoparticle surfaces, there was substantial discrepancy in the resulting optical characteristics. In UV–vis absorption measurements, as depicted in the black curves of Figure 3.2, both Janus (panel D) and BE (panels A–C) nanoparticles exhibited an exponential decay response with a small and broad peak at ca. 520 nm that was characteristic of the surface plasmon resonance of nanosized gold particles.\textsuperscript{21-23} Additionally, a small absorption band appeared at around 280 nm, which is consistent with the absorption profile of monomeric DAT ligands (blue curve in panel C). In fact, the peak became increasingly apparent with increasing DAT coverage on the nanoparticle surface (from BE-1 to BE-3 nanoparticles) as shown in panels A–C.
Scheme 3.3. Photopolymerization of the Diacetylene Moieties of the Janus Nanoparticles (Not to Scale; Actual Extent of Polymerization Varies)
UV irradiation ($\lambda = 254$ nm) was then exploited to initiate covalent cross-linking of the diacetylene moieties between neighboring particle-bound ligands (Scheme 3.3), and the UV–vis absorption spectra were shown as the respective red curves in the figure. One can see that a fairly broad and yet well-defined peak now started to emerge within the range of 280 and 350 nm, which most probably arose from the resulting oligomers of the diacetylene moieties. Furthermore, the intensity of this peak actually increases with increasing DAT coverage on the nanoparticle surface (from BE-1 to BE-3 nanoparticles in panels A–C). Interestingly, the peak intensity of the Janus nanoparticles appeared to be the greatest (panel D), although the DAT coverage was only comparable to that on BE-2 nanoparticles, implying that the efficiency of covalent cross-linking between the diacetylene moieties on the Janus nanoparticles was much greater than that on the BE nanoparticles, most probably as a result of the close proximity between the DAT ligands. 

In contrast, in the longer wavelength region, the absorption profiles were essentially the same as those before UV exposure (black curves). In previous studies, it has been shown that the carbon backbone of fully conjugated polydiacetylene (PDA) is planar, and the lowest energy optical transition ($\pi-\pi^*$) is located at about 620 nm. However, distortion of the conjugated carbon backbone because of disorder or strain may reduce the extent of orbital overlap and, hence, the average conjugation length. Therefore, the $\pi-\pi^*$ transition might shift to a higher energy (≈...
Figure 3.3. (A) Excitation and emission spectra of Janus (black curves) and BE-1 (red curves) nanoparticles before UV irradiation. (B) Excitation and emission spectra of Janus and BE nanoparticles after UV irradiation: Janus, black curves; BE-1, green curves; BE-2, red curves; and BE-3, blue curves. Solid (—) curves were collected at $\lambda_{ex} = 360$ nm and $\lambda_{em} = 420$ nm, dotted (…) curves were collected at $\lambda_{ex} = 401$ nm and $\lambda_{em} = 445$ nm, and dashed (---) curves were collected at $\lambda_{ex} = 430$ nm and $\lambda_{em} = 485$ nm. The particle concentrations were all ca. 0.5 mg/mL in THF.
540 nm) and render the polymer to appear red. For the Janus and BE nanoparticles in the present study, only a small number of DAT ligands on the spherical surface of the gold cores are likely to satisfy the stringent topological requirements for polymerization. Thus, it is most probable that the red-form absorption would dominate. This frequency happens to coincide with the surface plasmon absorption of the gold nanoparticles and, hence, becomes difficult to be distinguishable. Similar behaviors have been observed previously. For instance, Kanaras and Bartczak prepared gold nanoparticles (diameter 15.0 and 3.25 nm) stabilized by a full monolayer of thiol ligands with a diacetylene-oligo(ethylene glycol) conjugate. Photopolymerization of the diacetylene moieties produced no apparent variation of the corresponding UV-vis absorption profiles (except for a slight sharpness of the nanoparticle surface plasmon resonance).

Notably, both the Janus and the BE nanoparticles exhibited apparent fluorescence that was characteristic of polymerized diacetylene moieties, although the extent of polymerization on the Janus nanoparticles differed markedly from that on the BE nanoparticles, as the oligomers of diacetylene have been known to exhibit distinctly different fluorescence emissions depending on the conjugation length. Prior to UV exposure, both the Janus and the BE nanoparticles in solutions showed only one emission peak at $\lambda_{em} = 419$ nm when excited at $\lambda_{ex} = 366$ nm (solid curves); excitation at other wavelength positions did not lead to any apparent emission (dotted and dashed curves), as depicted in Figure 3.3A. This is characteristic of the fluorescence of monomeric diacetylene moieties. Interestingly, after exposure to UV
light (λ = 254 nm) for 30 min, besides the emission at \( \lambda_{em} = 419 \) nm (solid black curves), the solution of the Janus nanoparticles showed two additional well-defined emissions at longer wavelength positions, \( \lambda_{em} = 445 \) nm (when excited at \( \lambda_{ex} = 401 \) nm, dotted black curves) and \( \lambda_{em} = 484 \) nm (at \( \lambda_{ex} = 430 \) nm, dashed black curves), as shown in Figure 3.3B. These fluorescence characteristics are very analogous to those observed with monomers, dimers, and trimers of the diacetylene moieties in two-dimensional self-assembled monolayer of diacetylene derivatives.\(^{28}\) This suggests that a mixture of monomers, dimers, and trimers was produced after the Janus nanoparticles were exposed to UV irradiation. In contrast, no trimers of the diacetylene moieties were found when the BE nanoparticles were exposed to the same UV irradiation, and the fluorescence emission could only be ascribed to monomers and dimers. For instance, after UV exposure, BE-1 nanoparticles exhibited two emissions at \( \lambda_{em} = 419 \) nm (monomers, solid green curves) and 445 nm (dimers, dotted green curves), and no trimer emission was observed at 484 nm (dashed green curves). For BE-2 nanoparticles where the surface coverage of DAT ligands increased to 57.20%, the intensity of the dimer emission increased slightly while the trimer emission was still absent (red curves). With a further increase of the DAT surface coverage to 73.21% (BE-3 nanoparticles, blue curves), the dimer emission exhibited a further enhancement, and the trimer emission (\( \lambda_{em} = 484 \) nm) now started to emerge.

The discrepancy observed above between the fluorescence characteristics of the Janus and BE nanoparticles may be ascribed to the difference of the DAT ligand distributions on the nanoparticle surface. For the Janus nanoparticles, the DAT
ligands were concentrated on one hemisphere of the nanoparticles, and the close proximity between the ligands rendered it likely for the ligands to meet the topochemical principles for photopolymerization (Scheme 3.3). Consequently, formation of dimers and trimers was apparent as manifested by their characteristic emission profiles. For BE nanoparticles, however, the DAT ligands were mixed rather homogeneously with the hexanethiolate ligands on the entire nanoparticle surface. Therefore, the surface dilution rendered it difficult to have a large number of DAT ligands that were situated in close proximity. As a result, only dimers were produced, and higher orders of oligomers were formed only at significantly higher DAT surface coverage.

Importantly, the photoinduced cross-linking between the diacetylene moieties of neighboring DAT ligands led to marked enhancement of the structural integrity of the Janus nanoparticles. As mentioned earlier, mercapto derivatives on gold surfaces exhibit apparent surface diffusion even at ambient temperature. Therefore, the two types of ligands that were initially segregated on the Janus nanoparticle surface eventually became mixed rather homogeneously, analogous to the structure of BE nanoparticles. Yet, covalent cross-linking between the nanoparticle surface ligands is anticipated to help maintain the asymmetrical surface structure of the Janus nanoparticles. The hypothesis was proved by fluorescence measurements shown in Figure 3.4. It can be seen that for the Janus nanoparticles that had been subject to UV irradiation, after 30 days the three emission peaks remained well-defined at 419, 445, and 484 nm (black curves), and the relative intensity was virtually unchanged as
Figure 3.4. Excitation and emission spectra of Janus nanoparticles: black curves are the spectra collected where the nanoparticles were subject to UV irradiation and then were aged for 30 days, and red curves are those for the Janus nanoparticles that were aged for 30 days and then were exposed to UV lights. Solid (—) curves were collected at $\lambda_{\text{ex}} = 360$ nm and $\lambda_{\text{em}} = 420$ nm, dotted (···) curves were collected at $\lambda_{\text{ex}} = 401$ nm and $\lambda_{\text{em}} = 445$ nm, and dashed (---) curves were collected at $\lambda_{\text{ex}} = 430$ nm and $\lambda_{\text{em}} = 485$ nm. The particle concentration was ca. 0.5 mg/mL in THF.
compared to those before aging (Figure 3.3). In sharp contrast, when the Janus nanoparticles were first aged in solution at ambient temperature for 30 days and then were subject to UV irradiation, the intensity of the trimer emission was found to be minimal (red curves in Figure 3.4), and the overall fluorescence profiles became similar to those of BE nanoparticles (Figure 3.3), suggesting a structural evolution that most probably arose from the slow but apparent surface diffusion of monomeric thiol ligands on the nanoparticle surface.

3.3 Conclusion

In this study, Janus nanoparticles were prepared by taking advantage of the interfacial ligand-exchange reactions of hexanethiolate-protected gold nanoparticles with a mercapto derivative of diacetylene (with a terminal hydroxyl functional group). $^1$H NMR measurements showed that the protecting shell of the resulting nanoparticles consisted of ca. 50% hydrophobic hexanethiolates and 50% hydrophilic DAT ligands. Contact angle studies indicated that these two types of ligands were segregated on the two hemispheres of the nanoparticle surface, in contrast to the bulk-exchange counterparts. Consequently, the Janus nanoparticles behaved analogously to conventional surfactant molecules and could form stable superstructures in solvent media of varied polarity, as revealed in dynamic light scattering measurements. Importantly, because of the close proximity of the diacetylene moieties on the Janus nanoparticle surfaces, exposure to UV irradiation led to effective covalent cross-linking between neighboring ligands, as manifested by the unique fluorescence characteristics of diacetylene dimers and trimers, in sharp contrast to bulk-exchange
nanoparticles where the extent of ligand cross-linking was much limited as dictated by the topochemical principles for diacetylene polymerization. The cross-linking between the surface ligands also led to marked enhancement of the structural integrity of the Janus nanoparticles, as compared to unpolymerized Janus nanoparticles. This is critical in the further chemical functionalization and utilization of Janus nanoparticles.
3.4 References


Chapter 4

AgAu Bimetallic Janus Nanoparticles and Their Electrocatalytic Activity for Oxygen Reduction in Alkaline Media

4.1 Introduction

Janus nanoparticles with two distinctly different chemical hemispheres represent a new class of nanomaterials that behave analogously to conventional surfactants and may be exploited for controlled assembly as well as directional functionalization.\textsuperscript{1,2} Whereas the majority of research has thus far been focused on polymer-based Janus particles that may be up to the micrometer scale,\textsuperscript{3-7} recently several effective strategies have been developed in our laboratory for the preparation of much smaller, nanometer-sized transition-metal Janus particles with hydrophobic characters on one face and hydrophilic on the other.\textsuperscript{8,9} In these studies, alkanethiolate-passivated nanoparticles are used as the initial starting materials. A compact monolayer is then formed at the air\textendash{}water interface or deposited onto a solid substrate surface by the Langmuir methods, and ligand exchange reactions with hydrophilic mercapto derivatives in the water subphase or in a solution medium are initiated for the replacement of the original hydrophobic ligands by the hydrophilic ones on one side of the nanoparticles, leading to the generation of amphiphilic Janus nanoparticles. It should be noted that in these earlier studies,\textsuperscript{8,9} the metal cores remain unchanged. Thus, an immediate question arises. Is it possible to concurrently convert the monometallic cores into bimetallic ones with also an asymmetrical distribution of the metal elements? This is the primary motivation of the present study.

One may note that bimetallic nanoparticles are typically prepared by using two metal precursors that are reduced simultaneously forming bimetallic alloy cores. Of these, monolayer-protected alloy clusters are early examples of bimetallic
nanoparticles that can be stably isolated in dry form. The metal compositions in and on the core surface may differ significantly from the initial feed ratio of metal salts used in nanoparticle synthesis. Another common procedure involves the deposition of a second metal onto the surface of preformed nanoparticles and hence the production of core–shell nanoparticles where the thickness of the second metal layer in principle may be controlled by varied experimental parameters. Alternatively, galvanic exchange reactions have also been used to (partly or fully) replace the metal elements of the original nanoparticles forming new functional nanostructures of controlled metal compositions. Such reactions have, for example, been employed to replace Cu or Ag particles encapsulated in dendrimers by more noble metals (e.g., Au, Pt, and Pd) and to prepare bi- and trimetallic nanoparticles. Galvanic displacement reactions have also been used to prepare the bimetallic sulfides of PbCd and ZnCd, CoPt core–shell bimetallic nanoparticles, AuAg, PdAg, AuPd, and AuCu bimetallic alloy nanoparticles, etc. This is to take advantage of the different redox potentials of varied metal/ion couples where ions of more noble metals may be reduced by the less noble metal elements. It should be noted that in these early reports the two metal elements are presumed to be distributed homogeneously within the nanoparticles as the reactions take place in a single solution phase. Importantly, the introduction of a new metal element in the cores leads to an apparent variation of both the physical and chemical properties of the resulting nanoparticles, which may be exploited, for instance, for optical, electronic, as well as (electro)catalytic applications. In fact,
a number of catalysts for fuel cell electrochemistry are based on bimetallic nanoparticles.

It should be noted that fuel cells have been recognized as a promising clean and efficient power source for diverse applications. Of these, alkaline fuel cells (AFCs) have gained a great deal of attention because alkaline media provide a less corrosive environment to the catalysts and electrodes,\textsuperscript{20} the kinetics of oxygen reduction reactions (ORR) is more rapid in alkaline electrolytes than in acidic ones, and the chemical energy stored in small molecule fuels (such as hydrogen, hydrazine, and alcohols)\textsuperscript{21,22} and oxidants (oxygen) can be directly and efficiently converted into electricity, rendering AFCs a promising power supply for portable electronics. In AFCs, Ag-based catalysts have been examined as a substitute of Pt because of their obviously low costs and high stability in alkaline media; yet, typically a large amount of silver is required because of its relatively low catalytic activity. In recent years, a number of strategies have been proposed and employed to improve the ORR activity of Ag nanoparticles that typically involve manipulation of the elemental composition, size, and surface atomic arrangements of the nanoparticle catalysts. Among these, Ag-based alloy catalysts show significantly enhanced ORR activity as compared with pure Ag.\textsuperscript{23,24}

In the present study, we take advantage of the Langmuir methods as well as galvanic exchange reactions to prepare bimetallic nanosized AgAu Janus particles. Specifically, 1-hexanethiolate-passivated silver (AgC6) nanoparticles were used as the starting materials. A monolayer was deposited onto a glass slide surface by the
Langmuir–Blodgett method, which was then immersed into a solution of gold(I)-mercaptopropanediol (Au\(^1\)MPD) complex. Galvanic exchange reactions between the AgC6 nanoparticles and Au\(^1\)MPD led to the displacement of part of the Ag atoms on the nanoparticle cores with Au and concurrently the replacement of the original hydrophobic hexanethiolates with the more hydrophilic MPD ligands. Note that the reactions were restricted to the side of the nanoparticles that was in direct contact with the solution because of surface ligand intercalation between neighboring particles that impeded the accessibility of the bottom face to the solution ligands. The asymmetrical chemical structures of the resulting nanoparticles were characterized by a variety of spectroscopic measurements. Interestingly, the bimetallic Janus nanoparticles exhibited enhanced electrocatalytic activity in ORR as compared with the original monometallic Ag nanoparticles or the bimetallic nanoparticles that were prepared in a single phase (the so-called bulk-exchange particles), suggesting that interfacial engineering is key to the manipulation and optimization of the nanoparticle electronic properties and hence the interactions with oxygen and ultimately the ORR performance.

4.2 Results and Discussion

Previously it has been shown that galvanic exchange reactions of core metals occur when alkanethiolate-passivated metal nanoparticles mix with thiolate complexes of more noble metals in solution, forming bimetallic nanoparticles.\(^{16}\) Thus, the reactivity of AgC6 nanoparticles with Au\(^1\)MPD was first examined by UV-vis spectroscopic measurements, as the (partial) replacement of the Ag core atoms by Au
is anticipated to lead to a drastic variation of the nanoparticle optical properties. It is well-known that pure gold and silver nanoparticles exhibit distinctly defined surface plasmon resonance in the visible region at about 520 and 420 nm, respectively.\textsuperscript{25} In fact, for the as-prepared AgC6 nanoparticles, UV-vis spectroscopic measurements showed that the surface plasmon band was centered at 422 nm, as manifested by the black curve in Figure 4.1. Upon the addition of the Au\textsuperscript{1}MPD complex, core metal galvanic reactions occurred, and the surface plasmon band position was found to shift accordingly, for instance, to 442 nm after reactions for 5 h (red curve), 450 nm for 10 h (green curve), 467 nm for 20 h (dashed black/yellow curve), and 493 nm at 24 h (blue curve). Such a red-shift of the surface plasmon resonance is consistent with the fact that an increasing amount of Au was incorporated onto the silver core surface as the surface plasmon band position is sensitively dependent upon the elemental composition of the metal nanoparticles.\textsuperscript{26} Furthermore, the appearance of a single absorption band indicates that bimetallic nanoparticles are formed rather than a simple mixture of monometallic nanoparticles. Note that similar observations have been reported by Link et al. where they synthesized a series of gold–silver alloy nanoparticles and observed a linear blue-shift of the surface plasmon peak position with increasing silver content,\textsuperscript{27} by Mulvaney and co-workers where metallic Au was deposited onto Ag colloidal nanoparticle surfaces by chemical reduction,\textsuperscript{12} and by Shon et al. of galvanic exchange reactions between Ag nanoparticles and Au\textsuperscript{1} thiolate complexes.\textsuperscript{16}
Such unique chemistry was then exploited for the preparation of Janus nanoparticles with asymmetrical bimetallic cores by using an interfacial engineering procedure that we developed earlier (Scheme 1).\textsuperscript{9} Specifically, by confining the galvanic exchange reactions to only one face of the nanoparticles, it is envisaged that the resulting nanoparticles would exhibit not only a segregated distribution of the two metal elements in the core but also two faces of protecting ligands that are chemically different. As manifested in Scheme 1, a monolayer of AgC6 nanoparticles deposited onto a glass slide surface was immersed into a solution of Au\textsuperscript{I}MPD and the galvanic exchange reactions were limited to the top face of the nanoparticles, leading to the formation of Janus nanoparticles with bimetallic cores. To confirm the amphiphilic characters of the surface protecting layers of the resulting nanoparticles, the contact angle of the nanoparticle monolayers was monitored at different immersion time intervals (step ii). The result is depicted in Figure 4.2. It can be seen that, prior to the immersion of the nanoparticle monolayers into the Au\textsuperscript{I}MPD solution (i.e., at $t = 0$ h), the contact angle of the AgC6 nanoparticle film was $101.4 \pm 7.8^\circ$, which is consistent with those observed with self-assembled monolayers of alkanethiols on silver substrate surfaces.\textsuperscript{28,29} After 1 h of immersion, the contact angle decreased slightly to $98.2 \pm 6.1^\circ$. Further immersion led to a more rapid decrease of the contact angle, and at $t = 13$ h, it dropped drastically to $46.2 \pm 4.0^\circ$ and remained statistically invariant thereafter ($45.7 \pm 4.4^\circ$ at 30 h). Note that this contact angle is consistent with that of
Figure 4.1. UV–vis spectra of AgC6 nanoparticles after galvanic exchange reactions with Au\textsuperscript{1}MPD for varied periods of time (as specified in the figure legends). The spectrum of Janus nanoparticles was also included (magenta curve) where the nanoparticles were prepared by interfacial galvanic exchange reactions for 24 h. The concentrations of the particles were all ca. 0.5 mg/mL in THF.
MPD self-assembled monolayers on metal surfaces. These observations suggest the effective replacement of the original hydrophobic hexanethiolate ligands by the more hydrophilic MPD which reached equilibrium at around 13 h. Such a dynamic change of the contact angle of the nanoparticle monolayers with immersion time might be accounted for by the nanocrystalline morphology of the nanoparticles, where galvanic exchange reactions on alkanethiolate-protected silver nanoparticles presumably started with the surface defect sites (e.g., edges and vertices) and then propagated to the terrace sites. Similar behaviors have been observed previously in ligand exchange reactions of AuC₆ nanoparticles with 2-(2-mercaptoethoxy)-ethanol (MEA) and 3,5-octadiyne-1-ol-8-thiol (DAT) as the hydrophilic ligands. This indicates that while Au¹ was reduced into Au⁰ by the Ag core atoms, the MPD ligands were also incorporated into the nanoparticle surface protecting layer. In fact, the formation of bimetallic AuAg Janus nanoparticles was also manifested in UV–vis spectroscopic measurements with a broad absorption band at around 472 nm (magenta curve in Figure 4.1, for the sample prepared by reactions for 24 h) that is in the intermediate range between those of pure Ag and Au nanoparticles.

In addition, experimentally, we observed no loss of nanoparticles into the water/methanol solution during the entire experimental procedure, which indicates that the galvanic replacement reactions were limited only to the top face of the AgC₆ nanoparticles, as nanoparticles fully functionalized with the hydrophilic MPD ligands would have become dispersible in the reaction media of water/methanol mixed solvents. This may be ascribed to the inaccessibility of the bottom face of the
Figure 4.2. Contact angles of a Langmuir–Blodgett monolayer of AgC6 nanoparticles after being immersed in *ca.* 2.5 mg/mL Au\(^{1}\)MPD complex in methanol/water (v: v = 1: 1) at room temperature for different periods of time. Error bars reflect the standard deviations of at least eight independent measurements.
nanoparticles to the Au\textsuperscript{1}MPD complex because of ligand intercalation, which impeded interfacial mobility of the nanoparticles on the substrate surface and, hence, led to the formation of asymmetrically functionalized nanoparticles.

The bimetallic nature of the resulting nanoparticles was further manifested in scanning transmission electron microscopic measurements. Figure 4.3 depicts the representative high-resolution TEM micrographs of the (a) original AgC6, (b) bulk-exchange and (c) Janus nanoparticles. Note that the last two samples were prepared by galvanic exchange reactions of AgC6 nanoparticles with Au\textsuperscript{1}MPD for 24 h. It can be seen that the nanoparticles were all very well dispersed, indicating effective protection of the nanoparticles by the mercapto ligands before and after core metal galvanic exchange reactions. Also, the nanoparticle core size remained statistically unchanged. In fact, the average core diameter was found to be 5.70 ± 0.82, 5.79 ± 1.02, and 5.36 ± 0.85 nm, for the as-prepared AgC6, bulk-exchange, and Janus particles, respectively, as depicted in the right insets to Figure 4.3. Furthermore, the nanoparticles all exhibited well-defined crystalline lattice fringes, as highlighted in the left insets, with a spacing of 0.235 nm that may be ascribed to the (111) planes of both fcc silver\textsuperscript{31} and gold.\textsuperscript{32}

As bulk gold and silver exhibit very close lattice constants (0.408 and 0.409 nm, respectively), it is challenging to detect the distribution of Au on the Ag nanoparticle surface by their lattice fringes. This can be done, however, by elemental mapping based on energy-dispersive X-ray analysis (EDS). Figure 4.4 shows two
Figure 4.3. Representative TEM images of (a) AgC6 nanoparticles, (b) bulk-exchange, and (c) Janus nanoparticles. The last two samples were prepared by galvanic exchange reactions of AgC6 nanoparticles with Au^{1}MPD for 24 h. The scale bars are all 10 nm. Left insets show the corresponding high-resolution TEM micrographs with the scale bars of (a) 5 nm and (b and c) 2 nm. Right insets are the respective core size histograms.
representative elemental maps of a (a) Janus and (b) bulk-exchange nanoparticle, with the red symbols for silver and green for gold. It can be seen that for the Janus nanoparticles in panel (a) gold can be identified only on one side of the nanoparticles whereas the silver signals are distributed all over the nanoparticles. In sharp contrast, for the bulk-exchange nanoparticle in panel (b), both the Ag and Au elements are distributed rather homogeneously throughout the entire nanoparticle.

The incorporation of Au onto the Ag nanoparticles by galvanic exchange reactions was also manifested in XPS measurements. Figure 4.5 shows the XPS survey spectra of the (a) Ag 3d and (b) Au 4f regions for the Janus (bottom curves) and bulk-exchange (top curves) nanoparticles. The Ag 3d electrons can be readily identified at 368.00 and 374.10 eV for the bulk-exchange nanoparticles, whereas for the Janus counterparts, the binding energies blue-shifted slightly to 368.55 and 374.20 eV; meanwhile, a small red-shift was observed of the Au 4f electrons, which appeared at 84.20 and 88.15 eV for the bulk-exchange nanoparticles and 84.05 and 87.85 eV for the Janus nanoparticles. Note that these values (Table 4.1) are qualitatively comparable to those reported previously for AgAu bimetallic core–shell or alloy nanoparticles;\textsuperscript{9,33} and more interestingly, the increase (decrease) of the binding energies of the Ag 3d (Au 4f) electrons of the Janus nanoparticles, as compared to those of the bulk-exchange counterparts, suggests that (partial) charge transfer occurred from Ag to Au. While the detailed mechanism is not clear at this point, this appears to be facilitated by the asymmetrical distribution of Au on the
Figure 4.4. Representative false-color EDS elemental maps of a (a) Janus and (b) bulk-exchange nanoparticle with red symbols for Ag and green for Au. The samples are the same as those as in Figure 4.3.
nanoparticle surface, as well as by the segregated distribution of the polar MPD ligands from the apolar hexanethiolates in the Janus nanoparticles (and hence the formation of an apparent dipole) that stabilized the extra electron density on the gold sites; in contrast, the ligands were distributed rather homogeneously on the bulk-exchange nanoparticle surface and hence the nanoparticles carried zero dipole. Such a unique property of the Janus nanoparticles may be exploited for further improving the electrocatalytic activity of the nanoparticles in oxygen reduction, as manifested below.

Table 4.1. Binding Energies of the Ag 3d and Au 4f Electrons in Bulk-Exchange and Janus AgAu Nanoparticles and Their Au/Ag Atomic Ratios by XPS Measurements

<table>
<thead>
<tr>
<th></th>
<th>Ag 3d (eV)</th>
<th>Au 4f (eV)</th>
<th>Au/Ag atomic ratio</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Bulk-exchange</strong></td>
<td>368.00</td>
<td>374.10</td>
<td>1:16.3</td>
</tr>
<tr>
<td><strong>particles</strong></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td><strong>Janus</strong></td>
<td>368.55</td>
<td>374.20</td>
<td>1:21.9</td>
</tr>
<tr>
<td><strong>nanoparticles</strong></td>
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</table>

Furthermore, from the XPS measurements (Figure 4.5), the Au/Ag atomic ratio can be quantified. For Janus nanoparticle, the Au/Ag ratio was estimated to be 1:21.9, and a somewhat greater ratio was observed of the bulk-exchange particles at 1:16.3. Note that, based on the nanoparticle core diameters as determined by TEM measurements (Figure 4.3), the surface atoms constitute about 25% of the total atoms of the metal cores of these nanoparticles. This means that, in the preparation of the Janus nanoparticles, approximately 17% of the Ag atoms (and the associated hexanethiolate ligands) in the surface layer were replaced by Au (and MPD
Figure 4.5. XPS survey spectra of (a) Ag 3d and (b) Au 4f electrons for (bottom curves) Janus and (top curves) bulk exchange nanoparticles.
ligands), and 23% for the bulk-exchange nanoparticles. This change of the nanoparticle surface structures (and composition) is consistent with the UV-vis measurements in Figure 4.1 and the contact angles reported in Figure 4.2. Previously it was observed\textsuperscript{35} that, for an alkanethiol monolayer self-assembled on Au(111) thin films, the contact angle was about 112°, which decreased drastically to only 45° when 25% of the ligands were replaced by hydroxyl-terminated thiol molecules. In the present study, the contact angle was found to decrease from about 101° for a monolayer of the as-prepared AgC6 nanoparticles to 46° after galvanic exchange reactions with Au\textsuperscript{I}MPD for 24 h (forming the aforementioned Janus nanoparticles, Figure 4.2).

The nanoparticles prepared above were then used for the electrocatalytic reduction of oxygen, a critical reaction at fuel cell cathodes, and their activities were evaluated and compared. Note that from the experimental results presented above (Figure 4.4) it is likely that Au was deposited onto the Ag surface in the form of nanoscale clusters, which are anticipated to exhibit interesting (electro)catalytic activity, as evidenced in a series of previous studies.\textsuperscript{36,37} Experimentally, the AgC6 and AgAu bimetallic nanoparticles prepared above were loaded onto the glassy carbon disk of a rotating ring-disk electrode. The electrodes were first subject to repeated potential cycling within the potential range of +0.2 to +1.0 V in a nitrogen-saturated 0.1 M NaOH solution at a potential sweep rate of 100 mV/s, until steady voltammograms appeared, so as to expose part of the nanoparticle surfaces for
electrocatalytic reactions. The assessments of their electrocatalytic activities were then carried out in an oxygen-saturated 0.1 M NaOH solution.

Figure 4.6 depicts the RRDE voltammograms of the glassy-carbon disk electrode modified with a calculated amount of (a) AgC6, (b) bulk-exchange and (c) Janus nanoparticles in an oxygen-saturated 0.1 M NaOH solution at varied electrode rotation rates (from 400 to 2500 rpm). It can be seen that in all cases, at the disk electrode (solid curves) apparent cathodic currents started to emerge at potentials more negative than about ca. +0.8 V and reached a (quasi-)plateau at potentials more negative than +0.6 V. These observations were ascribed to the electroreduction of oxygen catalyzed by the respective nanoparticle catalysts. Note that the behaviors were rather consistent with those reported in the literature for Ag nanoparticles and single crystal electrodes,\textsuperscript{38,39} indicating the apparent ORR activity of the nanoparticles despite their organic capping layers. A more careful analysis shows that the onset potential of the oxygen reduction reactions actually varied with the nanoparticle catalysts, +0.792 V for the original AgC6 nanoparticles, and +0.809 V for the bulk-exchange AgAu nanoparticles, and +0.917 V for the Janus AgAu nanoparticles. This suggests that the electron-transfer kinetics of oxygen reduction was facilitated by the incorporation of a minimal amount of Au onto the Ag nanoparticle surface (Table 4.1), with the ORR activity increasing in the order of AgC6 < bulk-exchange < Janus AgAu nanoparticles.

In addition, the amounts of hydrogen peroxide generated during the oxygen reduction were quantified by collection experiments with the ring potential set at +1.4
Figure 4.6. RRDE voltammograms of a glassy-carbon disk-gold ring electrode with the disk modified with (a) as-prepared AgC6, (b) bulk-exchange, and (c) Janus nanoparticles in an oxygen-saturated 0.1 M NaOH solution. The metal loadings were (a) 2.38, (b) 2.44, and (c) 2.60 µg, as determined by thermogravimetric analysis. Electrode potential sweep rate was 10 mV/s, the ring potential was set at +1.4 V, and rotation rates were specified in the Figure legends.
V. From Figure 4.6, it can be seen that the ring currents (dashed curves) were all substantially smaller than those at the disk at all rotation rates, and decreased in the order of AgC6 < bulk-exchange < Janus nanoparticles. Importantly, from the ratio between the ring (I_R) and disk (I_D) currents, the number of electron transfer (n) in oxygen reduction can be estimated by \( n = 4I_D/(I_D + (I_R/N)) \).\(^{40}\) For instance, at 2500 rpm, the n values for the three nanoparticle catalysts were estimated to be 2.46 ± 0.02 for AgC6, 3.15 ± 0.10 for the bulk-exchange, and 3.36 ± 0.03 for the Janus nanoparticles within the potential range of +0.2 to +0.6 V. This indicates that oxygen was more likely to undergo four-electron reduction to OH\(^-\) with the bimetallic AgAu nanoparticles, whereas with monometallic AgC6 the final products appeared to be dominated by hydrogen peroxide.\(^{24,38,41-44}\) The latter is drastically different from the results observed in a previous study with adenosine 5’-triphosphosphate(ATP)-capped Ag nanoparticles,\(^{38}\) where oxygen were found to undergo four-electron reduction. This discrepancy most probably arose from the different chemical environments on the Ag nanoparticle surfaces. In the present study, the Ag cores remained partly passivated by hydrophobic hexanethiolate ligands, even after an electrochemical activation procedure as described above. This impedes the accessibility of the Ag surface by the reaction intermediates of oxygen reduction as well as electrolyte counterions. By contrast, the hydrophilic ATP ligands might be effectively removed from the nanoparticle surface rendering it readily accessible and thus facilitating the oxygen reduction reactions.\(^{38}\)
The electron-transfer kinetics was further analyzed by the Koutecky–Levich plots (Eq. 1a), as the disk voltammetric currents ($I_D$) may involve both kinetic ($I_k$) and diffusion ($I_d$) controlled contributions

$$\frac{1}{I} = \frac{1}{I_k} + \frac{1}{I_D} = \frac{1}{I_k} + \frac{1}{B\omega^{1/2}}$$  \hspace{1cm} (1a)

$$B = 0.62nFA\text{DO}^{2/3}\nu^{-1/6}$$  \hspace{1cm} (1b)

$$I_K = nAFkC_O$$  \hspace{1cm} (1c)

where $F$ is the Faradaic constant (96500 C/mol), DO is the diffusion coefficient of O$_2$ in 0.1 M NaOH aqueous solution ($1.93 \times 10^{-5}$ cm$^2$/s), $\nu$ is the kinematic viscosity of the solution ($1.09 \times 10^{-2}$ cm$^2$/s), CO is the oxygen concentration in O$_2$-saturated solutions ($1.26 \times 10^{-6}$ mol/cm$^3$), $\omega$ is the electrode rotation rate, $k$ is the electron-transfer rate constant, and $A$ is the geometric surface area of the electrode.\textsuperscript{45-47} Figure 4.7 shows the corresponding Koutecky–Levich plots ($I_D^{-1}$ vs. $\omega^{-1/2}$) for the three nanoparticle catalysts within the potential range of +0.58 to +0.82 V where kinetic contributions were significant. It can be seen that all experimental data exhibited good linearity and the slopes were rather consistent in each nanoparticle sample within the corresponding potential range. This observation is usually taken as a strong indication of a first-order reaction with respect to dissolved O$_2$.

Additionally, from the linear regressions in Figure 4.7, the kinetic currents ($I_k$) could also be estimated from the y-axis intercepts (Eq. 1c). This is manifested in the Tafel plot of Figure 4.8, where one can see that at all nanoparticle catalysts, the kinetic currents increased with increasingly negative electrode potentials, and more
Figure 4.7. Koutecky–Levich plots of (a) as-prepared AgC6, (b) bulk-exchange, and (c) Janus nanoparticles in oxygen reduction in an oxygen-saturated 0.1 M NaOH solution. Symbols are experimental data acquired from Figure 4.6, and lines are the corresponding linear regressions.
importantly, at all electrode potentials (from +0.58 to +0.82 V), the kinetic current increased by the order of AgC6 < bulk-exchange < Janus nanoparticles. For instance, the area-specific kinetic current density (J_s, I_k normalized by the disk geometrical area) at +0.68 V can be estimated to be 5.68 A/m^2 for AgC6, 8.75 A/m^2 for the bulk-exchange particles, and 40.64 A/m^2 for the Janus nanoparticles. It can be seen that whereas the current density of the bulk-exchange nanoparticles was only about 50% higher than that of AgC6, the activity of the Janus nanoparticles was more than seven times higher. Note that in a previous study with adenosine 5’-triphosphate capped-Ag nanoparticles (diameter 4.5 nm) or bulk polycrystalline silver,^38 the kinetic current density at similar potentials was 30 to 50 A/m^2.

Similar behaviors can be seen with the mass-specific kinetic current density (J_m, I_k normalized by the metal loading of the corresponding nanoparticles, Figure 4.8), as for practical applications, mass-specific activity is also an important parameter in the quantitative evaluation of the performance of precious metal catalysts. From Figure 4.8, the values of J_m at +0.68 V for the three nanoparticle catalysts can be found at 59.0 (AgC6), 88.6 (bulk-exchange nanoparticles), and 386.4 A/g (Janus nanoparticles), respectively. One can see that, in comparison with the original AgC6 nanoparticles, bulk-exchange AgAu nanoparticles again showed an activity that was 50% higher, and the Janus nanoparticles exhibited an even higher activity that was more than six times that of AgC6. This once again suggests that the Janus nanoparticles, despite a minimal loading of Au on the nanoparticle surface, represent the best catalysts within the present experimental context.
Figure 4.8. Variation of mass-specific kinetic current densities at varied electrode potentials. Solid symbols are experimental data obtained from the y-axis intercepts of the linear regressions in Figure 4.7, and lines are for eye-guiding only.
Figure 4.9. Tafel plots of the area-specific kinetic current densities at varied electrode potentials. Solid symbols are experimental data obtained from the y-axis intercepts of the linear regressions in Figure 4.7, and lines are for eye-guiding only.
Furthermore, it can be seen from Figure 4.9 that the Tafel plots of the three nanoparticle catalysts exhibit two linear segments of different slopes. At low current densities ($J_s < 20 \text{ A/m}^2$), linear regressions show that the slopes are 85.6 mV/dec for AgC6, 84.3 mV/dec for bulk-exchange nanoparticles, and 116.8 mV/dec for Janus nanoparticles; whereas at current densities $>20 \text{ A/m}^2$, the respective slope increases to 154.0, 130.4, and 263.4 mV/dec. Note that for oxygen electroreduction at nanoparticle catalyst surfaces, the Tafel slopes are typically found at 60 or 120 mV/dec, where the former corresponds to a pseudo two-electron reaction as the rate determining step and in the latter, the rate determining step is presumed to be the first-electron reduction of oxygen.\textsuperscript{51} The results from Figure 4.9 suggest that the reduction mechanism is similar for the AgC6 and bulk-exchange nanoparticles where the reactions were limited largely by a pseudo two-electron reduction reaction at low current densities and at high current densities the first electron transfer of oxygen was the rate-determining step (implying that subsequent reduction and O-O bond breaking was facile). Such a behavior has been observed with a pure Pt surface.\textsuperscript{51} By contrast, for the Janus nanoparticles, the oxygen reduction reactions were primarily determined by the first electron-transfer reaction of oxygen at low current densities; whereas at high current densities the Tafel slope (263.4 mV/dec) exhibited a rather large deviation from 120 mV/dec. Similar results were reported previously. For instance, in a previous study Ye and Crooks\textsuperscript{52} examined the electrocatalytic activity of dendrimer-capped Pt and PtPd alloy nanoparticles in oxygen reduction and observed Tafel slopes around 160 mV/dec at high overpotentials. These observations suggest that the adsorption of
oxygen and reaction intermediates played an increasingly important role in determining the electron-transfer dynamics of oxygen reduction reactions, as the kinetics of the reduction of adsorbed oxygen and cleavage of O-O bonds was enhanced at increasingly negative electrode potentials. These behaviors are consistent with the mechanism of oxygen reduction in alkaline media, as detailed below.

In previous studies of oxygen electroreduction on Ag in alkaline media, the reaction mechanism was found to be similar to that on Pt. The key steps may be summarized below

\[
\begin{align*}
O_2 + e^- & \rightarrow O_2^* \quad & (2a) \\
O_2^* + H^+ + e & \rightarrow HO_2^* \quad & (2b) \\
HO_2^* + H^+ + e & \rightarrow H_2O + O^* \quad & (2c) \\
O^* + H^+ + e & \rightarrow OH^* \quad & (2d) \\
OH^* + H^+ + e & \rightarrow H_2O + * \quad & (2e)
\end{align*}
\]

where asterisks denote surface-adsorbed species. Of these, the first-electron reduction of O$_2^*$ to HO$_2^*$ is proposed to be the rate-determining step (2a and 2b), and the subsequent reaction step (2d) involves the breaking of the O-O bond. Note that on a catalyst surface, if the adsorption of oxygen is too weak, the breaking of the O-O bond will be slow. In contrast, strong adsorption of oxygen can readily break the O-O bond, but at the expense of forming strongly bound O and OH species as a result of water oxidation. The binding of oxygen on silver is considerably less strong than that on Pt, thus pure Ag is less active for O$_2$ reduction than Pt because the weaker Ag-O$_2$,abs interaction makes the breaking of the O-O bond more difficult. Alloying with
gold appeared to lead to enhanced bonding with \( \text{O}_2 \), as gold nanoparticles, in particular, subnanometer-sized gold clusters, are known to exhibit apparent activity in oxygen adsorption and subsequent electroreduction,\(^{40}\) as a result of the increasing d-band vacancy for strong metal-\( \text{O}_2 \) interactions and weakened \( \text{O}–\text{O} \) bonds.\(^{56,57}\) Note that the Janus nanoparticles exhibited an even better performance than the bulk-exchange ones, although both showed a comparable Au coverage (Table 4.1). The detailed mechanism is not clear at this point, although there are several possible contributing factors such as electronically modified Au clusters, interfacial interactions between Au clusters and Ag, and spilling effects. Of these, the segregation of the hydrophilic and polar MPD ligands on the Janus nanoparticle surface might further facilitate charge transfer from Ag to Au, as evidenced in XPS measurements (Figure 4.5), further shifting the d-band center to the Fermi level for optimal oxygen adsorption and reduction.

Additionally, if the O and OH species produced during ORR (Eq. 2a–e) are strongly adsorbed onto the catalyst surface, further reduction of \( \text{O}_2 \) may be inhibited, since the activation energies for O and OH reduction have been found to be relatively high in the low overpotential region in which fuel cell cathodes would ideally be operated.\(^{56}\) The observed enhancement of the catalytic activity of the bimetallic AgAu (either bulk exchange or Janus) nanoparticles, as compared to that of the monometal AgC6 nanoparticle, may be correlated with the weakened adsorption of oxygen species (e.g., \( \text{O}_{\text{ads}} \) and \( \text{OH}_{\text{ads}} \)) on the Ag surfaces by the Au sites, as partial electron transfer occurred from Ag to Au (e.g., Figure 4.5). Such a phenomenon has also been
observed with other Ag-based\textsuperscript{23,24} or Pt-based\textsuperscript{58,59} alloys. Note that the bonding energies of O and OH on Au are in general higher than those on Ag, implying that the overall adsorption of oxygen species to form water would be facilitated on the bimetallic AgAu nanoparticles, as compared to monometallic Ag nanoparticles. That is, the incorporation of Au onto Ag nanoparticles forming surface alloys\textsuperscript{60-63} favors the ORR catalytic activity.

4.3 Conclusion

In this present study, bimetallic AgAu Janus nanoparticles were prepared by confining the galvanic exchange reactions of AgC\textsubscript{6} nanoparticles with the Au\textsuperscript{I}MPD complex to the top face of the AgC\textsubscript{6} nanoparticles. The asymmetrical distribution of the surface organic ligands was confirmed by contact angle measurements, whereas the bimetallic nature of the metal cores was evidenced in elemental mapping based on energy-dispersive X-ray analysis as well as XPS measurements. Despite a minimal loading of Au onto the Ag nanoparticle surface, the resulting bimetallic nanoparticles exhibited markedly enhanced electrocatalytic activity in oxygen reduction, as compared to the original monometallic Ag nanoparticles, and the electrocatalytic performance of the Janus nanoparticles was even better than that of the bulk-exchange counterparts. Notably, the area- and mass-specific current densities of the Janus nanoparticles were more than seven and six times that of the monometallic Ag nanoparticles, respectively. In the bulk-exchange nanoparticles, the two metal elements were presumably distributed evenly in the nanoparticle cores, whereas in the Janus nanoparticles, the segregated partition of polar MPD ligands from the apolar
hydrophobic hexanethiolates was likely to further facilitate electron transfer from Ag to Au, leading to additional improvement of the adsorption and reduction of oxygen. These results further demonstrate the significance of interfacial engineered catalyst surfaces, the Tafel slopes are typically found at 60 or 120 mV/dec, where the former corresponds to a pseudo two-electron reaction as the rate determining step and in the latter, the rate determining step is presumed to be the first-electron reduction of oxygen. The results from Figure 4.9 suggest that the reduction mechanism is similar for the AgC6 and bulk-exchange nanoparticles where the reactions were limited largely by a pseudo two-electron reduction reaction at low current densities and at high current densities the first electron transfer of oxygen was the rate-determining step (implying that subsequent reduction and O-O bond breaking was facile). Such a behavior has been observed with a pure Pt surface. By contrast, for the Janus nanoparticles, the oxygen reduction reactions were primarily determined by the first electron-transfer reaction of oxygen at low current densities; whereas at high current densities the Tafel slope (263.4 mV/dec) exhibited a rather large deviation from 120 mV/dec. Similar results were reported previously. For instance, in a previous study Ye and Crooks examined the electrocatalytic activity of dendrimer-capped Pt and PtPd alloy nanoparticles in oxygen reduction and observed Tafel slopes around 160 mV/dec at high overpotentials. These observations suggest that the adsorption of oxygen and reaction intermediates played an increasingly important role in determining the electron-transfer dynamics of oxygen reduction reactions, as the kinetics of the reduction of adsorbed oxygen and cleavage of O-O bonds was
enhanced at increasingly negative electrode potentials. These behaviors are consistent with the mechanism of oxygen reduction in alkaline media, as detailed below.

In previous studies of oxygen electroreduction on Ag in alkaline media, the reaction mechanism was found to be similar to that on Pt. The key steps may be summarized below:

\[
\begin{align*}
O_2 + * & \rightarrow O_2^* (2a) \\
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HO_2^* + H^+ + e & \rightarrow H_2O + O^* (2c) \\
O^* + H^+ + e & \rightarrow OH^* (2d) \\
OH^* + H^+ + e & \rightarrow H_2O + * (2e)
\end{align*}
\]

where asterisks denote surface-adsorbed species. Of these, the first-electron reduction of O$_2^*$ to HO$_2^*$ is proposed to be the rate-determining step (2a and 2b), and the subsequent reaction step (2d) involves the breaking of the O-O bond. Note that on a catalyst surface, if the adsorption of oxygen is too weak, the breaking of the O-O bond will be slow. In contrast, strong adsorption of oxygen can readily break the O-O bond, but at the expense of forming strongly bound O and OH species as a result of water oxidation. The binding of oxygen on silver is considerably less strong than that on Pt, thus pure Ag is less active for O$_2$ reduction than Pt because the weaker Ag-O$_2$ interaction makes the breaking of the O-O bond more difficult. Alloying with gold appeared to lead to enhanced bonding with O$_2$, as gold nanoparticles, in particular, subnanometer-sized gold clusters, are known to exhibit apparent activity in oxygen adsorption and subsequent electroreduction, as a result of the increasing d-
band vacancy for strong metal-O2 interactions and weakened O–O bonds.\textsuperscript{53,54} Note that the Janus nanoparticles exhibited an even better performance than the bulk-exchange ones, although both showed a comparable Au coverage (Table 4.1). The detailed mechanism is not clear at this point, although there are several possible contributing factors such as electronically modified Au clusters, interfacial interactions between Au clusters and Ag, and spilling effects. Of these, the segregation of the hydrophilic and polar MPD ligands on the Janus nanoparticle surface might further facilitate charge transfer from Ag to Au, as evidenced in XPS measurements (Figure 4.5), further shifting the d-band center to the Fermi level for optimal oxygen adsorption and reduction.

Additionally, if the O and OH species produced during ORR (Eq. 2a–e) are strongly adsorbed onto the catalyst surface, further reduction of O2 may be inhibited, since the activation energies for O and OH reduction have been found to be relatively high in the low overpotential region in which fuel cell cathodes would ideally be operated.\textsuperscript{53} The observed enhancement of the catalytic activity of the bimetallic AgAu (either bulk exchange or Janus) nanoparticles, as compared to that of the monometal AgC6 nanoparticle, may be correlated with the weakened adsorption of oxygen species (e.g., O_{ads} and OH_{ads}) on the Ag surfaces by the Au sites, as partial electron transfer occurred from Ag to Au (e.g., Figure 4.5). Such a phenomenon has also been observed with other Ag-based\textsuperscript{23,24} or Pt-based\textsuperscript{55,56} alloys. Note that the bonding energies of O and OH on Au are in general higher than those on Ag, implying that the overall adsorption of oxygen species to form water would be facilitated on the
bimetallic AgAu nanoparticles, as compared to monometallic Ag nanoparticles. That is, the incorporation of Au onto Ag nanoparticles forming surface alloys\textsuperscript{57-60} favors the ORR catalytic activity.
4.4 References


Chapter 5

Trimetallic Ag@AuPt Neapolitan Nanoparticles

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5.1 Introduction

As unique structural scaffolds, nanoparticles may be decorated with multiple functional moieties. Yet, in most prior research these functional moieties are distributed rather homogeneously on the nanoparticle surface. To further engineer the nanoparticle structures and manipulate the properties and functions, there has been a great deal of interest in the design and preparation of patchy nanoparticles with an asymmetrical distribution of the organic and/or metal components within the nanoparticles. Such directional engineering of the nanoparticles may then be exploited for an unprecedented control of the self-assembled nanoparticle structures.\(^1\)\(^-\)\(^4\) Towards this end, amphiphilic Janus nanoparticles have represented the first example of bi-patchy nanoparticles that exhibit two hemispheres of distinctly different chemical compositions and/or properties.\(^1\) Yet, is it possible to have more complicated chemical patterning of the nanoparticles with a multi-patchy surface structure? This is the primary motivation of the present study.

It should be noted that experimental preparation of such multipatchy particles has been mostly focused on (sub)micronized polymeric particles that are produced by, for instance, particle and nanosphere lithography, and glancing-angle deposition.\(^5\) In these, the self-assembly of block copolymers has been suggested as an effective route for the fabrication of functional patchy particles, where the composition and distribution of the solvophilic and solvophobic components are proposed to play a critical role in the manipulation of the interparticle interactions and hence organized assemblies.\(^6\)
In contrast, the study of nanometer-sized metal particles with patchy metallic compositions and/or organic capping layers is largely limited to theoretical simulations and modeling. For instance, Pons-Siepermann and Glotzer\textsuperscript{7} carried out computer simulations based on dissipative particle dynamics (DPD) to predict the patterns of a mixed monolayer consisting of three thiol derivatives self-assembled on gold nanoparticle surfaces. With a deliberate variation of four critical parameters: (a) nanoparticle core diameter, (b) degree of ligand immiscibility, (c) ligand chain length, and (d) monolayer composition, they predicted the formation of various patchy structures, including striped Janus particles, tri-patchy Neapolitan and Cerberus nanoparticles, etc.

It should be emphasized that whereas there has been much progress in theoretical simulations and modeling, experimental preparation of such multi-patchy nanoparticles has remained a great challenge. In the present study, we took advantage of our prior progress in the preparation of Janus nanoparticles with asymmetric organic capping patches,\textsuperscript{8-10} and demonstrated that trimetallic Ag@AuPt Neapolitan nanoparticles might be readily prepared by interfacial engineering based on the Langmuir methods and galvanic replacement reactions. The procedure is depicted in Scheme 5.1. Specially, 1-hexanethiolate-passivated silver (AgC6) nanoparticles were used as the starting materials. A compact monolayer was formed on the water surface of a Langmuir–Blodgett tough, into which a calculated amount of gold(I)-thiomalic acid (Au\textsuperscript{I}TMA) complex was injected. Galvanic exchange reactions between the AgC6 nanoparticles and Au\textsuperscript{I}TMA at the air\textbar water interface led to the displacement of
part of the Ag atoms on the bottom side of the nanoparticle cores with Au and concurrently the replacement of the original hydrophobic hexanethiolate ligands with the more hydrophilic TMA ones. The monolayer was then up-stroke deposited onto a glass slide surface by the Langmuir–Blodgett method (such that the hexanethiolate side was exposed), and immersed into a solution of platinum(II)-hexanethiolate (Pt\textsuperscript{II}C6) complex for the second galvanic replacement reactions. As both reactions were restricted to two opposite sides of the nanoparticles, the resulting particles exhibited a segregated distribution of three metal components (Ag, Au and Pt) as well as organic capping ligands. To the best of our knowledge, we believe that this is the first experimental demonstration of nanometer-sized trimetallic Neapolitan particles. As a control experiment, trimetallic Ag@AuPt nanoparticles were also prepared by galvanic exchange reactions of AgC6 nanoparticles with Au\textsuperscript{TMA} and Pt\textsuperscript{II}C6 in THF. The resulting nanoparticles were denoted as bulk-exchange nanoparticles.

5.2 Results and discussion

The structures of the resulting nanoparticles were first examined by transmission electron microscopic (TEM) measurements. Figure 5.1 depicts the representative TEM micrographs of the (A) original AgC6, (B) trimetallic Ag@AuPt bulk-exchange and (C) Neapolitan nanoparticles. It can be seen that the nanoparticles were all very well dispersed, indicating effective protection of the nanoparticles by the thiolate ligands before and after core metal galvanic exchange reactions. Also, the nanoparticle core size remained statistically unchanged. In fact, the average core diameter was found to be 5.70 ± 0.82 nm, 6.00 ± 0.75 nm, and 5.90 ± 0.76 nm for the
Scheme 5.1. Preparation of trimetallic Neapolitan and bulk-exchange nanoparticles by interfacial galvanic exchange reactions.
as-prepared AgC6, trimetallic bulk-exchange, and Neapolitan particles, respectively (right insets). Furthermore, the nanoparticles all exhibited well-defined crystalline lattice fringes, with a spacing of 0.23 nm, as highlighted in the left insets. This is consistent with the Ag(111) crystal planes,11 and implies that only a small fraction of the Ag atoms on the original nanoparticle surface was replaced by Au and Pt, in agreement with XPS measurements (vide infra).

The tri-patchy characteristics of the Neapolitan nanoparticles were then manifested in EDS elemental mapping. Figure 5.2 shows two representative elemental maps of (A) trimetallic bulk exchange and (B) Neapolitan nanoparticles with the red symbols for silver, green for gold and blue for platinum. It can be seen that for the bulk-exchange nanoparticles in panel (A) the three metal elements were distributed rather homogeneously throughout the entire nanoparticles. By contrast, for the Neapolitan nanoparticles in panel (B), whereas the silver signals can be identified all over the nanoparticles, the gold and platinum elements are clearly segregated on two opposite poles of the nanoparticles, as highlighted in the schematic of panel (C).

The replacement of part of the Ag atoms on the nanoparticle surface by Au and Pt led to an apparent variation of the nanoparticle optical properties. Figure 5.3 depicts the UV-vis absorption spectra of the AgC6, and trimetallic Ag@AuPt bulk-exchange and Neapolitan nanoparticles in THF. For the original AgC6 nanoparticles (solid curve), the surface plasmon resonance peak can be clearly identified at 419 nm.12 Yet for the trimetallic bulk-exchange (dotted curve) and Neapolitan (dashed curve) nanoparticles, the peak became broadened somewhat and red-shifted to 437
Figure 5.1. Representative TEM images of (A) AgC6 nanoparticles, (B) trimetallic Ag@AuPt bulk-exchange and (C) Neapolitan nanoparticles. The scale bars are all 10 nm. Left insets show the corresponding high-resolution TEM micrographs with the scale bars of 2 nm. Right insets are the respective core size histograms.
Figure 5.2. Representative false-color EDS elemental maps of (A) bulk-exchange and (B) Neapolitan nanoparticles with red symbols for Ag, green for Au and blue for Pt. The samples are the same as those as in Figure 5.1(B) and (C). Panel (C) is a schematic of the resulting Neapolitan nanoparticles.
Figure 5.3. UV-vis spectra of AgC6 nanoparticles (solid curve), trimetallic bulk-exchange (dotted curve) and Neapolitan (dashed curve) nanoparticles in THF at a concentration of about 0.5 mg mL$^{-1}$. 
nm, along with the emergence of a broad shoulder centered at around 589 nm. The first peak most likely arose from the damping of the Ag surface plasmon by the Au(Pt) overlayer, whereas the second peak might be ascribed to the deposition of Au (Pt) onto the Ag nanoparticle surface in the form of tiny clusters where alloying occurred at the bimetallic interface. Similar observations were reported with much larger Ag@AgAu metal core–alloy shell nanoparticles (ca. 18 nm in diameter) that were prepared also by galvanic exchange reactions, which were accounted for by the plasmon hybridization theory.\textsuperscript{13} In addition, unlike Ag and Au nanoparticles, Pt nanoparticles exhibit no well-defined surface plasmon resonance.\textsuperscript{12} Therefore, in the trimetallic Ag@AuPt nanoparticles the optical features were largely determined by the Ag and Au components. In fact, one may notice that such optical characteristics were also observed previously with bimetallic AgAu Janus and bulk-exchange nanoparticles prepared with the same AgC6 nanoparticles (Scheme 5.1),\textsuperscript{10,14} as well as Au@Ag and Ag@Au core–shell nanoparticles.\textsuperscript{14–16}

The incorporation of Au and Pt onto the Ag nanoparticles by galvanic exchange reactions was also manifested in XPS measurements. Figure 5.4 shows the XPS survey spectra of (A) Ag 3d, (B) Au 4f, and (C) Pt 4f electrons for the Neapolitan (bottom spectra) and bulk-exchange (top spectra) nanoparticles. By deconvolution fits, the Ag 3d electrons can be readily identified at 368.1 and 374.2 eV for the bulk-exchange nanoparticles, and for the Neapolitan counterparts, they are almost unchanged at 368.2 and 374.2 eV. Meanwhile, a rather apparent variation was observed for the Au4f electrons, which appeared at 83.7 and 87.5 eV for the bulk
exchange nanoparticles and red-shifted to 83.3 and 87.2 eV for the Neapolitan nanoparticles. In contrast, the binding energies of the Pt 4f electrons increased from 71.4 and 74.7 eV for the bulk exchange nanoparticles to 71.8 and 75.2 eV for the Neapolitan nanoparticles. Overall, these values are comparable to those reported previously for AgAu, AgPt, or AuPt bimetallic core–shell or alloy nanoparticles.\(^{10,17-19}\)

Yet, the apparent discrepancy of the Au 4f and Pt 4f binding energies between the bulk-exchange and Neapolitan nanoparticles seem to suggest that in comparison with the structurally symmetric bulk-exchange nanoparticles, the segregation of Au and Pt on two opposite poles of the Neapolitan nanoparticles led to an uneven distribution of electrons where partial charge transfer likely occurred from Pt to Au (the segregated distribution of the associated polar TMA ligands from the apolar hexanethiolates in the Neapolitan nanoparticles and hence the formation of an apparent dipole might also help stabilize the extra electron density on the gold sites\(^{10}\)). This may be accounted for by the difference of electronegativity of the three metal elements, Au (2.4) > Pt (2.2) > Ag (1.9).\(^{20}\)

Furthermore, based on the integrated peak areas, the atomic ratio of the metal elements can be estimated to be 1: 1.6: 5.6 for the bulk-exchange nanoparticles and 1: 2.0: 8.6 for the Neapolitan nanoparticles. That is, the fractions of the Ag core atoms that were replaced by Au and Pt combined was 31.7% and 25.9% for the bulk-exchange and Neapolitan nanoparticles, respectively. Note that based on the average core diameter of the nanoparticles as measured by TEM measurements (Figure 5.1), the surface atoms constituted about 25% of the total atoms of the metal cores of these
Figure 5 4. XPS survey spectra of (A) Ag 3d, (B) Au 4f and (C) Pt 4f electrons in trimetallic Ag@AuPt bulk-exchange (bottom curves) and Neapolitan (top curves) nanoparticles. Symbols are experimental data and lines are deconvolution fits. Data are summarized in Table 5.1.
Table 5.1. Binding energies of the Ag 3d, Au 4f and Pt 4f electrons in trimetallic Ag@AuPt bulk-exchange and Neapolitan nanoparticles and the Au/Ag/Pt atomic ratios by XPS measurements

<table>
<thead>
<tr>
<th></th>
<th>Ag</th>
<th>Au</th>
<th>Pt</th>
<th>Au/Pt/Ag atomic ratio</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Bulk-exchange</strong></td>
<td>368.1</td>
<td>374.2</td>
<td>83.7</td>
<td>71.4</td>
</tr>
<tr>
<td><strong>Neapolitan</strong></td>
<td>368.2</td>
<td>374.2</td>
<td>83.3</td>
<td>71.8</td>
</tr>
</tbody>
</table>

nanoparticles.\(^{21}\) This means that in the preparation of the bulk-exchange and Neapolitan nanoparticles, the galvanic exchange reactions were mostly limited to the top layers of the Ag cores. Also as the Au/Pt ratio is very close, these two nanoparticles may be approximated as structural isomers.

With regard to the organic capping layer, the first galvanic exchange reactions would incorporate TMA ligands onto the nanoparticle surface, whereas in the second step, the organic ligands remained unchanged (with Pt\(^{II}\)C6). Thus, the resulting Neapolitan nanoparticles are anticipated to exhibit a surface structure analogous to that of Janus nanoparticles.\(^{8-10}\) To confirm the amphiphilic characters of the surface protecting layers, a monolayer of nanoparticles was formed at the air–water interface and transferred onto a microscope glass slide by up- and down-stroke deposition, and the thin-film contact angles were measured. For the original AgC6 nanoparticles a consistent contact angle of 94.8 ± 5.1° was observed for both up- and down-stroke depositions, which is consistent with those observed with self-assembled monolayers of alkanethiols on silver substrate surfaces.\(^{22,23}\) In comparison, the Neapolitan nanoparticles showed a contact angle of 92.8 ± 5.6° when the nanoparticle film was
deposited in the up-stroke fashion (that is, with the hydrophobic face of the hexanethiolate ligands exposed), which is similar to that of AgC6 nanoparticles; however, the contact angle exhibited a marked diminishment to 30.8 ± 4.1° when the nanoparticle monolayers were deposited by the down-stroke method (with the hydrophilic side of the TMA ligands exposed). Note that the latter is consistent with that observed with a TMA self-assembled monolayer on Au thin film surfaces (27.4 ± 7.2°). These observations suggest the effective replacement of the original hydrophobic hexanethiolates ligands by the more hydrophilic TMA during galvanic exchange reactions, and the TMA and C6 ligands were segregated on the nanoparticle surface. Similar behaviors have been observed previously in galvanic exchange reactions of AgC6 nanoparticles with gold(I)-mercaptopropanediol (Au\textsuperscript{I}MPD) complex,\textsuperscript{10} and ligand exchange reactions of AuC6 nanoparticles with 2-(2-mercaptoethoxy)-ethanol (MEA)\textsuperscript{9} and 3,5-octadiyne-1-ol-8-thiol (DAT)\textsuperscript{24} as the hydrophilic ligands.

The incorporation of the TMA ligands into the nanoparticle surface-capping layer is further manifested in FTIR measurements. Figure 5.5 depicts the FTIR spectra of the original AgC6 nanoparticles, trimetallic Ag@AuPt bulk-exchange and Neapolitan nanoparticles, as well as the Au\textsuperscript{I}TMA and Pt\textsuperscript{II}C6 complexes. In comparison with the spectral data of the AgC6 nanoparticles (black curve), bulk-exchange (red curve) and Neapolitan nanoparticles (green curve) share the same vibrational features that are consistent with the vibrational characteristics of the 1-hexanethiolate ligands (which can also be observed with the Pt\textsuperscript{II}C6 complex, yellow
Figure 5.5. FTIR spectra of the AgC6 nanoparticles (black curve), trimetallic Ag@AuPt bulk-exchange (red curve) and Neapolitan (green curve) nanoparticles, along with the AuTMA (yellow curve) and PtC6 (blue curve) complexes.
curve), including the methyl and methylene C–H stretches between 2800 and 3000 cm\(^{-1}\), methylene C–H rocking at 1463 cm\(^{-1}\) and methyl C–H bending at 1377 cm\(^{-1}\).\(^{25}\) Meanwhile, several new features emerged for the bulk-exchange (red curve) and Neapolitan nanoparticles (green curve), including the O–H stretch at 3450 cm\(^{-1}\) and carboxylic C=O stretch at 1710 cm\(^{-1}\) (the peak at 1592 cm\(^{-1}\) suggests the presence of carboxylate anions in the TMA ligands) which are consistent with the vibrational characteristics of the Au\(^{I}\)TMA complex (blue curve). Note that the vibrational stretch of S–H (~2550 cm\(^{-1}\)) was not observed in any of the samples, indicating that the samples were free of excessive thiol ligands.

5.3 Conclusion

In this study a Langmuir-based interfacial engineering approach was developed for the first-ever preparation of trimetallic Neapolitan nanoparticles. Using 1-hexanethiolate-protected Ag nanoparticles as the starting materials, Ag@AuPt Neapolitan nanoparticles were prepared by two sequential galvanic exchange reactions with gold(I)-thiomalic acid and platinum(II)-hexanethiolates complexes. As these two reactions were confined on two opposite sides of the Ag nanoparticles, there was a clear segregation of the Au and Pt elements (and the corresponding organic capping ligands) on the nanoparticle surface, as manifested in EDS elemental mapping studies as well as spectroscopic measurements. Such an unprecedented level of engineering of the nanoparticle structures may pave the way towards increasingly deliberate manipulation of the nanoparticle properties and functions. This is being pursued in ongoing work and results will be reported in due course.
5.4 References


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Chapter 6

Janus Nanoparticles as Amphiphilic Surfactants for
Nanoparticle Phase Transfer

6.1 Introduction

“Janus” nanoparticles (JNPs), named after the two-faced Roman God Janus, refer to a unique class of nanoparticles that exhibit an asymmetrical structure including, for instance, two hemispheres of different shapes, chemical compositions, and/or surface functionality.\textsuperscript{1} Research of these unique nanomaterials has been attracting considerable attention because of their anisotropic chemical, optical, electronic, and magnetic properties.\textsuperscript{2-10} For organically capped nanoparticles, research of Janus nanoparticles is mostly focused on segregation of two kinds of chemical ligands on the nanoparticle surface forming, for instance, a hydrophobic hemisphere and a hydrophobic one.\textsuperscript{11-16} Recently, we have developed effective procedures based on interfacial engineering to prepare nanosized Janus particles.\textsuperscript{17} Experimentally, a monolayer of hydrophobic alkanethiolate-protected gold nanoparticles is formed at the air/water interface by using a Langmuir-Blodgett trough. Hydrophilic thiol ligands are then injected into the water subphase to initiate ligand exchange reactions, which are confined to the bottom face of the nanoparticles, leading to the generation of Janus nanoparticles.\textsuperscript{17} The amphiphilic structures have been confirmed on multiple length scales, ranging from contact angle measurements of nanoparticle ensembles to adhesion force studies of individual nanoparticles, and even to two-dimensional NMR studies based on nuclear Overhauser effect spectroscopy (NOESY) of the spin interactions between neighboring molecular ligands on nanoparticle surface.\textsuperscript{18-21}

With the amphiphilic characters, the resulting Janus nanoparticles behave as nanoscale analogs to conventional surfactant molecules. In fact, prior studies have
showed that Janus nanoparticles may be dispersed both in water and organic media forming stable (reverse) micelle-like aggregates.\textsuperscript{17,22} Another unique property of amphiphilic surfactants is that they may be used effectively as phase transfer catalysts.\textsuperscript{23-25} Thus, an immediate question arises. Will it be possible to use Janus nanoparticles as phase transfer reagents as well? This will be of significance in the preparation and engineering of diverse functional nanocomposites. Yet, studies along this line are relatively scarce. This is the primary motivation of the present study.

Herein, we carried out a detailed study to examine the phase transfer properties of Janus nanoparticles. The Janus nanoparticles were prepared by interfacial ligand exchange reaction of hydrophobic 1-hexanethiolate-protected gold nanoparticles with hydrophilic 1,2-mercapto-3-propanediol.\textsuperscript{17} Organically soluble 1-hexanethiolate-protected silver nanoparticles and fullerene (C\textsubscript{60}) were used as the illustrating examples in the phase transfer from organic to aqueous media catalyzed by the Janus nanoparticles, whereas water-soluble glutathione-protected silver nanoparticles and photoluminescent carbon nanoparticles were used in the phase transfer from water to an organic phase. A variety of experimental tools were used in the structural characterization, including transmission electron microscopy, dynamic light scattering, UV-Vis absorption and photoluminescence spectroscopy. The results highlight the effectiveness of amphiphilic Janus nanoparticles in the phase transfer of diverse nanoparticle materials.

\textbf{6.2 Results and Discussion}

\textbf{6.2.1 Amphiphilicity of Janus nanoparticles.}
We first tested the formation of oil-in-water micelle-like structures with AuC6-MPD Janus nanoparticles in a small amount of CH₂Cl₂ followed by the addition of a large excess of water. Experimentally, 0.05 mg of Janus nanoparticles was initially dispersed in 300 µL of CH₂Cl₂. After the addition of a large excess (5 mL) of water (o/w ratio 0.06:1), mechanical agitation led to the appearance of a rather uniform reddish solution, as depicted in Figure 6.1 (A), suggesting the homogeneous mixing of the CH₂Cl₂ and water phases. It should be noted that the solution remained stable without apparent phase separation for more than 3 days. This is in sharp contrast with pure solvents of (5 mL) water and (300 µL) CH₂Cl₂, which are immiscible even after extensive mechanical agitation (panel (B)). Markedly different behaviors are also observed with AuC6 nanoparticles. When 5 mL of water was added to the solution of AuC6 nanoparticles in 300 µL of CH₂Cl₂, after mechanical agitation the water phase remained clear, and at the bottom of the vial, dark brown color droplets can be found, which were the AuC6 nanoparticles in CH₂Cl₂ (note that the density of CH₂Cl₂ is higher than that of water, so the CH₂Cl₂ phase is at the bottom), as depicted in panel (C).

We also tested the possibility of forming water-in-oil reverse micelle-like structures with the same Janus nanoparticles. In a similar fashion, a same amount of Janus nanoparticles (0.05 mg) was dispersed in a large excess (5 mL) of CH₂Cl₂ and then a small amount (300 µL) of water was added (o/w ratio 1:0.06), mechanical agitation also led to the formation of a homogeneous solution, as manifested in panel (D), again in sharp contrast to the case with the same amounts of (5 mL) CH₂Cl₂ and
(300 µL) water only but without the Janus nanoparticles where water droplet could be clearly seen on the side of the vial (panel (E)) because of their immiscibility. Furthermore, the solvents of (5 mL) CH₂Cl₂ and (300 µL) water were not miscible either with AuC6 nanoparticles dispersed in CH₂Cl₂, as manifested in panel (F).

**Scheme 6.1.** Schematic structures of (A) oil-in-water and (B) water-in-oil vesicles formed by Janus nanoparticles.

The hydrodynamic diameters of the aggregate structures of the Janus nanoparticles in these different solvents were then evaluated by dynamic light scattering (DLS) measurements. When AuC6-MPD Janus nanoparticles were initially
Figure 6.1. Optical images of solutions after mechanical agitation. (A) 0.05 mg of AuC6-MPD Janus nanoparticles in 300 µL of CH₂Cl₂ with 5 mL of water; (B) 300 µL of CH₂Cl₂ with 5 mL of water; (C) 0.05 mg of AuC6 nanoparticles in 300 µL of CH₂Cl₂ with 5 mL of water; (D) 300 µL of water with 0.05 mg of AuC6-MPD Janus nanoparticles in 5 mL of CH₂Cl₂; (E) 300 µL of water with 5 mL of CH₂Cl₂; (F) 300 µL of water with 0.05 mg of AuC6 nanoparticles in 5 mL of CH₂Cl₂. The concentration of nanoparticles is all ca. 0.01 mg/mL.
dispersed in CH$_2$Cl$_2$, the average hydrodynamic diameter was found to be about 58.2 nm, about 10 times the physical core size of individual nanoparticles (5.0 nm, as determined by TEM measurements). This may be ascribed to the amphiphilic nature of the particles that self-assembled to minimize the exposure of the hydrophilic face to the solvent, as observed previously. It is interesting to note that with the addition of only a small amount of water (oil/w ratio 1:0.06) the size of the nanoparticle ensembles increased significantly to ca. 148.4 nm after mechanical agitation. As shown above in the optical images (Figure 6.1(D)), a homogeneous solution was formed with water dispersed into the CH$_2$Cl$_2$ solution of AuC$_6$-MPD Janus nanoparticles, likely in the form of reverse micelle-like multilayer vesicle structures with water droplets trapped in the cores. In the case where an oil-in-water dispersion was formed with a large excess of water was added into a CH$_2$Cl$_2$ solution of AuC$_6$-MPD Janus nanoparticles (oil/w ratio 0.06:1, Figure 6.1(A)), the average hydrodynamic diameter of the resulting nanoparticle assemblies was found to be ca. 302.8 nm. This is consistent with the formation of micelle-like superparticulate structures with CH$_2$Cl$_2$ droplets as the anchoring cores. The results are summarized in Table 1.

These observations clearly showed the amphiphilicity of Janus nanoparticles that might form (reverse) micelle-like superparticulate structures (Scheme 6.1). In the oil-in-water condition (panel (A)), AuC$_6$-MPD Janus nanoparticles self-assembled into a structure that was analogous to multilayer vesicles, with the hydroxyl-terminated MPD hemisphere situated on the outermost surface and hydrophobic oil
(CH₂Cl₂) trapped within the central cores. On the contrary, in the water-in-oil condition (panel (B)), an opposite orientation was mostly likely formed where the outermost surface of the nanoparticle ensembles would be the hydrophobic hexanethiolate hemispheres and water encapsulated in the ensemble cores.

UV-Vis measurements were also carried out to provide further insights into the amphiphilic characters of these Janus particles and information of aggregates formed at different conditions. The optical absorption profiles of the AuC6 (black curve) and AuC6-MPD Janus (red curve) nanoparticles in CH₂Cl₂ were depicted as Figure 6.2. From Figure 6.2 (A) it can be seen that the original AuC6 nanoparticles (black curve) exhibited an exponential decay profile (Mie scattering) with an absorption peak at 556 nm, characteristic of the surface plasmon resonance of nanosized gold particles.²³,²⁶,²⁷ For the AuC6-MPD Janus nanoparticles (red curve), the surface plasmon peak was broadened and red-shifted to 612 nm, suggesting enhanced interparticle electronic coupling which is consistent with the formation of nanoparticle aggregates as observed in DLS measurements. More interestingly, when a small amount of water was added to the Janus nanoparticle solution in CH₂Cl₂ (oil/w ratio 1:0.06, Figure 6.1(D)), the corresponding surface plasmon peak after mechanical agitation became further broadened and centered at 651 nm (green curve). A similar behavior can be seen when a large excess of water was added to the Janus nanoparticle solution in CH₂Cl₂ (oil/w ratio 0.06:1, Figure 6.1(D)), the surface plasmon band exhibited a further red shift to 668 nm (yellow curve). These
observations are in excellent agreement with the DLS results where larger nanoparticle aggregates were formed in the latter.

Taken together, these studies highlight the amphiphilic characters of Janus nanoparticles that may be exploited form oil-in-water or water-in-oil vesicle-like superstructures, akin to the conventional surfactant molecules. Such unique properties may be exploited for the phase transfer of a diverse range of materials between the organic and aqueous phases, as manifested below.

In 300 µL CH₂Cl₂ mixed with 5 mL of water (C) with and (D) without 0.05 mg of AuC₆-MPD Janus nanoparticles.

6.2.2 Transfer of hydrophobic nanoparticles from organic to aqueous phase.

In the first tests, hydrophobic hexanethiolate-protected silver (AgC₆) nanoparticles and fullerene (C₆₀) were employed as the illustrating examples to manifest the phase transfer properties of Janus nanoparticles from organic to aqueous media. AgC₆ and C₆₀ were initially dispersed in CH₂Cl₂. With the addition of a large excess of water (oil/w ratio 0.06:1), a homogeneous solution was formed when aided by Janus nanoparticles, as depicted in Figure 6.3 (A) and (C). Yet, in the absence of the Janus nanoparticles, the AgC₆ and C₆₀ remained at the bottom of the vials, as manifested by the dark brown CH₂Cl₂ droplets in panels (B) and (D), respectively.

Consistent results were obtained in DLS measurements. For the solution of Figure 6.3 (A), the average hydrodynamic diameter of the resulting nanoparticle
Figure 6.2. UV-Vis spectrum of AuC6 NPs (black curve), AuC6-MPD JNPs (red curve) in CH₂Cl₂ and AuC6-MPD JNPs after phase transfer of CH₂Cl₂ to water (green curve) and of water to CH₂Cl₂ (yellow curve). The concentration of all species in each solution is ca. 0.01 mg / mL.
Figure 6.3. Optical images of 0.05 mg of AgC6 NPs in 300 µL of CH₂Cl₂ mixed with 5 mL of water (A) with and (B) without 0.05 mg of AuC6-MPD Janus nanoparticles, and 0.05 mg of fullerene C₆₀.
aggregates is ca. 179.9 nm. This is markedly larger than that observed without the AgC6 nanoparticles (148.4 nm, Figure 6.1 A), suggesting that the AgC6 nanoparticles were most likely encapsulated in the CH₂Cl₂ cores as well as between the Janus nanoparticles in the vesicle layers. For the solution of Figure 6.3 (C), even larger nanoparticle aggregates were formed with an average hydrodynamic diameter of 274.5 nm as listed in Table 6.1. This is likely due to the formation of C₆₀ crystals within the Janus nanoparticle vesicles.

Table 6.1. Diameter of transferees in original solution and aggregations after phase transfer by AuC6-MPD JNPs

<table>
<thead>
<tr>
<th></th>
<th>AuC6-MPD</th>
<th>AuC6-MPD +AgC6</th>
<th>AuC6-MPD +C₆₀</th>
<th>AuC6-MPD +AgGSH</th>
<th>AuC6-MPD +CNP</th>
</tr>
</thead>
<tbody>
<tr>
<td>CH₂Cl₂</td>
<td>58.2</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>CH₂Cl₂-H₂O (1:0.06)</td>
<td>148.4</td>
<td></td>
<td>279.9</td>
<td>426.3</td>
<td></td>
</tr>
<tr>
<td>CH₂Cl₂-H₂O (0.06:1)</td>
<td>302.8</td>
<td>179.9</td>
<td>274.5</td>
<td></td>
<td></td>
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</tbody>
</table>

The transfer of hydrophobic AgC6 nanoparticles and C₆₀ from CH₂Cl₂ to water by AuC6-MPD Janus nanoparticles was further confirmed by UV-Vis absorption measurements, as shown in Figure 6.4. The characteristic SPR peak of AgC6 nanoparticles in CH₂Cl₂ can be found at 424 nm (Figure 6.4 (A), red curve);²⁸
Figure 6.4. UV-Vis adsorption spectrum of phase transfer of (A) AgC6 NPs and (B) Fullerene C₆₀ from CH₂Cl₂ to water. The concentration of all species in each solution is ca. 0.01 mg/mL.
and the addition of AuC6-MPD Janus nanoparticles led to the appearance of two absorption bands at 424 and 556 nm, consistent with the SPR absorption of the AgC6 and AuC6-MPD Janus nanoparticles, respectively, as manifested by the green curve in Figure 6.4 (A), indicating no intimate interactions between the two types of nanoparticles. However, after transfer to the aqueous phase (blue curve), the UV-vis absorption file became largely featureless with a weak broad bump within 600 to 800 nm, which might be ascribed to the formation of nanoparticle aggregates such that the SPR features were markedly broadened, in consistence with results from the aforementioned DLS measurements. The size-increase suggests that hydrophobic AgC6 NPs were trapped into vesicles from AuC6-MPD JNPs.

The UV-Vis spectra of C60 before and after phase transfer by Janus nanoparticles were depicted in Figure 6.4 (B). For C60 dispersed in CH2Cl2 (black curve), three absorption features can be seen at 208.2 nm, 256.3 nm, and 328.3 nm, which may be ascribed to the 81T1u ← 11A1g, 61T1u ← 11A1g, and 31T1u ← 11A1g transitions, respectively.29 The same features can be seen with the addition of Janus nanoparticles into the C60 solution, along with the emergence of a broad peak within the range of 500 to 600 nm that is ascribed to the gold Janus nanoparticles (red curve and Figure inset). However, when C60 was transferred to the aqueous phase by the Janus nanoparticles (green curve), the three absorption peaks of C60 virtually vanished, signifying the formation of C60 clusters,25 and the weak broad band centered at ca. 575 nm (figure inset) may be ascribed to the formation of ensembles of C60 and Janus nanoparticles. Note that as C60 is barely soluble in water, they are
most likely concentrated within the vesicles formed by the Janus nanoparticles in the form of microcrystals rather than individual molecules of C$_{60}$ (vide infra). Consistent results were obtained in photoluminescence measurements. As shown in Figure 6.5, C$_{60}$ exhibits a characteristic reddish orange PL peak at 730 nm, which was attributed to the triplet state of C$_{60}$ in solutions$^{30-32}$ and thin films.$^{33,34}$ Note that the PL intensity showed no obvious influence by mixing AuC6-MPD JNPs with C$_{60}$ in CH$_2$Cl$_2$. It suggests that no interactions between C$_{60}$ and AuC6-MPD JNPs within the mixture solution. However, the peak intensity remarkably increased after phase transfer into water, indicating higher concentration C$_{60}$ existed in the solution, consistent with results from UV-Vis spectral measurements that C$_{60}$ microcrystals were encapsulated with in Janus particle vesicles along with CH$_2$Cl$_2$ droplet.

The formation of superparticulate ensembles can also be visualized by TEM measurements. Figure 6.6 (A) depicts a representative TEM micrograph of the AuC6-MPD Janus particles after being transferred from CH$_2$Cl$_2$ to the water phase, where one can see a largely vesicle-like structure of about 160 nm in diameter constituting multiple layers of nanoparticles that surrounded an empty core. This again suggests the amphiphilicity of the Janus nanoparticles that self-assembled into a vesicle superstructure. In the phase transfer of C$_{60}$ from CH$_2$Cl$_2$ to water, one can see from Figure 6.6 (B) that C$_{60}$ molecules, represented by the light-contrast objects, largely clustered together to form microcrystals that were trapped among the AuC6-MPD Janus nanoparticles, as highlight by the white square. Furthermore, the fringe spacing
Figure 6.5. Excitation and emission spectra of C_{60} in CH_{2}Cl_{2} (black curve), mixed with AuC_{6}-MPD JNPs in CH_{2}Cl_{2} (red curve) and after transferring to water (green curve).
Figure 6.6. Representative TEM images of (A) AuC6-MPD JNPs alone in CH₂Cl₂–H₂O (o/w ratio 0.06:1), (B) with C₆₀ (inset shows crystal lattices of C₆₀ nanocrystals), and (C) with AgC6 NPs. (D) A representative STEM image of an aggregate formed with AgC6 and AuC6-MPD JNPs. Top inset is a schematic of the AgC6 nanoparticles encapsulated within the vesicles of AuC6-MPD Janus nanoparticles, and bottom inset shows the corresponding line scans of EDX elemental mapping with the red curve for Ag and blue curve for Au.
of the C$_{60}$ microcrystals was estimated to be 0.50 nm, which is consistent with the (220) planes (0.50074 nm) of face-centered cubic (fcc) C$_{60}$ crystals.$^{35,36}$ For the transfer of AgC6 nanoparticles, a vesicle-like structure can still be found, yet with a marked shrinkage of the void space in the center, as shown in Figure 6.6 (C). This is likely due to the encapsulation of the AgC6 nanoparticles in the oil cores of the vesicles formed by the Janus nanoparticles. In fact, line-scans based on EDX elemental analysis of a typical nanoparticle ensemble showed that the Ag profile (orange curve) was mostly enclosed within the Au signals (blue curve), as depicted in Figure 6.6 (D).

**6.2.3 Transfer of hydrophilic nanoparticles from water to organic phase.**

In this study, water-soluble glutathione-stabilized silver (AgGSH) and carbon (CNP) nanoparticles were used as the illustrating examples for phase transfer from water to CH$_2$Cl$_2$ by AuC6-MPD Janus nanoparticles. As illustrated in Figure 6.7, homogeneous solutions were obtained when a large excess of CH$_2$Cl$_2$ was added to the AgGSH or CNP solutions in water in the presence of AuC6-MPD Janus nanoparticles, as depicted in panels (A) and (C), respectively. In contrast, in the absence of the Janus nanoparticles, the water phase remained clearly separated from CH$_2$Cl$_2$, as manifested by the brown color layers on the CH$_2$Cl$_2$ surface in panels (B) and (D).

The dimensions of the nanoparticle ensembles were then determined by DLS measurements. For solution (A) as aqueous soluble AgGSH nanoparticles transferred to CH$_2$Cl$_2$ assisted by AuC6-MPD JNPs (oil/w ration 1:0.06) in Figure 6.7, the
average hydrodynamic diameter of stable aggregates was found to be 279.9 nm, about 125 times larger than that of the AgGSH nanoparticles alone in water (2.2 nm). On the other hand, for solution (C) of CNPs transfer to CH₂Cl₂ with AuC6-MPD JNPs (oil/w ratio 1:0.06) in Figure 6.7, the size of the nanoparticle ensemble was determined to be 426.3 nm, in comparison to 7.4 nm for individual CNP in aqueous solution. The results are summarized in Table 6.1.

The corresponding UV-vis absorption spectra were shown in Figure 6.8. For AgGSH nanoparticles in water, the SPR peak can be identified at 454 nm (black curve), characteristic of nanosized silver particles. After being transferred to the CH₂Cl₂ phase by the AuC6-MPD Janus nanoparticles, the absorption profile was largely featureless with a broad peak within the range of 550 to 800 nm. The broadening and red-shift of the surface plasmon resonance most likely arose from strong electronic interactions between the nanoparticles as a result of the formation of nanoparticle aggregates (red curve).

The formation of nanoparticle aggregates can be clearly seen in TEM measurements. Figure 6.9 depicts a representative nanoparticle ensemble with a roughly spherical shape of about 160 nm in diameter, similar to those of AgC6 and AuC6-MPD Janus nanoparticles in the aqueous solution (Figure 6.6). The vesicle-like structure is evidenced by the partial collapse of the ensemble, as highlighted by the yellow arrow in panel (A). Line scans based on EDX elemental analysis in panel (B) showed that indeed the silver signals (orange curve) were enclosed within the gold profile (blue curve).
Figure 6.7. Optical images of 0.05 mg AgGSH NPs in 300 µL water mixed with 5 mL CH₂Cl₂ (A) with and (B) without 0.05 mg AuC6-MPD JNPs, and 0.05 mg of carbon NPs in 300 µL water mixed with 5 mL CH₂Cl₂ (C) with and (D) without 0.05 mg AuC6-MPD JNPs. The concentration of all species in each solution is ca. 0.01 mg / mL.
Figure 6.8. UV-Vis adsorption spectrum of phase transfer of AgGSH NPs (black curve) in aqueous solution and after transferred to CH$_2$Cl$_2$ (red curve). The concentration of AgGSH NPs in each solution is ca. 0.01 mg / mL.
Figure 6.9. TEM (A) and STEM (B) images of the aggregate formed with AgGSH NPs and AuC6-MPD JNPs. In panel (B), top inset is a schematic of the AgGSH nanoparticles encapsulated within the vesicles of AuC6-MPD Janus nanoparticles, and bottom inset is the line-scan of EDX elemental analysis of a representative nanoparticle ensemble, with the aqua blue curve for gold and orange curve for silver.
Figure 6.10. Excitation and emission spectra of carbon NPs in water (black curve), after being transferred to CH$_2$Cl$_2$ with AuC6-MPD Janus nanoparticles (red curve). The concentrations of the nanoparticles are ca. 0.01 mg/mL.
For carbon nanoparticles, marked differences can also be seen in optical measurements. From the excitation and emission photoluminescence spectra in Figure 6.10, one can see that carbon nanoparticles in water (black curves) exhibited a well-defined excitation peak at 322 nm and a corresponding emission one at 444 nm, which have been ascribed to electronic transitions of phenanthrenequinone-like moieties on the nanoparticle surface.\textsuperscript{37,38} In contrast, when the carbon nanoparticles were transferred to the CH\textsubscript{2}Cl\textsubscript{2} phase by the Janus nanoparticles, the photoluminescence was substantially quenched (red curves). This quenching may be accounted for by the encapsulation and hence high local concentration of the carbon nanoparticles within the Janus nanoparticle vesicles as well as by the close proximity of gold nanoparticles to the carbon nanoparticles where metal nanoparticles are known to be effective luminescence quenchers.\textsuperscript{39}

6.3 Conclusion

The amphiphilicity of Janus nanoparticles was tested by a series of experiments. With a hemisphere of hydrophobic capping ligands and the other of hydrophilic ligands, Janus nanoparticles might be readily dispersed in both water and organic media and form oil-in-water micelle-like or water-in-oil reverse micelle-like superparticulate structures by mechanical agitation. This unique property was then exploited for the transfer of hydrophobic nanoparticles (e.g., AgC6 and C\textsubscript{60} nanoparticles) from CH\textsubscript{2}Cl\textsubscript{2} to water as well as for the transfer of water-soluble AgGSH and carbon nanoparticles from water to CH\textsubscript{2}Cl\textsubscript{2}, in sharp contrast with the homogeneously capped AuC6 nanoparticles. In these tests, the formation of vesicle-
like nanoparticle ensembles was clearly visualized in TEM measurements, with the shells consisting of multiple layers of Janus nanoparticles and guest nanoparticles primarily in the cores. Consistent results were obtained in DLS, UV-vis, and photoluminescence measurements. The study further highlights the analogous behaviors of Janus nanoparticles to conventional surfactant molecules in the formation of (reverse) micelle-like structures and the applications of phase transfer leading to the formation of organized composites.
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Chapter 7

Graphene Quantum Dot-Supported Platinum Nanoparticles: Defect-Mediated
Electrocatalytic Activity in Oxygen Reduction
7.1 Introduction

In polymer exchange membrane fuel cells (PEMFC), both the oxidation of fuel molecules at the anode and reduction of oxygen at the cathode necessitate the use of effective catalysts so that sufficiently high current density is generated for practical applications. Of these, oxygen reduction reactions (ORR) have long been recognized as a bottleneck that largely limits the fuel cell performance because of the complex reaction mechanism and sluggish electron-transfer kinetics. Platinum-based nanoparticles have been used extensively as the catalysts of choice for ORR. These catalysts are generally dispersed onto supporting substrates with high specific surface areas and good electrical conductivity such as carbon black, carbon nanotubes, zeolite, tungsten carbides, Magneli phases of titanium oxides and indium tin oxides. In the resulting composite structures, the substrates are generally thought to help stabilize the nanoparticles and improve the durability of the nanoparticle catalysts. Additionally, studies have shown that the electronic interactions between the metal nanoparticles and the supporting substrates may also play a significant role in determining the electrocatalytic activity as a result of the manipulation of the electronic energy of the metal nanoparticles and hence the interactions with oxygen. Recently, graphene derivatives have been attracting particular interest as a new functional support in fuel cell electrocatalysis due to their low cost, high surface area, high conductivity, and high chemical inertness that may facilitate electron-transfer reactions at the electrode surface and hence improve catalyst stability and durability. In these studies, graphene sheets are generally produced
from bulk graphite by the Hummers method through chemical oxidation and exfoliation with strong acids and oxidizing reagents. Therefore, the graphene surface is decorated with various oxygen-containing functional groups (the products are hence commonly referred to as graphene oxide). Whereas the oxygen-containing groups on graphene oxide have been proposed to enhance Pt-support interactions, stabilize the nanoparticle catalysts, and prevent π-π stacking between the graphene sheets, it has been claimed that the higher the graphitization degree of the carbon supports, the higher the electrochemical stability for carbon supported Pt catalysts. Thus, the oxygenated species are generally removed from the graphitic structures so as to restore the hybridized sp2 graphitic network for enhanced conductivity and stability of the graphene structures by chemical reduction and/or thermal treatment. Yet, in a recent study based on DFT calculations, it was proposed that structural defects of graphene quantum dots (GQDs) might be exploited to promote charge transfer from platinum to oxygen as well as to manipulate the binding of reaction intermediates on the Pt surface, leading to enhancement of the ORR activity. In fact, we demonstrated experimentally that platinum nanoparticles supported on GQDs indeed exhibited a markedly enhanced electrocatalytic performance with a more positive onset potential, higher specific activity as well as stability, as compared to commercial Pt/C, which was ascribed to the intimate electronic interactions between Pt nanoparticles and nanosized GQDs that manipulated the dissociative adsorption of oxygen and the binding of reaction intermediates on the Pt surface. Therefore, one immediate question arises. Is there an
optimal concentration of structural defects within the GQDs that leads to maximal electrocatalytic activity of the Pt-GQD nanocomposites for ORR? This is the primary motivation of the present work.

Note that the structural defects of GQDs may be manipulated by rather simple chemical processes. For instance, we have shown that hydrothermal treatment may be used to remove oxygen-contained groups on carbon nanoparticle surfaces in a controllable fashion, which is manifested by the enhancement of the nanoparticle photoluminescence as a result of the removal of surface trap states through dehydration and decarboxylation processes.\(^{34}\) A similar hydrothermal procedure was also used in the conversion of graphene oxide to stable graphene suspension in water.\(^{35}\) In these closed systems of relatively high temperatures and internal pressures, the degree of \(\pi\)-conjugation and hence the concentration of structural defects may be readily engineered by a deliberate control of the heating temperature and reaction time. Therefore, in the present study, we adopted a literature procedure to prepare GQDs from carbon fibers, where the stacked submicrometer domains of traditional pitch-based carbon fibers were broken down to nanosized GQDs (1 to 4 nm with 1 to 3 layers in thickness) by acid treatments and chemical exfoliation.\(^{36}\) Then, GQDs were used as supporting substrates for platinum nanoparticles by hydrothermal co-reduction of GQDs and platinum precursors. The defect concentrations in GQDs were controlled by varying the heating temperature and reaction time of hydrothermal treatment and quantified by Raman and X-ray photoelectron spectroscopic (XPS) measurements. The electrocatalytic activity of the
resulting nanocomposites (Pt/G) in oxygen reduction was then examined and compared in acid electrolyte solutions. Voltammetric measurements showed that while oxygen was effectively reduced to water at all nanoparticle catalysts, the electrocatalytic performance of the Pt/G nanocomposites exhibited volcano-shaped dependence on the defect concentration of the hydrothermally treated GQDs. The results were accounted for by the manipulation of the electronic interactions between the Pt nanoparticles and the nanosized GQDs through the GQD defects and their impacts on the adsorption of oxygen and reaction intermediates.

7.2 Results and Discussion

Figure 7.1 shows the representative TEM images of the Pt/G nanoparticles prepared at various temperatures for different periods of time. It can be seen that the dark-contrast objects are platinum nanoparticles, which are dispersed rather homogeneously on the graphene surface that appears as a low-contrast background. Statistical analysis based on more than 200 nanoparticles in each sample, as manifested in the core size histograms in Figure 7.1 insets, shows that the majority of the Pt nanoparticles are in the narrow range of 2.5 to 3.0 nm in diameter when the hydrothermal temperatures were kept within the range of 140 °C to 180 °C, and at the higher temperature of 200 °C, the nanoparticles are markedly larger at 8 to 12 nm in diameter. Such a discrepancy of the nanoparticle core size (Table 7.1) might be ascribed to the variation of the concentration of GQD structural defects, which can be deliberately controlled by hydrothermal conditions. Note that the GQD structural defects likely serve as the anchoring sites for platinum precursors and the growth of
platinum nanoparticles. At high hydrothermal temperatures, the diminishment of the concentration of the structural defects renders it difficult to effectively passivated the Pt nanoparticles, hence leading to a marked increase of the particle size. Furthermore, in high resolution TEM studies (Figure 7.2), clearly defined lattice fringes can be identified, with a spacing of 0.236 nm. These are consistent with the (111) crystalline planes of fcc Pt.
Figure 7.1. Representative TEM micrographs of GQD-supported Pt nanoparticles prepared by hydrothermal treatment at various temperatures for different periods of time: (A) 140 °C, 6 h; (B) 140 °C, 12 h; (C) 160 °C, 3 h; (D) 160 °C, 6 h; (E) 160 °C, 12 h; (F) 180 °C, 3 h; (G) 180 °C, 6 h; (H) 180 °C, 12 h; (I) 200 °C, 3 h; (J) 200 °C, 6 h; and (K) 200 °C, 12 h. Scale bars are all 10 nm except for panel (I) where it is 50 nm.
Figure 7.2. Representative HRTEM micrographs of GQD-supported Pt nanoparticles prepared by hydrothermal treatment at different temperatures for various period of time: (A) 140 °C, 6 h; (B) 140 °C, 12 h; (C) 160 °C, 3 h; (D) 160 °C, 6 h; (E) 160 °C, 12 h; (F) 180 °C, 3 h; (G) 180 °C, 6 h; (H) 180 °C, 12 h. Scale bars are all 5 nm except for panels (D) and (G) where it is 2 nm.
Table 7.1. Summary of the structures and properties of Pt/G nanoparticles prepared at different hydrothermal temperatures for varied periods of time: average diameters ($d$, nm), $I(D)/I(G)$ ratio from Raman measurements, fraction of defective carbon ($\chi_d$, %) from XPS measurements, effective electrochemical surface area (ECSA, m$^2$/g$_{Pt}$), onset potential (V) and kinetic current density ($J_k$, A/m$^2$) at +0.90 V.

<table>
<thead>
<tr>
<th>Temperature</th>
<th>$d$ (nm)</th>
<th>$I(D)/I(G)$</th>
<th>$\chi_d$ (%)</th>
<th>ECSA (m$^2$/g$_{Pt}$)</th>
<th>Onset Potential (V)</th>
<th>$J_k$ (A/m$^2$ at +0.90 V)</th>
</tr>
</thead>
<tbody>
<tr>
<td>140 °C, 6 h</td>
<td>2.92 ± 0.46</td>
<td>1.49</td>
<td>64.6</td>
<td>13.96</td>
<td>0.87</td>
<td>-</td>
</tr>
<tr>
<td>140 °C, 12 h</td>
<td>3.18 ± 0.51</td>
<td>1.26</td>
<td>54.7</td>
<td>14.37</td>
<td>0.96</td>
<td>-</td>
</tr>
<tr>
<td>160 °C, 3 h</td>
<td>2.91 ± 0.39</td>
<td>1.35</td>
<td>43.8</td>
<td>15.43</td>
<td>0.96</td>
<td>2.48</td>
</tr>
<tr>
<td>160 °C, 6 h</td>
<td>2.83 ± 0.42</td>
<td>1.27</td>
<td>32.5</td>
<td>15.72</td>
<td>0.96</td>
<td>0.60</td>
</tr>
<tr>
<td>160 °C, 12 h</td>
<td>2.87 ± 0.43</td>
<td>1.20</td>
<td>21.6</td>
<td>16.03</td>
<td>1.02</td>
<td>29.2</td>
</tr>
<tr>
<td>180 °C, 3 h</td>
<td>2.78 ± 0.43</td>
<td>1.32</td>
<td>38.5</td>
<td>15.96</td>
<td>0.91</td>
<td>-</td>
</tr>
<tr>
<td>180 °C, 6 h</td>
<td>2.90 ± 0.37</td>
<td>1.21</td>
<td>23.2</td>
<td>17.71</td>
<td>1.03</td>
<td>24.6</td>
</tr>
<tr>
<td>180 °C, 12 h</td>
<td>2.85 ± 0.48</td>
<td>1.17</td>
<td>16.9</td>
<td>16.49</td>
<td>0.96</td>
<td>2.43</td>
</tr>
<tr>
<td>200 °C, 3 h</td>
<td>8.23 ± 5.61</td>
<td>1.16</td>
<td>29.2</td>
<td>12.44</td>
<td>0.80</td>
<td>-</td>
</tr>
<tr>
<td>200 °C, 6 h</td>
<td>7.86 ± 5.56</td>
<td>1.05</td>
<td>24.0</td>
<td>11.98</td>
<td>0.83</td>
<td>-</td>
</tr>
<tr>
<td>200 °C, 12 h</td>
<td>10.67 ± 7.42</td>
<td>0.93</td>
<td>6.1</td>
<td>12.07</td>
<td>0.86</td>
<td>-</td>
</tr>
</tbody>
</table>
The formation of Pt-GQD nanocomposites was manifested in FTIR measurements. Figure 7.3 depicts the FTIR spectra of the as-prepared GQDs and Pt/G composites prepared under various hydrothermal conditions. All samples exhibit one broad peak at about 3430 cm\(^{-1}\), which is attributed to the hydroxyl groups of the GQDs (and residual water).\(^{40}\) For the as-prepared GQDs (black curve), several strong peaks can also be identified at 1685 cm\(^{-1}\) (C=O carboxyl or carbonyl stretching vibrations), 1350 cm\(^{-1}\) (O–H deformation in the C–OH group), and 1135 cm\(^{-1}\) (C–O–C asymmetric stretching vibration in epoxide), suggesting the presence of various oxygenated species on the GQD surfaces. In addition, two strong vibrational bands can be seen at 1606 and 1443 cm\(^{-1}\) which were attributed to the C=C stretching vibration of un-oxidized graphitic (sp\(^2\)) domains.\(^{41}\) Almost identical vibrational features can be seen with the Pt/G-140-6h sample (red curve), signifying that hydrothermal treatment under this condition did not lead to a marked change of the GQD structures.

For other Pt/G hybrid nanoparticles, however, apparent differences can be seen. First, the O–H vibrations diminished markedly, and the C=O and C–O–C stretches almost disappeared, signifying effective removals of these functional moieties from the GQD surfaces. Second, the C=C stretches exhibited an apparent red-shift to 1593 and 1410 cm\(^{-1}\) (Pt/G-140-12h, green curve), 1583 and 1405 cm\(^{-1}\) (Pt/G-160-3h, yellow curve), 1593 and 1429 cm\(^{-1}\) (Pt/G-160-6h, blue curve), 1587 and 1431 cm\(^{-1}\) (Pt/G-160-12h, magenta curve). This may be accounted for by the
Figure 7.3. FTIR spectra of Pt/G nanoparticles prepared by hydrothermal treatments at different temperatures for various periods of time (specified in figure legends). The spectrum for the as prepared GQDs is also included as the black curve.
restoration and hence growth of the Csp² domains in GQDs. With a further increase of the hydrothermal temperature the change was minimal, as the C=C stretches now appeared at 1602 and 1436 cm⁻¹ for Pt/G-180-3h (aqua blue curve), 1602 and 1431 cm⁻¹ for Pt/G-180-6h (grey curve), 1603 and 1441 cm⁻¹ for Pt/G-180-12h (brown curve), 1606 and 1455 cm⁻¹ for Pt/G-200-3h (dark green curve). For the Pt/G-200-6h (chartreuse curve) and Pt/G-200-12h (dark blue curve) samples, the C=C stretches can be found at 1599 and 1356 cm⁻¹, consistent with the G and D bands observed in Raman spectroscopic measurements (Figure 7.4 below).

A more quantitative assessment of the GQD defects was then carried out by Raman spectroscopic measurements. From Figure 7.4, one can see that the series of Pt/G nanocomposites all exhibited two bands at ca. 1593 cm⁻¹ and 1352 cm⁻¹, corresponding to the G band and D band of graphitic nanostructures, respectively. Note that the G band is assigned to the E₂g phonon of the sp² carbons, while the D band is a breathing mode of the κ-point phonons of A₁g symmetry. A prominent D band is an indication of structural disorder in the GQDs, originating from defects associated with vacancies, grain boundaries and amorphous carbon species, which has been observed extensively with chemical exfoliated graphene oxide; and the ratio (I(D)/I(G)) of the D and G band intensity may be exploited for the quantitative assessment of the relative concentration of structural defects within the graphitic carbon matrix. Table 7.1 lists the I(D)/I(G) values for the series of Pt/G hybrid nanoparticles prepared under different hydrothermal conditions. There are several
Figure 7.4. Raman spectra of Pt/G nanoparticles prepared by hydrothermal treatments at different temperatures for various periods of time (specified in figure legends).
aspects that warrant attention. First, for the same reaction time, increasing hydrothermal temperature led to a decrease of the I(D)/I(G) ratio. For the magenta curve. This may be accounted for by the restoration and hence growth of the Csp² domains in GQDs. With a further increase of the hydrothermal temperature the more effective removal of structural defects (and restoration of the Csp² domains) at higher temperature and growth of the Csp² domains. Additionally, at any given temperature, the I(D)/I(G) ratio also decreases with increasing reaction time. For instance, at the hydrothermal temperature of 160 °C, the I(D)/I(G) ratio decreased from 1.35 at 3 h to 1.27 at 6 h and 1.20 at 12 h. Same behaviors can be seen at other hydrothermal temperatures. Thus, within the present experimental context, the lowest I(D)/I(G) ratio was observed at 0.93 with the Pt/G nanocomposites prepared at 200 °C for 12 h. These observations confirm that the hydrothermal treatment is indeed an effective method in removing defects in carbon nanostructures and the defect density can be readily controlled by experimental conditions (temperature, reaction time, etc.), in good agreement with results of the FTIR measurements (Figure 7.3).³⁵

Such a structural variation was also quantified by XPS measurements. Figure 7.5 depicts the survey spectra of the (A) C1s and (B) Pt4f electrons of the Pt/G nanocomposites prepared at different temperatures by hydrothermal treatment. In panel (A), for the Pt/G-140-6h sample, deconvolution of the C1s electron spectra revealed four major components of the carbon 1s electrons: sp² carbon at 284.7 eV (yellow curve),⁴⁷-⁵¹ carbons in C-OH at 286.2 eV (blue curve),⁵² in C=O at 287.4 eV (magenta curve) and in COOH at 289.9 eV (aqua blue curve) bonds.³⁶,⁵³,⁵⁴
Figure 7.5. XPS spectra of (A) C1s and (B) Pt4f electrons of the Pt/G nanoparticles prepared by a hydrothermal procedure at different temperatures for various periods of time (specified in figure legends). Black curves are experimental data and colored curves are deconvolution fits.
Figure 7.6. Cyclic voltammograms of GQD-supported Pt nanoparticles prepared by hydrothermal treatment at different temperatures for various periods of time, which were specified in the figure legends. Pt mass loadings were all about 3 mg (Table 7.3). Potential sweep rate 0.1 V/s. The charge associated with hydrogen adsorption/desorption was used to quantify the electrochemical surface areas of the respective catalysts, as summarized in Table 1.
Table 7.2. XPS data of Pt/G composites

<table>
<thead>
<tr>
<th>Temperature</th>
<th>Sp² C</th>
<th>C-OH</th>
<th>C=O</th>
<th>C(=O)OH</th>
<th>4f 7/2</th>
<th>4f 5/2</th>
</tr>
</thead>
<tbody>
<tr>
<td>140 °C, 6 h</td>
<td>284.69</td>
<td>286.18</td>
<td>287.42</td>
<td>289.87</td>
<td>71.10</td>
<td>74.41</td>
</tr>
<tr>
<td>140 °C, 12 h</td>
<td>284.72</td>
<td>286.15</td>
<td>287.80</td>
<td>289.56</td>
<td>71.13</td>
<td>74.40</td>
</tr>
<tr>
<td>160 °C, 3 h</td>
<td>284.69</td>
<td>286.15</td>
<td>287.75</td>
<td>289.21</td>
<td>71.04</td>
<td>74.30</td>
</tr>
<tr>
<td>160 °C, 6 h</td>
<td>284.69</td>
<td>286/02</td>
<td>287.64</td>
<td>289.42</td>
<td>71.02</td>
<td>74.29</td>
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<tr>
<td>160 °C, 12 h</td>
<td>284.67</td>
<td>286.10</td>
<td>287.69</td>
<td>289.26</td>
<td>70.87</td>
<td>74.22</td>
</tr>
<tr>
<td>180 °C, 3 h</td>
<td>284.75</td>
<td>286.20</td>
<td>287.85</td>
<td>289.26</td>
<td>70.97</td>
<td>74.26</td>
</tr>
<tr>
<td>180 °C, 6 h</td>
<td>284.75</td>
<td>286.16</td>
<td>287.75</td>
<td>289.46</td>
<td>70.90</td>
<td>74.21</td>
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<tr>
<td>180 °C, 12 h</td>
<td>284.69</td>
<td>286.04</td>
<td>287.64</td>
<td>289.17</td>
<td>70.98</td>
<td>74.24</td>
</tr>
<tr>
<td>200 °C, 3 h</td>
<td>284.67</td>
<td>286.15</td>
<td>287.85</td>
<td>289.26</td>
<td>71.04</td>
<td>74.34</td>
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<td>286.23</td>
<td>287.85</td>
<td>289.32</td>
<td>71.05</td>
<td>74.35</td>
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<td>200 °C, 12 h</td>
<td>284.75</td>
<td>286.17</td>
<td>287.47</td>
<td>289.26</td>
<td>71.08</td>
<td>74.39</td>
</tr>
</tbody>
</table>

Further confirms the formation of various oxygenated functional moieties on the GQD surfaces. If one defines all non-sp² carbon as the structural defects, one can see that whereas the binding energies remained virtually unchanged (Table 7.2), the defect concentration in the Pt/G nanocomposites decreased markedly with increasing hydrothermal temperature and prolonging reaction time, as manifested by the apparent diminishment of the non-sp² carbon peaks. In fact, from the top panel of
Figure 7.6, one can see that (i) during the hydrothermal treatment, C=O and COOH defects might be more readily removed, leaving C-O as the primary defects remaining in the GQDs (blue peaks); and (ii) the defect concentration reaches a minimum (~20%) and correspondingly Csp\(^2\) fraction reaches a maximum (~80%) at Pt/G-160-12h. These observations are consistent with the Raman spectroscopic results (Figure 7.3 and Table 7.1). In fact, the atomic ratio of defective carbons to total carbon exhibited a roughly linear increase with the I(D)/I(G) ratio, from 6.1% at I(D)/I(G) = 0.93 to 64.8% at I(D)/I(G) = 1.49, suggesting a direct correlation between these two measurements. From panel (B) of Figure 7.4, the binding energies of the Pt4f electrons in the Pt/G nanocomposites can all be identified at around 71.0 and 74.4 eV where both the doublet energies and spin–orbit coupling are consistent with those of metallic platinum (Table 7.2).\(^{55,56}\) Interestingly, from Table 7.2, it can be seen that both binding energies of the Pt4f electrons first decreased with increasing temperature from 140 to 180 °C, and then increased when the hydrothermal temperature increased to 200 °C. Specifically, the lowest binding energies for Pt4f\(7/2\) and Pt4f\(5/2\) among the series can be found at 70.9 eV and 74.2 eV for Pt/G-160-12h (and only slightly higher with Pt/G-180-6h). In contrast, the binding energies are the highest at 71.1 and 74.4 eV for both Pt/G-140-6h and Pt/G-200-12h. Interestingly, among the three major defects (C-OH, C=O, and COOH), the corresponding binding energy of the C1s electrons in C=O was 287.7 eV for Pt/G-160-12h, but markedly lower at 287.4 eV for both Pt/G-140-6h and Pt/G-200-12h, whereas those for C-OH and COOH were virtually invariant. This discrepancy suggests that charge transfer likely occurred
from Pt to GQD that was dictated largely by the polar carbonyl (C=O) moieties on the GQD surfaces, and this charge transfer reached a minimum in the Pt/G-160-12h and Pt/G-180-6h samples among the series, because of low concentrations of the polar C=O and COOH structural defects (Figure 7.6). Interestingly, electrochemical measurements indicate that these two samples exhibited the best electrocatalytic activities in ORR among the series, as detailed below.

Table 7.3. Elemental analysis of Pt/G composites

<table>
<thead>
<tr>
<th>Temperature</th>
<th>Area C1s</th>
<th>Area Pt 4f</th>
<th>Ratio C:Pt</th>
<th>Pt loading (%)</th>
<th>Pt mass loading (mg)</th>
</tr>
</thead>
<tbody>
<tr>
<td>140 °C, 6 h</td>
<td>22753</td>
<td>26463</td>
<td>7.34</td>
<td>11.99</td>
<td>3.30</td>
</tr>
<tr>
<td>140 °C, 12 h</td>
<td>7975</td>
<td>8775</td>
<td>7.76</td>
<td>11.42</td>
<td>3.14</td>
</tr>
<tr>
<td>160 °C, 3 h</td>
<td>7672</td>
<td>8796</td>
<td>7.45</td>
<td>11.84</td>
<td>3.26</td>
</tr>
<tr>
<td>160 °C, 6 h</td>
<td>13791</td>
<td>16270</td>
<td>7.24</td>
<td>12.14</td>
<td>3.34</td>
</tr>
<tr>
<td>160 °C, 12 h</td>
<td>16447</td>
<td>22428</td>
<td>6.26</td>
<td>13.77</td>
<td>3.79</td>
</tr>
<tr>
<td>180 °C, 3 h</td>
<td>6422</td>
<td>7853</td>
<td>6.98</td>
<td>12.53</td>
<td>3.45</td>
</tr>
<tr>
<td>180 °C, 6 h</td>
<td>19615</td>
<td>24997</td>
<td>6.70</td>
<td>12.99</td>
<td>3.57</td>
</tr>
<tr>
<td>180 °C, 12 h</td>
<td>19606</td>
<td>20296</td>
<td>8.25</td>
<td>10.82</td>
<td>2.97</td>
</tr>
<tr>
<td>200 °C, 3 h</td>
<td>9150</td>
<td>10194</td>
<td>7.66</td>
<td>11.54</td>
<td>3.17</td>
</tr>
<tr>
<td>200 °C, 6 h</td>
<td>14163</td>
<td>14589</td>
<td>8.29</td>
<td>10.77</td>
<td>2.96</td>
</tr>
<tr>
<td>200 °C, 12 h</td>
<td>17922</td>
<td>20053</td>
<td>7.63</td>
<td>11.59</td>
<td>3.19</td>
</tr>
</tbody>
</table>

Furthermore, from the integrated peak areas in the XPS measurements, the concentration of Pt in the Pt/G nanocomposites can be quantified. The results are
summarized in Table 7.3, where one can see that the platinum loading (Pt/C atomic ratio) was quite consistent among the nanocomposite series at between 11% and 14%.

The electrocatalytic activity of the resulting Pt/G nanocomposites was then examined for oxygen reduction reactions. Figure 7.6 shows the steady-state cyclic voltammograms of a glassy carbon electrode modified with a same amount of Pt/G in a 0.1 M HClO₄ solution saturated with nitrogen. Note that the Pt mass loading was estimated by XPS measurements to be between 3.1 and 3.8 mg (Table 7.3). All samples exhibited the well-defined butterfly voltammetric features of platinum in nitrogen-saturated acid electrolytes. Of these, a pair of broad voltammetric peaks can be seen within the potential range of +0.6 and +1.0 V, which are ascribed to the formation of platinum oxide in the anodic scan and reduction of the oxide in the return sweep. Two additional pairs of voltammetric peaks appeared between 0 and +0.3 V. These are due to hydrogen adsorption/desorption on the platinum surface. Based on the integrated areas of these voltammetric features, the effective electrochemical surface area (ECSA) of the nanoparticle catalysts were calculated to be between 12 and 18 m²/gₚt. The results are listed in Table 1.
Figure 7.7. RRDE voltammograms of GQD-supported Pt nanoparticles prepared by hydrothermal treatment at different temperatures for various period of time: (A) 140 °C, 6 h; (B) 140 °C, 12 h; (C) 160 °C, 3 h; (D) 160 °C, 6 h; (E) 160 °C, 12 h; (F) 180 °C, 3 h; (G) 180 °C, 6 h; (H) 180 °C, 12 h; (I) 200 °C, 3 h; (J) 200 °C, 6 h; and (K) 200 °C, 12 h. Catalyst loadings were all 27.5 µg. Potential sweep rate 5 mV/s and electrode rotation rates are specified in figure legends. Ring potentials were all set at +1.5 V.
The electrocatalytic activity in oxygen reduction was then examined by voltammetric measurements in an oxygen-saturated 0.1 M HClO₄ solution. Figure 7.7 shows the RRDE voltammograms of the glassy carbon disk electrode modified with Pt/G nanoparticles with the electrode rotation rate varied from 100 rpm to 2500 rpm. There are at least two aspects that warrant attention here. First, nonzero cathodic currents at the disk electrode (I₉) became clearly identified as the electrode potential was swept in the negative direction, and the currents increased with increasing electrode rotation rates, signifying the apparent electrocatalytic activity of the Pt/G nanoparticles in oxygen reduction. Second, the corresponding ring currents (I₉) at +1.5 V were about 3 orders of magnitude lower than those of the disk, signifying that only minimal amounts of peroxide intermediates were produced during oxygen reduction and hence high efficiency of the Pt/G nanoparticles in the electrocatalytic process. In fact, the number of electron transfer (n) during oxygen reduction can be estimated by the ratio between the disk and the ring currents,⁵⁴,⁵⁷,⁵⁸

\[
n = 4 \cdot \frac{I_D}{I_D + I_R/N}
\]  

(8.1)

where N is the collection efficiency (37%) of the RRDE electrode,⁵⁷ as depicted in Figure 7.8. It can be seen that at sufficiently negative potentials, all electrodes exhibited \( n \approx 4.00 \), indicating that oxygen was fully reduced into water, \( \text{O}_2 + 4\text{H}^+ + 4\text{e} \rightarrow 2\text{H}_2\text{O} \). Yet the onset potential for oxygen reduction was markedly different, as listed in Table 7.1. Among the series, the onset potentials decreases in the order
Figure 7.8. Variation of the number of electron transfer (n) in oxygen reduction with electrode potential. Curves are average values of experimental data calculated from the RRDE voltammograms at all rotation rates in Figure 7.7 by using equation 7.1.
of Pt/G-180-6h (+1.03 V) > Pt/G-160-12h (+1.02 V) > Pt/G-180-12h > Pt/G-160-3h
> Pt/G-140-12h (+0.96 V) > Pt/G-180-3h (+0.91 V) > Pt/G-140-6h (+0.87 V) > Pt/G-
200-12h (+0.86 V) > Pt/G-200-6h (+0.83 V) > Pt/G-200-3h (+0.80 V). That is, Pt/G-
180-6h and Pt/G-160-12h are among the best in the series with the most positive
onset potential.

The electron-transfer kinetics involved were then quantified by the Koutecky–Levich analysis (equation 7.2), as the disk currents ($I_D$) might include both kinetic ($I_k$)- and diffusion ($I_d$)-controlled contributions,

$$\frac{1}{I_D} = \frac{1}{I_k} + \frac{1}{I_d} = \frac{1}{I_k} + \frac{1}{B\omega^{1/2}} \quad (7.2a)$$

$$B = 0.62nFAC_0D_0^{2/3}v^{-1/6} \quad (7.2b)$$

$$I_k = nAFkC_0 \quad (7.2c)$$

where $F$ is the Faradaic constant (96500 C/mol), $D_0$ the diffusion coefficient of O$_2$ in
0.1 M HClO$_4$ aqueous solution (1.93×10$^{-5}$ cm$^2$/s), $v$ the kinematic viscosity of the
solution (9.87×10$^{-3}$ cm$^2$/s), $C_0$ the oxygen concentration in O$_2$-saturated solutions
(1.18 mM), $\omega$ the electrode rotation rate, $k$ the electron-transfer rate constant, and $A$
the geometric surface area of the electrode.$^{61-63}$ The Koutecky–Levich plots ($I_D$ vs.
$\omega^{-1/2}$) of all Pt/G nanoparticles within the respective kinetically controlled region.

First, one can see that all experimental data exhibited good linearity, and the slopes
were rather consistent with each nanoparticle sample. This indicates that the oxygen
reduction proceeded at the Pt/G nanoparticle catalysts as a first-order reaction with
respect to dissolved oxygen.
Figure 7.9. Tafel plot of the Pt/G nanoparticles for oxygen reduction. Symbols are experimental data obtained by linear regressions of the K-L plots with equation (7.2). Lines are for eye-guiding only. Curves are average values of experimental data calculated from the RRDE voltammograms at all rotation rates in Figure 7.8 by using equation 7.1.
Figure 7.9 is the Tafel plot. It can be clearly seen that at all Pt/G nanoparticle catalysts the kinetic current densities increased with increasingly negative electrode potentials, and more importantly, within the electrode potential range of +0.80 V to +1.00 V, the kinetic current densities with Pt/G-160-12h and Pt/G-180-6h were at least an order of magnitude higher than those of other Pt/G samples. For instance, the area-specific current density ($J_k$, $I_k$ normalized by the respective effective electrochemical surface area as listed in Table 7.1) at +0.90 V was 29.2 and 24.6 A/m$^2$ for these two catalysts, respectively, but only 2.48 A/m$^2$ for Pt/G-160-3h, 2.43 A/m$^2$ for Pt-180-12h, and 0.60 A/m$^2$ for Pt/G-160-6h (for the rest, the currents were too small to measure).

These are significantly greater than that observed with Pt/G nanocomposites prepared without hydrothermal treatment (14.5 A/m$^2$), and more than an order of magnitude higher than that of commercial Pt/C.$^{33}$ In terms of mass activity, the Pt/G-160-12h and Pt/G-180-6h samples also stood out as the best among the series at 468.1 A/g$_{Pt}$ and 435.7 A/g$_{Pt}$ at +0.90 V, respectively. Note that these have reached the DOE target for 2015 (440 A/g$_{Pt}$ at +0.90 V), and are also superior to most of Pt alloying catalysts reported so far, such as PtPd nanodendrites (240 A/g),$^{59}$ PtAu (200 – 300A/g),$^{63}$ and PtCuCoNi nanotubes (190 A/g).$^{64}$ In contrast, the mass activity was only 40.1 A/g$_{Pt}$ for Pt/G-180-12h, 38.3 A/gPt for Pt/G-160-3h, and 9.4 A/gPt for Pt/G-160-6h.

This remarkable performance of the Pt/G nanocomposites for oxygen reduction might be accounted for by the impacts of the GQD structural defects on the
Figure 7.10. Variation of the ORR kinetic current density at +0.85 (solid circles) and +0.90 V (empty circles) with GQD structural defects manifested as the defect concentrations from XPS measurements (Figure 7.5) and I(D)/I(G) ratio in Raman spectroscopic measurements (Figure 7.4).
reaction dynamics of ORR. In a recent study based on density functional theory calculations of a Pt_{13} nanoparticle supported on a monovacancy defective graphene nanosheet,\textsuperscript{32} it was found that the defective graphene support not only lowered the activation energy for oxygen (O\textsubscript{2}) dissociation by promoting charge transfer from Pt to O\textsubscript{2} but also decreased the energy barrier of the rate-limiting step by weakening the binding of the HO\textsuperscript{*} species. Indeed drastic enhancement was observed with GQD-supported Pt nanoparticles in ORR, in comparison to commercial Pt/C catalysts.\textsuperscript{33} In the present study, the results presented above demonstrate that the performance may be further enhanced by a deliberate manipulation of the GQD structural defects, as shown in Figure 7.10. Using the kinetic current densities at +0.85 V (solid circles) and +0.90 V (empty circles) as the examples, we can see that the electrocatalytic activity of the Pt/G nanocomposites exhibited volcano-shaped dependence on the defect concentrations quantified by XPS measurements (Figure 7.5) and on the I(D)/I(G) ratio determined by Raman spectroscopic measurements (Figure 7.4), with the best activity in the series both corresponding to the Pt/G-160-12h and Pt/G-180-6h samples. This means that there exists an optimal defect concentration within the GQDs for maximal ORR activity of the Pt/G hybrid nanoparticles. This may be ascribed to the intimate interactions between the graphene support and platinum nanoparticles that led to deliberate manipulation of the platinum d-band center and hence the charge transfer dynamics of oxygen reduction.\textsuperscript{32}

Mechanistically, in oxygen reduction, it has been known that the electron-transfer kinetics and hence the electrocatalytic performance depend rather sensitively
on the adsorption of oxygen and reaction intermediates such as $O^*$ and $HO^*$ intermediates on the Pt surface. In fact, studies have shown that the optimal catalytic activity for ORR may be achieved when oxygen adsorption is 0.1 eV weaker than that on single-crystal platinum electrode surfaces.$^{65-67}$ Thus, ideally a balance has to be struck between the strength of intermediate adsorption and reaction kinetics. This may be achieved by a deliberate variation of the GQD structural defects as a result of partial charge transfer from platinum that weakens the adsorption of oxygen and reaction intermediates. In the present study, the experimental results suggest that an optimal structure may be found at about 20% defect concentration of the GQD supports. Whereas higher concentration of the GQD defects may afford more substantial charge transfer from Pt to GQD, the electronic conductivity of the GQDs support may suffer and hence compromise the electron transfer kinetics of oxygen reduction.

7.3 Conclusion

In this study, graphene quantum dots (GQDs)-supported platinum nanoparticles were prepared by hydrothermal co-reduction of Pt(II) precursors and GQDs within the temperature range of 140 to 200 °C for various periods of time. TEM measurements showed that the Pt nanoparticles exhibited rather consistent core size when the hydrothermal temperature was controlled between 140 and 180 °C, and at higher temperatures (200 °C), the particle core size was found to increase drastically, which was accounted for by the diminishment of the structural defects of the GQDs that weakened the anchoring and passivation of the platinum nanoparticles.
Interestingly, the GQD structural defects, which were examined and quantified by FTIR, Raman and XPS spectroscopic measurements, were found to strongly impact the electrocatalytic activity of the resulting Pt/G nanocomposites in oxygen reduction. On the basis of the onset potential, number of electron transfer involved, and kinetic current density, the Pt/G-160-12h and Pt/G-180-6h nanoparticles were found to exhibit markedly enhanced electrocatalytic activity as compared to the rest of the series, with the mass activity reaching the DOE target for 2015. This suggests an optimal defect concentration of about 20% of non-sp^2 carbons in GQDs as determined by XPS measurements, or an I(D)/I(G) ratio of about 1.2 in Raman spectroscopic measurements. The results are rationalized by the manipulation of the adsorption of oxygen and reaction intermediates on platinum by the GQD structural defects as partial charge transfer might occur from Pt to GQD defects. Additional concentrations might arise from the effects of structural defects on the electronic conductivity of the nanocomposites catalysts. The results presented herein are significant in that the strategy may lead to the development of a new paradigm in the design, manipulation and optimization of nanoparticle catalysts for fuel cell electrochemistry.
7.4 Reference


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Chapter 8

Ferrocene-Functionalized Carbon Nanoparticles

8.1 Introduction

Carbon nanoparticles represent a unique form of carbon-based nanomaterials that, similar to their well-known cousins of fullerenes and carbon nanotubes, exhibit interesting optical and electronic properties that may be exploited for extensive applications in diverse areas.\(^1,2\) Typically, carbon nanoparticles are prepared by laser ablation of a graphitic target\(^3,4\) or by electrochemical treatments of carbon nanotubes.\(^5\) More recently it was demonstrated that nanosized carbon particles could also be produced by oxidative treatments of carbon soot which were collected from the incomplete combustion of candles or natural gas.\(^6-8\) High-resolution transmission electron microscopic (HRTEM) measurements showed that the as-produced nanoparticles exhibited a crystalline graphitic core with the core surface decorated with various oxygenated functional moieties where the quinone-like derivatives gave rise to unique electrochemical and spectroscopic characteristics.\(^7,8\) By taking advantage of the chemical reactivity of carbon surfaces, it is anticipated that the material properties of carbon nanoparticles can be further manipulated by controlled chemical functionalization. This is the primary motivation of the present study.

It has been rather well-known that carbon surfaces can be readily functionalized by (electro)chemical grafting of diazonium derivatives, where a strong covalent C–C bond is formed between the functional ligand and the carbon substrate.\(^9-12\) Such a unique interfacial bonding interaction may be exploited to initiate intraparticle electronic coupling between particle-bound functional moieties, as the carbon nanoparticles exhibit a graphitic core with an \(sp^2\) carbon network that serves
as a conducting medium. It should be noted that the recent observation of nanoparticle-mediated electronic communication is primarily limited to transition-metal nanoparticles functionalized with conjugated metal–carbon covalent bonds at the metal–ligand interface such as Ru=carbene π bonds and Ru–C≡ bonds.\textsuperscript{13-17} Therefore, chemically functionalized carbon nanoparticles offer a unique structural framework within which the impacts of the core–ligand interfacial bonding interactions on intraparticle charge delocalization and hence nanoparticle optical and electronic properties can be examined.

In the present study, we functionalized carbon nanoparticles with 4-ferrocenylphenyldiazonium and determined the surface concentration by X-ray photoelectron spectroscopic (XPS) measurements. We then examined the impacts of ferrocenyl functionalization on the spectroscopic and electrochemical characteristics of the nanoparticles by exploiting the ferrocenyl moieties as the electrochemical probe and the photoluminescence characteristics of the carbon nanoparticles as the optical yardstick. The results suggest that electronic communication occurred between the nanoparticle-bound ferrocenyl moieties at mixed valence, although the electronic coupling was somewhat weak and consistent with the behaviors of Class I/II compounds as defined by Robin and Day.\textsuperscript{18} This indicates that, to a limited extent, the C(sp\textsuperscript{2})–C(sp\textsuperscript{2}) interfacial bonding interactions offer a new pathway towards the manipulation of the chemical and physical properties of carbon nanoparticles. In contrast, with the insertion of an sp\textsuperscript{3} carbon spacer (CH\textsubscript{2}) between the phenyl and ferrocenyl moieties, the ferrocenyl groups were found to behave
independently, as reflected in electrochemical and spectroscopic measurements, indicating the effective turn-off of intraparticle charge delocalization by the saturated spacer.

8.2 Results and discussion

The incorporation of the ferrocenyl moieties onto the carbon nanoparticle surface was first confirmed by FTIR measurements. Figure 8.1 depicts the FTIR spectra of the carbon nanoparticles before and after reactions with 4-ferrocenylphenyldiazonium. In comparison with the spectral data of the as-prepared carbon nanoparticles (blue curve), several new features emerged for Fc-CNPs (black curve) which are consistent with the vibrational characteristics of the ferrocenyl and phenyl moieties, including 3068 cm\(^{-1}\) (\(v_{\text{C-H}}\)), 1600 cm\(^{-1}\) (\(v_{\text{C=C, phenyl}}\)), 1450–1506 cm\(^{-1}\) (\(v_{\text{C=C, ferrocenyl}}\)), 1018 cm\(^{-1}\) (\(\delta_{\text{C-H}}\)), and 820 cm\(^{-1}\) (\(\pi_{\text{C-H}}\)). These vibrational bands can also be clearly identified with monomeric 4-ferrocenylaniline (red curve). Note that the vibrational stretches of N–H (~3450 cm\(^{-1}\)) and C–N (1295 cm\(^{-1}\)) are very well-defined with 4-ferrocenylaniline, and disappeared in the ferrocene-functionalized carbon nanoparticles, indicating that the Fc-CNP samples were free of excessive aniline monomers.

Furthermore, as reported previously, the as-prepared carbon nanoparticles exhibited various oxygenated species on the surface, which was manifested with the carbonyl vibrational band (\(v_{\text{C=O}}\)) at 1724 cm\(^{-1}\). Interestingly, this band became weakened rather substantially with the Fc-CNP sample, most probably as a consequence of superhydride reduction during the ferrocene functionalization process.
Figure 8.1. FTIR spectra of the as-produced (CNPs, blue curve) and ferrocene-functionalized (Fc-CNPs, black curve) carbon nanoparticles, along with that for the monomeric 4-ferrocenyl-aniline (red curve).
(it is likely that the broad peak around 3400 cm$^{-1}$ includes contributions from both the resulting hydroxyl moieties as well as residual water).

The attachment of the ferrocenyl moieties onto the carbon nanoparticles was also manifested in XPS measurements (Figure 8.2). The C1s electrons can be clearly identified at 284.4 eV, consistent with the graphitic nature (sp2 carbons) of the carbon nanoparticles;\textsuperscript{7} whereas the two peaks at 719.9 eV and 707.3 eV can be assigned to the Fe2p$^{1/2}$ and Fe2p$^{2/3}$ electrons of the ferrocenyl moieties.\textsuperscript{21} Based on the integrated peak areas of the C1s and Fe2p electrons, the elemental ratio between Fe and C in the Fc-CNP samples is estimated to be ca. 0.52%. By assuming a spherical structure of the graphitic core of the carbon nanoparticles (dia. 4.8 ± 0.6 nm),\textsuperscript{7} this corresponds to about 31.9 ferrocene moieties per nanoparticle, or a surface coverage of 7.32 × 10$^{-11}$ mol cm$^{-2}$. Note that this is significantly smaller than the saturated surface coverage of ferrocene-terminated self-assembled monolayers on gold surfaces (3.2 × 10$^{-10}$ mol cm$^{-2}$).\textsuperscript{22}

The impacts of surface functionalization by the ferrocenyl moieties on the particle opto-electronic properties were then examined by electrochemical and spectroscopic measurements. Figure 8.3(A) shows the square wave voltammograms (blue solid curve) of the Fc-CNP sample at a concentration of 6 mg mL$^{-1}$ in DMSO with 0.1 M TBAP as the supporting electrolyte at a gold disk electrode in the dark. It can be seen that within the potential range of −0.2 to +0.6 V there are two pairs of voltammetric peaks with the peak potentials at +0.068 V and +0.355 V, respectively. The former can be ascribed to the charge transfer reactions of oxygenated functional
Figure 8.2. XPS surveys of the C1s and Fe2p electrons in ferrocenyl-functionalized carbon nanoparticles. In the bottom panel, the red curve is the smoothed profile of the experimental data (black curve).
Figure 8.3. Square wave voltammograms (SWVs) of ferrocene-functionalized carbon nanoparticles (Fc-CNPs) acquired (A) in the dark or (B) under UV photoirradiation (370 nm) at a gold electrode in 0.1 M tetrabutylammonium perchlorate (TBAP) in DMSO. Electrode surface area 2.63 mm², particle concentration 6 mg mL⁻¹, increment of potential 4 mV, amplitude 25 mV and frequency 15 Hz. Solid curves are the experimental moieties on the carbon nanoparticle surface that are analogous to phenantheraquinone derivatives, as observed previously with the as-prepared carbon nanoparticles, whereas the latter is attributable to the particle-bound ferrocenyl moieties that underwent one-electron oxidation to ferrocenium, Fc → Fc⁺ + e. In fact, consistent voltammetric profiles were observed with data and dashed lines represent the deconvolution of the voltammetric features.
moieties on the carbon nanoparticle surface that are analogous to phenanthraquinone derivatives, as observed previously with the as-prepared carbon nanoparticles, whereas the latter is attributable to the particle-bound ferrocenyl moieties that underwent one-electron oxidation to ferrocenium, \( \text{Fc} \leftrightarrow \text{Fc}^\dagger + e \). In fact, consistent voltammetric profiles were observed with the ferrocenyl complexes produced by the reduction of 4-ferrocenylphenyldiazonium with superhydride (not shown). More interestingly, deconvolution of the experimental data shows that the broad ferrocenyl peak actually consists of two closely spaced voltammetric waves (green and red dashed curves) with the formal potentials \( (E^\circ') \) at +0.318 V and +0.396 V, respectively (note that the summation (black dashed curve) of these individual voltammetric profiles, along with that from the nanoparticle surface species (yellow dashed curve), exhibits excellent agreement with the experimental data), and both of these two subpeaks exhibited a peak splitting \( (\Delta E_p) \) less than 20 mV, consistent with the reversible kinetics of ferrocene electron-transfer reactions. This observation strongly suggests that intraparticle electronic communication occurred between the nanoparticle-bound ferrocenyl moieties at mixed valence, most probably as a result of the covalent grafting of the ferrocenyl ligands onto the graphitic particle cores where the \( \text{sp}^2 \) carbon matrix serves as a conducting medium for intraparticle charge delocalization. Yet the somewhat small difference of the formal potentials \( (\Delta E^\circ' = 78 \text{ mV}) \) indicates that the electronic coupling between the ferrocenyl metal centers is relatively weak. In fact, according to the classification by Robin and Day, the Fc-CNPs appeared to behave as a Class I/II compound.
It should be noted that the ferrocenyl moieties are covalently bridged by a spacer that consists of two phenylene units and a nanosized particle core. Despite this long chemical separation, intraparticle intervalence transfer between the particle-bound ferrocenyl moieties is resolvable voltammetrically. This is in contrast with a previous study\textsuperscript{23} where methylated binuclear ferrocene derivatives bridged by a \textit{p}-phenylene unit were found to exhibit two clearly reversible, one-electron voltammetric peaks with a potential spacing ranging from 70 to 120 mV, signifying apparent electronic communication between the ferrocenyl moieties; whereas the incorporation of a \textit{p}-biphenylene spacer led to the appearance of a single reversible oxidation peak that corresponded to the simultaneous transfer of two electrons per dimer, indicating diminishment of the electronic coupling between the two ferrocenyl centers.

It should be noted that the surface coverage of the ferrocenyl moieties on the carbon nanoparticles was far less than a full monolayer (Figure 8.2). Thus the contribution of electrostatic (through-space) interactions to the appearance of intervalence transfer between the particle-bound ferrocenyl moieties at mixed valence is anticipated to be minimal. In other words, the observed intervalence transfer is most likely due to through-bond interactions, akin to those observed previously with Ru nanoparticles functionalized with Ru=carbene $\pi$ bonds or Ru–C≡ bonds.$^{13-17}$

This argument was further supported by the voltammetric data obtained when the Fc-CNP solution was exposed to UV (370 nm) photoirradiation, as manifested in Figure 8.3(B). It can be seen that whereas the overall voltammetric features remained
practically unchanged and two subpeaks can also be deconvoluted from the broad voltammetric wave at $\sim+0.40$ V, the potential separation ($\Delta E^{\circ}$) between these two subpeaks was found to increase to about $107$ mV, suggesting that intraparticle charge delocalization might be facilitated by photoexcitation due to the photogenerated free electrons from the biphenylene bridge (vide infra). This is also consistent with the control experiment where an aniline derivative was synthesized with a $\text{CH}_2$ spacer inserted between the ferrocenyl and the phenylene moieties, i.e., $\text{Fc}–\text{CH}_2–\text{C}_6\text{H}_4–\text{NH}_2$, and the corresponding diazonium was used to functionalize the nanoparticles by using the same experimental procedure detailed in the Experimental section. The resulting nanoparticles (denoted as $\text{FcCH}_2$-CNPs) exhibited two pairs of voltammetric peaks in SWV measurements, and deconvolution could not resolve any additional peak (Figure 8.4), no matter whether the voltammograms were acquired in the dark or under UV irradiation. The first peak at $E^{\circ} = +0.071$ V is almost the same as that observed with $\text{Fc}$-CNP (Figure 8.3), which was, again, ascribed to the charge transfer reactions of oxygenated functional moieties on the carbon nanoparticle surface; whereas the second peak at $E^{\circ} = +0.240$ V was attributed to the redox reactions of nanoparticle-bound ferrocenyl moieties. The fact that only one pair of voltammetric peaks was observed for the ferrocenyl moieties in $\text{FcCH}_2$-CNP whereas two pairs for the $\text{Fc}$-CNP sample strongly discounts the hypothesis that the latter was a result of different binding sites on the CNP surface. Instead, the discrepancy of the voltammetric behaviors between these two nanoparticle samples strongly suggests that the intraparticle charge delocalization might be effectively turned off by the
insertion of an sp³ carbon spacer, consistent with our earlier studies with Ru nanoparticles.¹³-¹⁷

The notion that electronic coupling occurred between the nanoparticle-bound ferrocenyl moieties at mixed valence was also manifested in near-infrared (NIR) spectroscopic measurements by using NOBF₄ as the oxidizing reagent. Figure 5 shows the NIR absorption spectra of Fc-CNPs in DMSO with the addition of varied amounts of freshly prepared NOBF₄. It can be seen that with the addition of NOBF₄, two prominent absorption bands started to emerge at 1454 and 1950 nm, and as depicted in the figure inset, their peak intensities exhibited volcano-shaped dependency on the amount of NOBF₄ added, which is analogous to the unique NIR features of biferrocene derivatives at mixed valence. In sharp contrast, the NIR profile of the FcCH₂-CNP sample remained practically unchanged with the addition of a comparable amount of NOBF₄ (Figure 8.6).

These behaviors are consistent with the results in our previous studies where nanoparticle-mediated intraparticle intervalence transfer was observed with functional moieties bound onto metal nanoparticle surfaces by conjugated metal–carbon
Figure 8.4. Square wave voltammograms of FeCH$_2$-CNP nanoparticles acquired (top) in the dark or (bottom) under UV photoirradiation (370 nm) at a gold electrode in 0.1 M tetrabutylammonium perchlorate (TBAP) in DMSO. Electrode surface area 2.63 mm$^2$, particle concentration 3 mg/mL, increment of potential 4 mV, amplitude 25 mV and frequency 15 Hz. Solid curves are the experimental data and dashed lines represent the deconvolution of the voltammetric features.
covalent bonds.\textsuperscript{13-17, 24} For instance, previously we observed that when ferrocenyl moieties were bound onto Ru nanoparticle surface by a Ru=\(\pi\) bond or Ru–C≡ bond, two pairs of voltammetric peaks appeared with a potential spacing of about 200 mV, rendering the nanoparticle materials to behave as Class II compounds. The much smaller \(\Delta E'^{\circ}\) observed above with Fc-CNPs suggests that the C(sp\textsuperscript{2}, graphitic)–C(sp\textsuperscript{2}, phenyl) interfacial bonding interactions exhibit a much lower bonding order and therefore are less efficient in facilitating intraparticle charge delocalization. With an increase of the bonding order by photoirradiation with UV lights, enhanced electronic communication was observed between the particle-bound ferrocenyl moieties (Figure 3(B)).

The optical properties of the ferrocenyl-functionalized nanoparticles (Fc-CNPs) were then examined by UV-vis and photoluminescence spectroscopic measurements. Figure 8.7 depicts the UV-vis absorption spectra of the carbon nanoparticles before (blue curve) and after (red curve) ferrocenyl functionalization, along with that for 4-ferrocenylaniline (black curve). It can be seen that the original carbon nanoparticles exhibited a broad peak at around 365 nm, which was ascribed to the quinone-like functional moieties, such as 9,10-phenanthraquinone, on the nanoparticle surface.\textsuperscript{7,8} By contrast, after ferrocene functionalization, this peak essentially disappeared, suggesting the effective removal of the quinone-like functional moieties from the nanoparticle surface by superhydride, which is consistent with results from the FTIR measurements (Figure 8.1).\textsuperscript{7,8} Furthermore, in comparison with the absorption profile of monomeric 4-ferrocenylaniline,
Figure 8.5. Near-infrared (NIR) spectra of ferrocene-functionalized carbon nanoparticles (Fc-CNPs) with the addition of varied amounts of NOBF$_4$ in DMSO. The starting solution of the carbon nanoparticles was 2 mL at a concentration of 0.1 mM, and the concentration of the NOBF$_4$ solution was 5 mM. Totally 720 µL NOBF$_4$ was added to the solution at an increment of 20 µL. Inset shows the variation of the absorbances at 1454 nm and 1950 nm with the amounts of NOBF$_4$ added.
Figure 8.6. Near-infrared (NIR) spectra of FcCH$_2$-CNPs with the addition of varied amounts of NOBF$_4$ in DMSO. The starting solution of the carbon nanoparticles was 2 mL at a concentration of 0.1 mM, and the concentration of the NOBF$_4$ solution was 5 mM. Totally 800 µL NOBF$_4$ was added to the solution at an increment of 25 µL. Inset shows the variation of the absorbances at 1965 nm, 1896 nm, and 1436 nm with the amounts of NOBF$_4$ added.
three absorption peaks can be identified with Fc-CNPs, corresponding to the $\pi-\pi^*$ (260 nm) and $d-d$ (294 nm and 465 nm) electronic transitions that are characteristic of the ferrocenyl moiety.\textsuperscript{25}

The corresponding photoluminescence spectra of the carbon nanoparticles were then presented in Figure 8.5. It can be seen that the original CNPs in water (black curves) exhibit a very well defined excitation peak at 330 nm and an emission peak at 440 nm, as observed previously, which was accounted for by the electronic transitions of functional species on the nanoparticle surface.\textsuperscript{7,8} However, after ferrocenyl functionalization (red curves), the nanoparticles became soluble in DMSO and exhibited a substantial red-shift of the excitation peak to 376 nm and a small shift of the emission peak to 448 nm. Remarkably, the resulting photoluminescence characteristics are very similar to those observed with conjugated organic oligo biphenylene vinylene molecules based on biphenylene motifs linked together through double bonds.\textsuperscript{26} This observation is in agreement with the above argument that apparent electronic coupling occurred between the particle-bound ferrocenyl moieties because the chemical bridge that covalently connected these ferrocenyl groups behaved equivalently to a conjugated biphenylene unit, as manifested in the voltammetric and NIR measurements (Figure 8.3 and 9.5). Furthermore, as the chemical bridge serves as the photoactive site, the molecular conductance may be enhanced by photoirradiation, leading to improved intraparticle charge delocalization, as observed experimentally (Figure 8.3).
Figure 8.7. UV-vis spectra of the as-produced (CNPs) and ferrocene-functionalized (Fc-CNPs) carbon nanoparticles, as well as the monomeric 4-ferrocenylaniline. The CNPs were dispersed in water whereas the Fc-CNP and Fc-aniline samples were in DMSO.
Interestingly, the Fc-CNP photoluminescence properties can be further manipulated by the charge state of the peripheral ferrocenyl units. From Figure 8.8, it can be seen that the excitation ($\lambda_{ex}$) and emission ($\lambda_{em}$) peak positions exhibited an insignificant variation when the amount of NOBF$_4$ added was less than 320 µL, where less than half of the ferrocenyl sites were oxidized to positively charged ferrocenium (Figure 8.5). Further additions of NOBF$_4$ led to a rather drastic red-shift for both $\lambda_{ex}$ and $\lambda_{em}$. For instance, when the ferrocenyl moieties were fully oxidized (720 µL), the excitation peak ($\lambda_{ex}$) shifted to 393 nm and the emission profile became broadened significantly with the center of the peak ($\lambda_{em}$) moved to 502 nm. Concurrently, the fluorescence intensity diminished with the oxidative conversion of ferrocene into ferrocenium. These observations may again be accounted for by the nanoparticle-mediated electronic coupling between the peripheral ferrocenyl moieties. Specifically, the positively charged ferrocenium sites most likely (i) served as electron acceptors and thus quenched the fluorescence emitted from the biphenylene chemical spacer, and (ii) helped stabilize the photoexcited electrons by virtue of intraparticle charge delocalization which lowered the energy of the nanoparticle excited states and hence red-shift of the electronic transitions, as observed experimentally.

Additional contributions to the manipulation of the nanoparticle photoluminescence probably arose from the nitrosation of the aromatic rings of the nanoparticle graphitic cores as well as the formation of quinone-like derivatives by the oxidation of hydroxyl species on the particle surface by NOBF$_4$, as both been
Figure 8.8. Photoluminescence spectra of the as-produced (CNPs) and ferrocene-functionalized (Fc-CNPs) carbon nanoparticles. The solutions were the same as those in Figure 8.5 and 9.7.
Figure 8.9. UV-vis spectra of Fc-CNPs with the addition of varied amount of NOBF₄. The solutions were the same as those in Figure 8.8.
known to behave as efficient electron acceptors.\textsuperscript{8,27,28} In fact, upon the addition of NOBF\textsubscript{4}, UV-vis measurements of the Fc-CNP nanoparticle solution showed that the absorption peak at 365 nm re-emerged and the intensity increased with the amount of NOBF\textsubscript{4} added (Figure 8.9).

8.3 Conclusion

Ferrocenyl-functionalized carbon nanoparticles were prepared by covalent grafting of 4-ferrocenylphenyldiazonium onto the nanoparticle surface. FTIR measurements confirmed the successful attachment of the ferrocenyl moieties onto the nanoparticle surface and XPS measurements showed that there were \textit{ca.} 31.9 ferrocenyl moieties per nanoparticle. Interestingly, apparent electronic coupling between the nanoparticle-bound ferrocenyl moieties was observed in voltammetric measurements, where two pairs of voltammetric waves were identified with a potential spacing of about 78 mV, signifying that the nanoparticles behaved as a Class I/II compound, as defined by Robin and Day. Further supporting evidence was manifested in NIR measurements where two prominent peaks started to emerge at 1454 nm and 1950 nm with the addition of NOBF\textsubscript{4} that oxidized the peripheral ferrocenyl moieties into ferrocenium, and the peak intensities displayed volcano-shaped dependence on the amount of NOBF\textsubscript{4} added, indicating intraparticle intervalence transfer at mixed valence. These results strongly suggest that by virtue of the C(sp\textsuperscript{2})–C(sp\textsuperscript{2}) interfacial bonding contacts, a rather delocalized chemical bridge was established between the nanoparticle-bound ferrocenyl units, which might be further enhanced by UV photoirradiation of the nanoparticle solution, with the
potential spacing found to increase to 107 mV. Because of the nanoparticle-mediated charge delocalization, the particle photoluminescence characteristics were found to be further manipulated by the charge states of the peripheral ferrocenyl moieties. This study suggests that surface chemical functionalization may be exploited as an effective mechanism in the manipulation of nanomaterials optical and electronic properties.
8.4 References


