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Ultrafast Charge Transfer between Light Absorber and Co$_3$O$_4$ Water Oxidation Catalyst across Molecular Wires Embedded in Silica Membrane

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Supporting Information

ABSTRACT: The mechanism of visible light-induced hole transfer from a molecular light absorber, in the form of a free-base porphyrin, coupled to a Co$_3$O$_4$ nanoparticle catalyst for water oxidation by a molecular wire (p-oligo(phenylenevinylene) featuring three aryl units) is investigated by transient absorption spectroscopy. The wires are covalently anchored on the Co$_3$O$_4$ surface and embedded in a dense, yet ultrathin (2 nm), silica layer that separates light absorber and catalyst. The porphyrin is electrostatically adsorbed on the silica surface, and aqueous colloidal solutions of the core-shell particles are used for transient optical measurements. Pulsed optical excitation of the porphyrin results in rapid injection of the photogenerated hole onto the molecular wire and concurrent formation of reduced light absorber in less than 1 picosecond (ps). Ultrafast charge separation was monitored by transient absorption of the wire radical cation, which is given by bands in the 500 to 600 nm region and at 1130 nm, while formation of reduced porphyrin was characterized by absorption at 700 nm. Forward transfer of the hole to Co$_3$O$_4$ catalyst proceeds in 255 ± 23 ps. Ultrafast transfer of positive charge from the molecular assembly to a metal oxide nanoparticle catalyst for water oxidation is unprecedented. Holes on Co$_3$O$_4$ recombined with electrons of the reduced sensitizer with biphasic kinetics on a much longer time scale of ten to several hundred nanoseconds. The unusually efficient hole transfer coupling of a molecular light absorber with an Earth-abundant metal oxide catalyst by silica-embedded p-oligo(phenylenevinylene) offers an approach for integrated artificial photosystems featuring product separation on the nanoscale.

1. INTRODUCTION

Nanostructured metal oxides of late transition metals, in a variety of morphologies, have recently emerged as robust, Earth-abundant catalysts for water oxidation.1–14 Although average turnover frequencies per exposed surface metal site of oxide catalysts for oxygen evolution are only on the order of 10$^{-2}$ O$_2$ molecules per second,1,15–17 the very high densities of sites per geometrical area of nanostructured catalysts enables productive use of the majority of injected charges for starting fresh catalytic cycles. However, for use in artificial photosystems, efficient charge transfer coupling of the oxide to a light absorber remains a formidable challenge. This holds especially if energy loss caused by mismatched potentials of light absorber and catalyst is to be held at a minimum in order to ensure conversion of a maximum fraction of the absorbed solar photon energy to chemical energy stored in the products.

For molecular light absorbers, which offer the advantage of precise potential matching by tuning of the electronic properties through synthetic modifications, early studies by Mallouk have established rates in the millisecond range for hole transfer (positive charge) between Ru tris-bipyridyl type light absorbers ((Ru(bpy)$_3$)$_2^+$) and Ir oxide nanocluster catalysts.18,19 As a consequence of the rather slow rates, efficiency degrading back transfer of separated electrons resulted in low photocatalytic quantum yields. Improvements have been achieved by introducing molecular relays akin to the tyrosine-histidine bridge of Nature’s photosystem II, resulting in a 3-fold increase of the quantum yield.19–21 On the other hand, visible light-induced hole transfer from a Ru(bpy)$_3$ sensitizer to a molecularly defined metal oxide structure, in the form of polyoxometalate, was found to occur within a nanosecond, suggesting that ultrafast kinetics in the case of metal oxide nanocluster catalysts might be feasible.22 While the photon flux at maximum solar intensity (1500 photons s$^{-1}$ nm$^{-2}$) alone does not require such high charge transfer rates,23 ever-present competing charge transfer processes that degrade productive use of the separated charges require forward hole transfer rates of a few nanoseconds or even picoseconds for acceptable water oxidation quantum yields to be realized.

Fast hole transfer between light absorbers and metal oxide catalysts is of particular importance for artificial photosystem designs that aim at closing the photosynthetic cycle of CO$_2$ reduction by H$_2$O on the nanoscale, while also separating products by a membrane, which is essential for the efficient photo-reduction of CO$_2$ to liquid fuel products.24 We have

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recently demonstrated ultrathin dense phase silica layers (2–3 nm) as O2 impermeable, proton transmitting separation membranes.25,26 Tight control of charge transport between a light absorber on one side of the silica membrane and a Co oxide catalyst for water oxidation on the other was accomplished by embedded molecular wires composed of p-oligo(phenylenevinylene) featuring three aryl units.16,17 Energy-selective hole or electron transport across the membrane was achieved by tuning the HOMO and LUMO potentials of energy-selective hole or electron transport across the membrane, as demonstrated by visible light photoelectrochemical measurements on planar constructs.26 Using aqueous colloidal solutions of spherical Co3O4−SiO2 core−shell nanoparticles with embedded wire molecules, [Ru(bpy)3]2+ visible light sensitizer, and sacrificial electron acceptor-revealed diffusion-controlled hole transfer to the Co3O4 core via embedded molecular wires.17 From this result, a lower limit of the kinetic rate constant for hole transfer from light absorber to Co3O4 via silica-embedded molecular wire of 106 s−1 was inferred.

An essential open question is whether ultrafast hole transfer between a molecular light absorber and a metal oxide catalyst for water oxidation can be achieved in order to outcompete efficiency degrading pathways, and whether this is feasible even in the presence of a silica separation membrane. The latter is required for realizing acceptable efficiency for CO2 photoreduction by H2O to dense phase products. Here we report the direct detection and kinetic evaluation of hole transfer between a molecular light absorber and a Co3O4 nanoparticle catalyst, coupled via molecular wires embedded in an ultrathin silica layer, by transient optical absorption spectroscopy. While inorganic heterobinuclear units such as ZrOCO are our target light absorbers for integrated artificial photosystems,4,25 free-base porphyrin offered spectroscopic properties particularly suitable for ultrafast optical monitoring. The findings reveal unusually efficient hole transfer coupling of a porphyrin chromophore and the metal oxide catalyst via a p-oligo(phenylenevinylene) cast into silica, thus opening up nanoscale artificial photosystems designs with built-in membrane separation.

2. EXPERIMENTAL SECTION

Sample Preparation and Characterization. A surfactant-assisted solvothermal method reported previously was used for preparing ~4 nm sized Co3O4 nanoparticles.17,25 Molecular wires, of the type cesium 4-(E)-4-(E)-(1,3-dihydroxy-2-(hydroxymethyl)-propan-2-yl)carbamoyl)styryl)styryl)benzenesulfonate (hereafter abbreviated as PV3), were synthesized according to a reported procedure16 and attached to Co3O4 nanoparticle surfaces using O-(6-chlorobenzotriazol-1-yl)-NNN,N′-tetramethyluronium hexafluorophosphate (HCTU) peptide coupling agent, as described in an earlier paper,17 with the exception of using a tip-sonicator for efficient particle dispersion (Branson Ultrasonic model Sonifier, 3–4 W, 1 s on/1 s off). In short, PV3 (0.0081 g, 13 μmol) and HCTU (0.0017 g, 0.0042 mmol) were put in a 50 mL Schlenk paper,17 with the exception of using a tip-sonicator for e-

Figure 1. TEM image of Co3O4−SiO2 core−shell particles. The lattice distance is 0.25 ± 0.01 nm and corresponding to the Co3O4(311) plane (PDF number 01-071-0816).

For casting the molecular wires into silica, the Co3O4−PV3 particles were dispersed in 90 mL of ethanol while continuously stirring the solution. Five milliliters of ammonia, 10 mL of water, and 0.05 mL of tetraethyl orthosilicate (TEOS) were added to the solution, which was stirred for 4 h while tip-sonicating with repetitive cycles of 1 s on/1 s off at 4 W. The temperature was maintained at 40 °C. The resulting core−shell nanoparticles, with embedded molecular wires (abbreviated Co3O4−PV3−SiO2) were collected by repeated (3×) centrifugation (12 500 rpm for 15 min at 10 °C). The precipitate was resuspended and subsequently collected and concentrated 2.5× in a 20 mL vial. The volume was completed to 20 mL and the dispersion kept overnight to settle. Any precipitate was removed, and the resulting solution was used for spectroscopic experiments. A similar procedure was employed for core−shell samples without PV3 wires, which were used for control experiments. Samples were uniform core−shell nanoparticles consisting of a crystalline Co3O4 core (5 nm diameter) and an amorphous SiO2 shell (2 nm), as shown by TEM images presented in Figure 1.

Transient Absorption Spectroscopy. The ultrafast laser pump beam was produced by a Coherent Libra Ti:sapphire regenerative amplifier coupled to a Coherent OPerA Solo optical parametric amplifier. The 430 nm output (700 nJ pulse−1, 0.3 mm diameter) of ≤150 fs duration at 1 kHz repetition rate was directed toward the...
3. RESULTS

3.1. Spectroscopic Characterization of Core–Shell Particles with Adsorbed Sensitizer. Figure 2 trace 1 shows the UV–vis spectrum of a colloidal aqueous solution of Co3O4–SiO2 core–shell particles with PV3 wire molecules embedded inside the silica shell and free-base porphyrin H2P electrostatically adsorbed on the SiO2 surface (Co3O4–PV3–H3P). The spectrum of the same particles without adsorbed H2P is shown in trace 2 for comparison (Co3O4–PV3–SiO2). The spectrum of H2P adsorbed in SiO2 nanoparticles is presented in trace 3. Optical absorption by the charge transfer transitions of the Co3O4 core particle causes the tail that rises from the near-infrared toward the UV region and the weak broad maximum between 700 and 800 nm. The difference spectrum for the 450–800 nm range is shown on an expanded scale in the inset of Figure 2. The strong broad absorption between 300 and 400 nm is due to the PV3 π-π* transition. From the intensity, a loading of 210 PV3 molecules per core–shell particle is derived (4 PV3 nm−2). The intense Soret band of H2P adsorbed on SiO2 nanoparticles at 432 nm and Q-bands at 527, 555, 597, and 653 nm are in agreement with recent literature,31 spectral traces with broad maxima at 600 and 850 nm are observed following excitation of the Soret band of H2P at the same wavelength, a modest fraction of the laser pulse energy is transmitted with a 150 fs pulse at 430 nm. Because the Co3O4 absorbs at the near-infrared toward the UV region and the weak broad maximum between 700 and 800 nm, it is most likely due to charge transfer interaction between ground-state porphyrin and PV3, with electron density partially shifted from the wire molecule to the porphyrin. The integrity of molecular wires embedded in silica shells was confirmed by infrared spectroscopy. As shown in Figure S1, the fingerprint FT-IR spectrum of embedded PV3 molecules agrees well with the spectrum of the free wire molecule.

3.2. Ultrafast Optical Spectroscopy of Visible Light-Induced Charge Transfer. Time-resolved optical measurements were initiated by excitation of the Soret band of H2P visible light sensitizer within Co3O4–PV3–SiO2 H3P assemblies with a 150 fs pulse at 430 nm. Because the Co3O4 absorbs at the same wavelength, a modest fraction of the laser pulse energy is transmitted with a 150 fs pulse at 430 nm. Because the Co3O4 absorbs at the same wavelength, a modest fraction of the laser pulse energy is transmitted with a 150 fs pulse at 430 nm. Because the Co3O4 absorbs at the same wavelength, a modest fraction of the laser pulse energy is transmitted with a 150 fs pulse at 430 nm. Because the Co3O4 absorbs at the same wavelength, a modest fraction of the laser pulse energy is transmitted with a 150 fs pulse at 430 nm. Because the Co3O4 absorbs at the same wavelength, a modest fraction of the laser pulse energy is transmitted with a 150 fs pulse at 430 nm. Because the Co3O4 absorbs at the same wavelength, a modest fraction of the laser pulse energy is transmitted with a 150 fs pulse at 430 nm. Because the Co3O4 absorbs at the same wavelength, a modest fraction of the laser pulse energy is transmitted with a 150 fs pulse at 430 nm. Because the Co3O4 absorbs at the same wavelength, a modest fraction of the laser pulse energy is transmitted with a 150 fs pulse at 430 nm. Because the Co3O4 absorbs at the same wavelength, a modest fraction of the laser pulse energy is transmitted with a 150 fs pulse at 430 nm. Because the Co3O4 absorbs at the same wavelength, a modest fraction of the laser pulse energy is transmitted with a 150 fs pulse at 430 nm. Because the Co3O4 absorbs at the same wavelength, a modest fraction of the laser pulse energy is transmitted with a 150 fs pulse at 430 nm. Because the Co3O4 absorbs at the same wavelength, a modest fraction of the laser pulse energy is transmitted with a 150 fs pulse at 430 nm. Because the Co3O4 absorbs at the same wavelength, a modest fraction of the laser pulse energy is transmitted with a 150 fs pulse at 430 nm. Because the Co3O4 absorbs at the same wavelength, a modest fraction of the laser pulse energy is transmitted with a 150 fs pulse at 430 nm. Because the Co3O4 absorbs at the same wavelength, a modest fraction of the laser pulse energy is transmitted with a 150 fs pulse at 430 nm. Because the Co3O4 absorbs at the same wavelength, a modest fraction of the laser pulse energy is transmitted with a 150 fs pulse at 430 nm. Because the Co3O4 absorbs at the same wavelength, a modest fraction of the laser pulse energy is transmitted with a 150 fs pulse at 430 nm. Because the Co3O4 absorbs at the same wavelength, a modest fraction of the laser pulse energy is transmitted with a 150 fs pulse at 430 nm. Because the Co3O4 absorbs at the same wavelength, a modest fraction of the laser pulse energy is transmitted with a 150 fs pulse at 430 nm. Because the Co3O4 absorbs at the same wavelength, a modest fraction of the laser pulse energy is transmitted with a 150 fs pulse at 430 nm. Because the Co3O4 absorbs at the same wavelength, a modest fraction of the laser pulse energy is transmitted with a 150 fs pulse at 430 nm. Because the Co3O4 absorbs at the same wavelength, a modest fraction of the laser pulse energy is transmitted with a
581, and a shoulder at 622 nm, which are characteristic of the H2P(S1) excited state as reported in the literature.32 For further verification, transient absorption traces of H2P adsorbed on SiO2 particles, shown in Figure S2, were compared with transient absorption traces of Co3O4−SiO2·H2P of Figure 3B. The comparison confirms the absence of the broad transient absorption originating from direct 430 nm excitation of Co3O4 (Figure 3A) (note that the transient bleach of ground-state H2P Q bands (at 522, 555, 597, and 653 nm) is more pronounced for this sample than for the Co3O4−SiO2·H2P samples (shown in Figure 3B) because a substantially larger fraction of H2P is excited by 430 nm light (differences in photon loss by scattering and absorption by Co3O4). Hence, for ultrafast transient spectra of core−shell particles with molecular wires embedded in the silica and adsorbed H2P, the 430 nm excitation causes absorption peaks at 509, 539, 579, 633, and 1130 nm coinciding with absorption peaks of the one-electron-oxidized PV3 wire molecules (abbreviated PV3+).34 In addition, the intensity at 633 nm contains a contribution from absorption by H2Pred.33 Previously measured transient radical cation spectra of PV3 wire molecules anchored on SiO2 nanoparticles sensitized by [Ru(bpy)3]3+ in aqueous solution show similar spectral structure.16 Small differences between the radical cation spectrum generated by hole transfer from [Ru(bpy)3]3+ and the spectra of Figure 3C are due to spectral overlap with the H2P ground-state bleach, with the pattern of decreasing features exactly matching the H2P(S0) Q-band peaks in the 500−650 nm region.

The presence of transient spectral signatures from H2Pred and PV3+ indicates injection of photogenerated holes from the sensitizer to the wire. Comparison of transient absorption spectra of Co3O4−PV3−SiO2·H2P samples (Figure 3C and 3D) with those of (wire-free) Co3O4−SiO2·H2P systems, which show electronically excited H2P (Figure 3B), indicates that no electronically excited singlet H2P is present in the Co3O4−PV3−SiO2·H2P system at 1 ps and beyond. Hence, charge separation is complete within 1 ps. As can be seen in Figure 3C, a pronounced absorbance bleach was detected at 485 nm from Co3O4−PV3−SiO2·H2P. To aid identification of this bleach feature, reference measurements were performed on an analogous system with the Co3O4 nanoparticle core replaced by a SiO2 core (SiO2−PV3−SiO2·H2P). No such absorbance loss below 500 nm was observed upon excitation of the SiO2−PV3−SiO2·H2P system (Figure
4A), demonstrating that the negative 485 nm signal is only observed in the presence of the Co oxide core. Furthermore, the 485 nm bleach is absent for Co$_3$O$_4$−SiO$_2$·H$_2$P core−shell particles that lack embedded PV$_3$ (Figure 3B), indicating that the negative signal requires electronic linkage between light absorber and Co$_3$O$_4$. Therefore, we attribute the bleach at 485 nm to charge transfer from the wire molecule to Co$_3$O$_4$. Because a hole is injected onto PV$_3$ upon H$_2$P reduction, the bleach is assigned to arrival of a hole from PV$_3^+$ onto the Co oxide core, yielding Co$_3$O$_4$(h$^+$). The resulting charge-separated state is Co$_3$O$_4$(h$^+$)$^-$PV$_3$·H$_2$P$_{red}$. As shown in Figure 4B, the assignment of this transient bleach feature to Co$_3$O$_4$(h$^+$) is further supported by the observation of a bleach at wavelengths shorter than 550 nm when exposing aqueous colloidal solution of Co$_3$O$_4$ nanoparticles to Ce(IV), which is well-known to induce water oxidation by hole injection into Co$_3$O$_4$ particles. It is important to note that the bleach below 500 nm caused by direct absorption of the 430 nm photolysis pulse by Co$_3$O$_4$ and the dip at 480 nm in the first time slice of Figure 3C originating from excitation of the H$_2$P$^{red}$−PV$_3$ ground-state absorption both get smaller on the ps time scale, opposite to the kinetic behavior of the 485 nm bleach attributed to hole transfer to Co$_3$O$_4$.

None of the transient absorptions associated with H$_2$P$_{red}$ or Co$_3$O$_4$(h$^+$) of the Co$_3$O$_4$−PV$_3$−SiO$_2$·H$_2$P system were observed for Co$_3$O$_4$−SiO$_2$·H$_2$P particles that did not have wire molecules embedded in the silica shell. Instead, excited singlet H$_2$P(S$_1$) bands are detected as mentioned above (Figure 3B). The observed decay time of the H$_2$S(S$_1$) state is 580 ± 50 ps, which represents the internal relaxation time of the sensitizer and competes with charge transfer to the wire in the case of the fully assembled Co$_3$O$_4$−PV$_3$−SiO$_2$·H$_2$P system.

For elucidating the kinetics of the charge transfer processes in Co$_3$O$_4$−PV$_3$−SiO$_2$·H$_2$P assemblies, the 1130 nm absorption of PV$_3^+$ and the 695 nm band of H$_2$P$_{red}$ were selected to represent the transient behavior because they exhibit the least overlap with other spectral features. We note that in the visible region the 509 nm band follows the same kinetics within uncertainty as the 1130 nm band. However, for clarity, only the 1130 nm band is shown and discussed further. Figure 5A and

![Figure 4](image-url)

**Figure 4.** (A) SiO$_2$−PV$_3$−SiO$_2$·H$_2$P ultrafast optical spectra upon 430 nm (150 fs) excitation. H$_2$P$_{red}$ bands are at 498 and 695 nm, and PV$_3^+$ peaks at 509 (shoulder), 539, 579, 633 nm. No transient bleach is observed at 485 nm. From dark purple to light yellow: 1.07; 2.55; 4.01; 6.50; 17.3; 38.2; 91.0; 319; 1560; 2110 ps. (B) Static difference UV−vis spectrum of Co$_3$O$_4$ oxidized with Ce(IV) from Co$_3$O$_4$. A bleach at 485 nm is observed.

![Figure 5](image-url)

**Figure 5.** Kinetic behavior of molecular wire and porphyrin bands. (A) 695 nm absorption of H$_2$P$_{red}$. (B) 1130 nm band of PV$_3^+$. (C) Fit of decay of the PV$_3^+$ and H$_2$P$_{red}$ species. Solid traces are least-squares fits according to eqs 1−3. The inset shows the kinetic behavior of the 485 nm bleach attributed to Co$_3$O$_4$(h$^+$). Baseline treatment: The peak area at 695 nm was calculated by fitting a Gaussian-shaped band with cubic baseline that follows the Co$_3$O$_4$ transient absorption shape near 695 nm. These were used for the kinetic calculations and plots shown in panel C. In panels A and B, background subtracted spectra are presented. The 695 nm peak was smoothed by seven-point binomial smoothing, while for the 1130 band raw data are shown.

![Figure 6](image-url)

**Figure 6.** Recovery of the 485 nm bleach, shown in Figure 6A, follows biphasic kinetics, with most occurring on the time scale of 10 ns with a slower phase extending to about 1 μs, as displayed in Figure 6B. While colloidal solutions of spherical Co$_3$O$_4$−PV$_3$−SiO$_2$ core−shell...
nanoparticles were found to provide optimal sensitivity for transient spectroscopic studies, water molecules are unable to access the Co oxide surface; hence, catalytic activity cannot be monitored with these samples. However, we have previously shown that water oxidation catalysis occurs upon hole injection into CoOx via PV3 wires for CoOx−PV3 particles prior to casting of silica.15 The CoOx−silica core−shell construct for actual water oxidation has nanotube geometry where the inside surface of the CoOx nanotube is open and accessible to the Co oxide surface; hence, catalytic activity cannot be included in the kinetic model. The latter process takes place because no sacrificial acceptor is present for removing transferred electrons or holes. The equations for the kinetic model are (in absorbance units)

\[
A_{(\text{CoO}_x \text{−PV3 } \cdot \text{H}_2\text{P})}^i(t) = A_{0(\text{CoO}_x \text{−PV3 } \cdot \text{H}_2\text{P})} e^{-(k_1 + k_2)t} 
\]

for the decay of the initial charge-separated wire−porphyrin state, and

\[
A_{(\text{CoO}_x \text{−PV3 } \cdot \text{H}_2\text{P})}^f(t) = A_{0(\text{CoO}_x \text{−PV3 } \cdot \text{H}_2\text{P})} \left( \frac{k_2}{k_1 + k_2} \right) \left(1 - e^{-(k_1 + k_2)t} \right) 
\]

for the rise of the transferred hole in the CoOx particle. \(k_1\) is the rate constant for back electron transfer, \(k_2\) is the rate constant for hole transfer from PV3 to CoOx, and \(A_0\) is the initial absorbance of the CoOx(h+)−PV3-H2Pred species. The decay of the PV3′ band at 1130 nm follows the kinetics of eq 1 while the temporal behavior of the 485 nm bleach is described by eq 2. The kinetics of the 695 nm absorbance of H2Pred is described by

\[
A_{(\text{H}_2\text{P})}^f(t) = A_{0(\text{CoO}_x \text{−PV3 } \cdot \text{H}_2\text{P})} \left( \frac{k_d}{k_1 + k_2} \right) e^{-(k_1 + k_2)t} 
\]

3.3. Kinetic Analysis. Based on these data, the simplest kinetic model we can conceive of for the excited-state processes upon excitation of the H2P light absorber is presented in Scheme 2. Hole transfer from the H2P sensitizer excited at 430 nm to embedded PV3 wires produces PV3+ and H2Ppred within hundreds of femtoseconds. Competition between back hole transfer from PV3′ to H2Pred to regenerate ground state and forward hole transfer from PV3+ to CoOx determines the rate of decay of the wire radical cation and the reduced H2P on the time scale of tens to hundreds of picoseconds. These processes are temporally separated from the much slower recombination of the hole on Co oxide (CoOx(h+)) and H2Ppred to regenerate the CoOx−PV3−SiO2−H2P ground state. The latter process takes place because no sacrificial acceptor is present for removing transferred electrons or holes. The equations for the kinetic model are (in absorbance units)

\[
A_{(\text{CoO}_x \text{−PV3 } \cdot \text{H}_2\text{P})}^i(t) = A_{0(\text{CoO}_x \text{−PV3 } \cdot \text{H}_2\text{P})} e^{-(k_1 + k_2)t} 
\]

for the decay of the initial charge-separated wire−porphyrin state, and

\[
A_{(\text{CoO}_x \text{−PV3 } \cdot \text{H}_2\text{P})}^f(t) = A_{0(\text{CoO}_x \text{−PV3 } \cdot \text{H}_2\text{P})} \left( \frac{k_2}{k_1 + k_2} \right) \left(1 - e^{-(k_1 + k_2)t} \right) 
\]

for the rise of the transferred hole in the CoOx particle. \(k_1\) is the rate constant for back electron transfer, \(k_2\) is the rate constant for hole transfer from PV3′ to CoOx, and \(A_0\) is the initial absorbance of the CoOx(h+)−PV3-H2Pred species. The decay of the PV3′ band at 1130 nm follows the kinetics of eq 1 while the temporal behavior of the 485 nm bleach is described by eq 2. The kinetics of the 695 nm absorbance of H2Ppred is described by

\[
A_{(\text{H}_2\text{P})}^f(t) = A_{0(\text{CoO}_x \text{−PV3 } \cdot \text{H}_2\text{P})} \left( \frac{k_d}{k_1 + k_2} \right) e^{-(k_1 + k_2)t} 
\]

Least squares fits of the kinetics of the 1130 and 695 nm bands give \(k_1 + k_2\) values (2.0 ± 0.16 × 1010 s−1 (1/e decay time of 50 ± 4 ps) for the 1130 nm band, and (2.1 ± 0.2) × 1010 s−1 (1/e decay time of 48 ± 5 ps) at 695 nm. The values for \(k_1 + k_2\) of the two bands agree within uncertainties. As can be seen from the inset of Figure 5C, the kinetic behavior of the 485 nm bleach assigned to CoOx(h+) follows that of the 1130 and 695 nm species, but the uncertainty of the absorbance changes is substantially larger than for the PV3′ and H2Ppred bands, primarily due to the more extensive spectral overlap with neighboring bands. Therefore, the 485 nm feature was not included in the kinetic fits. According to eq 3, \(k_2/(k_1 + k_2)\) is equal to the ratio of the asymptotic absorbance of H2Ppred (approximated by the fit value of the asymptotic absorbance of the 695 nm band taking data points over the initial 300 ps) and the starting absorbance of H2Ppred, which is 0.0036/0.0181 = 0.20. Hence, \(k_1 = (1.6 ± 0.2) × 10^{10} \text{s}^{-1} (62 ± 6 \text{ ps})\), \(k_2 = (3.9 ± 0.4) × 10^9 \text{s}^{-1} (255 ± 23 \text{ ps})\). While the value of \(k_2\) obtained from curve fitting is close to the uncertainty of the fit value of \(k_1\)
+ $k_a$, the asymptotic amplitude of H$_2$P and the concurrent observation of the 485 nm bleach clearly show hole transfer to Co$_3$O$_4$.

As can be seen from Figure 6B, the recovery of the 485 nm bleach is multiphasic with most of the back transfer of holes occurring in the initial 10 ns followed by slower processes extending to one $\mu$s. The absorbance vs log t plot shows a biexponential fit with time constants and amplitude $k_{a1} = (1.24 \pm 0.06) \times 10^4$ s$^{-1}$ (81.4 $\pm$ 3.8 ns), $A_1 = 4.9 \times 10^{-4}$, and $k_{a2} = (1.4 \pm 0.4) \times 10^6$ s$^{-1}$ (700 $\pm$ 200 ns), $A_2 = 9.4 \times 10^{-5}$.

4. DISCUSSION

According to the Weller equation, the energetics for charge separation between excited H$_2$P sensitizer and embedded PV3 wire molecule is

$$G_0(\text{kcal-mol}^{-1}) = 23.06 \times [e^0(PV3^-/PV3) - e^0(H_2P/H_2P^{\text{red}}) - w(H_2P^{\text{red}}/H_2P) + w(PV3/H_2P) - \Delta G_{00}]$$

where $e^0(PV3^-/PV3) = 1.01$ V (SCE in butyronitrile), $e^0(H_2P/H_2P^{\text{red}}) = -1.19$ V (SCE in pyridine), and $\Delta G_{00} = 43.8$ kcal mol$^{-1}$ (energy of H$_2$P(S$_1$)). The Gibbs free energy part (i.e., not taking into account the $w$ term) is $+6.9$ kcal mol$^{-1}$. The large positive charge of H$_2$P (+8) and the small dielectric constant of SiO$_2$ (3.9) inflate the electrostatic part of the free energy ($w(H_2P^{\text{red}}/H_2P) - w(PV3/H_2P)$), for which 6.7 kcal mol$^{-1}$ is calculated at a separation of 0.2 nm, and for larger separations. Taking the maximum value of 6.7 kcal mol$^{-1}$ (0.2 nm), we estimate that the energy of the charge-separated PV3$^+$/H$_2P^{\text{red}}$ state is 22.4 kcal mol$^{-1}$ smaller than the absorbed photon energy at 430 nm, as shown in Scheme 2. Hence, the observed subpicosecond formation of oxidized molecular wire and reduced porphyrin implies that hole transfer occurs from vibrationally excited S$_1$ and possibly the S$_2$ state, according to the pico-ns lifetime of these unrelaxed levels designated as H$_2$P* in Scheme 2. Such a rapid primary charge separation ensures that hole transfer to the wire dominates over slower reaction and recombination pathways. The forward transfer of the hole on the wire moiety of Co$_3$O$_4$–PV3$^+$/SiO$_2$/H$_2P$ to Co$_3$O$_4$ to yield Co$_3$O$_4$(h$^+$)–PV3–SiO$_2$/H$_2P^{\text{red}}$ is energy neutral or exoergic by $8.1$ kcal mol$^{-1}$ (700 $\pm$ 200 ns), $A_2 = 9.4 \times 10^{-5}$.

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oxidation step was reported for a Ru polyoxotungstate \([\text{Ru}_4\text{O}_4(\text{OH})(\text{H}_2\text{O})_2]_4(\gamma\text{-SiW}_{10}\text{O}_{40})_5^{10-}\) catalyst coupled to a metal polypyridine sensitizer \([\text{Ru}(bpy)_2(dpbb)]^{2+}\) (dpbb = 4,4’-diphosphonic acid-2,2’-bipyridyl). The very large electrostatic interaction of dye and POM molecule due to the high negative charge of the latter and the positive charge of the former may be an important factor for the high rate of hole transfer. In the general area of dye-sensitized semiconductor electrodes, ultrafast hole injection from an excited coumarin light absorber to p-type NiO electrode is well established. Hammarstroem found 200 fs transit time for hole transfer from (anchored by carboxyl group) excited coumarin C343 to NiO, which in turn enabled efficient electron transfer from the excited dye to a coadsorbed artificial hydrogenase.

For incorporating a molecular light absorber–metal oxide assembly into a complete artificial photosystem, transfer of electrons concurrently produced upon photoexcitation to an acceptor and subsequently to catalytic sites for CO2 reduction needs to occur on a time scale that is fast compared to reverse hole transfer. For excited molecular (organic or organometallic) light absorbers, subpicosecond electron transfer to the conduction band of semiconductor or molecular catalysts has been demonstrated, outpacing the 60 ps hole recombination time observed here by approximately 2 orders of magnitude.

For the specific Co oxide core–silica shell nanoscale design pursued here, heterobimetallic ZrOCo light absorbers covalently anchored on the silica shell surface and coupled to an Ir oxide nanoparticle catalyst for water oxidation were shown to drive CO2 reduction by H2O to CO and O2 with a respectable quantum yield of 17%. Studies are in progress to determine whether such favorable charge transfer kinetics similarly apply to ZrOCo–wire–Co3O4 systems.

5. CONCLUSIONS

Ultrafast transient absorption spectroscopy of photoinduced hole transfer from a molecular light absorber to Co oxide catalyst across silica-embedded p-oligo(phenylenevinylene) allowed the direct observation of charge arrival on the wire molecule, which takes place in less than 1 ps. Subsequent forward transfer of the positive charge to the Co oxide particle occurred within 250 ps, exceeding known hole transfer rates from anchored molecular light absorbers to metal oxide catalyst particles for water oxidation by several orders of magnitude.

The finding reveals unusually efficient hole transfer coupling, made possible by the p-oligo(phenylenevinylene) linkage between a visible light absorber and a metal oxide catalyst. A key task ahead is to gain a detailed understanding of the factors that render anchored organic moieties with this structure to be efficient hole transfer conduits to metal oxide catalysts.

Ultrafast hole transfer from molecular light absorbers to metal oxide catalysts for water oxidation is essential for achieving high quantum efficiency of photodriven water oxidation. The fast transfer is achieved here by separation of light absorber and oxygen-evolving catalyst by a 2 nm thick silica layer, which can also function as a proton-conducting, O2-impermeable membrane. This assembly opens up capabilities for developing artificial photosystems that incorporate separation of water oxidation catalysis from the incompatible environment of light absorber and reduction catalyst by an ultrathin membrane while maintaining efficient electronic coupling between the components. Such systems are currently being explored in our laboratory.

ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/jacs.7b01070.

Figures S1 and S2, showing FT-IR spectra of silica-embedded wire molecules and ultrafast absorption spectra of control samples (PDF)

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Notes

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