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Solvents Effects on Charge Transfer from Quantum Dots

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S Supporting Information

ABSTRACT: To predict and understand the performance of nanodevices in different environments, the influence of the solvent must be explicitly understood. In this Communication, this important but largely unexplored question is addressed through a comparison of quantum dot charge transfer processes occurring in both liquid phase and in vacuum. By comparing solution phase transient absorption spectroscopy and gas-phase photoelectron spectroscopy, we show that hexane, a common nonpolar solvent for quantum dots, has negligible influence on charge transfer dynamics. Our experimental results, supported by insights from theory, indicate that the reorganization energy of nonpolar solvents plays a minimal role in the energy landscape of charge transfer in quantum dot devices. Thus, this study demonstrates that measurements conducted in nonpolar solvents can indeed provide insight into nanodevice performance in a wide variety of environments.

To design efficient devices using nanoscale components (nanodevices), the charge transfer pathways between nanostructures must be understood in a predictive way. Numerous studies have used time-resolved spectroscopy techniques to determine the rate-limiting steps in charge transfer between individual components in nanodevices.^{1–8} These studies are typically conducted using liquid phase samples, and the effect of the local solvent environment on the charge transfer process has proven difficult to investigate.^{5,9} Understanding the influence of the solvent is important since nanodevices are often synthesized and tested in one environment, but ultimately deployed in a different environment. For example, colloidal semiconductor quantum dots (QDs) are typically prepared and characterized in organic solvents, but often attached to surfaces as films in photovoltaics.¹⁰ Solvent molecules can alter the charge transfer process by perturbing the dielectric layer, or through the dynamic configuration rearrangements (electronic and conformational) of the solvent molecules at the nanomaterial surface during charge transfer process.⁵ Therefore, rational design and characterization of nanomaterials requires that we understand solvent effects. In this Communication, using a combination of novel experiments and theoretical insights, we show that charge transfer dynamics measurements conducted in nonpolar solvents are indeed

relevant for understanding nanodevices operating in air or vacuum.

Prior investigations utilized liquid phase transient absorption spectroscopy (TA), and showed that polar solvents can significantly alter the charge transfer rate.¹¹ However, to dissolve nanoparticles into solvents with different polarities, it is typically necessary to alter the ligand coverage or swap ligands entirely, convolving solvent effects with ligand effects. This makes it difficult to isolate the effect of the solvent alone.

In this Communication, we overcome this technical challenge by utilizing a velocity map imaging spectrometer^{12,13} coupled with a nanoparticle aerosol source (nano-VMI).^{14–16} This allows us to perform a time-resolved photoelectron spectroscopy experiment (PES, Figure 1a) on isolated nano-

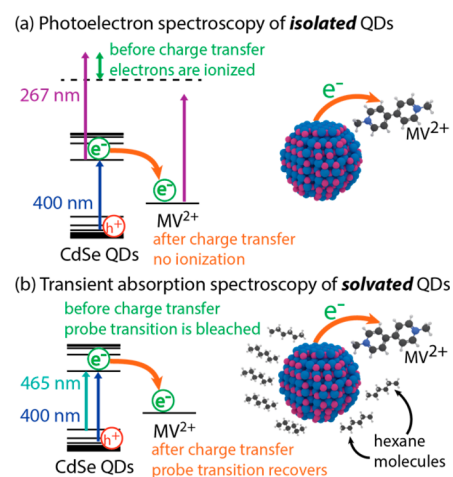


Figure 1. (a) Photoelectron spectroscopy (PES) detects electrons in order to follow charge transfer dynamics in *solvent-free* quantum dots (QDs—ligands are present, but not depicted here). A 400 nm pump pulse excites electrons, and before (or without) charge transfer, they can be ionized by a delayed 267 nm probe pulse. Once transferred to MV, the probe photon energy is insufficient to ionize the electron. (b) The transient absorption (TA) measurement follows the same dynamics by observing a time-dependent absorption change in *solvated* QDs. Here, before (or without) charge transfer, the probe transition is bleached, due to the presence of the excited electron, resulting in a decrease in absorption. By comparing PES and TA, we can isolate the effect of the solvent, hexane, on charge transfer.

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particles in vacuum. To eliminate complications arising from the use of different ligands, we implement gas phase nano-VMI spectroscopy on quantum dots with identical ligand coverage as in solution phase. Here, we unambiguously characterize the influence of a commonly used nonpolar solvent (hexane) on charge transfer by comparing nano-VMI data with solution phase TA measurements conducted on the same quantum dot sample. Specifically, we compare gas-phase PES and solution-phase TA measurements of the charge transfer rate between CdSe QDs and methyl viologen (MV^{2+}) cations (Figure 1) to characterize the influence of the solvent (hexane) on this process. We selected the CdSe-MV complex for these studies because it is a well characterized system that exhibits fast and efficient charge transfer.^{4,7,17–19} Furthermore, hexane is frequently used as a solvent for the synthesis and characterization of QDs; thus, it is important to determine whether it influences charge transfer between the QD and the electron acceptor.

To prepare the charge-transfer system, we adsorbed MV dye to octadecylamine-capped CdSe QDs with a diameter of 2.3 nm in solution (see Supporting Information (SI) for sample preparation details). We then used ultraviolet–visible absorption and fluorescence spectroscopies to characterize the static spectral features of CdSe QDs and CdSe-MV complexes. The absorption spectra of both samples show a peak at 480 nm (Figure 2a) that corresponds to the $1S(e)-1S_{3/2}(h)$ transition.

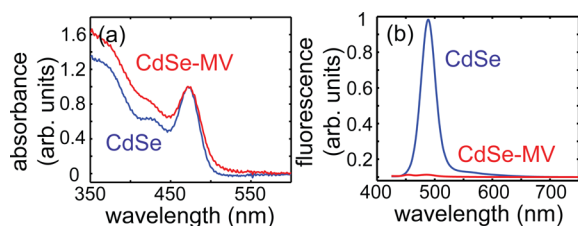


Figure 2. (a) The similarity of the UV–vis absorption spectra of CdSe and the CdSe-MV in solution reveals that the addition of MV does not alter the quantum confinement of the CdSe QDs. (b) The quench in the fluorescence spectra upon addition of MV indicates that electrons excited in the CdSe transfer to MV.

The CdSe-MV spectrum shows slightly broadened peaks, which is likely due to the excitonic coupling of the $1S(e)$ exciton state to the LUMO level of MV.²⁰ The fact that all of the peaks are preserved demonstrates that adding MV to the CdSe does not significantly influence quantum confinement in the QD. The quenching of the CdSe fluorescence peak upon the addition of MV (Figure 2b) indicates that the MV molecules successfully attach to the QD surfaces and that excited electrons in the CdSe QDs migrate to the MV faster than the rate of radiative decay.^{17,19,21}

Before addressing the effect of solvent molecules on charge transfer processes, we first verified that PES can indeed be used to track excited state dynamics, through comparison with TA measurements of electron dynamics occurring within CdSe QDs. Experimental details of the PES and TA experiments are described in the SI. In the PES experiment, the 400 nm pump pulse excites electrons primarily to the $1S(e)$ level (leaving a deeper hole in the valence band, based on the assignment of features in UV–vis absorption spectra^{22–25}), while a time-delayed 267 nm probe pulse ionizes the excited electron (Figure 1a). Therefore, immediately after the creation of $1S$ electrons, the photoelectron signal is enhanced. The decay of

the photoelectron signal reflects the decay of the $1S$ population due to both radiative and nonradiative relaxation. In the TA experiment, we monitor the dynamics of the bleach of the $1S(e)-1S_{3/2}(h)$ transition (Figure 1b), which also probes the population of electrons in the $1S$ state.^{25,26} Therefore, both the TA and the PES measurements probe the $1S$ electron population. In both experiments the fluence of the 400 nm pump pulse is selected so that an electron is excited in less than 10% of QDs in the interaction region, in order to minimize the effects from multiple excitons in a single quantum dot.

The difference between the two measurements is the presence (TA) or absence (PES) of surrounding solvent molecules. In the absence of charge transfer (i.e., no MV attached), we expect identical results from TA and PES, because the solvent should not strongly affect the dynamics that take place inside of the QD. Indeed, we do observe good agreement between the TA and PES measurements (Figure 3a,

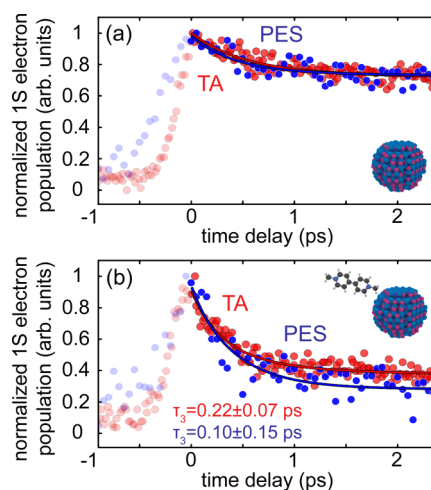


Figure 3. (a) In the absence of MV^{2+} , the $1S$ electron population only decays slightly on a few picosecond time scale. (b) When MV is attached to the QDs, a ~ 100 fs decay is seen, indicating charge transfer from the QD to the MV. There is no significant difference between the decay rates obtained from the TA and PES experiments, indicating that the hexane solvent molecules have a minimal effect on the charge transfer process.

Table S1) demonstrating that PES has the ability to follow exciton dynamics. Both measurements of CdSe QDs (Figure 3a) show a fast rise at $t = 0$, followed by a small initial decay and a long plateau. To quantify these dynamics, they were fit with a double exponential decay convoluted with the instrument-response-function (IRF, Table S1). The slow component is beyond the temporal range of the delay stage, which is consistent with the few nanosecond radiative lifetime of the $1S$ electron.²⁷ The small fast component results from the small fraction of electrons that undergo faster decay. While the presence or absence of solvent molecules could have an effect on carrier trapping at surface states,^{28–31} we do not observe such effects. This is indication that the CdSe QD surface is well passivated and that the ligand coverage (i.e., passivation) is identical for the two measurements. We note that the difference between the two measurements at $t < 0$ results from the fact that the 267 nm pulse used in the PES experiment excites hot electrons, which can then be ionized by the 400 nm pulse. Thus, the TA experiment and the PES experiment probe different processes in the $t < 0$ regime. In this paper, we focus

only on the band edge electron dynamics ($t > 0$), where TA and PES can be directly compared.

Having verified that PES can track charge dynamics in CdSe QDs, we can now apply it to study charge transfer in the CdSe-MV complex. In this case we see a faster decay of the PES signal (Figure 3b) and, therefore, the 1S electron population, due to electron transfer to the MV LUMO (from which the electron cannot be ionized by the 267 nm probe, Figure 1a). The TA measurements conducted on the same sample also detect faster decay in the 1S electron population when MV is adsorbed, seen as the faster recovery of the bleach of the $1S(e)-1S_{3/2}(h)$ transition. We fit the CdSe-MV kinetics using a triple exponential decay convoluted with the IRF, fixing two of the time constants with the values determined in the absence of MV. The newly extracted time constant (τ_3) is indicative of an electron transfer rate of 220 ± 70 fs (TA) and 100 ± 150 fs (PES) (Figure 3b, Table S2), which are in agreement with previous studies in organic solvents.^{4,17} The charge transfer rates obtained in both measurements are the same within the fitting error (one standard deviation). This indicates that the presence of hexane has a negligible effect on the charge transfer process. We note that these recovered τ_3 values are very close to the time scale of the instrument response functions of the TA and PES experiments, leading to the large errors seen in the fit values (Table S1).

The negligible influence of the hexane solvent molecules can be understood through the solvent electronic polarization model developed by Kim and Hynes.³²⁻³⁶ In this model, solvent molecules contribute to the charge transfer reorganization energy through both the electronic polarization and the orientational polarization. Since hexane is nonpolar, reorientation of the molecules does not alter the electron distribution. Therefore, the orientational contribution vanishes. Alternatively, the solvent molecules can influence the charge transfer by the redistribution of their electron populations. The electronic contribution will only be significant when the charge transfer reaction is fast compared to the solvent electronic polarization rate. This can be characterized by the ratio between the rates of charge transfer and solvent electronic polarization, $\rho = 2\beta/(\hbar\omega)$, where β is the electronic coupling factor and ω is the electronic transition frequency of the solvent.³⁴ We estimated β using the broadening²⁰ of the absorption spectra of the QDs upon the MV adsorption (Figure 2a), which is approximately 0.05 eV. Since hexane does not absorb in the visible region, its electronic transition energy, $\hbar\omega$, is > 3 eV.^{34,36} Therefore, $\rho < 0.02$, which means that the solvent electronic polarization is rapid compared to the charge transfer process (nonadiabatic). As a result, neither the electronic nor the orientational polarization of hexane contributes significantly to the reorganization energy, and consequently, one would not expect solvent reorganization to have a large influence on the charge migration dynamics of the CdSe-MV complex. Furthermore, from this analysis we predict that the influence on QD charge transfer of any nonpolar transparent solvent should be minimal, as long as the charge transfer process is slower than a few femtoseconds, which is true for most charge-transfer processes. This is not necessarily the case for polar solvents, where the orientational reorganization energy can affect the charge transfer process, so that dynamic solvent effects must be considered.^{37,38}

In conclusion, we investigated the influence of the solvent on charge transfer between quantum dots and methyl viologen by comparing dynamics measured using solvent-free two-photon

photoelectron spectroscopy with those measured by solution-phase transient absorption spectroscopy. We first verified that photoelectron spectroscopy is a viable method of measuring excited electron dynamics in quantum dots. After this verification, we applied this technique to study a charge transfer reaction. The good agreement in the charge transfer dynamics obtained by solvent-free and solution phase spectroscopies indicates that common nonpolar organic solvents, such as hexane, have a negligible influence on the charge transfer process between quantum dots and electron acceptor molecules. We explain this observation using theoretical insights that have not previously been applied to nanocrystals. Our results indicate that kinetic data measured by transient absorption spectroscopy, under nonpolar solvent environments, can be used to infer nanodevice behavior in air or vacuum. In the future, this approach can also be used to investigate polar solvents, to gain a general picture of the solvent effects on charge transfer on the nanoscale. This knowledge will provide another tunable parameter to manipulate the charge motion in nanodevices.

■ ASSOCIATED CONTENT

📄 Supporting Information

Further experimental, sample preparation, and fitting details. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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Notes

The authors declare no competing financial interest.

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