Minimizing Electron–Hole Recombination on TiO₂ Sensitized with PbSe Quantum Dots: Time-Domain Ab Initio Analysis

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Supporting Information

ABSTRACT: TiO₂ sensitized with quantum dots (QDs) gives efficient photovoltaic and photocatalytic systems due to high stability and large absorption cross sections of QDs and rapid photoinduced charge separation at the interface. The yields of the light-induced processes are limited by electron–hole recombination that also occurs at the interface. We combine ab initio nonadiabatic molecular dynamics with analytic theory to investigate the experimentally studied charge recombination at the PbSe QD–TiO₂ interface. The time-domain atomistic simulation directly mimics the laser experiment and generates important details of the recombination mechanism. The process occurs due to coupling of the electronic subsystem to polar optical modes of the TiO₂ surface. The inelastic electron–phonon scattering happens on a picosecond time scale, while the elastic scattering takes 40 fs. Counter to expectations, the donor–acceptor bonding strengthens at an elevated temperature. An analytic theory extends the simulation results to larger QDs and longer QD–TiO₂ bridges. It shows that the electron–hole recombination rate decreases significantly for longer bridges and larger dots and that the main effect arises due to reduced donor–acceptor coupling rather than changes in the donor–acceptor energy gap. The study indicates that by varying QD size or ligands one can reduce charge losses while still maintaining efficient charge separation, providing design principles for optimizing solar cell design and increasing photon-to-electron conversion efficiencies.

 SECTION: Energy Conversion and Storage; Energy and Charge Transport

Dye-sensitized solar cells (DSSCs) constitute an alternative to silicon-based solar cells and represent a cost-effective framework to achieve solar energy conversion based on a hybrid of organic-chromophore and semiconductor-based technologies. Electron transfer (ET) and electron–hole recombination across the dye/semiconductor interface play vital roles in determining the voltage and current of DSSCs. Since the original publication by O’Regan and Grätzel, a wide range of experiments have been conducted to investigate electron dynamics in dye–TiO₂ systems, using time-resolved laser spectroscopy to study electron evolution in real time. Most studies have focused on electron injection because the initial charge separation is the primary event, leading the conversion of solar energy into electric current and chemical activity. To achieve high efficiency, one requires fast injection of hot electrons from a chromophore to the TiO₂ conduction band (CB) and slow electron–hole recombination and energy loss to heat. The latter processes occur by coupling to vibrational modes. Compared with the electron injection, studies of electron–hole recombination are much fewer, with observed time scales ranging from subpicoseconds to milliseconds. If an injected electron that has already reached TiO₂ bulk returns to the surface and recombines with the positive charge on the chromophore, the current is reduced. Therefore, the role of electron–hole recombination is particularly important for solar cell efficiency. Our group has initiated time-domain ab initio modeling of electron dynamics occurring at chromophore–semiconductor interfaces, including photoexcited charge separation, delocalization, relaxation, electron trapping at the surface, back-ET to the chromophore or electrolyte, and regeneration of the neutral chromophore by ET from electrolyte. Subsequently, we have investigated the closely related photoinduced charge separation at interfaces of TiO₂ with water, quantum dots (QDs), and graphene. QD-sensitized semiconductor solar cells (QDSCs) have been receiving more recent attention because QDs are superior to molecular chromophores in many aspects. QDs have larger absorption cross sections than molecules. QD spectral response can be tuned simply by changes in size. Thus, QDs made from the same material can be made to absorb sunlight over a broad range of wavelengths. In addition, QDs can increase solar cell voltage and current by either extracting hot charge carriers or generating multiple electron–hole pairs. Zhu and coworkers found that scattering of photoexcited electrons in PbSe QDs occurs faster than electron cooling. Consequently, hot electrons can be extracted faster than they lose energy to phonons, thereby potentially increasing the solar cell voltage. Modeling these experiments directly, we used ab initio nonadiabatic molecular dynamics (NAMD) to demonstr...
strate that the photoinduced ET from a PbSe QD into a TiO₂ surface competes successfully with electron relaxation inside the QD. Following the experimental study of the electron injection dynamics, the same group reported recombination of the electron in the TiO₂ surface with the hole in the PbSe QD occurring on the 1.6 ± 0.1 ps time scale. Modeling such nonradiative electron–hole recombination in real time and at the atomic level can provide fundamental insights and novel design concepts for solar cell development. Because rapid charge recombination decreases solar cell current and hence efficiency, it is particularly important to understand how to slow the recombination.

We employ a combination of time-domain atomistic simulation and analytic theory to analyze in detail the mechanism of the electron–hole recombination at the PbSe QD–TiO₂ interface and to provide guidelines for minimizing charge losses. We show that the recombination occurs due to coupling of the electronic subsystem to high-frequency polar optical modes. The inelastic electron–phonon scattering requires a picosecond, in excellent agreement with the experiment. The elastic scattering, which determines the lifetime of the coherent quantum-mechanical superpositions between the donor and acceptor states, is much shorter, 40 fs. In contrast, with the ultrafast photoinduced charge separation in the same system, which involves a donor state delocalized between the PbSe QD and TiO₂ surface, both donor and acceptor states for the electron–hole recombination are localized on the corresponding materials. Counter to intuition, the donor–acceptor bonds become shorter at a higher temperature. Analytic arguments indicate that the recombination rate reduces with increasing length of the QD–TiO₂ and QD size. The dependence arises primarily due to changes in the donor–acceptor coupling. Changes in the donor–acceptor energy gap also give a weaker dependence. The study suggests that one can control and minimize losses of photogenerated charges in QD–TiO₂ systems by judicious choice of QD diameter, ligands, and QD–TiO₂ binding.

The simulations were performed by the quantum-classical fewest-switches surface-hopping technique implemented with the time-dependent Kohn–Sham scheme and including a semiclassical correction for quantum decoherence. The decoherence times were computed using the optical-response formalism, as described in ref 31. A more detailed description of the theoretical technique is given in the Supporting Information. The approach has been applied to study ET and relaxation in many systems, including fullerene–QD interfaces, graphene, carbon nanotubes, nanoribbons, semi-conducting, and metallic nanocrystals.

The simulation cell (Figure 1), is the same as in our paper on the photoinduced electron injection in the PbSe QD–TiO₂ system. The geometry optimization, electronic structure, and adiabatic MD calculations were carried out using the Vienna ab initio simulation package (VASP). The nonlocal exchange and correlation energies were treated with the Perdew–Burke–Ernzerhof (PBE) functional, based on the generalized gradient approximation (GGA). The projector-augmented wave (PAW) approach was used to describe the interaction of the ionic cores with the valence electrons. The DFT+U correction was used with the on-site $U = 5.5$ eV applied to the Ti 3d electrons. After relaxing the geometry at 0 K, repeated velocity rescaling was used to bring the temperature of the TiO₂–PbSe system to 100 K, corresponding to a midrange temperature used in the experiment. After that, a 2 ps adiabatic MD simulation was performed in the microcanonical ensemble. To simulate ET from the TiO₂ surface to the PbSe QD, several hundred geometries were selected randomly from the 2 ps adiabatic MD trajectory and used as initial conditions for the NAMD. A description of the method can be found in refs 9, 10, and 42. The nuclear time step for the equilibration and production runs was set to 1.0 fs. The electronic time step for NA dynamics was 1.0 attosecond.

Figure 1 shows top and side views of the system relaxed at 0 K (left panel) and a snapshot from the MD run at 100 K (right panel). Geometries obtained from DFT+U are very similar to those from DFT. The PbSe QD and TiO₂ surface bind because both possess unsaturated chemical bonds. These bonds reconstruct to minimize the surface energy. The reconstruction is not perfect, leaving an opportunity for the bonding. Comparing the zero- and finite-temperature geometries, we observe that the two Pb–O bonds connecting the QD to the TiO₂ surface decrease by ~0.05 Å from 2.594 and 2.695 Å at 0 K to about 2.55 and 2.65 Å at ambient temperature. This may appear surprising because typically bonds elongate with increasing temperature due to anharmonicity and break at a high temperature. The overall system expands with increasing temperature, as expected. At the same time, the bonds between the two subsystems contract slightly. The bonding strengthens because thermal fluctuations disrupt the fully optimized structure of the TiO₂ surface and PbSe QD, creating additional bonding opportunities. A similar effect was observed at the graphene–TiO₂ interface, rationalizing why the photoinduced electron injection from metallic graphene into TiO₂ is faster than the electron–hole recombination expected in most metals. QD displacement in the plane of the TiO₂ surface is the largest amplitude motion. The top and side views in Figure 1 illustrate that the QD translates and rotates with respect to the bidentate PbSe–TiO₂ bridge. The bulk topology of this small PbSe nanocrystal remains intact at the finite temperature. The out- and in-plane displacements of the surface oxygen atoms have a strong effect on the electron–hole
recombination. These are the fasted motions available to the system. They change surface polarization, affecting the donor and acceptor wave functions, and create the strongest NA coupling.

Figure 2a presents the energy level diagram for the PbSe QD–TiO2 interface, and Figure 2b gives the projected density of states of the simulated system. The photoinduced dynamics start with excitation of an electron from the valence band (VB) to a conduction band (CB) of the PbSe QD. The electron is rapidly transferred to the CB of TiO2. Having relaxed to the bottom of the TiO2 CB, the electron can return to the lowest energy excited state of the QD, reducing solar cell efficiency. The latter process is under consideration in the present work.

Figure 3 displays the electron densities of the donor and acceptor states for the back ET process. The ET dynamics depend on the electronic energy gap and donor–acceptor coupling. The strength of the coupling is related directly to the amount of mixing between the donor and acceptor wave functions. Here the donor state is localized on the TiO2 substrate and the acceptor state is entirely on the QD. The situation leads to a weaker coupling for the back ET compared with the coupling driving the photoinduced charge separation in the same system. The photoexcited state for the charge separation is already delocalized between the two materials. (See figure 3a in ref 12.) Therefore, one expects slower electron–hole recombination than separation.

The autocorrelation function (ACF) of the donor–acceptor energy gap describes how the gap at a particular time depends on its value at earlier times. In general, poorly correlated random motions give ACFs that decrease rapidly form 1 to 0. Changes that are results of well-correlated periodic vibrations lead to ACFs that oscillate between 1 and −1. Fourier transform (FT) of the ACF characterizes the phonon modes that couple to the electronic subsystem and accommodate the excess energy released during the back ET. The ACF also defines the semiclassical decoherence correction in the NAMD simulation.29,30 The ACF decays rapidly on a 15 fs time scale (Figure 4a) due to coupling of the electronic subsystem to multiple phonon modes. After the rapid initial decay, the ACF shows partial revivals, suggesting the presence of a few dominant modes.

Figure 4b characterizes the vibrational modes that drive the electron–hole recombination. The dominant peak at 671 cm⁻¹ is close in frequency to the 685 cm⁻¹ Raman-active phonon of rutile.45,46 The small peak at 540 cm⁻¹ is close in frequency to the 667 cm⁻¹ hole recombination. The dominant peak at 671 cm⁻¹ can be attributed to an overtone of the longitudinal-optical (LO) phonon of rutile.45,46 The high-frequency modes of TiO2 create the strongest electron–phonon coupling both because they are polar and because O is the lightest atom in the system. Polar modes have a strong electrostatic effect on the electronic wave functions. Light atoms create high-energy phonon quanta that best match the electronic energy gap.

The optical pure-dephasing function, characterizing elastic electron–phonon scattering, is shown in Figure 5a. It is computed from the ACF using the second-order cumulant approximation, as described in ref 31. The open circles in Figure 4a represent a double-Gaussian fit, \( f(t) = B \exp(-0.5(t/\tau_e)^2 + (1 - B) \exp(-0.5(t/\tau_h)^2). \) The fitting parameters are \( B = 0.40, \tau_e = 15 \text{ fs}, \) and \( \tau_h = 57 \text{ fs}. \) The pure-dephasing time, defined by \( B\tau_e + (1 - B)\tau_h, \) is equal to 40 fs. This time scale is typical of nanoscale materials.31

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**Figure 2.** (a) Energy level diagram and (b) projected density of states (PDOS) in the TiO2–QD system. The photoinduced dynamics start by excitation of an electron from the valence band (VB) to a conduction band (CB) of the PbSe QD. The electron is rapidly transferred to the CB of TiO2. Having relaxed to the bottom of the TiO2 CB, the electron can return to the lowest energy excited state of the QD, reducing solar cell efficiency. The latter process is under consideration in the present work.

**Figure 3.** Charge densities of (a) donor and (b) acceptor states localized on the TiO2 slab and the QD, respectively.

**Figure 4.** (a) Autocorrelation function (ACF) of the donor–acceptor energy gap and (b) Fourier transforms (FT) of the donor–acceptor energy gap. The dominant 667 cm⁻¹ peak seen in panel b can be attributed to a high-frequency optical Raman-active mode of rutile TiO2.

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The ET transfer from the TiO$_2$ surface to the PbSe QD occurs via a nonradiative transition and reflects inelastic electron–phonon scattering. The time-dependent population of the donor state demonstrated the evolution of the electron–hole recombination process (Figure 5b). The direct DFT calculation gives a 0.1 eV donor–acceptor energy gap and a 0.7 ps time scale, which is about two times faster than the experimental time.\(^\text{24}\) To compare the simulation to the experiment more directly, we scaled the energy gap to the experimental value of 0.3 eV and repeated the NAMD simulation. The result is a 1.3 ps time (Figure 5b), in good agreement with the experiment. Such rapid electron–hole recombination is detrimental to solar cells, leading to reduction of charge carrier concentration. Next, we discuss how to minimize the recombination by varying the length of a bridge connecting the QD to the TiO$_2$.\(^\text{48}\) and the QD size.

The NA coupling strength is related to the wave function overlap between donor and acceptor states. It is common to assume that the coupling decays exponentially with increasing separation between donor and acceptor. Hence, we assume that the NA coupling depends on the QD–TiO$_2$ distance as NA = Aexp(−β|x|). Here x is the QD–TiO$_2$ distance, A is the NA coupling without the ligand, and β is the damping factor.\(^\text{49,50}\) Typical values of the damping factor β are around 0.1 to 0.2 Å\(^{-1}\).\(^\text{51}\) To investigate the dependence of the ET rate on the ligand length x, we take β = 0.2 Å\(^{-1}\) and repeat the NAMD simulations for x = 20, 30, 40, and 50 Å. The parameter A is the NA coupling of the original simulation. The charge-recombination rates are plotted on a semilogarithmic scale in Figure 6a. The rate decays rapidly as the bridge length increases. Therefore, an increase in the length of the linker between TiO$_2$ and QD serves to reduce nonradiative electron–hole recombination\(^\text{48}\) and optimize solar-cells performance. It should be noted that this strategy will also reduce the photoinduced charge separation rate. An optimal bridge length should achieve a balance between the forward and backward ET rates.

The ET rate also depends on the QD size.\(^\text{23,24}\) Changes in the QD size affect both donor–acceptor coupling and energy. The band gap of the PbSe QD decreases with increasing QD diameter, as described in ref 52 for PbSe QDs with diameters ranging between 1 and 10 nm. Because the return of the electron from TiO$_2$ to the PbSe QD occurs by a transition from the bottom of the TiO$_2$ CB to the QD LUMO,\(^\text{24}\) decreasing the QD gap lowers the LUMO energy and increases the donor–acceptor gap. Changing the QD size also alters the QD wave function. The electronic structure of QDs can be approximated using a finite-depth spherically symmetric well.\(^\text{53,54}\) The overlap of the donor and acceptor wave functions is determined by the tail of the QD wave function extending onto TiO$_2$. The finite-depth well model predicts that this overlap is inversely proportional to the QD volume. Therefore, we assume that the NA coupling decreases with increasing QD radius, r, as NA = B/r\(^3\). The constant B is determined by the NA coupling computed for the simulated QD (Figure 1).

Modeling the effect of the QD size on the electron–hole recombination rate, we repeated the NAMD simulations by scaling the energy gap and NA coupling, as previously described. The resulting rates are shown in Figure 6b. The Figure also shows data separating the overall effect into contributions from the energy gap and the NA coupling. The change in the energy gap has a much smaller impact on the electron–hole recombination than the change in the NA coupling. The overall effect of increasing QD size on the rate is significant, which is consistent with the experimental observations.\(^\text{24}\) The data show that larger QDs suppress electron–hole recombination. Larger QDs provide additional advantages. For instance, they absorb more sunlight photons over a broader wavelength range due to higher absorption cross sections and smaller energy gap. An increase in the QD size is easier to achieve in experiment than an increase in the ligand length because the same precursors and synthetic procedure can be used. The finite well model of the QD electronic structure predicts very strong dependence of the electron–hole recombination rate on the QD size (Figure 6b). The effect in realistic systems is likely smaller because the QD–TiO$_2$ coupling can arise from states localized on the QD surface and therefore can be much less dependent on the QD size. Furthermore, the finite well model predicts significant energy gaps between QD electronic states, as observed spectroscopically. However, atomistic calculations predict much higher state densities.\(^\text{35}\) Higher energy QD levels can contribute to the process, reducing the donor–acceptor energy gap.

In summary, we have performed NAMD simulations combined with time-domain DFT, characterizing in detail
transfer of the photogenerated electron from a TiO₂ surface to a PbSe QD. The simulated time scale agrees well with the experimental observation. The simulations indicate that the recombination is largely promoted by a high-frequency optical Raman-active mode of TiO₂. Lower frequency optical modes contribute to a lesser extent. The elastic electron–phonon scattering time is an order of magnitude shorter than theinelastic time. The donor and acceptor states are strongly localized on the corresponding materials. This is in contrast with the photoinduced charge separation in the same system, which starts from a QD state that is delocalized onto TiO₂ and which is significantly faster than the charge recombination. Compared with the optimized structure at 0 K, the PbSe–TiO₂ bonding becomes stronger at an elevated temperature because thermal fluctuations disrupt the fully optimized structure, creating additional bonding opportunities. This effect is counterintuitive because most bonds weaken and break with increasing temperature. Model simulations suggest that charge recombination can be suppressed exponentially by increasing either the ligand length or QD size. Changes in both donor–acceptor coupling and energy gap lead to the exponential dependence, with the coupling providing a more significant contribution. The study provides valuable insights into the dynamics of interfacial charge recombination and nonradiative energy losses, detrimental to a wide variety of applications, including photovoltaics, solar hydrogen production, and catalysis.

■ ASSOCIATED CONTENT

1 Supporting Information

Description of the theoretical approaches. 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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