Dimensionality of Nanoscale TiO$_2$ Determines the Mechanism of Photoinduced Electron Injection from a CdSe Nanoparticle

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ABSTRACT: Assumptions about electron transfer (ET) mechanisms guide design of catalytic, photovoltaic, and electronic systems. We demonstrate that the mechanism of ET from a CdSe quantum dot (QD) into nanoscale TiO$_2$ depends on TiO$_2$ dimensionality. The injection into a TiO$_2$ QD is adiabatic due to strong donor–acceptor coupling, arising from unsaturated chemical bonds on the QD surface, and low density of acceptor states. In contrast, the injection into a TiO$_2$ nanobelt (NB) is nonadiabatic, because the state density is high, the donor–acceptor coupling is weak, and multiple phonons accommodate changes in the electronic energy. The CdSe adsorbant breaks symmetry of delocalized TiO$_2$ NB states, relaxing coupling selection rules, and generating more ET channels. Both mechanisms can give efficient ultrafast injection. However, the dependence on system properties is very different for the two mechanisms, demonstrating that the fundamental principles leading to efficient charge separation depend strongly on the type of nanoscale material.

KEYWORDS: Nonadiabatic molecular dynamics, time-domain density functional theory, semiconductor quantum dots, electron-vibrational interaction, adiabatic electron transfer

 Increased environmental and economic concerns have prompted the development of new technologies to harvest energy from our solar system.$^1$–$^3$ Recent efforts have led to the use of nanomaterials as building blocks for next-generation energy conversion devices.$^4$–$^12$ In particular, heterostructured materials composed of metal oxides have attracted substantial attention and have shown promise in photocatalysis, photovoltaics, and other applications.$^{13}$–$^{24}$ Because of this, understanding the general photophysics is critical to a variety of applications and is important basic science for developing these materials. The most common metal oxide used for light harvesting and utilization is titanium dioxide (TiO$_2$), which suffers from two fundamental problems, such as (1) a large UV spectral band gap that only utilizes 1–5% of the sunlight reaching the Earth surface and (2) charge carrier recombination that causes electrons and holes to recombine before they can initiate the photoreduction.$^{25}$–$^{28}$

To overcome these inefficiencies, one can use semiconductor quantum dots (QDs), for example, CdSe, PbS, and PbSe, to photosensitize TiO$_2$ and improve its optical activity in the visible and near-infrared regions of the solar spectrum.$^{29}$–$^{34}$ These nanocrystals are easily tunable to absorb light at almost any wavelength, are thermally stable, and are photochemically robust. When combined with TiO$_2$, the semiconductor QDs form type II band alignment, indicating that photoexcited electrons in the conduction band (CB) of the nanocrystal can be injected into the CB of TiO$_2$.$^{17,35}$ Photoinjection of electrons is ultrafast, causing the electron and hole in the QD to separate and reducing charge recombination.$^{36}$–$^{38}$ The efficiency of the charge injection is often low because of other major competitive pathways, leading to an undesired loss of the photogenerated electrons due to charge trapping on QD surfaces and charge recombination during transport through the semiconductor oxide substrate.$^{39}$ Recently, highly ordered one-dimensional (1D) nanostructures, for example, nanotubes, nanowires, and nanorods, have received considerable attention as a solar material.$^{5,40}$–$^{47}$ They provide significant improvement in the charge transport and photoconversion efficiency compared to planar photoelectrodes and assemblies of zero-dimensional (0D) QDs.$^{48,49}$ We have conducted a systematic study to characterize the photoinjection mechanism of electrons across CdSe/TiO$_2$ interfaces by varying the shape of the semiconductor nanostructures.

Here, we report time-domain ab initio simulations of the photoinduced electron transfer (ET) from an excited CdSe QD to a TiO$_2$ QD and a TiO$_2$ nanobelt (NB), respectively. We
focus on the effect of the acceptor dimensionality on the ET properties and consider implications of the obtained results in developing next-generation photocatalytic and photovoltaic materials. Our simulations mimic the recent experimental work of Kamat and co-workers\textsuperscript{50} and Zhang and co-workers.\textsuperscript{43} Good agreement with the experimental data is achieved. The study establishes that the ET proceeds mainly by the adiabatic mechanism for the quasi 0D acceptor and by the nonadiabatic (NA) mechanism for the 1D acceptor. Both mechanisms give efficient injection; however, they have very different dependence on system properties. The adiabatic mechanism requires strong donor–acceptor coupling, and hence it is very sensitive to the binding interaction. In contrast, the NA mechanism operates for weak donor–acceptor coupling. It requires high density of acceptor states and phonon modes to accommodate changes in the electronic energy during NA transitions. Detailed analysis of the simulation data rationalizes the origin of the fundamental difference between the TiO\textsubscript{2} QD and NB, and provides important insights into the charge-separation processes. Because the ET dependence on system properties varies strongly for the two mechanisms, the study demonstrates that the design principles guiding efficient photoinduced charge separation are strongly influenced by system dimensionality.

Figure 1 presents a schematic for electron injection from the CdSe QD to TiO\textsubscript{2} along with a diagram explaining the adiabatic and NA ET mechanisms. An absorbed photon promotes an electron from the CdSe QD ground state, which is located energetically in the semiconductor TiO\textsubscript{2} band gap, to an excited state that is resonant with the TiO\textsubscript{2} CB. After excitation, an electron is injected from the QD to the TiO\textsubscript{2} surface, typically on an ultrafast time scale. Following the transfer, the electron diffuses into the bulk, simultaneously relaxing to the bottom of the CB and losing its energy to vibrations. The transfer of the electron from the photoexcited donor (CdSe QD) to the acceptor (TiO\textsubscript{2}) can occur either adiabatically by passing over a transition state barrier or nonadiabatically by hopping between donor and acceptor states, generally away from a transition state transition.

The electron dynamics simulations are carried out using the mixed quantum-classical approach\textsuperscript{51} with implementation of the fewest switching surface hopping technique\textsuperscript{52} within the time-dependent density functional theory in the Kohn–Sham representation.\textsuperscript{51,53} In this approach, the electrons are treated quantum mechanically, while the nuclei are classical. The method has been previously applied to study ET and relaxation dynamics at interfaces of inorganic semiconductors with molecular chromophores,\textsuperscript{54} QDs,\textsuperscript{55} and graphene;\textsuperscript{56} in carbon nanotubes,\textsuperscript{57} nanoribbons,\textsuperscript{58} fullerene,\textsuperscript{59} semiconducting,\textsuperscript{60} and metallic\textsuperscript{61} nanocrystals, and in biological systems.\textsuperscript{51} The approach allows for direct mimicking of numerous time-domain experiments and provides an atomistic description of chemical and physical processes and interactions. Details of this approach can be found elsewhere.\textsuperscript{62}

The geometry optimization, electronic structure, and adiabatic MD simulations were carried out with the Vienna ab initio simulation package (VASP).\textsuperscript{63,64} The nonlocal exchange-correlation interactions were treated with the Perdew–Burke–Ernzerhof (PBE) functional\textsuperscript{65} based on the generalized gradient approximation. The projector-augmented wave (PAW) approach was used to describe the interaction of the ionic cores with the valence electrons.\textsuperscript{66,67} After the geometries were fully optimized at 0 K, uniform velocity rescaling was used to bring the temperature of the TiO\textsubscript{2}–CdSe systems to 300 K. Then, a 1.5 ps adiabatic MD simulation were performed in the microcanonical ensemble with a 1.5 fs atomic time-step. The nuclear trajectories from this adiabatic MD were used to sample the initial conditions and to carry out the NAMD simulations. The atomic structures of the QD (47 TiO\textsubscript{2} units) and NB (48 TiO\textsubscript{2} units) were carved out from the anatase structure, which was found to be active in light absorption and photon-to-current conversion and was prevalent in the experiments.\textsuperscript{68} The dominant-area facet of the QD and NB is (101), which is stable and reactive.

Figure 2 depicts the optimized and finite-temperature geometries of the simulated systems. The first system includes a Cd\textsubscript{13}Se\textsubscript{13} QD directly attached to the TiO\textsubscript{2} QD as implemented in the recent experimental study.\textsuperscript{50} The second system involves the Cd\textsubscript{13}Se\textsubscript{13} QD connected to the TiO\textsubscript{2} NB. The CdSe QD is thermodynamically stable and preserves the topology of the bulk at room temperature. A comparison of the systems at 0 and 300 K indicates that thermal fluctuations impact the system geometries. The top part of Figure 2a shows the top and side views of the QD–QD system relaxed at 0 K and a system geometry from the MD run at 300 K. Comparing the zero- and finite-temperature geometries, we observe that the CdSe QD remains bound to the TiO\textsubscript{2} QD substrate at room temperature and that a Se–O bond at 0 K (1.940 Å) is broken at room temperature to form a Se–Se bond (2.410 Å). In the system geometry optimized at 0 K, the lengths of the three Cd–O bonds are 2.230, 2.230, and 2.340 Å, while they
become 2.250, 2.210, and 2.180 Å in the sample MD geometry. Their corresponding bond angles fluctuate as well. It is particularly important for the adiabatic ET mechanism, that the strong chemical interaction between the donor and acceptor species is preserved at room temperature.

In the QD−NB system (Figure 2, bottom), the CdSe QD is bound to TiO2 at 0 K through two Se−Ti bonds with bond lengths of 3.030 Å. Already at 0 K, the donor−acceptor interaction is weaker for the TiO2 NB than TiO2 QD. This is because the QD has less perfect surfaces and more unsaturated chemical bonds than the NB. As temperature increases to 300 K, the CdSe−TiO2 interaction decreases significantly. As a result, the average separation grows, leading to Se−Ti bond breaking and weak donor−acceptor coupling.

The binding energies between the CdSe and TiO2 subsystems are equal to 1.714 and 1.134 eV for the TiO2 QD and NB, respectively. These values support the above conclusion obtained by considering the system geometries at 0 and 300 K. The interaction is stronger for the TiO2 QD than the TiO2 NB. Similar calculations performed with the TiO2 surfaces terminated with hydroxyl bonds, Figure S1 of Supporting Information, give a stronger difference in the binding energies. The values are 3.360 and 0.965 eV for the TiO2 QD and NB, respectively. Chemical termination of the TiO2 surface has a strong effect on the TiO2 QD system, because the termination greatly reduces the number of defect states and unsaturated chemical valences. With less need to accommodate the defects, the structure of the hydroxyl-terminated TiO2 QD becomes more bulklike. The chemical interaction between the TiO2 QD and the CdSe QD is more favorable now, because TiO2 has well-defined free bonds to interact with CdSe, and because “self-healing” of the TiO2 surfaces no longer competes with the CdSe−TiO2 binding interaction. Note that the TiO2 atoms interacting with CdSe are not terminated by hydroxyls. Chemical termination of the TiO2 NB slightly decreases the binding energy, because addition of the hydrogen atoms introduces weak repulsion by preventing CdSe from closely approaching the TiO2 slab. The data obtained with both bare and chemically terminated TiO2 surfaces support the conclusion that the TiO2−CdSe interaction is stronger for the TiO2 QD than the TiO2 NB.

Figure 3 shows representative electron densities of the donor and acceptor states at room temperature. In both systems, the density of the electron donor is delocalized over the whole QD and a small amount of the photoexcited electron density spills into the TiO2 substrate due to direct CdSe−TiO2 coupling in the absence of a bridge. The acceptor state in the TiO2 QD is spread nearly uniformly across the QD. The asymmetry seen in the provided example agrees between the donor and acceptor states. Both states have higher density on the left side of the picture, maximizing the state overlap.

An isolated TiO2 NB has delocalized band states. However, the acceptor states seen in the QD−NB system are localized, because the adsorbed donor breaks the symmetry. A calculation performed with a 50% thicker TiO2 NB, Figure S2 of Supporting Information, also shows the symmetry breaking. The donor−acceptor coupling is weaker for the QD−NB than QD−QD system; the key role is played by the NA coupling induced by phonon modes. Symmetry breaking relaxes selection rules and helps to couple to more phonons, therefore, increasing the NA ET rate.

As a result of a weaker donor−acceptor coupling and a large ensemble of available phonon modes, the excited electron is transferred from the QD donor state to the NB acceptor state by a NA transition. The excess electronic energy is deposited into vibrational modes. In contrast, due to a strong donor−acceptor interaction in the QD-QD system the excited electron is injected into the acceptor state adiabatically, by passing over a transition state barrier (Figure 1). A representative evolution of
the donor and acceptor state energies are shown for the NB system in Figure S3 of Supporting Information.

In general, the photoinduced electron injection from CdSe into TiO$_2$ occurs through a combination of adiabatic and NA mechanisms. Our simulations allow us to separately the two contributions quantitatively.$^{19}$ Adiabatic ET occurs by a change in the localization of the occupied state from CdSe to TiO$_2$, whereas NA ET involves a change in the state occupations during which electron hops from a state localized on CdSe to a state localized on TiO$_2$. Strong interaction between the donor and acceptor systems leads to adiabatic transfer. During adiabatic transfer, the electron remains in the same (adiabatic) electronic state, and the presence of other states, that is, the density of states, is not important. The NA mechanism operates when the interaction between the donor and acceptor systems is weaker. Often described by perturbation theory, such as Fermi’s golden rule, the NA transfer rate is directly proportional to the density of acceptor states. In present, the donor–acceptor coupling is stronger for the TiO$_2$ QD due to imperfections of the QD surface, as evidenced by the stronger CdSe/TiO$_2$ binding energy. The density of acceptor states is higher for the TiO$_2$ NB, because it is a higher dimensional system.

Figure 4 depicts the average ET dynamics at the interface of the CdSe and TiO$_2$ systems. The ET coordinate is defined by integrating the photoexcited electron density over the region of the simulation cell occupied by the electron acceptor. The ET data were fitted to the exponential function $y = A \exp(-x/t)$, where $t$ is the ET time constant, $A$ represents the amplitudes of the adiabatic, NA, and overall ET. The total, adiabatic, and NA ET contributions are shown in Figure 4 by the solid black, red dashed, and blue dash-dotted lines, respectively. In the CdSe–TiO$_2$ QD system, the NA ET contribution is very small, and the ET process is dominated entirely by the adiabatic ET.

The story differs for the CdSe–TiO$_2$ belt. Our calculations indicate that the photoinduced electron injection occurs by the NA mechanism. The large negative contribution of the adiabatic mechanism at the concluding stage of the photoinduced ET dynamics in the TiO$_2$ NB system is an artificial boundary effect. We confirmed this fact by performing the calculation on the TiO$_2$ NB system with the surface terminated by hydroxyl groups, Figure S4 of Supporting Information. The results of the calculations with and without the hydroxyl termination agree for the first 50 fs of the dynamics and disagree at a later time, because hydroxyls introduce different boundary conditions. Both simulations confirm that the photoinduced ET from the CdSe QD into the TiO$_2$ NB occurs by the NA mechanism.

The photoinduced ET from the CdSe QD into the TiO$_2$ QD and NB occur on similar time scales, 105 and 92 fs, respectively. These results correspond to the faster end of the broad range of the experimental injection times measured for a variety of CdSe–TiO$_2$ systems.$^{37,50,70}$ In particular, the simulated times are in excellent agreement with the 1.68 $\times$ 10$^{-13}$ s$^{-1}$ transfer rate measured by Kamat and co-workers for their smallest CdSe nanoparticle (2.8 nm diameter).$^{37}$ One expects the simulated dynamics to be faster than the measured time scales in general, because the systems used in the calculations are smaller than those in the experiment. The reduced system size implies that both the donor–acceptor electronic coupling and the NA electron–phonon coupling are stronger and that the photoexcited state is located spatially closer to TiO$_2$ CB states.

It may be surprising at first glance that the distinct ET mechanisms, adiabatic in the TiO$_2$ QD and NA in the TiO$_2$ NB, can give similar injection times. This phenomenon is known from the literature on dye-sensitized TiO$_2$ solar cells.$^{21}$ Adiabatic ET is fast in most systems. NA ET is fast because of the high density of TiO$_2$ acceptor states.

Vibrational motions of the atoms play crucial roles in the interfacial injection dynamics. Not only they are responsible for the fluctuation of the energy and localization of the photoexcited states; they also drive both adiabatic and NA ET, modulate the state localizations and donor–acceptor coupling, and are responsible for the electron-vibrational relaxation. To characterize their effects on the ET process, we identified the phonon modes that couple to the electronic subsystem and promote the ET. Figure 5 shows the influence spectra obtained by taking Fourier transforms of the autocorrelation functions (ACF) of the photoexcited state energy and localization. Because state localization depends on both state energies and donor–acceptor coupling, the additional modes seen in the localization spectra characterize the effect of vibrational motions on the donor–acceptor coupling.

Comparison of the data for the TiO$_2$ QD and NB systems (Figure 5) immediately shows that the ET into the TiO$_2$ NB couples to a much broader range of vibrational modes than the ET into TiO$_2$ QD. This fact rationalizes the efficiency of the NA mechanism in the NB system: NA ET relies on the Na electron–phonon coupling and involves a redistribution of the electronic energy lost during a NA transition into vibrations. The photoexcited state energy in the QD system oscillates with a distinct frequency around 150 cm$^{-1}$ in the range of QD acoustic modes that modulate QD size and shape. In contrast, in addition to the acoustic mode the energy spectrum of the belt shows optical mode frequencies between 600 and 800 cm$^{-1}$ and even higher frequency overtones. The localization spectra exhibit more frequencies than the energy spectra, because the donor–acceptor coupling is more sensitive to atomic positions than the state energy.

The inserts of Figure 5 depict the ACF of the photoexcited state energy and localization. They quantify the memory of the corresponding fluctuations. Both energy and localization ACFs show a significantly faster decay for the belt compared to the QD due to coupling of the electronic subsystem to more
The main difference in the two systems studied in the present work resides in the local interaction between the donor and acceptor species. The TiO$_2$ NB represents an infinite flat TiO$_2$ surface without defects. The TiO$_2$ QD represents a finite system with imperfections. If the TiO$_2$ dot is made significantly larger, it will resemble an infinite TiO$_2$ surface. At the same time, the differences will remain, for instance, due to the differences in synthetic procedures. Typically, nanocrystals have rough surfaces, involving different crystallographic directions, defects, steps and other imperfections. These increase the strength of chemical bonding, since TiO$_2$ defect sites have unsaturated chemical valences that can form strong bonds with CdSe. The effective density of TiO$_2$ acceptor states decreases, because only states localized in the donor—acceptor interaction region can couple to the CdSe donor state. The stronger donor—acceptor interaction and lower density of available acceptor states favors the adiabatic mechanism. In contrast, well-defined ideal TiO$_2$ surfaces, represented by the TiO$_2$ NB, result in a weaker donor—acceptor coupling and a higher density of available acceptor states. As a result, the electron transfer is NA. When extrapolated to large particles, our TiO$_2$ QD simulation represents systems with rough surfaces and multiple defects, while the TiO$_2$ NB simulation exemplifies systems with nearly ideal surfaces.

In summary, the electronic structure and mechanisms of the photoinduced interfacial ET have been investigated in the CdSe−TiO$_2$ systems in real time and at the atomistic level, using the state-of-the-art approach combining time-domain DFT with NAMD. It has been shown that the ET mechanism is dictated by the acceptor dimensionality; it is adiabatic for the quasi 0-D QD acceptor and NA for the 1D NB acceptor. Both mechanisms can give efficient and ultrafast injection; however, the dependence of injection on system properties is very different for the two mechanisms. The adiabatic mechanism requires strong donor—acceptor coupling, and therefore, it is very sensitive to the CdSe−TiO$_2$ binding, presence and length of a bridge, and so forth. In contrast, the NA mechanism operates if the donor—acceptor coupling is weak. It requires a high density of acceptor states and availability of phonon modes to accommodate changes in the electronic energy during NA transitions. The NA ET is not particularly sensitive to the CdSe−TiO$_2$ binding. Rather, its efficiency depends on the photoexcitation energy, QD size, NB thickness, and so. The adiabatic mechanism operates in the TiO$_2$ QD system, because the chemical binding between CdSe and TiO$_2$ is strong due to imperfection in the TiO$_2$ QD surface. The NA mechanism is efficient with the TiO$_2$ NB, because the coupling is weak, while the density of the NB acceptor states and the range of available phonon modes are high. The CdSe adsorbant breaks the symmetry of delocalized band-type states of the TiO$_2$ NB, creating localized acceptor states. The symmetry breaking relaxes the donor—acceptor and NA coupling selection rules, generating more ET channels. The clearly demonstrated effect of system dimensionality on the mechanism of the photoinduced ET provides important guidelines for design of nanoscale light-harvesting materials.

### ASSOCIATED CONTENT

#### Supporting Information

Structures of the systems under investigation with TiO$_2$ surfaces terminated by hydroxyl groups, results for electron transfer dynamics in the TiO$_2$ nanobelt system with hydroxyl termination, representative evolution of the donor and acceptor state energies in the nanobelt system, and acceptor state density in a 50% thicker TiO$_2$ nanobelt. This material is available free of charge via the Internet at http://pubs.acs.org.

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**Notes**

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