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Recent Advances in Quantum Dot Surface Chemistry

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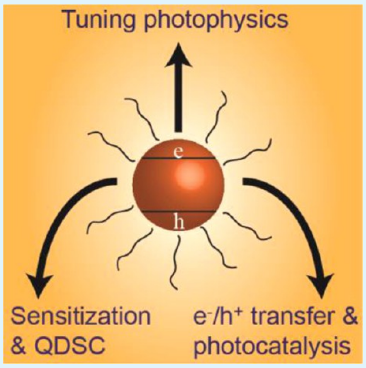
ABSTRACT: Quantum dot (QD) surface chemistry is an emerging field in semiconductor nanocrystal related research. Along with size manipulation, the careful control of QD surface chemistry allows modulation of the optical properties of a QD suspension. Even a single molecule bound to the surface can introduce new functionalities. Herein, we summarize the recent advances in QD surface chemistry and the resulting effects on optical and electronic properties. Specifically, this review addresses three main issues: (i) how surface chemistry affects the optical properties of QDs, (ii) how it influences the excited state dynamics, and (iii) how one can manipulate surface chemistry to control the interactions between QDs and metal oxides, metal nanoparticles, and in self-assembled QD monolayers.



KEYWORDS: *quantum dots, surface chemistry, electron transfer, hole transfer, trap state*

SURFACE CHEMISTRY AS A TOOL TO TUNE PROPERTIES OF QUANTUM DOTS

The ability of chemists to synthesize high-quality, size- and shape-selective semiconductor nanocrystals has made materials science, physics, and engineering disciplines embrace them as building blocks in nanotechnology. In particular, these semiconductor nanocrystals gain most of their attention for photovoltaic, optoelectronic, and electronic applications from their size-dependent optical properties.[1−8] The size-dependent optical and electronic properties of semiconductor nanocrystals or quantum dots (QD) arise from the quantum confinement effect; a property of semiconductors that is evident as the diameter of a nanoparticle approaches that of the Bohr-exciton radius.[9−11] For instance, CdS, CdSe, and CdTe are commonly studied semiconductors that experience quantum confinement effects when their particle diameters are less than ~5−6 nm,[12] ~11 nm,[13,14] and 7.3 nm,[15] respectively. The consequence of small particle diameters is that QDs have a high ratio of surface atoms to atoms confined to the core. As this ratio of surface to core atoms increases, the properties of the surface atoms begin to dominate the properties of the entire particle. These surface atoms are chemically different than the core atoms due to the termination of the semiconductor lattice at the QD surface. These atoms are typically undercoordinated because of the steric hindrance between passivating ligands coordinated at the surface,[16] an effect that has been confirmed by NMR, FTIR, EXAFS, and Rutherford backscattering spectroscopic studies of the QD surface.[17−20]

The undercoordination of the surface atoms can be remediated (to a degree) through the "passivation" of these surface atoms by the use of inorganic shells such as ZnS, CdSe, and CdTe.[22−28] Left unpassivated, atoms on the QD surface are thought to have "dangling bonds", which are essentially unbonded orbitals that protrude from the QD surface and are thought to be the origin of charge trapping states.[29−32] The adsorption/reaction of organic molecules, oxygen and semiconductor layers have all been shown to have unique effects on the optical properties of the QD by binding at these free sites.[22,33]

An example of the effect that a chemical adduct can have on QD optical properties is band-edge emission quenching through the addition of thiol functionalized molecules.[21,34−38] One study on 3-mercaptopropionic acid (3-MPA) has reported the quenching of band-edge emission upon exchange with ligands native to the QD surface, shown in Figure 1.[21] Concurrent with band-edge quenching is the appearance of a broad, lower energy emission arising from the electron trapping states that are energetically below the conduction band-edge. Ligand exchange with 3-MPA results in a broad emission across most of the visible spectrum and gives the QD emission a white-light appearance. The attachment of a bifunctional molecule to the QD surface allows for the unique opportunity to tune the optical properties of QDs as well as serve as an anchor to bind QDs to another surface such as a metal oxide. This has applications both in QD solar cells as well as field effect transistors (FETs) and other electronic and optoelectronic devices. Studies involving these interactions have demonstrated better loading of QDs on a surface as well as better film formation.[39] The use of conductive linker molecules, such as metal chalcogenide capping agents, have been shown to eliminate the insulating organic molecules on the QD surface

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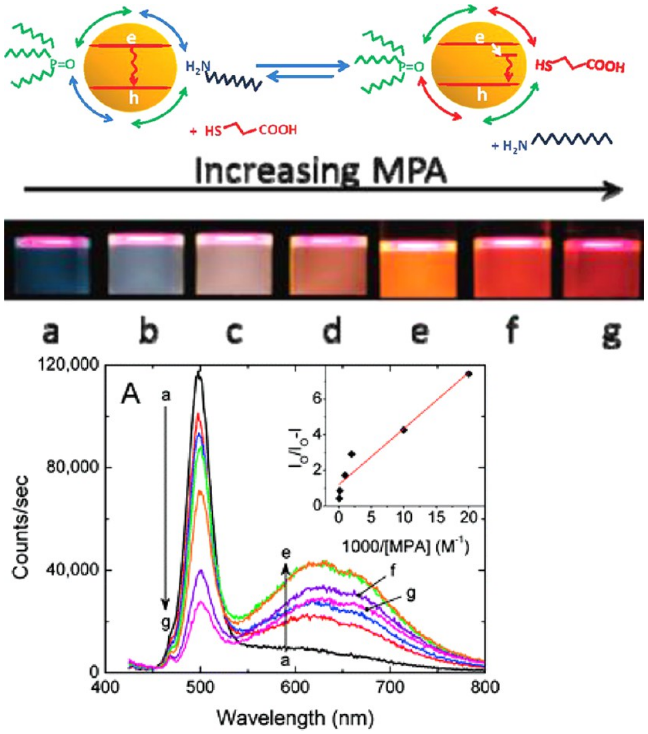

Figure 1. Top: Ligand exchange between dodecylamine and 3-mercaptopropionic acid leading to the tuning of emission. Bottom: Corresponding changes in the emission spectra showing the quenching of band-edge emission and increasing trap emission for a solution of QDs treated with (a) 0 M, (b) 50 μM, (c) 100 μM, (d) 500 μM, (e) 1 mM, (f) 5 mM, and (g) 10 mM 3-MPA. Reprinted with permission from ref 21. Copyright 2010 American Chemical Society.

and allow for the formation of highly ordered and highly conductive films of QDs.[40−42]

The manipulation of QD surface chemistry has also been shown to enhance the performance of quantum dot sensitized solar cells (QDSCs).[43] Numerous studies have shown the effects of the use of various organic passivants on QDSC performance. One of the promising manipulations of QD surface chemistry comes from the passivation of QD trap sites with various inorganic layers such as ZnS.[44−47] These inorganic layers serve to reduce nonradiative recombination in QDSCs thus increasing the probability of electron injection. These effects present new ways to tune QD optical properties to the specific need of the application while also exposing the sensitivity of QDs to changes in the chemical environment.

Here we discuss the photophysical and photochemical aspects of QD surface chemistry with three major thrusts (Figure 2): (i) the effect of surface chemistry on the optical and electronic properties of QDs and how these changes effect the charge recombination dynamics of QDs; (ii) electron and hole transfer mediated by surface bound species; and (iii) surface modification to tailor the interactions between QDs and other semiconductors, metal oxides, metal nanoparticles, and organic materials for device applications.

OXIDATIVE REACTIONS ON THE QD SURFACE

a. Photoluminescence Studies. Several studies of surface oxidation have made use of PbSe nanocrystals. Monitoring the band-edge photoluminescence (PL) of PbSe QDs, Klimov and coworkers have shown that QDs are sensitive to oxidation over the course of a 24 h time period.[48] Presence of oxygen atoms bound to the surface show a brief period of PL quenching from oxygen induced trap states,[49] however, in some cases the PL can eventually recover to higher intensities. The initial quenching is a result of a fast rate of nonradiative recombination (k_{nr}), which competes with the radiative process. The recovery of the band edge PL indicates the reversibility of the reaction which is discussed later in this manuscript. Using XPS and TEM, Klimov and his coworkers have also shown that the exposure of PbSe QDs to air results in the formation of oxides (SeO_2 and $PbSeO_3$) on the QD surface that desorb and reduce the nanoparticle size.

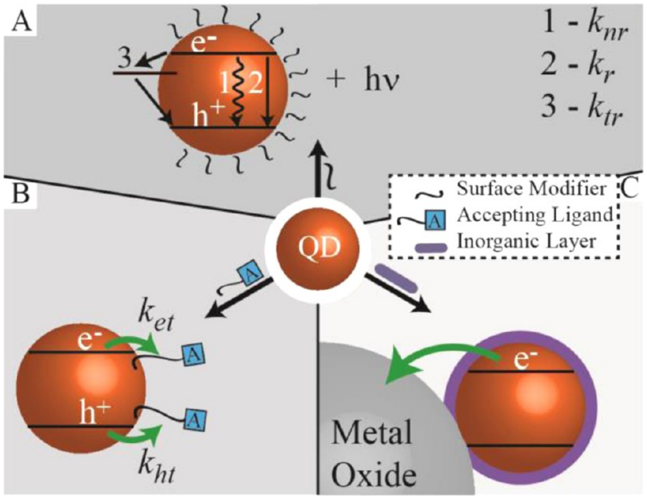

Figure 2. Illustration of the three main areas of interest for QD surface chemistry: (A) effects on QD optical properties and excited state dynamics, (B) the capture and shuttling of electrons/holes, and (C) the influence of surface chemistry on electron transfer between QDs and other surfaces.

A study from Wen shows the degradation of the QD surface in CdSe/CdS dot-in-rod structures through photoluminescence spectroscopy.[50] Specifically, they show that the pump fluence of the irradiation source can drastically affect the rate at which these structures are modified by oxidation. By increasing the thickness of the CdS rod that encases the CdSe QD, it was possible to suppress the rate at which the CdSe is oxidized. An interesting effect noted both by Wen and Rumbles was that there is a brief period of photoluminescence enhancement when the trap states on the QD surface are remediated by the physisorption of oxidative species.[51] The physisorption of these species calls into question the different mechanisms for O_2 adsorption to the QD surface, specifically raising the question of why some reports show a reversible transformation with oxygen and others show an irreversible reaction on the QD surface.

b. Physisorption and Chemisorption of Oxygen. Two different mechanisms of oxygen adsorption to the CdSe surface (Figure 3) have been shown in a study that makes use of a CdSe/ZnS core/shell system.[52] Physisorption of molecular oxygen is a process that can be reversed by purging the sample with an inert gas such as argon or nitrogen or by degassing the sample with vacuum.[48] Chemisorption involves a reaction on the QD surface that forms the aforementioned oxides which desorb from the surface and often result in the etching of the QD to smaller sizes. A similar study from Muller focuses on the PL quantum yield of CdSe/ZnS nanocrystals in different media, vacuum purged versus oxygenated.[53] This study supports the finding that rapid exposure to oxygen results in a reversible

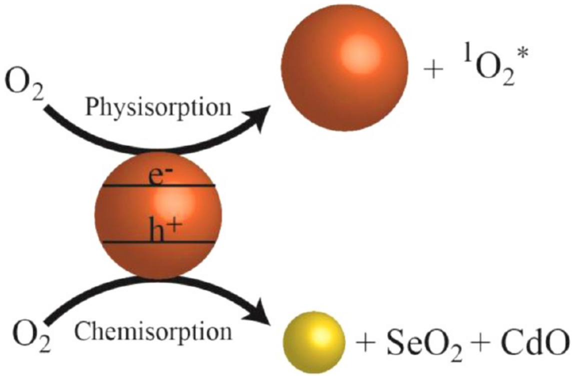

Figure 3. Two separate mechanisms for oxygen adsorption to II−IV semiconductors exist: (i) physisorption and (ii) chemisorption.

physisorption of oxygen to the QD surface. It was concluded in this study that while the QD surface is clearly prone to instabilities, surface degradation can be avoided or reversed at short time scales by purging a QD solution with an inert gas.

c. Reactions on the CdSe Surface. Recent studies from our group have provided additional insight into the oxidation of CdSe films in an ambient atmosphere. When the CdSe QDs were deposited on a semiconductor oxide (TiO_2) an irreversible transformation of CdSe was observed following the illumination with visible light.[54] It was evident from this study that the photooxidation of CdSe films was enhanced by the presence of a metal oxide that is capable of readily accepting electrons. The excitation of CdSe in the presence of a metal oxide results in electron injection into TiO_2 which is quickly scavenged by surrounding O_2. The accumulated holes thus induce the anodic corrosion of CdSe. This mechanism is also highlighted in the work of Ahmed et al., who further demonstrates that smaller QDs are oxidized at a faster rate than larger.[55] The larger surface/volume ratio in smaller particlse is expected to increase the rate of oxidation.

It was also shown that the photooxidation reaction is based on the length of time that QDs are stored in toluene suspension as well as the environment (combinations N_2/O_2 and light/dark) surrounding the suspension.[56] The storage of CdSe QDs in an ambient atmosphere and ambient lighting resulted in the oxidation of the QDs as evident from the changes in the absorption and emission spectra. The extent of degradation was found to be dependent on the number of post-synthesis washes (1 wash versus 4 wash). Oxides on the CdSe surface from the parent particle desorb, resulting in an etching process that decreases the overall QD size. X-ray absorption near edge structure (XANES) analysis, shown in Figure 4, confirmed the presence of SeO_2 on the QD surface following air oxidation. These results are also supported by XPS studies that confirm the formation/desorption of SeO_2.[57]

The oxidation of the nanocrystal surface was also shown to have implications on the excited state dynamics of CdSe QDs.[56] Reaction with oxygen introduces defect states on the QD surface and results in an increased probability of recombination for photogenerated carriers and a faster decay from the excited state. A comparison of excited state dynamics was made with similar size CdSe QDs (pristine). The study confirmed that the increase in recombination rate of oxidized QDs was not a result of the decrease in QD size that is associated with this etching process, but because of the oxidation of the QD surface and introduction of trap states.

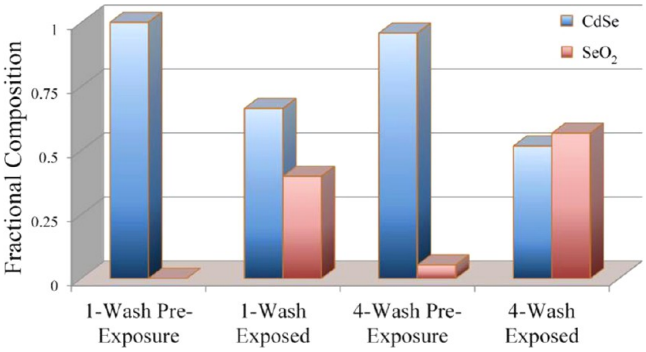

Figure 4. XANES results illustrating the dependence of the extent of total oxidation on the number of post-synthesis washes. Reprinted with permission from ref 56. Copyright 2012 American Chemical Society.

d. Thermodynamic Considerations for CdSe/PbSe. XPS studies have provided further insight into the oxidation products formed on the QD surface. The work of Klimov and Alivisatos groups suggest that a compound oxide ($CdSeO_3$ = -104.5 kcal/mol and $PbSeO_3$ = −352 kJ/mol or $PbSeO_4$ = −402 kJ/mol) are the thermodynamically favored products for the oxidation of CdSe and PbSe.[48] It should be noted that the Pb and Cd atoms on the QD surface are typically coordinated by the capping ligands leaving Se to be easily oxidized. Although the thermodynamically favorable products ($XSeO_3$ or $XSeO_4$ where X = Pb, Cd) exist on the surface the more likely mechanism is for the formation and desorption of SeO_2 as Se atoms are more accessible.[19,48] According to Wrighton, cadmium based chalcogenide species such as CdSe and CdTe have oxidation potentials of 0.29 and −0.14 (vs SCE), respectively. At potentials more positive than these values, the oxidation of these species is possible given that kinetic considerations are taken into account.[58]

e. The Role of Solvent in Mediating Photooxidation. A study from Sykora's group suggested that the solvent can also mediate the photooxidation of QDs.[59] If UV-light with energy on the order of 3−5 eV is used to excite the solvent molecules (e.g., hexane or toluene), it can subsequently participate in energy transfer processes with dissolved oxygen resulting in the formation of singlet oxygen. Singlet oxygen is a highly reactive species which is capable of oxidizing the QDs at the surface, a process that has also been demonstrated previously with CdTe nanocrystals suspended in H_2O.[60] On a similar note it has been suggested that CdSe has the capability to create singlet oxygen without the help of the solvent, which implies that CdSe accelerates its own photooxidation as it creates singlet oxygen near the QD surface.[61]

Santhosh and coworkers have found a way to decelerate oxidation by employing the use of ionic liquids as the coordinating/suspending solvent.[62] The ionic liquid (IL), 1-methyl-(11-undecanethiol)immidazolium bromide, was designed specifically to passivate and protect CdTe QDs while also keeping them suspended in the solvent. This solvent plays a dual role in passivating the QD surface and protecting it from molecular oxygen. One of the reasons that the QD surface is protected from O_2 is because of its low solubility in the IL (<0.2 mM) when compared to chloroform or toluene (9.8 mM).[61,63,64] This method appears to offer greater protection for the QD surface than those that employ the use of typical passivating ligands such as TOPO and TDPA.

FUNCTIONALIZATION OF QDS WITH ELECTRON DONATING AND ACCEPTING LIGANDS

The most commonly used approach to modulate the optical properties of a semiconductor is by variation of its size, as in the case of QDs, or its shape, as in the case with nanowires, nanosheets, and nanorods. An emerging method for controlling QD optical properties (such as the absorption profile and PL quantum yield) is through control of surface chemistry via exchange reactions that remove native ligands such as trioctylphosphine oxide (TOPO), trioctylphosphine (TOP), tetradecylphosphonic acid (TDPA), or hexadecylamine (HDA).[65] Many of these ligand exchange reactions often strip the nanoparticle of its ligands when refluxed in pyridine for an extended period of time.[66−69] Pyridine is only weakly bound to the QD surface and is easily replaced by the desired ligands upon introduction to the suspension.

Many recent studies have focused on the effect of these ligand exchange reactions on the charge separated state of the excited QD.[70−74] Deactivation from the QD excited state is dictated by the nonradiative, k_{nr}, and radiative, k_r, processes and which can be influenced directly through QD surface modification. For applications in QDSCs, it is important to understand the kinetics associated with the deactivation of the excited state to the ground state, as the rate with which the excited state decays strongly affects the probability of electron injection into TiO_2. To utilize this aspect, many chemists focus on ways to increase the average lifetime of the excited state through the binding of different chemical passivants to the QD surface.

Typical studies focus on the ability of certain organic ligands to either withdraw or donate electrons, the ability of which is usually attributed to the structure of the molecule (i.e., its functional groups, aromaticity and conjugation).[73,74] Other studies have focused on the use of bi-functional molecules to assist in the deposition of thin films of QDs either for use in electronic devices such as FETs or for use in photovoltaics.[21,40,41,72] The choice of molecule used in these studies is typically based on its ability to promote charge separation and transfer charge across semiconductor interface.

a. Thiols versus Amines. Ligand exchange reactions have been used to modulate the optical properties, link QDs to a substrate or promote the stabilization of QDs in a polar solvent such as water.[75−78] What many studies do not take into account are the effects that the binding of these molecules have on QD optical properties and how they vary from one semiconductor to the next. For instance, several reports show the enhancement of band edge PL upon binding of a thiol molecule to the CdTe or CdS surface whereas others report a decrease in PL intensity of CdSe QDs with other complexing thiols.[36,38,77,78] Also, several studies have shown PL enhancement upon the binding of a ligand with an amine group to the CdSe surface.[72,79,80]

The binding of thiol ligands on the surface strongly influences the electron and hole wavefunctions.[77,81] In addition, thiol molecules are easily oxidized and thus quench band edge PL in CdSe QDs by extracting holes from the surface.[38] The effect of this process is different in CdTe particles because of the relative position of their valence bands, illustrated in Figure 5. Because the valence band edge for CdTe is 1.0 V and CdSe is 1.7 V (versus SHE), we expect molecules with a HOMO located in between these two values is likely to extract holes from CdSe but not CdTe.[38] The difference in valence band potentials for bulk CdTe and CdSe results in remarkably different external quantum efficiencies in liquid junction devices. The polysulfide redox couple is not capable of scavenging holes from the CdTe surface, resulting in anodic corrosion of the QD and the exchange of Te for sulfide ions in the electrolyte.[82]

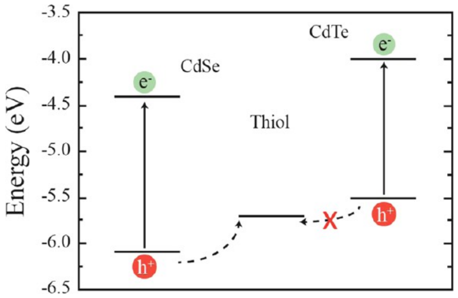

Figure 5. Electrochemical potential for the HOMO of a thiol-functionalized molecule plotted alongside the bulk bandgap of CdSe and CdTe. Illustration adapted with permission from ref 38. Copyright 2004 American Chemical Society.

Amine-functionalized molecules are typically seen as capable of enhancing the photoluminescence of QDs however there are some conflicting reports in the literature.[70,71,83] This argument has been realized and explained as a duel effect of both the structure of the specific ligand as well as the ratio of ligands to QDs.[36,72] Also, it has been shown that primary amines are ideal ligands for QDs because their HOMOs are typically located below the valence band of most semiconductors which means that there is no hole trapping occurring from the binding of the ligand.[37] The same study also points out that primary amines offer better control over binding than secondary and tertiary amines. The single alkyl chain of the primary amine reduces steric hindrance on the QD surface and thus allows more ligands to bind. A recent study from our group demonstrates the effect of varying degrees of passivation with *β*-alanine (*β*-Ala).[72] Within a certain concentration range (region I, Figure 6), the PL quantum yield increases while the emission lifetime increases. As the concentration shifts to region II, a quenching process dominates and results in a decreased quantum yield and a decrease in the rate of radiative recombination.

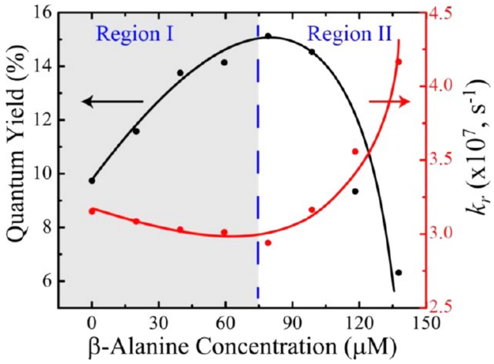

Figure 6. Effect of various concentrations of *β*-Ala on the photophysical properties of CdSe QDs. Reprinted with permission from ref 72. Copyright 2013 American Chemical Society.

b. Aromatic Ligands. The interest in aromatic molecules as ligands lies with the pi-conjugation structure. This conjugated structure offers the possibility to extract and stabilize photogenerated charges from the QD surface, shown in Figure 7. Several studies in the past have shown the ability of

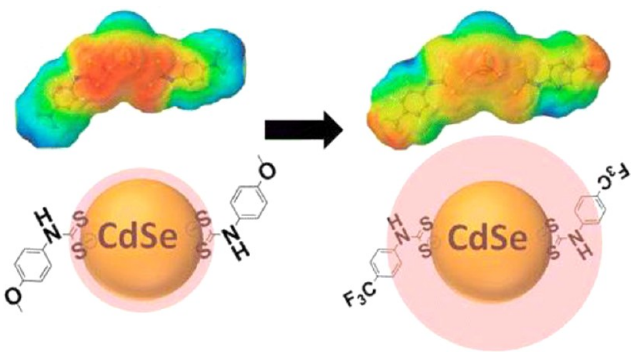

Figure 7. Illustration of hole wavefunction delocalizing over the structure of an aromatic ligand. Reprinted with permission from ref 71. Copyright 2012 American Chemical Society.

these aromatic molecules to bind to the QD surface and alter the lifetime of the excited state and the PL quantum yield,[35,70,84,85] whereas another has noted an enhanced stability against oxidation because of hole transfer and stabilization on the aromatic ligand.[74] A report from Dibbell et al. emphasizes the ability of these molecules to transport charge from the QD surface to a metal oxide substrate.[86] This particular study shows that these molecules not only have an added benefit of being able to accept charge but that the conjugated structure can also transport that charge to an accepting metal-oxide substrate.

A recent study from Weiss and coworkers has shown that a series of para-substituted derivatives of aniline have the ability to extract and stabilize holes.[87] The ability of the para-substituent to activate or deactivate the aromatic ring and influence hole capture from the QD is shown in another work by Weiss using a dithiocarbamate molecule.[71] The hole transfer and its stabilization on the aromatic ligand demonstrated in this study could play an important role in the development of QDSCs, as hole transfer is thought to be one of the factors limiting the device efficiencies.[88,89]

c. Polymer Encapsulation. QD-polymer hybrids have become a popular research area that bridge materials chemistry and polymer chemistry.[90−95] Many recent studies show the effectiveness of polymer matrices in completely encapsulating QDs and forming an interconnected QD network.[96] The functionality of the polymer serves to bind the QD in the matrix while also proving to be useful in passivating the QD surface and aiding in the separation of photogenerated charge.[97,98] This has a significant application in both biology and optoelectronics as the QDs are thought to be more stable when passivated by a large coordinating polymer instead of a small organic ligand. These polymer matrices are also being researched for use in solar cell applications wherein the polymer enhances the hole-extraction and transport properties of the cell.

Fogg and coworkers have shown PL quenching with increased passivation of the QD surface by a methylcyclotetradodecene polymer matrix[99] while a report from McPherson and coworkers have shown that the enhancement of band edge PL intensity and the reduction in emission from mid-gap states following encapsulation of QDs in copoly(4-ethylphenol/4-hydroxythiophenol). The appearance of lower energy emission is normally suggestive of new recombination sites at the QD surface.[100] A study from Moffitt and coworkers shows the enhancement of band edge PL in a polymer that also contains Cd^{2+} cations. This treatment appears to play some role in slowing nonradiative recombination while also better protecting CdS QDs from oxidation observed over the course of a 60 day storage in toluene.[101] Similarly, Wang and coworkers show the importance of polymer chain length in modulating the band edge and surface luminescent states as well as the PL lifetime.[102] The ability of poly(dimethyl siloxane) (PDMS), poly(vinyl pyrrolidone) (PVP) and poly(butadiene) in passivating the CdSe surface and modulating the properties of the emissive states has also been realized.[103] These and many other studies in the literature point out the ability of polymers to encase a QD and not only affect the optical properties but to stabilize these particles in new solvents and protect them from oxidation.[98,104−113]

d. QD-Ligand Binding: A Molecular Orbital Diagram. There are several studies that report the importance of redox potentials (conduction/valence band as well as HOMO/LUMO positions) of the QD and the binding moiety in determining the effect that the binding event has on the QD optical properties.[114] The location of semiconductor valence band in relation to ligand HOMO positions play an important role in charge transfer reactions that may occur at this interface. As mentioned previously, Wuister explains that one thiol molecule may not have the same effect on CdSe as it does on CdTe depending on the oxidation potential of its HOMO.[38] Other studies have shown the role that the positions of the ligand HOMO/LUMO with respect to the CdSe conduction and valence bands play in the electronic structure on the QD surface.[70,115,116]

This molecular orbital picture is deconvoluted by Ellis and coworkers, Figure 8, and demonstrates how a molecule bound to the QD surface can affect the electronic structure of the atoms located on the surface.[117] This illustration is especially helpful when trying to predict how a ligand will affect the behavior of n-type and p-type particles. A reducing ligand has the ability to donate electron density into a p-type particle but not to an n-type particle while an oxidizing ligand has the ability to pull electron density out of both. This is of course a generalization; however the degree to which each of these is true of course depends on the locations of the semiconductor Fermi level as well as the respective positions of the ligand bonding orbitals and the QD midgap states. These MO diagrams present an easy way that we can tailor QD surface chemistry through the use of adsorbates with the proper HOMO/LUMO levels.

e. Ligands with Noncoordinating Substituents. An interesting finding of some recent studies is that the unbound substituents on a ligand can affect that molecule's influence on QD surface chemistry. For instance, several studies show the dependence of the PL intensity on the pH of the solution.[77,118−120] This pH effect can be witnessed as a direct result of carboxylic groups and other pH sensitive functionalities on the ligand that are unbound to the QD surface. The change in pH causes a change in the ability of a molecule to donate or accept electron density from the QD surface, thus modulating the PL quantum yield.

Liu et al. have shown that the effect of a metalated ligand on the PL intensity of CdSe QDs.[121] This study shows the effect that nonbinding substituents located on the ligand can have on the QD surface chemistry. Liu and coworkers first witness a slight increase in band edge PL intensity from the exchange of native ligands with dihydrolipoic acid (DHLA). Subsequently, they treat these QDs with a combination of NaOH and Zn^{2+} and see doubling in the band edge PL from that of the

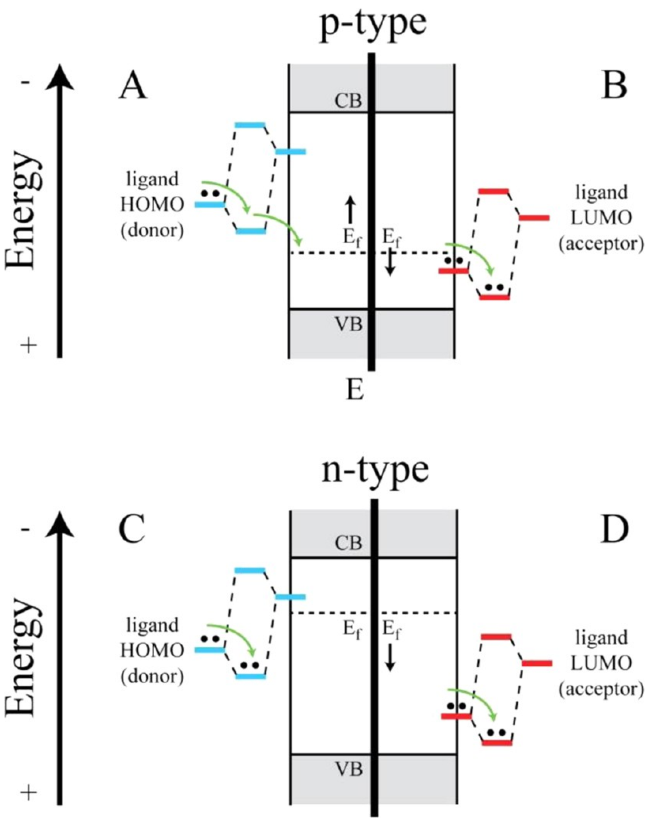

Figure 8. Molecular orbital diagram illustrating (A) an electron-donating and (B) an electron-accepting ligand bound to a p-type QD and (C) an electron-donating and (D) an electron-accepting ligand bound to an n-type QD. This figure was adapted from reference 117. (Copyright American Chemical Society).

untreated CdSe, shown in Figure 9. By using metalated and unmetalated DHLA, this study illustrates the importance of these nonbinding substituents on the optical properties of CdSe QDs.

f. Ligand Binding Mechanisms. Several studies use Langmuir adsorption isotherms or the Stern−Volmer approximation to model ligand binding to a QD surface. In many of these examples, ligand binding to the QD surface is a reversible reaction which means that it is concentration dependent.[36] Munro and coworkers have generated Langmuir binding isotherms for CdSe nanocrystals synthesized via several different methods. The main finding of this study was that the number of ligand binding events could be correlated to the synthetic approach. Different synthetic methods result in a varied amount of vacant Cd sites on the QD surface. This results in a varying degree of ligands bound to the QD surface and thus a variation in the photophysical properties. Meanwhile, several reports have also used a Langmuir adsorption isotherm to model the binding affinity of TOPO for the CdSe surface determining a binding coefficient of 1 × 10^2 M^{-1}.[67,122,123] Similar binding coefficients have been determined for several aldehydes and ketones as well as C60 and C70 by Ellis and coworkers.[114,124]

Figure 9. Qualitative photoluminescence of QDs passivated with DHLA (left) and DHLA following a treatment of NaOH and $Zn(NO_3)_2$ (right). Reprinted with permission from ref 121. Copyright 2010 American Chemical Society.

A work from Breus et al. reveals the nature of the quenching mechanism in thiol capped CdSe/ZnS QDs.[78] Using Stern−Volmer kinetics, it was possible to establish nonlinear quenching mechanisms for bi-functional molecules (thiol and carboxylic groups). Although the thiol functional group is responsible for the majority of the quenching, they show that the carboxylic group also contributes to quenching based on the nonlinearity of the Stern−Volmer plot. It was also determined that the quenching of QD emission is a static process from the PL lifetime data. The replacement of weakly bound ligands with a strongly bound thiol-functionalized molecule is an irreversible process and the emission quenching witnessed by these adsorbates is only due to thiol molecules bound to the surface of the QD and not a collisional quenching process.

SURFACE CHEMISTRY AND CHARGE/ENERGY TRANSFER

In the previous section, we discussed the effect that molecular adsorbates have on the electron structure of the QD surface. This section looks at the effect that organic ligand binding has on interfacial electron and hole transfer for QDSC applications. Of particular interest are bi-functional molecules that are used to chemically link QDs to metal oxides such as TiO_2. This linkage has been shown to increase the loading of the substrate with the QD sensitizer when compared to a linkerless approach.[2,125−129] The binding of these molecules to QD surface sites has still been shown to affect the rate of electron transfer between QDs and the metal oxide substrate.[130] Several groups have attempted to define which functional groups have such an effect and if the proper manipulation of surface chemistry can be used to increase the efficiency of electron injection in QDSCs.[21,72,131−135]

a. Linker Molecules. Watson and coworkers have shown the importance of molecular linkers in mediating charge transfer processes between QDs and metal oxides. One report stresses the influence of phenylene-based molecules in increasing the rate of charge transfer between CdS QDs and TiO_2 substrates.[86] They found that the conjugated pi-bonds available to molecules such as 4-mercaptobenzoic acid allow for a more efficient rate of charge transfer. The electron wavefunction extends from the QD surface to access these pi-bonds and delocalize onto the ligand structure. Increasing the effective volume of the electronic wavefunction, results in an increased spatial overlap between the electron-donating species (QD) and the electron-accepting species (TiO_2). This increase in electronic coupling of the two states results in an increase in the rate of electron transfer.[132,133]

Other reports demonstrate the affect that the binding functional groups have on electron transfer rates. A recent study from our group focused on the use of *β*-alanine (*β*-Ala) as a linker molecule to replace the commonly used 3-MPA or mercaptoacetic acid (MAA).[72] Molecules with thiol functional groups have been shown to create charge carrier trapping states on the QD surface, which are thought to hinder the rate of electron injection into TiO_2 from QDs.[21] By linking QDs to TiO_2 with amine-functionalized molecules instead of thiols, fewer traps are created on the QD surface, which causes an increase in the electron transfer rate, shown in Figure 10A. Rates of electron transfer are calculated from example kinetic decays shown in Figure 10B. For a detailed account on the calculation of electron transfer rates see reference 72.

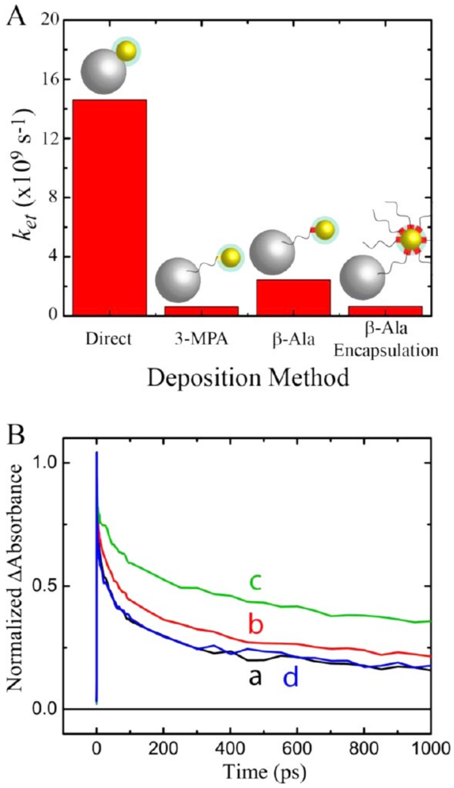

Figure 10. (A) Summary of k_{et} for 4 deposition methods. Comparison of 3-MPA to *β*-Ala shows the effect of thiol/amine function group on k_{et}. (B) Representative kinetic traces from transient absorption experiments. Reprinted with permission from ref 72. Copyright 2013 American Chemical Society.

A report from Wise and coworkers shows the effect that the binding moiety has on the electron accepting state.[134] Through the use of structurally similar linkers (phenylene bridges with a thiol functional group for binding to PbS) they show that the functional group that binds to TiO_2 ($-SiX_3$, $-COOH$, $-PO_3H_2$, and $-SO_3Na$) can make an impact on the electron transfer rate. These functional groups have the ability to influence the density of accepting states on the TiO_2 surface, which shows the importance of maintaining favorable surface chemistry both on the electron-donating and -accepting sides of the QD-linker-MO systems.[134]

b. Ligands and Energy Transfer. CdSe QDs have been shown to transfer energy to the adjacent dye molecules via Forster resonance energy transfer (FRET) or Dexter energy transfer (DET) mechanisms.[136−142] The majority of the published work involves the demonstration of distance dependent energy transfer and the use of QD antennas for photoelectrochemical solar cells.[143] In a recent study, our group has made use of this process to extend the photoresponse of quantum dot solar cells (QDSC) into the near infrared. The strategy of linking QDs to mesoscopic TiO_2 film with a bifunctional linker capable of absorbing red and near infrared light is demonstrated in Figure 11.[135] In this study, CdSe was linked to TiO_2 using a squaraine dye (SQSH) functionalized with both carboxylic and thiol groups. The strategy of using a chromophore as a linker facilitates a two-step mechanism of energy transfer from CdSe to the SQSH followed by electron transfer from SQSH to TiO_2. This CdSe-SQSH-TiO_2 architecture shows enhanced power conversion over the SQSH-TiO_2 and CdSe-TiO_2 controls as the energy transfer and electron transfer processes are coupled during the QDSC operation.

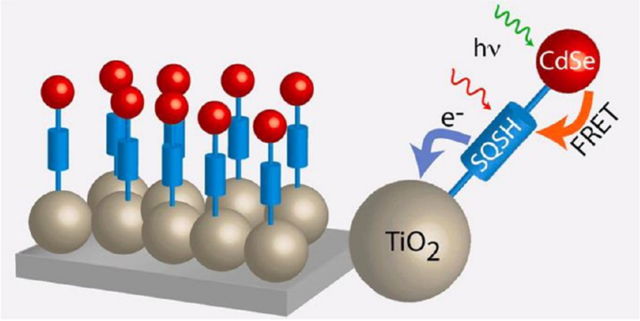

Figure 11. Energy transfer from CdSe to SQSH linker/dye synchronized with electron transfer between SQSH and TiO_2. Reprinted with permission from ref 135. Copyright 2012 American Chemical Society.

c. Surface Treatments and Biosensing. Energy transfer between QDs and surface-bound ligands is also utilized in the field of biosensing. These QD-biomolecule systems make use of FRET, chemiluminescence resonance energy transfer (CRET), and electron transfer to provide means of detecting pathogens, matching tissue, and analyzing of genetic disorders.[144,145] One study from Willner and coworkers demonstrates the reaction of hemin-G-quadruplex/thrombin and hemin-G-quadruplex/ATP complexes with bound conjugates of CdSe/ZnS/anti-thrombin and CdSe/ZnS/anti-ATP, respectively.[146] The reaction of these DNAzymes with their aptamers results in a CRET process with the bound QDs that is detectable even at low concentrations of the analytes. The CRET process was also shown to be useful in detecting multiple DNA targets in the same solution by utilizing QDs of various sizes each functionalized by their respective hairpin nucleotides.[147] Each hairpin nucleotide is opened by the DNA target, allowing the target to react with the hemin-G-quadruplex and engage in CRET with the bound CdSe/ZnS QDs.

d. ZnS Treatment. The synthesis of CdSe/ZnS core/shell particles was first reported by Bawendi in 1997.[22] This treatment is favorable for QDs such as CdSe and $CuInS_2$ because of minimal lattice mismatch with ZnS as well as the type I bandgap, illustrated in Figure 12, which confines photogenerated charges to the core of CdSe. The adsorption of a ZnS shell results in a decreased rate of nonradiative recombination from the excited state due to the passivation of under-coordinated surface atoms.[22,45,148−153] This property has enabled the use of the ZnS layer in QDSCs resulting in an enhanced performance from devices treated with this layer.

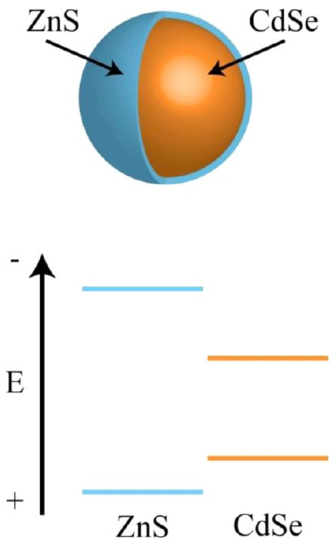

Figure 12. Type I band alignment of CdSe/ZnS core−shell nanoparticles.

Vinayakan et al. have demonstrated that the optimal ZnS shell thickness for 4.2 nm QDs is 2 monolayers (0.65 nm) for use in bioimaging applications; an area of research where the quenching effects that are associated with charge transfer are undesirable.[154] A two-monolayer-thick coating suppresses electron transfer between phenothiazine and the CdSe core while a thicker coating does not further increase the PL quantum yield. This study illustrates the importance of optimizing the ZnS layer based on the application. A thick layer is desired for bioimaging but not for QDSCs because it would limit the charge transfer processes necessary for QDSC function.[155] A study from Raymo and coworkers demonstrates the suppression of electron transfer out of the CdSe core to methyl viologen by increasing the ZnS layer thickness to 5.1 nm.[156] Although the ZnS layer has the benefit of reducing recombination (thus increasing the lifetime of the charge separated state) on the surface of CdSe nanoparticles, it comes with the consequence of limiting electron transfer by increasing the distance between donor and acceptor states.

e. Exchange of Cd^{2+} with Cu^{2+}. Recent studies have reported the exchange of surface Cd^{2+} cations with Cu^{2+}. Toshisharu and coworkers demonstrate that this exchange is generally an undesirable process resulting in the reduction in photovoltaic efficiency.[157] The diffusion of Cu species into the QD structure is generally difficult to avoid given the relatively low protection that the QD surface has from small ionic species. Alivisatos and coworkers have demonstrated that this replacement reaction can be manipulated into giving well-structured Cu_2X (X = S or Se) particles.[158] By simply adding a methanolic solution of Cu to a solution of CdSe nanorods, they report that Cd is fully replaced and that the nanorod structure is fully retained. This represents a useful method for the well-controlled synthesis of Cu_2S nanoparticles.

f. Multiple Exciton Generation and Surface Bound Species. Efficient manipulation of multiple exciton generation is a highly sought-after understanding for materials used in photovoltaic applications.[159,160] In theory, this phenomenon could reduce the energy loss by thermalization of carriers to the band-edge states of a semiconductor. In recent years, many studies have focused on the ability to generate multiple excitons with one photon in order to eliminate this loss of energy in photovoltaic devices. Lian and coworkers have published several papers tracking the effect of surface bound species on generating and harvesting multiple excitons from QD architectures.[161−164]

A number of reports focus on the ability of surface adsorbed molecules to extract electrons from multiexcitons before recombination.[161,162] One study demonstrates that it is possible to extract electrons on a time scale (12 ps) that is faster than multiexciton annihilation as long as the number of acceptors adsorbed to the surface is above a certain threshold (in this case 4.1 rhodamine B molecules).[161] Other reports utilize methylene blue to find that electrons can be extracted in 2 ps (from PbS and CdSe) and that up to 3 electrons can be removed from one CdSe QD.[162,163] Also observed is that nanoparticle shape can play a role in the number of excitons extracted by adsorbed methyl viologen (MV^{2+}) molecules. Quantum rods have been shown to be able to donate more than 21 electrons to adsorbed methyl viologen which far exceeds the limit in QDs. Shape effects are a direct result of the larger nanoparticle volume allowing for a longer multiexciton lifetime.[164]

g. Surface Chemistry and Photocatalysis. To provide insight into the function of CdSe QDs for photocatalytic applications, charge transfer reactions between CdSe and MV^{2+} have previously been performed in reverse micelle configuration.[165,166] The reverse micelle configuration allows the study of charge transfer reactions with quantum confined semiconductor nanoparticles (of well-defined size) while eliminating the insulating ligand shell that is native to the QD surface when particles are grown by the typical hot injection method. Removal of this ligand shell allows the experimental determination of charge transfer rates in a well-controlled environment that is free from hindrance by these long alkyl chain organic ligands.

The first effort of this study illustrates the use of TiO_2 to increase both the quantum yield of MV^{2+} reduction from 0.1 to 0.2. This system also results in an increased rate of electron transfer in CdSe-TiO_2-MV^{2+} (2.74×10^{11} s^{-1}) from the non-TiO_2 mediated transfer in CdSe-MV^{2+}(2.25×10^{10} s^{-1}). This study illustrates that the close proximity of MV^{2+} to the CdSe, Figure 13, surface upon reduction allows for fast back electron

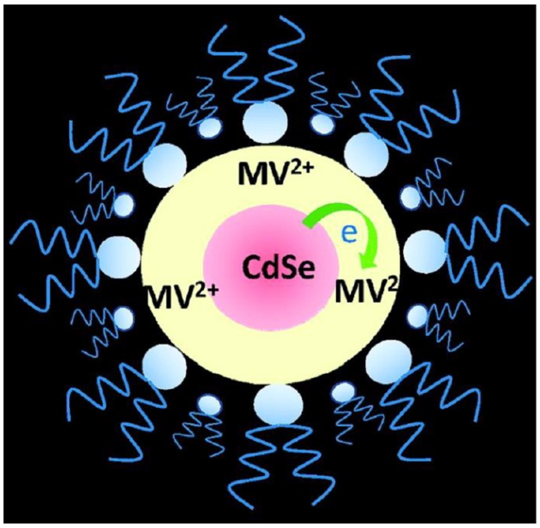

Figure 13. Electron transfer from CdSe nanoparticles to MV^{2+} molecules. Reprinted with permission from ref 165. Copyright 2009 American Chemical Society.

transfer to CdSe. The use of TiO_2 in mediating the charge transfer process allows for faster charge separation with a longer lived reduction product.[165]

A similar study focuses on the electrodic property of Pt nanoparticles in similar confined media. Micelles containing Pt nanoparticles, CdSe QDs and MV^{2+} were studied via transient absorption spectroscopy. The rate of electron transfer from the QDs was 10 times faster in the presence of both MV^{2+} and the Pt nanoparticles when compared to electron transfer to only MV^{2+}. This shows that Pt nanoparticles have the ability to collect and store charge in these systems and also highlights the usefulness of experiments done in the micellar configuration.

h. Identification of the S^{2-} Radical. One important mechanism to understand, specifically for liquid junction QDSCs, is the hole transfer process from the CdSe surface to the electrolyte species. A previous study from our group follows this hole transfer process by monitoring the generation of the sulfide radical, Figure 14, when transferring holes from CdSe QDs to S^{2-}/S_n^{2-} electrolyte.[167] This study reports a hole transfer rate 8.5×10^7 s^{-1} and demonstrates that slow hole transfer from CdSe to S^{2-}/S_n^{2-} is likely a major bottleneck to device performance. Using nanosecond flash photolysis and pulse radiolysis experiments, we generated the sulfide radical ($S^{-\bullet}$) signal. This same signal ($S^{-\bullet}$ or $Se^{-\bullet}$) has been seen in hole trapping events that occur on the QD surface. This and other previous work open the door for further studies on oxidation products of hole transfer out of II−VI semiconductors.[168−170]

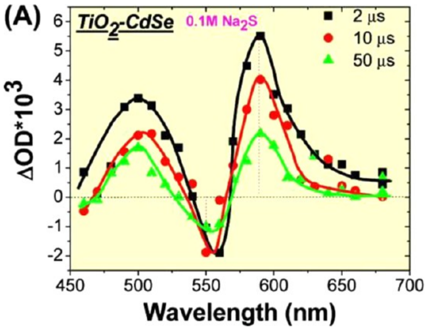

Figure 14. Sulfide radical spectrum generated by nanosecond flash photolysis. Reprinted from ref 167. Copyright 2011 American Chemical Society.

i. Self-Assembly and Surface Chemistry. The assembly of well-ordered highly-conductive layers from colloidal nanoparticles is an important step in the fabrication of nanoparticle-based electronic devices such as LEDs, FETS, and other nanoelectronic devices.[171] Self-assembly of QD monolayers is often chemically induced using bifunctional molecules such as SnS_4^{2-} or through the use of different techniques such as Langmuir−Blodgett (LB).[40,41,172] The focus of many of these studies is to find linkers that will assemble well-ordered layers of QDs into highly conductive films for use in electronic devices. Solution processing of films is an important strategy for the fabrication of devices because it eliminates the need for expensive lithographic techniques that would otherwise need to be used in order to make films in such a precise manner.[173,174]

j. Film Formation with Organic Capping Agents. Formation of self-assembled monolayers of organic-capped QDs has been studied extensively in the past. One of the most common ways to form a monolayer of these particles is through the use of a Langmuir−Blodgett (LB) technique, which forms films at the liquid−liquid or water air interface. LeBlanc and coworkers demonstrate the formation of these films at the water−air interface from QDs capped with TOPO and 1-octadecanethiol.[172] The properties of the films were found to be highly dependent on the capping agent used. QDs capped with TOPO formed close-packed monolayers that are limited to the length of the TOPO ligand, whereas those capped with ODT underwent alkyl chain interdigitation thus having a smaller interparticle distance. This change in interparticle radius has been shown to be a major factor in determining the conductivity of these QD films.[175]

A report from Gigli and coworkers shows the importance of the passivating ligands for the optical properties of QDs and in the packing of self-assembled films.[176] By replacing the native ligand, oleic acid in this case, with arenethiolate anions they note that the film packing formation changes from hexagonal to cubic, Figure 15. The arenethiol molecule is also responsible for participating in charge transfer reactions on the QD surface, which are shown in the red-shifting of the QD absorption spectrum. This shows the delocalization of holes out onto the

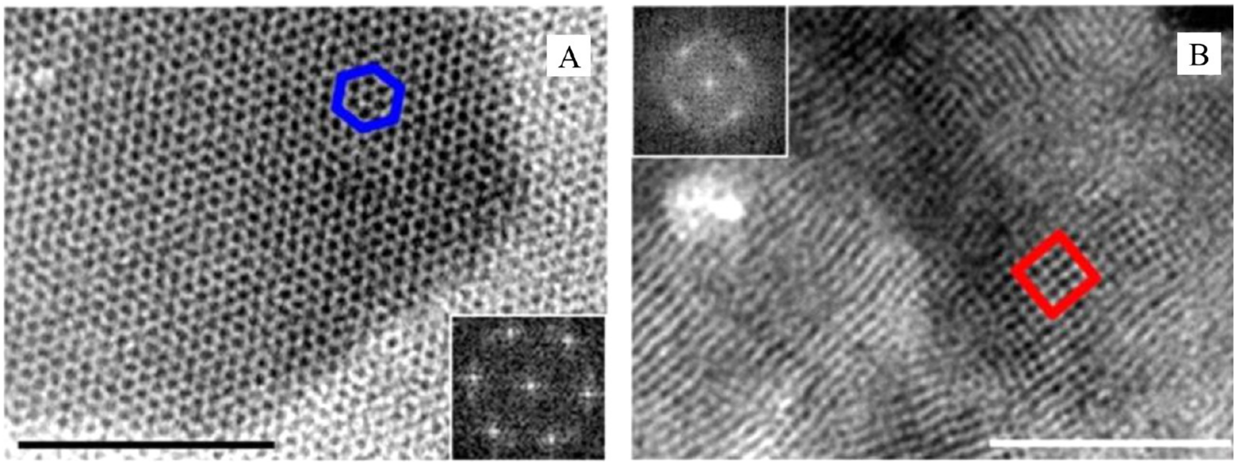

Figure 15. Transmission electron micrographs of (a) oleic-acid-capped and (b) arenethiolate-capped PbS QDs in a close packed film. Packing formation is either hexagonal or cubic depending on the ligands on the QD surface. Reprinted with permission from ref 176. Copyright 2013 American Chemical Society.

ligand structure implying that films of PbS/arenethiolate are likely to be more conductive than the PbS/oleic acid films.

A similar observation on film conductivity was reported by Rogach and coworkers using films of thioglycolic-acid-capped CdSe and CdTe QDs.[177] Using a layer-by-layer deposition approach, they show quenching of band-edge PL intensity for CdTe nanocrystals in alternating films of CdSe and CdTe. This quenching effect is attributed to charge tunneling between nanocrystals, implying that these films are more conductive than films of just CdSe or CdTe.

Bawendi and coworkers report increased photoconductivity for films of QDs treated with butylamine, aniline, 1,6-diaminohexane, 1,4-phenylenediamine, tri-*n*-butylphosphine and NaOH. These results were highly independent of the ability of the molecule to cross-link QDs or the ability of aromatic molecules to increase the conductivity of the film. The increase in photocurrent was attributed to the increased passivation of the QD surface by the smaller amine molecules as well as the decreased interparticle separation induced by the ligand exchange reaction.[178]

k. Film Formation with Inorganic Linkers. Several factors play into the formation of ordered QD films. Factors such as substrate morphology, solvent wetting, and solvent drying rates all factor into film uniformity. Talapin and coworkers demonstrate the conductivity of thin films of PbTe QDs capped with organic ligands at a low value of 1×10^{-13} S/cm^{-1}. Low conductivity is thought to be caused by the large interparticle distances that are a common result of the organic capping ligands. These films were then treated with hydrazine, removing the oleic acid capping agent, allowing for a decrease in interparticle separation (demonstrated with TEM) and results in a ten-fold increase in conductivity in films used as FETs. These hydrazine treatments give rise to a new class of passivants that replace organics while also chemically linking QDs with a conductive bridge.[179]

Recent reports from Talapin and coworkers have demonstrated the replacement of native ligands with metal chalcogenide capping agents such as $Sn_2S_6^{4-}$, $Sn_2Se_6^{4-}$, $In_2Se_4^{2-}$, and $HgSe_2^{2-}$. These ligands are useful for solubilizing QDs in highly polar solvents such as water, ethanolamine, formamide, and DMSO while retaining photoluminescence properties to an extent.[40] The benefit presented by these linkers is the increased conductivity of the films when compared to organic molecules. One report from Talapin and coworkers shows an electrical conductivity of 2.7 S cm^{-1} for a film cast from PbSe colloids passivated by K_4SnTe_4 that were deposited from suspension in formamide.[41] Another report from the same research group finds electron mobilities for $In_2Se_4^{2-}$- and S^{2-}-capped QDs that are up to an order of magnitude higher than films formed out of organic passivated QDs.[180,181]

■ LIGHT HARVESTING WITH QD SURFACE MANIPULATION

In this last section, we discuss the application of these QD surface manipulations in QDSCs, illustrated in Figure 16. The ability of the aforementioned organic and inorganic passivants to enhance photovoltaic performance has been shown on many accounts. Basic studies of the surface chemistry are important for understanding the reactions that affect the optical properties and excited state dynamics of QDs that are bound to oxide surfaces such as TiO_2. These basic studies are complementary to the new advances made in the fabrication of QDSCs and better illustrate the mechanisms behind performance enhancement of these photovoltaic devices. In this section, we focus on cases where QD surface chemistry has been manipulated in order to enhance the performance of these devices.

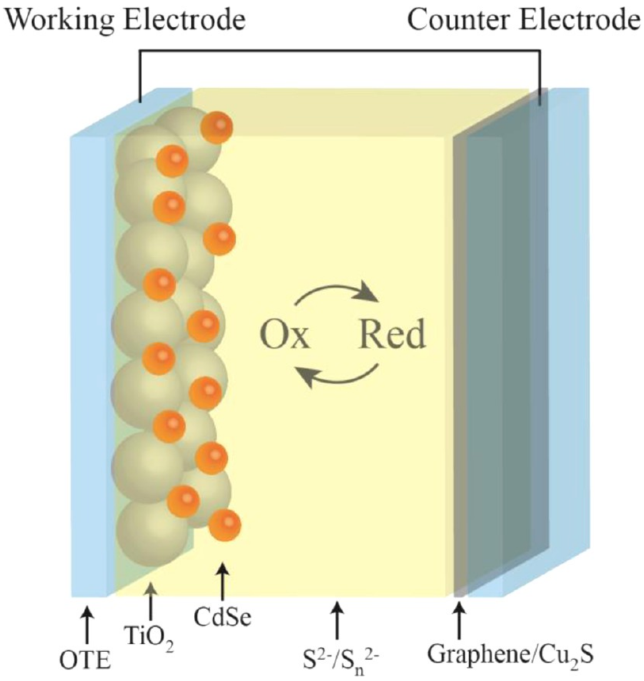

Figure 16. Schematic of a typical liquid junction quantum-dot-sensitized solar cell.

a. ZnS Layer. One of the most common manipulations of surface chemistry is the use of ZnS to passivate the QD surface in QDSCs fabricated via the successive ionic layer adsorption and reaction (SILAR) method. Briefly, the SILAR method of QDSC fabrication allows for the in situ growth of semiconductor sensitizer directly on the TiO_2 substrate by alternating the immersion of the electrode in cation and anion precursors of the sensitizer.[182−184] This method has since been applied to the same ZnS layer that is commonly used to create core−shell structures of QDs, allowing for the addition of ZnS to the surface of the QDs that are deposited onto TiO_2. This results in a decrease in the rate of recombination for QDs and an increase in the photovoltaic enhancement.[185] This effect has been witnessed for CdSe, CdSeS, CdS, $CuInS_2$, and PbS QDSCs.[44,46,186−190]

Sambur et al. have demonstrated the effect of ZnS on the photostability of CdSe core deposited on a single-crystalline TiO_2.[128] Their report (Figure 17) shows that QDs capped with ZnS display higher photocurrent at 20 h of illumination time than CdSe core QDs show after 2.5 h. This increased stability in the I^-/I_3^- shows how the ZnS shell protects the CdSe core from oxidation by the electrolyte, which is a property that should extend to other oxygenated environments. As shown in Figure 10, the linker molecule also influences the rate constant of the charge injection process.

b. Organic Treatments and Linker Molecules. Because of the ability of linker molecules to effectively load the TiO_2 substrate with QDs, this deposition approach has been applied for use in QDSCs. These QD-linker-MO systems have been shown to have increased photon conversion efficiencies when compared to those where a linker is not used. The enhancement in this case is usually based on number of QDs loaded onto the substrate.[191,192] One result from Bisquert's

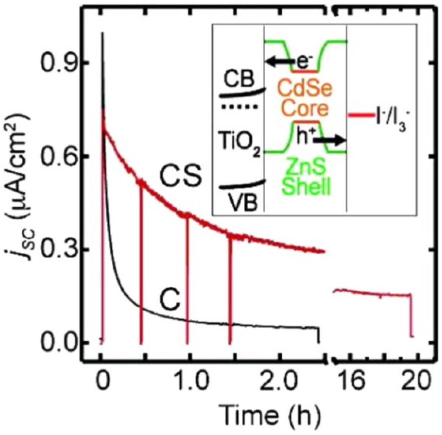

Figure 17. Increased photocurrent stability of CdSe QDs in I^-/I^{3-} passivated by a layer of ZnS. Reprinted with permission from ref 128. Copyright 2010 American Chemical Society.

group shows that the incident photon conversion efficiency (IPCE) can be increased by use of the proper linking molecule between CdSe and TiO_2. In particular this study shows the distance dependence of the IPCE performance as well as the increase in performance with the use of cysteine compared to 3-MPA.[193] Cysteine has an amino substituent that 3-MPA does not. The extra amino group makes the molecule much more electron rich and much more likely to extract holes. This hole-extraction process is likely the reason why cysteine is a much more efficient linker when compared to 3-MPA and MAA.[193]

c. Quantum Dot-Polymer Hybrid Solar Cells. Recent efforts have been made toward the inclusion of a hole-conducting polymer layer in QD photovoltaic devices. These polymer layers can be used in place of the liquid electrolyte; resulting in all solid-state devices that avoid the problems associated with a liquid redox couple. An example of a hole conducting polymer that has been used in hybrid devices is MEH-PPV (poly(2-methoxy,5-(2′-ethyl)-hexyloxy-*p*-phenylenevinylene)).[194] The use of this polymer in these devices proves the concept of hybrid solar cells but also reveals that the TOPO layer, which is innate to the QD surface, hinders the transfer of holes to the polymer.

Another polymer that is commonly used in hybrid devices is P3HT (poly(3-hexylthiphene)).[195−199] Several reports have seen power conversion efficiencies above 1% with the by employing P3HT as a hole transport medium.[200,201] One report from Bawendi and coworkers demonstrates the attachment of CdS nanoparticles to P3HT nanowires. This architecture results in hybrid solar cells that perform at an efficiency of 4.1%.[201]

One interesting study from Seo and coworkers shows the enhancement of photovoltaic performance in PbS/P3HT solar cells after a post-fabrication treatment with acetic acid.[202] The mechanism behind this enhancement is thought to be a ligand exchange reaction between acetic acid and oleic acid that is on the surface of the PbS colloids. The exchange of oleic acid for the shorter acetic acid ligands would likely decrease the distance separating PbS and P3HT. The closer proximity of the two species increases charge transfer at this interface, resulting in higher performing devices.

Another polymer that is commonly used in these inorganic−organic hybrid devices is PEDOT:PSS (poly(3,4-ethlyenedioxythiophene):poly(styrenesulfonate)).[203] Used in conjunction with PbSe, these devices have performed as high as 4.6%.[204] Armstrong and coworkers demonstrate the exchange of native ligands on the CdSe surface with 3,4-propylenedioxythiophene.[205] These ligands were then cross-linked with the PEDOT polymer via electropolymerization. These films show higher conductivity when compared with films of PEDOT polymer and also demonstrate a way to chemically link nanoparticles to hole-transport polymers and increase conductivity of devices made in this way.

■ OUTLOOK

Since the initial realization of size quantization effects, semiconductor quantum dots have made their impact on a variety of disciplines. Despite the emergence of several different nanostructures (e.g., nanowires, nanorods, nanoribbons, tripods, nanoforest, etc.), the 0D semiconductor nanocrystals continue to intrigue the researchers with unusual properties. Whether used as a biological probe or a light-harvesting antenna, semiconductor QDs continue to dominate nanoscience research. The ability to modify the QD surface with a desired molecule or capping layer has opened up a new dimension in achieving tailored functionalities.

Use of semiconductor QDs as a building block in designing inorganic−organic hybrid assembly is expected to be the focus of future research activities. In particular, the scientific community continues to view photovoltaic devices as promising candidates to fulfill the world's need for a sustainable energy source. Although QDSCs are leading candidates to fill this void, further improvement in photostability and photoconversion efficiency is needed before commercialization of photovoltaic devices is realized. The majority of the efforts to date have been controlling the size and shape of nanostructure and controlling the optical and electronic properties through synthetic manipulation. As discussed in this feature article, surface chemistry of QDs plays an important role in dictating the overall excited state dynamics. Tuning the QD properties through chemical manipulation of the surface is likely to expand the scope of semiconductor nanoscience research in the near future.

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Notes

The authors declare no competing financial interest.

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