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Viewpoint: Challenges in Colloidal Photocatalysis and Some Strategies for Addressing Them

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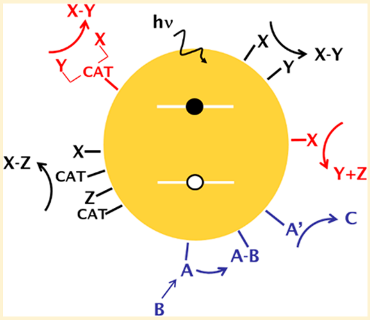
ABSTRACT: Colloidal semiconductor nanocrystals, or "quantum dots" (QDs), have several optical and chemical properties that give them the potential to enable nonincremental increases in the efficiencies of many types of photocatalytic reactions relevant for energy conversion and organic synthesis. Colloidal photocatalysts have many desirable characteristics of both heterogeneous and homogeneous catalysts but come with their own particular set of challenges. This viewpoint outlines some of the obstacles one first encounters when driving reactions with these colloids and offers some strategies for overcoming these obstacles, including ways to extend their excited state lifetimes, prevent corrosion by photogenerated holes, and choose a surface chemistry and buffering system for maximum colloidal stability over a range of environmental conditions.



INTRODUCTION

Redox reactions are used by living systems to store energy in chemical bonds and subsequently release it, as in the processes of photosynthesis, cellular respiration, fermentation, and combustion, or to eliminate free radicals, as in the disproportionation of superoxide. In synthetic chemistry, redox reactions drive conversion of one functional group to another, change the degree of saturation of a carbon backbone or ring, and allow for coupling of molecular fragments.

Light is a versatile energy input for redox reactions. Its frequency (color), intensity, pulse duration, and pulse pattern are controllable precisely and remotely. It can drive reactions when applied as a broadband source, like a lamp, or a single-wavelength source, like a laser, and varying its parameters can be used to investigate the reaction mechanistically. Photooxidants/reductants are excited state electron acceptors/donors (relative to some redox partner) that absorb light energy and convert it to electrochemical potential. In photoredox-based catalysis, this electrochemical potential drives a chemical transformation through excited-state single- or multicharge transfer from the catalyst to the substrate of interest. A photoredox catalyst can perform this function many (ideally, an infinite number of) times if either (i) it is both the photooxidant and the photoreductant for a reaction, or (ii) there are sacrificial terminal oxidants or reductants in the sample that regenerate the catalyst.

Driving a redox reaction with visible or even near-infrared light rather than UV light, when possible given required redox potentials, maximizes energy efficiency, minimizes side products,[1] and, when relevant, allows us to best take advantage of the solar spectrum, which peaks in irradiance around 500 nm (blue-green). Heterogeneous photocatalysis is dominated by the use of nanostructured films of TiO_2, which, unsensitized, has an absorption onset of ~380 nm.[2,3] Homogeneous photocatalysis is dominated by systems sensitized by Ru and Ir coordination compounds; these chromophores have peak absorbances at wavelengths as long as 450 nm for tris(bipyridine)ruthenium(II) chloride[4] or 420 nm for *fac*-tris(2-phenylpyridine)iridium.[5,6] The most synthetically well-defined excitonic colloidal nanocrystals (cadmium and lead chalcogenides, copper−indium chalcogenides, and indium phosphide semiconductor nanocrystals, or "quantum dots" (QDs)), however, have size- and material-tunable band-edge absorbances throughout the entire visible and much of the near-infrared spectrum, with quantum confinement-enhanced reduction potentials up to −2.4 V vs SCE ($CuInS_2$ QDs)[7] and oxidation potentials up to +1.9 V vs SCE (CdS QDs).[8]

The typical homogeneous photocatalytic system has two components: (i) a photosensitizer, which absorbs a photon and forms an excited state, and (ii) a catalyst, which accepts charge carriers from the photosensitizer and performs the desired chemical transformations. Colloidal QDs have already been shown to act as photosensitizers but also as solo photocatalysts (where they perform both sensitizer and catalyst functions) in multielectron and proton-coupled multielectron reactions relevant to energy conversion and organic synthesis such as CO_2 reduction and C−C coupling reactions.[7,9−12] The most widely used QDs contain no precious metals, unlike the ubiquitous Ru and Ir complexes, and many types, including highly reducing $CuInS_2$ QDs, are also heavy metal-free. By using a QD as a solo photocatalyst, we can dispose of the sensitizer−co-catalyst paradigm, so many photocatalytic reaction mixtures based on QDs are relatively simple. Under the right conditions, QD systems are remarkably stable, reaching turnover numbers (TONs) of 10^4−10^5 for reactions such as the reduction of protons,[9] nitrobenzene,[8] or dinitrogen,[13] although below we suggest strategies for improved photostability. The

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use of QDs as solo photocatalysts, or, in some cases, their spontaneous assembly with a molecular co-catalyst, avoids slow, diffusion-mediated sensitizer-catalyst redox-reactions *without* the need for covalent synthesis to link sensitizer to catalyst.[7,14] Importantly, the surface ligands of the QD are typically only very weakly coupled to the electronic structure of their cores, so we can change the ligands on the QD to access a variety of solvents, to change the permeability of the ligand layer to selectively adsorb certain substrates,[12] or to create a certain type of adsorption site, without changing the redox potentials and absorption spectra of the particles. This property is in stark contrast to coordination compounds, where ligand identity and electronic structure are highly coupled. With QDs as photocatalysts, we can, with certain surface chemistries (as discussed below), work in acidic water.[15] QDs form stable and optically clear dispersions in a variety of solvents (with the right ligands), so we can study catalytic reaction mechanisms in solution using NMR and high signal-to-noise optical spectroscopy. The excited states of QDs that are precursors to the photoredox reactions are emissive, so we can monitor the fluorescence of the QDs to measure their redox activity with respect to a given substrate or photocatalyst.

Listed above is some of what we *know* we can do with QDs as photocatalysts. What can we *potentially* do? One can imagine, with the field's current level of synthetic and postsynthetic control of surface chemistry at the nanoscale, decorating the surfaces of the particles with specific binding sites and "second coordination spheres" for substrates that mimic active sites of enzymes or the most selective, efficient synthetic molecular catalysts. Given the extremely small (~10 meV[16,17]) splitting between the singlet-like and triplet-like excitons in QDs, we could use the high energy triplet-like "dark" excitons to access reactive triplet states of molecules that have singlet states that are too short-lived to be precursors to chemistry. We could use the field's many techniques for controllable self-assembly of QDs[18−20] to build photosynthetic reaction center mimics, where light energy is funneled to a catalytic site, such that photocatalysis is efficient even in low-light conditions.

Before we realize these more sophisticated applications of QD photocatalysts, we need to delineate and tackle some basic challenges. Some of these challenges have been around a long time in the field of semiconductor photochemistry but must be readdressed in light of the larger scope of reactions now being attempted, the newest surface chemistries, and the expanded library of semiconductor materials available for the QD cores. Here we describe some of the most consistent challenges we encounter in using QDs as sensitizers and photocatalysts for chemical reactions and offer some possible solutions. We hope these solutions are generally useful, but the most important goal of this article is to compile common constraints and limitations of QD-based photocatalytic systems so that each researcher can design solutions for their own particular system or reaction.

■ EXTENDING THE QD'S EXCITED STATE LIFETIME

A large majority of homogeneous photocatalytic systems utilize Ir- or Ru-based organometallic dyes as photosensitizers to deliver redox equivalents to molecular substrates. A primary advantage of these dyes is that they undergo fast (~1−10 ps) intersystem crossing to form triplet excited states with microsecond lifetimes.[5,21,22] The strong oscillator strengths of band-edge electronic transitions of QDs are useful for photocatalysis, but they are accompanied by fast radiative recombination and typical excited state lifetimes of 10−100 ns.[23−26] For some reactions, these lifetimes are sufficient, but, in order to use QDs as light absorbers for photocatalysis of the largest possible set of reactions with a high quantum efficiency and minimum QD degradation, we must develop strategies that extend the lifetime of the QD excited state, enough to allow for high yields of extraction of both the electron and hole in the particular reaction mixture of interest.

While the fundamental limit to the excited-state lifetime of a chromophore is the radiative lifetime of that species, nonradiative decay processes of the photogenerated charge carriers shorten the excited-state lifetime and decrease the photoluminescence quantum yield (PL QY) of the chromophore. By using QDs with high PL QYs (>30%), we maximize the excited-state lifetime and increase the chances that the desired reaction occurs. Zinc, cadmium, and lead-chalcogenide core-only QDs are regularly synthesized with PL QYs of up to 50%,[27] 100%,[28,29] and 80%,[30,31] respectively. Copper and indium-based core-only QDs typically suffer from lower PL QYs, but they can be improved significantly by shelling with another material such as CdS[32] or ZnS.[33,34]

In addition to surface passivation, inorganic shelling creates an "energetic heterojunction"[35,36] that extends the excited-state lifetime by decreasing the overlap of electron and hole wave functions. Bawendi and co-workers showed that, by coating a CdTe core with a thin shell of CdSe, a "type II" interfacial alignment where the electrons are delocalized to the shell while the holes are confined in the core, one can extend the radiative lifetime of the exciton by a factor of 120 from that of bare CdTe QDs (Figure 1).[37] Peng and co-workers demonstrated that the radiative lifetime of quasi-type II CdSe/CdS core−shell QDs increases with increasing thickness of CdS shell[38] through a decrease in wave function overlap of the charge carriers, a key determinant in the radiative rate.[39,40] One can synthesize other type II structures such as CdSe/ZnSe QDs with radiative lifetimes as long as a microsecond.[41−43] This strategy clearly accomplishes the goal of prolonging the excited state but does so at the cost of localizing one of the carriers (usually the hole, which, as discussed below, is typically more difficult to extract in any circumstance). One therefore might consider using segmented quantum rod heterostructures rather than spherical core−shell heterostructures to achieve a large degree of charge separation in the excited state so that the wave functions of both carriers overlap to some degree with the QD surface.

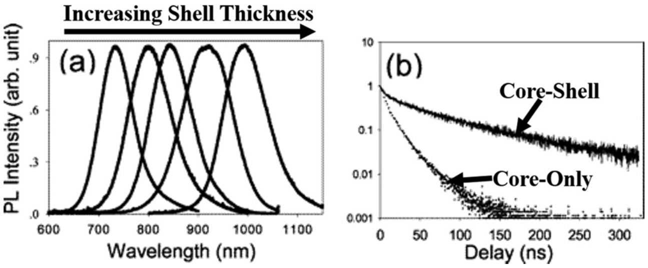

Figure 1. (A) Normalized room-temperature photoluminescence spectra of CdTe/CdSe (core/shell) QDs with a constant core size and differing shell thicknesses. With increasing shell thickness, the electron−hole overlap decreases and the emission shifts to lower energy. (B) Normalized photoluminescence intensity decays of CdTe QDs with (solid) and without (dotted) CdSe shells. The CdSe shell extends the PL lifetime of the QDs by a factor of 6. Adapted from ref 37. Copyright 2003 American Chemical Society.

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Another approach to creating long-lived excited states in QDs is to chemically dope the QDs with ions that serve as temporary charge carrier trap sites. Chemical doping can be achieved either in situ by adding the dopants directly into the reaction flask, or postsynthetically, by exposing the QD to cations that slowly exchange with cations in the QD's surface and lattice. Peng and co-workers demonstrated that the excited state lifetimes of ZnSe/ZnS core/shell QDs doped in situ with Mn^{2+} increased from ∼50 to 1000 μs, with nearly single-exponential decay dynamics.[44] Gamelin and co-workers demonstrated that Cu^+- and Ag^+-doped CdSe QDs have radiative lifetimes of microseconds. They proposed that photoinduced holes trap on the dopants (Cu^+ or Ag^+), such that the primary QD emission originates from recombination of delocalized electrons with localized holes.[45] Chemical doping has also been extended to III−V semiconductors such as Cu^+-doped InP QDs.[46]

One particularly interesting example of exploiting charge carrier trapping to extend the excited state lifetime of a QD without intentional doping is $CuInS_2$ QDs. Numerous spectroscopic studies have concluded that the fluorescence of these QDs primarily originates from the recombination of delocalized electrons and localized holes that are trapped on the Cu^+ ions within the lattice structure.[46−51] Coating the QDs with a layer of ZnS or CdS further increases the excited-state lifetime to microseconds.

■ EXTRACTING PHOTOGENERATED HOLES

For use of QDs as sensitizers or photocatalysts in photoredox catalysis, one must balance the rates of the electron and hole extraction from the QD because the accumulation of charge carriers greatly accelerates the chemical degradation of the QDs. Of particular concern is the accumulation of holes, which can induce the oxidation of the chalcogenide[52] or surface ligands. Photoelectron-driven degradation is not as much of a concern as QD ligands are usually anionics with high reduction potentials, and reduction of the inorganic core results in the formation of metallic sites on the QD surface (which are useful for catalytic reactions[53]). For QDs with cadmium and copper as cations, the effective mass of the electron is a factor of 3−4 smaller than that of the hole; therefore, the electron is more strongly confined, more delocalized, and easier to extract than the hole.[54] While the electron transfer lifetimes from a QD to a bound molecular acceptor are typically on the subpicosecond to single nanosecond time scales,[39,55−60] hole transfer lifetimes range from nanoseconds to microseconds.[39,61,62] Furthermore, ligands with thiolate binding groups, which are commonly used because of the high affinity of thiolates for "soft" metal ions like Cd^{2+} and Pb^{2+}, often have oxidation potentials within the bandgap of the QD so that they act as hole traps competitive with the intended hole scavenger or substrate in the system.[8,63,64] Trapping of holes on thiolate ligands decreases the probability of corrosion of the particles but increases the probability of precipitation because oxidized thiolates form disulfides, which have low affinity for the QD surface and easily desorb. Alternatives to thiolates, such as phosphonopropionate,[65,66] should be considered unless the reaction mixture contains an excess of thiols to replace desorbed ligands.[8]

One option to balance carrier extraction rates is to slow electron extraction by, for example, decreasing driving force or electronic coupling for the electron transfer reaction. On its face, this approach seems counterproductive but is a good option when the redox-driven chemistry is much slower than the redox reaction itself, and fast electron transfer creates long-lived (and therefore vulnerable) catalytic intermediates. In the following, we instead focus on strategies for increasing the rate of hole extraction from nanocrystals.

A straightforward yet limiting solution for hole accumulation-driven QD degradation is to initiate the catalytic cycle with hole transfer from the QD to a substrate.[11,12,67] This "hole-transfer first" strategy (Figure 2) entirely avoids the accumulation of holes in the QD core or on its surface, and the intrinsically fast rate of electron transfer inhibits the accumulation of electrons. Caputo et al. achieved up to 80000 TON for C−C coupling reactions using CdSe QDs that acted first as photo-oxidants and then reductants,[11] however, this strategy limits the scope of catalytic reactions that can be performed with QDs and does not necessarily eliminate all hole-driven degradation processes.

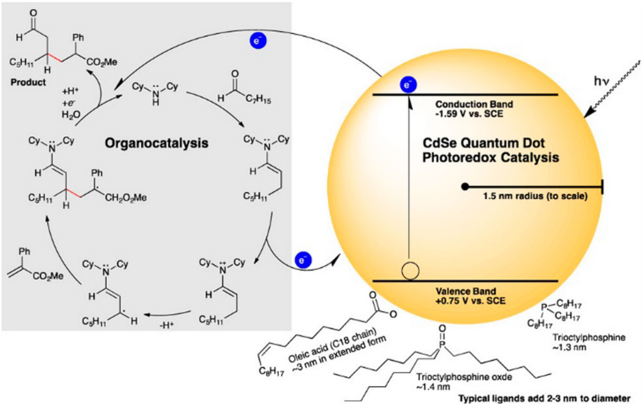

Figure 2. A typical photoredox catalytic scheme incorporating an organocatalyst (cycle in gray box) and a QD photoredox catalyst (right, yellow sphere) acting as both a one-electron oxidant and a one-electron reductant. In this reaction, photoexcited hole transfer from the QD to the substrate occurs before the electron transfer. Adapted from ref 11. Copyright 2017 American Chemical Society.

An alternative is to utilize molecular hole shuttles to perform a fast initial extraction of the photogenerated hole from the QD and then shuttle it to a waiting scavenger or substrate molecule; such shuttles have been shown to accelerate the removal of holes from QDs and enhance the efficiency of catalytic systems.[68,69] Hole shuttles, however, introduce two major limitations to the system: (i) the "effective" oxidation potential of the QD is dictated by the chosen hole shuttle, and (ii) the QD and the hole shuttle must be strongly electronically coupled to enable hole extraction competitive with hole trapping to a surface or lattice site. Such electronic coupling typically requires a covalent linkage of the shuttle to the QD surface. We have shown one type of linkage to be particularly effective: a molecular hole shuttle coupled to the QD through a so-called "exciton delocalizing ligand". Hole delocalizing ligands, such as phenyldithiocarbamate (PTC), mix with the valence band of QDs and result in a decrease in the confinement barrier for the excitonic hole.[70] We have demonstrated that hole transfer from a CdS QD to a phenothiazine hole shuttle through a PTC linker occurs faster than 300 fs.[71,72]

Alternatively, one can synthesize a type II core−shell QD structure, such as CdS/ZnSe QDs,[35] that localizes the hole wave function to the shell; in this case, the shell serves as the hole shuttle and interacts with the desired substrate. These type II core−shell structures can enhance the rate of hole transfer

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but will concurrently slow down the rate of electron transfer, as the electron is confined to the QD core. The electron is still accessible and may react with a substrate, depending on the shell thickness and the driving force for the reduction reaction. With this type of core−shell architecture, one ideally utilizes a thin-shell such that extracting the electron is still feasible. For example, Ganguli and co-workers demonstrated they could extract photoinduced electrons in TiO_2/CuS core−shell nanorods for the photocatalytic degradation of methylene blue despite the electrons' being confined to the TiO_2 core.[73] If this confinement is a problem in balancing carrier extraction rates, the hole delocalizing ligand is a better option.

■ OPTIMIZING LIGANDS TO ENSURE PERMEABILITY, SOLUBILITY, COLLOIDAL STABILITY, AND SELECTIVE INTERACTIONS WITH CO-CATALYSTS

Colloidal QDs are typically synthesized via hot-injection or heat-up methods[74] in the presence of surfactants with long aliphatic chains, such as oleic acid,[75−77] oleylamine,[78] and/or tetradecylphosphonic acid.[79,80] These surfactants serve as the "native ligands" that passivate the surface of the nanocrystals and solubilize them in nonpolar media. These bulky native ligands often insulate the QD from the adsorption of potential substrates and decrease the QD's catalytic activity. It is therefore sometimes necessary to remove or replace at least a portion of the native ligand shell to disorder it and maximize its permeability to the species of interest. A recent study by Zhang et al.[81] showed that, upon introducing intermolecular disorder within the QD ligand shell by replacing some of oleate ligands with octylphosphonate, the initial rate of a modular C−C coupling reaction, photocatalyzed by the QDs, increases by a factor of 2.3, and the energy efficiency (turnovers per Joule of photons absorbed) of the reaction improves by a factor of 1.6.

In other cases, the reaction of interest proceeds in polar media and requires a complete exchange of the nonpolar native ligands of QDs by polar (usually shorter) ligands. Mercaptoalkanoates[82−90] and ammonium-alkanethiolates[91,92] are among the most frequently used ligands for these exchange reactions, as QDs capped by these charged ligands are readily soluble in water.[93] In addition, zwitterionic amino acids[94−96] with either thiolate or imidazole binding groups, as well as neutral 3-mercatopropanol,[7] have been reported as ligands to solubilize QDs in water and DMSO. QDs dissolved in polar media are generally prone to degradation and flocculation due to either photodriven oxidation[96,97] or proton-induced desorption[98] of their ligands. There are two commonly utilized approaches to address this challenge. One option is to use ligands that are analogous to thiolates but are less susceptible to oxidation such as 3-phosphonopropionic acid[66] or poly imidazole.[99−101] The other option is to synthesize multidentate thiolate ligands that have a much higher binding affinity toward the QD surface than their monodentate analogues. Mattoussi and co-workers have demonstrated that dihydrolipoic acid-based molecules and polymers with two,[102−105] four,[15,106] and more[107,108] binding groups solubilize and colloidally stabilize QDs in water, even at pH 3.[103] Eisenberg and co-workers have designed and synthesized molecules with trithiolate binding groups and carboxylate tail groups that are much less likely to desorb from the surface of QDs than monothiolates during photocatalytic proton-reduction reactions.[87,109,110]

Nonspecific binding of molecules to nanoparticles is a well-recognized problem for their use in biological applications[111] but can also inhibit their catalytic activity. In complex chemical environments, it is often necessary to use electrostatics to localize co-catalysts[10,83,85,112,113] or substrates[55,114,115] on the QD surface or facilitate their diffusion toward the surface of QDs,[116] therefore allowing specific QD-molecule interactions to outcompete nonspecific binding of catalyst poisons or spectator species. For example, King and co-workers reported a series of QD-sensitized photocatalytic reactions using enzymes as co-catalysts and suggested that the attraction between the QD and the enzyme is electrostatic in nature (Figure 3).[10,13,83,112] Through this electrostatic assembly of QDs and MoFe proteins, they achieved TONs as high as 10^4 for the nitrogen fixation reaction. Peterson et al. combined optical measurements with electronic structure calculations to conclude that the binding of positively charged methylviologen on the surface of CdS QDs preferentially takes place on the electron-rich sulfur sites.[56] Young et al. also observed simultaneous two-electron transfer from the biexciton state of a 3-mercaptopropionate-capped CdS QD to a single viologen derivative using transient absorption spectroscopy and attributed this efficient process to the close contact and strong electronic coupling between the QD and the electron acceptor, enabled by their electrostatic attraction.

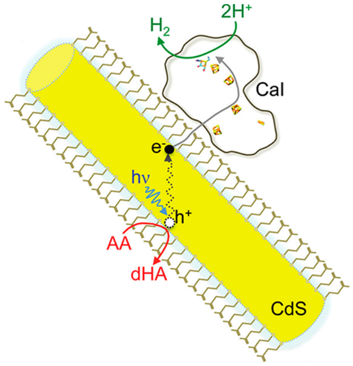

Figure 3. Electrostatic assembly of 3-mercaptopropionic acid (MPA) capped CdS nanorods and *Clostridium acetobutylicum* [FeFe]-hydrogenase I (CaI) used in the photocatalytic reduction of protons to H_2. The strong electrostatic interactions between the nanorods and protein enable efficient electron transfer from the excited nanorod to the protein. Ascorbic acid (AA) is used as the sacrificial electron donor, and dehydroascorbic acid (dHA) is its oxidation product. CdS and CaI are drawn to scale, while MPA molecules are enlarged by ~5×. Adapted from ref 83. Copyright 2012 American Chemical Society.

■ DEFINING "ACTIVE SITES"

While molecular catalysts have a limited number of modes for interacting with substrates and bulk semiconductors are typically synthesized with a set of known facets and defects, hot-injection approaches to colloidal QD synthesis produce QDs with chemically and electronically heterogeneous surfaces. The variety of coordination environments and ligand densities on the surface of a single QD, and the tunability of this surface chemistry, allows for binding of substrates through a range of binding modes and geometries.[8,11,56,117] While these properties make QDs attractive for screening potential reactions or for using one type of QD to catalyze multiple types of reactions, it is a challenge to determine the types of QD−substrate or QD−co-catalyst binding modes that are catalytically active for the desired reaction, and to minimize side reactions.

The field has however made much progress in describing (qualitatively and quantitatively) the chemical nature of both covalent and noncovalent interactions between various molecules and QD surfaces. For example, Peterson et al., provided evidence that methyl viologen adsorbs electrostatically to CdS QD surfaces with the bipyridyl core lying flat on the QD surface.[56,118] By changing the stoichiometry of the QD surface from Cd-enriched to S-enriched, the affinity of the methyl viologen for the surface increased. Cation/anion enrichment of QD surfaces can be accomplished during QD synthesis[119] or postsynthetically through dilution of the QDs[56] or the introduction of additional metal salts.[120]

While these procedures can be used to create binding sites for molecules, they do not afford atomic-level synthetic control of the QD surface as effectively as postsynthetic shelling procedures or surface treatments that produce QDs with well-defined facets (Figure 4).[28,40,121−127] These postsynthetic modifications typically afford the thermodynamically favorable products by introducing reagents or ligands at high temperatures (>200 °C) with long reaction times (>10 min); the QDs produced are reproducibly highly crystalline with low polydispersity.

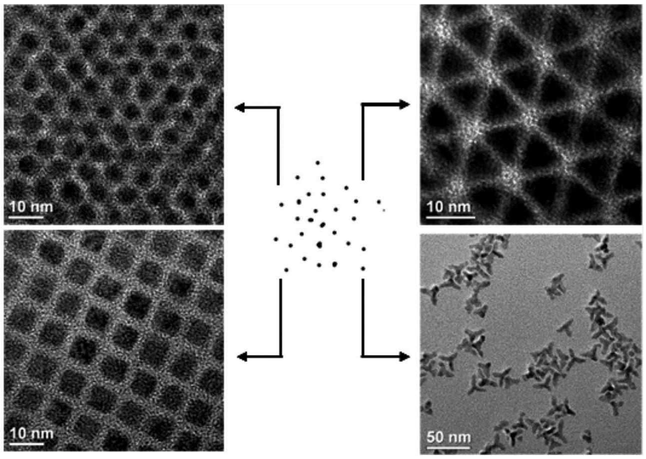

Figure 4. By varying the injection temperature, the same Cd and Se precursors can be used to generate a variety of nanoparticle shapes (spheres, cubes, tetrahedra, and tetrapods) with different ratios of {100} to {111} facets while maintaining a zinc blende CdSe structure. Adapted with permission from ref 127. Copyright 2009 American Chemical Society.

Anisotropic colloidal nanocrystals such as nanorods (NRs)[128−131] and nanoplatelets (NPLs)[132−135] have large areas of well-defined surface without any postsynthetic treatment. During the synthesis of these materials, the reactivity/stability of the different nanocrystal facets is modified through the coordinating ligand environment, which leads to anisotropic growth and well-defined crystal terminations. These materials can be exploited to determine the reactivity of different facets with the desired substrate through systematic comparisons of QDs, NRs, and NPLs.

A final consideration is that, even with a well-defined nanocrystal surface, the large number of potential adsorption sites on a QD is disadvantageous for multielectron redox reaction, such as the water splitting reaction or CO_2 reduction, because the QD, upon successive excitations, is more likely to distribute its photogenerated carriers among several molecular acceptors than to deliver more than one redox equivalent to a single catalytic site or substrate. In these cases, an excess of QD (relative to either the co-catalyst or the substrate) ensures that no more than one molecule adsorbs per QD but, of course, lowers the quantum efficiency of the system because many QDs have no associated redox partner. If a co-catalyst is used, Lian et al., have found that a static association between the QD sensitizer and the co-catalyst (as opposed to a diffusion-limited interaction) provides the best chance of efficient sensitization.[7,85,87,136−138] Metal co-catalysts can be directly deposited onto the surface of the QD; this strategy has been employed for Ni,[68,139] Pt,[57] Pd,[140] and other transition metals (Figure 5).

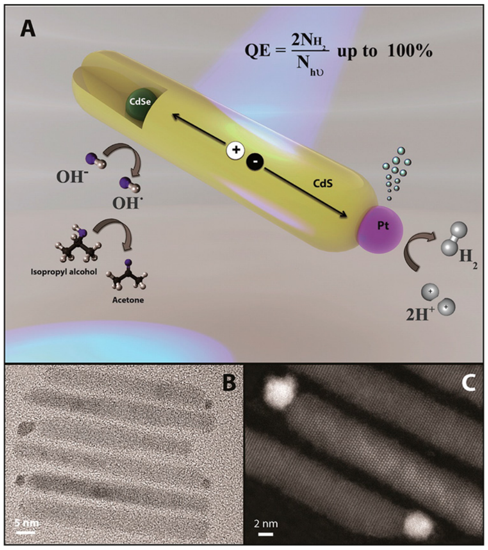

Figure 5. (A) Illustration of CdSe/CdS nanorods, with a Pt-metal co-catalyst selectively deposited on one end of the nanorod, used in the photocatalytic reduction of protons to H_2. The Pt-metal site allows for efficient accumulation of photoinduced electrons at a single site. (B) TEM and (C) high-resolution HAADF micrographs of a few representative metal-tipped CdSe/CdS nanorods. Adapted with permission from ref 69. Copyright 2016 American Chemical Society.

■ OPTIMIZING SOLVENT AND/OR pH

The large surface area-to-volume ratios of QDs makes them vulnerable to adventitious adsorbates and corrosion; these concerns are particularly relevant to photocatalysis, which involves electronically excited electrons and holes. The reaction conditions are therefore an important consideration when optimizing not only reactivity but stability. While QDs are generally stable in nonpolar solvents such as hexanes, chloroform, and toluene, many desired reactions occur in polar organic solvents or water. QDs can be solubilized in polar protic solvents such as methanol and ethanol through ligand exchange; however; these solvents are easily oxidized by some QDs[139] and are known to bind to the QD surface.[141] QDs can be solubilized in polar aprotic solvents such as dimethyl sulfoxide,[7] *N*,*N*-dimethylformamide, and ethylene glycol,[116] but purification of products from these solvents is difficult due to their high boiling points. Acetone and acetonitrile are commonly used in photocatalysis, but they are inconvenient for colloidal catalysis because very few types of ligands solubilize QDs in these solvents. Co-solvent systems composed of mixtures of polar/nonpolar solvents promote QD solubility while allowing the desired reaction to proceed.

For aqueous reactions involving QDs, the sample must be at a pH value where both the QDs are soluble and the reaction proceeds. While the known sensitivity of the QD's optical properties to changes in pH is advantageous for QD-based sensors,[142,143] this sensitivity is problematic when choosing reaction conditions. In very acidic environments (below pH 5), QDs with the most common water-solubilizing ligands (mercaptoalkanoates[144]) tend to aggregate and precipitate from the dispersion due either to (i) protonation of the carboxylate group ($pK_a \geq 4.8$),[145] which reduces electrostatic repulsion among the QDs and allows for hydrogen bonding of the ligand shells, or (ii) protonation of the thiolate headgroups (where the pK_as of the corresponding thiols are depressed significantly from their values for the free thiols due to binding with the metal ion). Protonation of thiolate headgroups desorbs the ligands and induces agglomeration.[98] One solution to problem (i) is to substitute the solubilizing tail group for one that will remain charged at acidic pH such as an amine[146] or a sulfonate.[147] A solution to problem (ii) is to use a bidentate (or polydentate) ligand such as dihydrolipoic acid; these ligands are known to limit ligand desorption at low pH[9,148] but, of course, still suffer from aggregation due to protonation of their terminal carboxylate groups.[149] The ideal water-solubilizing ligand for acidic conditions would therefore have a polydentate binding group with an amine or sulfonate terminal group.

In basic environments (above pH 10), hydroxide ions pose a problem for QD-based catalysis. The hydroxide ion often acts as a competitive acceptor for the photogenerated hole in the QD and, upon oxidation, produces reactive radical intermediates that potentially oxidize other molecules in solution.[68,150] While hydroxide radicals can be used as "hole shuttles" to enhance the rate of hole transfer in the system,[69] their use is limited to systems where the oxidation potential of hydroxide ions is more positive than the substrate. Furthermore, hydroxide ions have been shown to serve as X-type ligands which can potentially to bind to catalytic sites on the QDs, effectively "poisoning" the catalyst.[151]

Finally, in considering the proper pH value at which to run a photocatalytic reaction, note that cadmium and lead-chalcogenide QDs can, with the proper hole scavenger, efficiently reduce protons to hydrogen gas without the addition of a co-catalyst. This characteristic is desirable if proton reduction is the reaction of interest but undesirable if it competes with another reduction reaction (like CO_2 reduction).[53]

■ FINDING AN "INERT" BUFFER SYSTEM

For the reasons outlined in the previous section, QDs with many surface chemistries are suited to reactions in only mildly acidic or basic conditions (~pH 6−9).[68] Ideally, the pH of the sample would be controlled both during sample preparation and throughout the duration of the reaction with a buffer. The addition of reagents during sample preparation often induces large changes in pH, which can irreversibly degrade the QDs through aggregation, ligand stripping, or surface reconstruction. For example, for reactions involving photocatalytic CO_2 reduction, one typically observes a large decrease in the solution pH (~5.7) after purging the sample with CO_2 due to the formation of carbonic acid.[14,152] Buffers are also crucial for maintaining a constant proton/hydroxide ion concentration during a reaction, which is particularly relevant for proton-coupled electron-transfer (PCET) reactions that employ protons from the solution as reagents/products.[153] However, one must choose the buffer system carefully if the reaction mixture contains QDs to avoid degradation, poisoning, and aggregation.

Many commonly employed buffers can lead to degradation of QDs through stripping of surface atoms. Good's buffers comprise more than 20 commonly used buffers, often zwitterions with multiple charged or polar functional groups that were originally designed to be used in biological systems with large effective buffering ranges.[154−156] These functional groups, however, sequester metal ions such as the ones typically used in QDs: Cd^{2+}, Pb^{2+}, and Zn^{2+}.[157,158] Consequently, these buffers can lead to QD degradation by dissolution.[159] When choosing a buffer for reactions catalyzed by QDs, we are limited to those that do not complex with the surface of the QDs.[157] For example, the photoluminescence of QDs is stable for days in the presence of Tris buffer, while ethylenediaminetetraacetic acid (EDTA) leads to aggregation and degradation in minutes.[159,160]

Even if a particular buffer does not degrade the QD, it can still interfere with catalysis by binding to the surface of the QD. The majority of Good's buffers have amine or sulfonate groups, which are good ligands for metal ions on the QD surface.[161] Phosphates and phosphonates will also adsorb.[66] This binding leads to the displacement of weakly bound ligands and "poisons" the QD catalyst by occupying potential adsorption/reaction sites for substrates.[144] One solution is the use of excess QD ligands as the buffering agent for the solution; this method prevents ligand removal and should not completely block the QD surface. This option is limited though, as many commonly used ligands only buffer in very specific pH ranges and/or are weak buffers.[65]

Finally, some buffers induce QD aggregation. The solubility of QDs and other colloids is known to be sensitive to the ionic strength of the solution.[162] To maintain a constant pH during a reaction requires buffer salts at concentrations of ~10−100 mM, which is often high enough to lead to nanoparticle aggregation.[160,163] One solution is to use a buffer that also serves as a sacrificial reagent for the reaction; ascorbic acid is typically used as both the buffer and sacrificial electron donor for QD-catalyzed proton reduction (Figure 6).[9] This approach limits the number of charged molecules in solution while allowing for a sufficiently high buffer concentration. This strategy requires careful monitoring of the pH during the reaction because the buffering molecules are consumed.

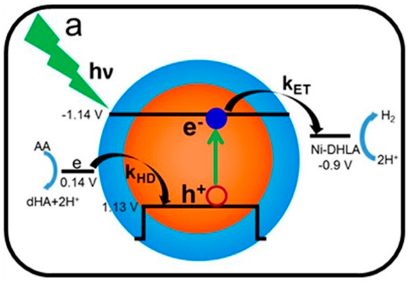

Figure 6. Schematic illustrating photoreduction processes for H_2 generation using a CdSe/CdS core/shell QD as the photosensitizer, a Ni-dihydrolipoic acid (DHLA) complex as the catalyst, and ascorbic acid (AA) as the sacrificial donor (HT, hole transfer; ET, electron transfer). Energy levels for a typical core/shell CdSe/CdS QD, AA, and Ni-DHLA catalyst are given versus the normal hydrogen electrode (NHE). Adapted with permission from ref 125. Copyright 2016 American Chemical Society.

The challenges we have outlined above are substantial but also technical in nature; none, we suspect, is so inherent to semiconductor nanocrystals that it cannot be overcome with the right combination of semiconductor core and surface functionalization. Overcoming them will allow the field to access a large range of photocatalytic reactions relevant for both energy conversion and organic synthesis and will set us up to exploit some of the more exotic properties of these materials to make nonincremental advances in the science and applications of light-driven chemistry.

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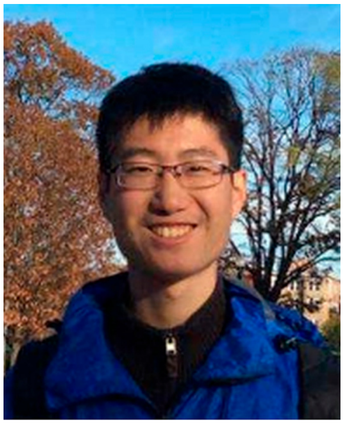

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