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Electrochemical Reduction of CO₂ at a TiO₂ Electrode using Quantum Dots as Multi-electron Funnels

**Emily A. Weiss
Northwestern University
633 Clark St.
Evanston, IL 60208-0001**

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Electrochemical Reduction of CO₂ at a TiO₂ Electrode using Quantum Dots as Multi-electron Funnel

Emily A. Weiss, Dept. of Chemistry, Northwestern University

A fundamental difference between colloidal quantum dots (QDs) and organic chromophores is the ability of a QD to mediate multiple charge transfer reactions due to band-edge degeneracy, which allows QDs to accommodate multiple excitons or injected charge carriers, and the availability of multiple sites for charge acceptors to adsorb to QD surfaces. Lead chalcogenide QDs have the highest band-edge degeneracy of the commonly prepared types of QDs. The original goal of this project was to determine the suitability of lead chalcogenide QDs as multi-electron redox centers for shuttling of electrons from a bulk semiconductor to a molecular substrate, in order to catalyze chemical reactions. The PI and her group realized early on in the project that, before they could explore the redox activity of QDs within an electrochemical cell, they needed to determine the fundamental mechanisms of electron exchange between QDs and small molecules, and to optimize the ligand shell of the QDs to provide maximum charge injection/extraction efficiency while maintaining electronic passivation of the QD surface, and thereby preventing chemical corrosion of the QD.

While Marcus theory is, in principle, just as applicable to charge transfer processes in QD-molecule systems as it is to molecular systems, the use of Marcus theory to predict the rate of charge separation involving QDs is, in practice, complicated by various heterogeneities and distributions of the chemical and electronic properties of the QD surface. The common theme of the work performed for this project is discovery (and quantitative modeling) of the relationship between the properties of the QD surface and the rate and mechanism charge transfer process.

With respect to these goals, the group has made substantial progress using lead sulfide (PbS) QDs with molecular charge-transfer partners in the solution-phase, and has begun to explore the potential for PbS QDs to participate in multi-electron transfer. Below are descriptions of the work performed with three donor-acceptor systems, and what was learned about the structural and electronic features of colloidal QD-organic complexes that influence the rate of interfacial charge separation.

System 1: PbS QD (hole donor) – Aminoferrocene (hole acceptor).¹

Malicki *et al.*¹ demonstrated that the structure of the native ligand shell of the QD influences the ability of a small molecular redox partner to access the surface of a QD. Addition of aminoferrocene (amFc) to a solution of PbS QDs passivated with oleate increases the rate of decay of the excited state of the QD due to photoinduced hole transfer from the QD to amFc. Nuclear Overhauser effect spectroscopy (NOESY NMR) indicated that amFc molecules adsorb to the surfaces of PbS QDs passivated with OA. In contrast, for QDs of the same size passivated with decanethiolate (DT), addition of amFc does not affect the excited state decay, and the 1-D NOESY NMR spectrum does not contain any evidence for surface-bound amFc. Hole transfer activity is thus correlated with adsorption of amFc to the surface of the QD, as gated by the ligand shell. Quantitative ¹H NMR measurements reveal similar numbers of bound OA and DT native ligands, so a difference in number density of the passivating ligands is not responsible for the difference in PHT behavior. Two hypotheses for the mechanism governing the change in PHT activity upon ligand exchange from OA to DT are (i) DT chains are more tightly packed (either in a liquid-like or

crystalline motif) than OA chains on the surface of a PbS QD and thus do not present any gaps large enough to allow amFc to penetrate the ligand shell, and (ii) the thiolate head group of DT forms a much stronger bond to the Pb^{2+} than does the carboxylate head group of OA, so amFc cannot effectively compete with DT for available binding sites on the QD. While it is currently unclear which of these mechanisms dominates (work is ongoing), these results highlight the importance of the ligand shell in gating the access of a molecular redox couple to the surface of the QD. It is therefore the permeability of this ligand shell, and not its thickness, that determines the probability of charge transfer.

System 2: PbS QD (electron donor) – Substituted Benzoquinones (electron acceptors).^{2,3}

The organic ligand shell that chemically stabilizes, electronically passivates and solubilizes colloidal QDs also presents a physical barrier that impedes a molecular redox partner's approach to the QD surface, and limits the number of available sites per QD for adsorption of molecular redox partners. Once the "empty" sites on a QD surface are occupied by adsorbed redox-active molecules, some QD-molecule systems – specifically those for which the rate of excitonic decay in the QD is slower than the average rate of collisions between QDs and freely diffusing redox-active molecules – also participate in collisionally gated photoinduced charge transfer. The lifetime of an exciton in PbS QDs ranges from 1 to 3 μs ; the group's work on PbS QD-benzoquinone (BQ) systems shows that this timescale is long enough to **enable both collisionally gated and static photoinduced electron transfer from solution-phase PbS QDs to freely diffusing and adsorbed BQ molecules**, respectively.² A combination of picosecond and microsecond transient absorption dynamics reveals the involvement of two mechanisms by which benzoquinone induces the decay of the excited state of the QDs: (i) electron transfer to BQ molecules adsorbed to the surfaces of PbS QDs and (ii) collisionally gated electron transfer to freely diffusing BQ.² Together, these two mechanisms quantitatively describe the quenching of photoluminescence upon addition of BQ to PbS QDs in dichloromethane solution.

This work represents the first quantitative study of a QD-ligand system that undergoes both adsorbed and collisionally gated photoinduced charge transfer within the same sample, and demonstrates that the availability of a collisionally gated pathway improves the yield of electron transfer from PbS QDs to BQ by an average factor of 2.5 over that for static electron transfer alone. Fewer than 1% of collisions between PbS QDs and BQ molecules result in electron transfer, which indicates the diffusing BQ molecules have to permeate through the oleate ligand shell to a location close enough to the inorganic core of the QD in order to participate in PET before exciton recombination. This observation provides further evidence for the role of the organic ligand shell in determining the accessibility of the inorganic QD core to molecular redox partners. Incidentally, the lifetime of an exciton in CdSe or CdS QDs is two orders of magnitude shorter ($\sim 10\text{-}50$ ns) than in PbS QDs, and thus does not allow enough time for collisional charge transfer to occur.

In a study of the photoinduced electron transfer process between PbS QDs and a series of BQs with various alkyl substituents on the central ring, the group studied the **influence of the size and shape of alkyl-substituted benzoquinone (s-BQ) acceptors on the efficiency with which they participate in static and collisional photoinduced electron transfer with oleate-coated PbS QDs**.³ Each of a series of alkyl-substituted BQ molecules participates in collisional electron transfer with oleate coated PbS QDs, but

only s-BQ molecules with one or fewer substituents participate in static electron transfer with PbS QDs. Larger s-BQ molecules generally have fewer adsorption sites available on the surface of a PbS QD and do not permeate through the oleate ligand shell as easily as smaller s-BQ molecules. The distribution of substituents on the BQ ring affects both the ability of an s-BQ to adsorb to the surface of a PbS QD and its collisional quenching efficiency. Having at least one side of the BQ ring unsubstituted increases the ability of a s-BQ molecule to participate in static PET more than having a sterically unhindered oxygen atom, but having a sterically unhindered oxygen atom enhances the collisional quenching efficiency of a s-BQ molecule. The observation that the efficiencies of static and collisional PET depend differently on the substitution pattern of a s-BQ indicates that the orientations of a s-BQ molecule of the surface of a PbS QD that enable static electron transfer are not the same as the orientations that enable collisional electron transfer. The study also resulted in a model for the effect of molecular volume on the change in free energy associated with transfer of s-BQ from dichloromethane solution into the oleate ligand shell surrounding the QDs. This model yields a parameter that provides a quantitative measure of the permeability of the organic adlayer of the QDs.

Our observation of collisional electron transfer from PbS QDs to s-BQ molecules that do not participate in static PET demonstrates directly that a molecular redox partner does not have to be adsorbed to the surface of a QD in order to participate in photoinduced charge transfer with the QD. Removing the requirement for a surface binding group enables a greater synthetic flexibility in the design of molecular redox partners for colloidal QDs. Furthermore, this work demonstrates that the ability of the molecular redox partner to permeate the organic shell of a QD should be an important criterion in the design of components for QD based photoelectrochemical systems.

System 3: PbS QD (electron donor) – Tetracyanoquinonodimethane (electron acceptors).⁴

This study demonstrated that PbS QDs coated in oleate ligands form **ground state multi-electron charge transfer complexes** with tetracyanoquinonodimethane (TCNQ) acceptors.⁴ Addition of TCNQ to PbS QDs in chloroform solution results in the spontaneous formation of features in the visible and mid-infrared absorption spectra of the mixture that correspond to reduced (anionic) TCNQ. The spin-lattice relaxation time of oleate protons and the concentration of reduced TCNQ have identical dependencies on the molar ratio TCNQ:QD; therefore, the decrease in spin-lattice relaxation time is due to the formation of paramagnetic centers upon electron transfer from the QD to TCNQ, and every electron transfer event occurs at the QD surface. There were no features corresponding to delocalized holes that would form upon oxidation of the QD core in the near-infrared or mid-IR absorption spectra of the QDs. The absence of these features, in conjunction with evidence that a molecular source of S^{2-} reduces TCNQ (but a molecular source of Pb^{2+} does not), indicated that sulfur anions on the surfaces of the QDs, and not the QD cores, were the electron donors to TCNQ. The maximum number of reduced TCNQ molecules formed per QD is 4.5. The number of TCNQ molecules a QD is able to reduce likely depends on the number of available adsorption sites for TCNQ on the QD surface, present either initially or made available by displacement of weakly-bound Pb^{2+} -oleate complexes from the surface of the QD.

There thermodynamic spontaneity of the electron transfer reaction between PbS QDs and TCNQ allowed mechanistic analysis of the electron transfer process with steady state methods: NMR and FT-

IR. Monitoring the response of spin-lattice relaxation times of oleate ligands on the QD to charge separation confirmed that electron transfer is occurring on the surface of the QD, and elucidated the role of surface ligand displacement in the formation of donor-acceptor complexes. This type of information will also be useful in analyzing and optimizing systems for photoinduced multi-electron transfer processes involving QDs.

Publications Resulting from the AFOSR-funded Work

- 1) Malicki, M.; Knowles, K. E.; Weiss, E. A. Gating of hole transfer from photoexcited PbS quantum dots to aminoferrocene by the ligand shell of the dots *Chemical Communications, Advance Article*.
- 2) Knowles, K. E.; Malicki, M.; Weiss, E. A. Dual-pathway photoinduced electron transfer from PbS quantum dots to a molecular acceptor *Journal of the American Chemical Society* **2012**, *134*, 12470-12473.
- 3) Knowles, K. E.; Malicki, M.; Tagliazucchi, M.; Swenson, N. K.; Weiss, E. A. Influence of the size of substituted benzoquinones on their ability to participate in static and collisional electron transfer with photoexcited PbS quantum dots *in preparation (to be submitted May 2013)*.
- 4) Knowles, K. E.; Malicki, M.; Parameswaran, R.; Cass, L. C.; Weiss, E. A. Spontaneous multi-electron transfer from the surfaces of PbS quantum dots to TCNQ *submitted*.

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Abstract

This project aimed to determine the fundamental mechanisms of electron exchange between colloidal lead sulfide (PbS) quantum dots (QDs) and small molecules, and to optimize the ligand shell of the QDs to provide maximum charge injection/extraction efficiency while maintaining electronic passivation of the QD surface, and thereby preventing chemical corrosion of the QD. The use of standard models to predict the rate of charge separation involving QDs is, in practice, complicated by various heterogeneities and distributions of the chemical and electronic properties of the QD surface. The common theme of the work performed for this project is discovery (and quantitative modeling) of the relationship between the properties of the QD surface and the rate and mechanism charge transfer process. With respect to these goals, the group has made substantial progress using PbS QDs with molecular

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charge-transfer partners in the solution-phase, and has begun to explore the potential for PbS QDs to participate in multi-electron transfer. This report describes the work performed with three donor-acceptor systems – lead sulfide QDs and an aminoferrocene hole acceptor, lead sulfide QDs and substituted benzoquinone electron acceptors, and lead sulfide QDs and a tetracyanoquinonodimethane electron acceptor – and what was learned about the structural and electronic features of colloidal QD-organic complexes that influence the rate of interfacial charge separation. Some key conclusions are that (i) it is the permeability of the ligand shell of the QD, and not its thickness, that determines the probability of charge transfer; (ii) QDs with long-lived excited states can participate in both static (adsorbed) and collisionally gated charge transfer with small molecules; (iii) both the molecular volume and the shape of a small molecule influences its ability to adsorb to the surface of the QD to participate in static charge transfer, and to permeate the ligand shell to participate in collisional charge transfer; and (iv) QDs can form ground state multi-electron charge transfer complexes with molecules of appropriate redox potentials. The charge donors in these cases may be surface ions, rather than the QD core.

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- 1) Malicki, M.; Knowles, K. E.; Weiss, E. A. Gating of hole transfer from photoexcited PbS quantum dots to aminoferrocene by the ligand shell of the dots *Chemical Communications, Advance Article*.
- 2) Knowles, K. E.; Malicki, M.; Weiss, E. A. Dual-pathway photoinduced electron transfer from PbS quantum dots to a molecular acceptor *Journal of the American Chemical Society* 2012, 134, 12470-12473.
- 3) Knowles, K. E.; Malicki, M.; Tagliazucchi, M.; Swenson, N. K.; Weiss, E. A. Influence of the size of substituted benzoquinones on their ability to participate in static and collisional electron transfer with photoexcited PbS quantum dots in preparation (to be submitted May 2013).
- 4) Knowles, K. E.; Malicki, M.; Parameswaran, R.; Cass, L. C.; Weiss, E. A. Spontaneous multi-electron transfer from the surfaces of PbS quantum dots to TCNQ submitted.

Changes in research objectives (if any):

The original goal of this project was to determine the suitability of lead chalcogenide QDs as multi-electron redox centers for shuttling of electrons from a bulk semiconductor to a molecular substrate, in order to catalyze chemical reactions. The PI and her group realized early on in the project that, before they could explore the redox activity of QDs within an electrochemical cell, they needed to determine the fundamental mechanisms of electron exchange between QDs and small molecules, and to optimize the ligand shell of the QDs to provide maximum charge injection/extraction efficiency while maintaining electronic passivation of the QD surface, and thereby preventing chemical corrosion of the QD. This report describes the group's substantial progress toward these goals.

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