Pathways of Quantum Dot Degradation during Photocatalysis

Florence Y. Dou, Emily Nishiwaki, Helen Larson, Tallie Zion, Hao A. Nguyen, and Brandi M. Cossairt*

Department of Chemistry, University of Washington, Seattle, Washington, USA 98195

*Email: cossairt@uw.edu

Abstract

CdS QDs are widely employed as photocatalysts for reactions such as hydrogen evolution, and its degradation under aerobic, aqueous conditions is well understood. However, despite evidence of aggregation and precipitation of CdS QD photocatalysts under inert conditions, catalyst speciation and degradation are under-explored. In this work, we demonstrate that during a reductive dehalogenation reaction, CdS QDs undergo surface ligand etching, leading to loss of colloidal stability and the formation of micro-crystalline cadmium metal deposits. We hypothesize that this results from the accumulation of electrons on the QD surface. In addition, we demonstrate a high catalytic TOF of 0.67 s^{-1} and show evidence of mild surface sulfur oxidation and formation of an ammonium salt by-product of the hole quencher. This work adds to our atomic-level understanding of the reactions occurring at the QD surface during photocatalysis and ultimately uncovers design principles that will allow the design of more stable and efficient catalysts.

Cadmium chalcogenide quantum dots (QDs) have been the material of choice for visible light photoredox catalysis mainly due to their wide band gaps, tuneable band edge potentials, and high absorptivity, making them suitable for both reduction and oxidation reactions.[1] CdSe and CdS have bulk band gaps of 1.7 eV and 2.4 eV, respectively, and may be tuned across the visible spectrum. CdS can access more challenging reactivity or higher turnover frequency due to its greater driving force for charge transfer. In addition, CdS nanocrystals of both dot and rod morphologies have been demonstrated as viable catalysts for several organic reactions.[2,3]

However, CdS catalysts are susceptible to photo-degradation, which significantly hinders catalytic activity and the practical implementation of this system at scale. The photo-corrosion of CdS catalysts in aqueous conditions has been well documented.[4,5] It is thought that there are two main pathways of irreversible photo-oxidation – 1) accumulation of excess holes leading to elemental sulfur formation and leached cadmium ions (Eq. 2) and 2) the reactivity of surface sulfides with molecular water or oxygen to form sulfates (Eq. 3).[4] Common strategies to alleviate this decomposition center around rapidly extracting photogenerated holes to prevent their reactivity with S^{2-} on the surface via construction of heterojunctions with materials such as metal oxides or metal catalysts.[6] These strategies have been shown to confer stability and enhanced activity.

$$\mathrm{CdS} + h\upsilon \rightarrow e^{-} + h^{+} \text{ (Eq. 1)}$$

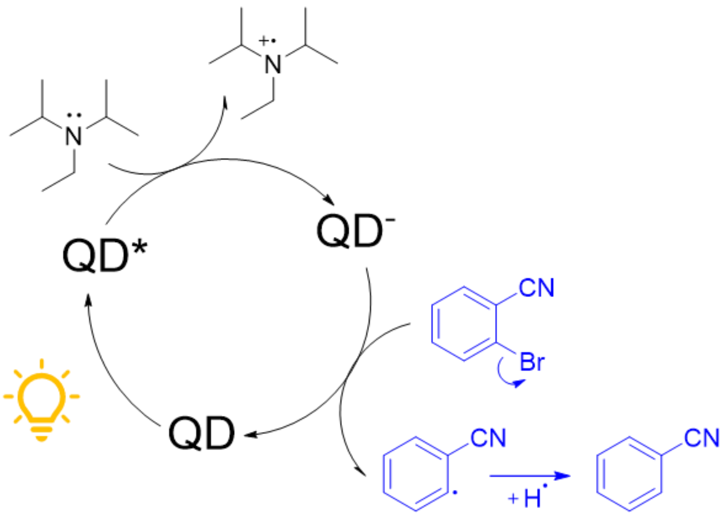
$$\mathrm{CdS} + 2\mathrm{H_2O} \rightarrow \mathrm{Cd^{2+}}_{(aq)} + \mathrm{S} + \mathrm{H_2} + 2\mathrm{OH^{-}} \text{ (Eq. 2)}$$

$$\mathrm{CdS} + 2\mathrm{O_2} \rightarrow \mathrm{Cd^{2+}} + \mathrm{SO_4^{2-}} \text{ (Eq. 3)}$$

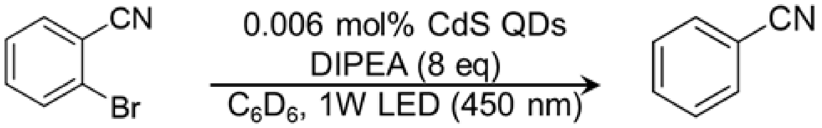
In non-aqueous colloidal systems, photo-corrosion resulting from catalysis has also been observed. CdSe QDs have been shown to exhibit aggregation and changes in color.[7] CdS QDs undergo increases in absorbance scattering typically indicative of loss of colloidal stability, both after catalysis and under illumination with common hole quenchers such as N,N-diisopropylethylamine (DIPEA).[2,8] In a study by Bartlett et al., CdS QDs used in the photo-oxidation of benzylamine showed a modest increase in surface SO_4^{2-} species under inert conditions measured by XPS.[9] These issues are typically addressed via additives to the reaction mixture such as large amounts of excess capping ligand, or a high catalyst loading where some amount of catalyst is sacrificed. Despite this, there remains a lack of understanding and characterization of QD degradation during organic photocatalysis, which ultimately hinders the design of more stable, efficient, and scalable systems.

In this work, we use a simple dehalogenation model reaction catalyzed by CdS QDs to characterize the photo-decomposition products and propose a mechanism of QD degradation during photocatalysis. We find that concurrent with product formation, we observe ligand etching, loss of colloidal stability, and the formation of microscale deposits of metallic cadmium. We also observe evidence of surface sulfide oxidation to sulfates. We propose that these are QD surface-localized reactions resulting from an imbalance of charge carriers during the constant flux of catalysis. With this concrete characterization of catalyst speciation, we can design more stable catalysts and gain a more atomistic understanding of QD photocatalysis.

We chose a reductive dehalogenation studied by the König group as a model reaction for studying QD speciation during catalysis.[8] The proposed mechanism (Scheme 1) is as follows – a photoexcited QD is reductively quenched by DIPEA to generate a charged, anionic QD. Next, a single electron transfer to the substrate 2-bromobenzonitrile occurs, triggering a C-X bond cleavage event with bromide as the leaving group and regenerating a neutral QD. Finally, the molecular radical abstracts an H atom from DIPEA or solvent to form the product, benzonitrile.



Scheme 1. Proposed mechanism of reductive dehalogenation of 2-bromobenzonitrile (blue) by CdS QDs with DIPEA as the sacrificial hole quencher.



Scheme 2. Optimized reaction conditions for photocatalysis.

We first attempted to recreate literature conditions using 5 nm oleate-capped CdS QDs (Figure S1) as our catalyst instead of ZnSe/CdS core/shell QDs. We note that the energetics of electron transfer to the substrate between the two systems should be comparable, as the electron wavefunction delocalizes to the CdS shell in the type-II ZnSe/CdS system. We observed complete conversion of 2-bromobenzonitrile to benzonitrile after 24 hours but found that a large amount of grey-black precipitate had accumulated after catalysis (Figure S2).

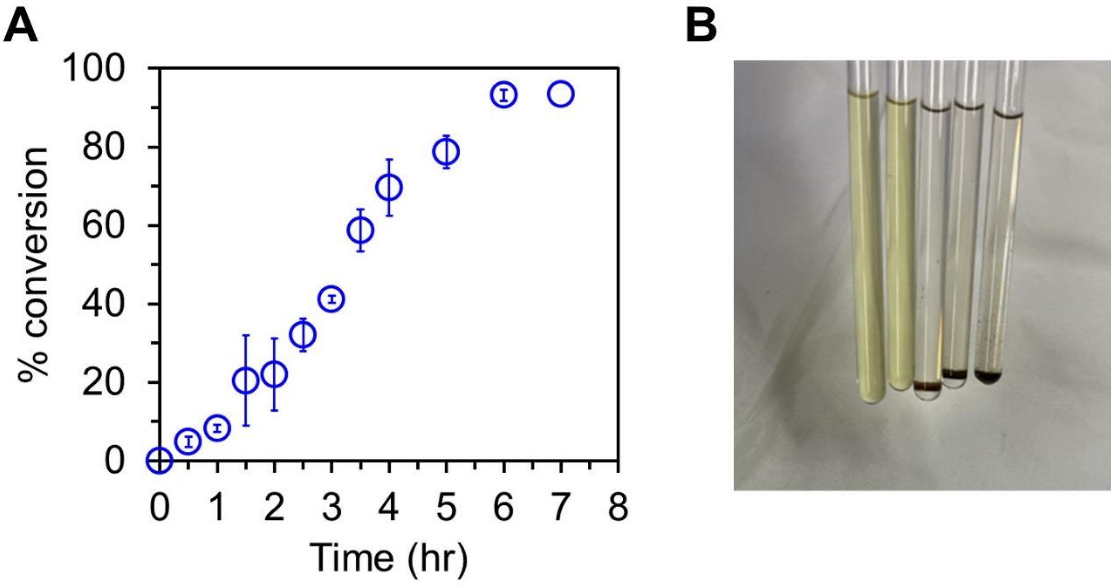


Figure 1. Conversion of 2-bromobenzonitrile to benzonitrile. (A) Quantification by ^{1}H NMR spectroscopy (Figure S3). (B) Image showing complete depletion of visible CdS absorbance accompanied by the formation of black precipitate over time (left to right).

We next attempted to optimize catalysis conditions by lowering the catalyst loading from the reported 0.6 mol % (320 nmol) to 0.006 mol % (3.2 nmol) and performing the reaction directly in deuterated C_6D_6 instead of hexanes (Scheme 2). At this lower loading, we again observed a large amount of precipitation accompanied by complete depletion of visible CdS absorbance (Figure 1B). Despite the precipitation, we report an impressive TOF of 0.67 s^{-1} and a product formation rate that remained consistent over time (Figure 1A). This suggests that the CdS is still catalytically active despite undergoing apparent chemical changes. We observed no product formation in the absence of light or QD.

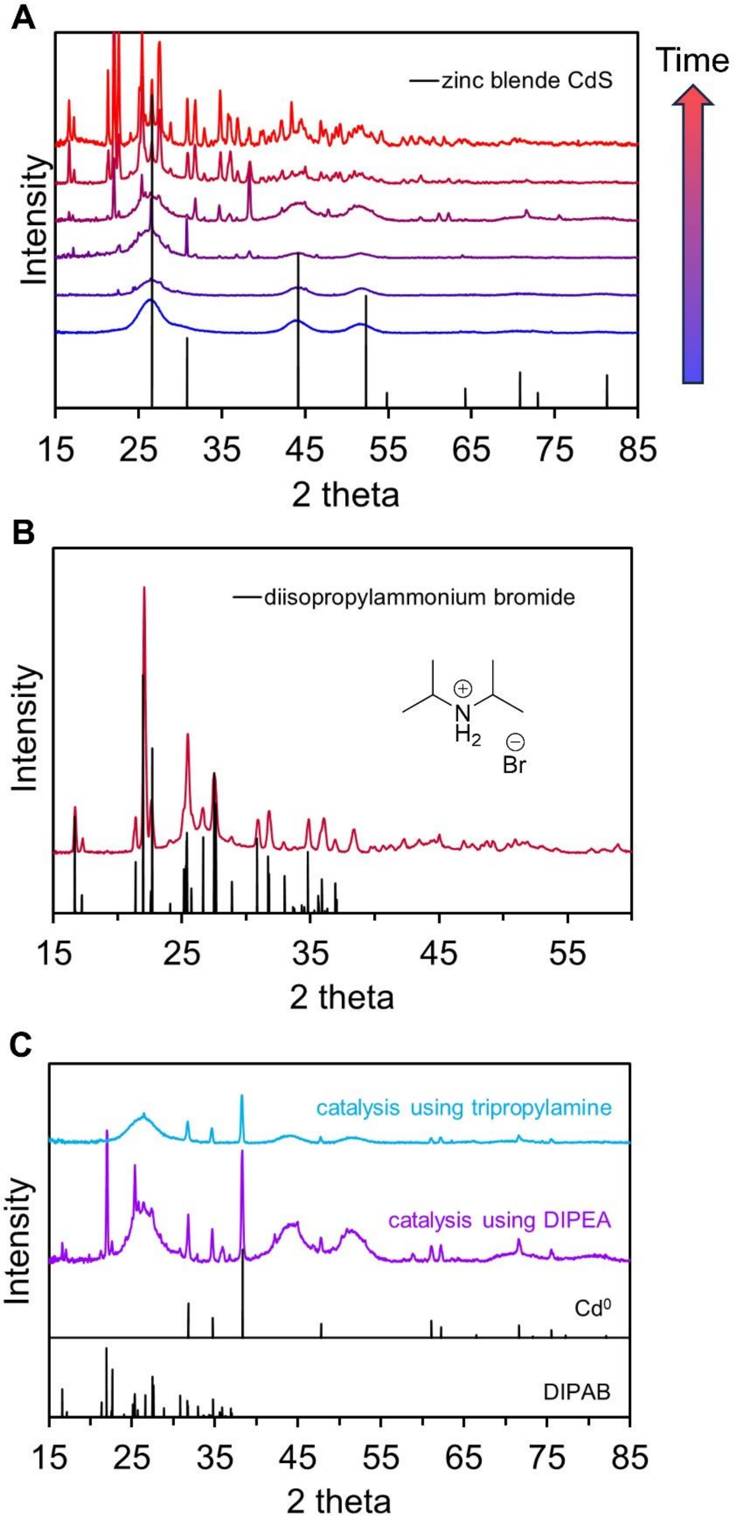


Figure 2. XRD patterns of precipitate over the course of the reaction. (A) Precipitate from 0-7 hours (bottom to top). (B) Precipitate showing formation of DIPAB salt. (C) Precipitate showing

the formation of cadmium metal using DIPEA or tripropylamine as the hole quencher for the reaction.

We used powder X-ray diffraction (XRD) to identify and characterize the precipitate formed during catalysis. From Figure 2A, we observe the persistence of broad features assigned as zinc blende CdS with sharper features growing in over time. We can calculate the crystalline domain sizes of CdS using the Scherrer equation, and we find that the CdS domains are ~ 3 nm (Table S1). The CdS appears to remain nanocrystalline but may have been slightly etched from their original size of 5 nm. We corroborate this with evidence of ligand etching during catalysis by ^{1}H NMR spectroscopy (Figure S4). The persistence of nanocrystalline CdS is consistent with the observation of continuous product formation. We analyzed later time points (Figure 2B) and observed the formation of diisopropylammonium bromide (DIPAB) crystals. This confirms the mechanism of H atom abstraction from DIPEA to form an iminium ion, followed by hydrolysis to form the ammonium salt.[10] By ^{1}H NMR spectroscopy, we see the ammonium protons as a broad peak at later time points and acetone as a hydrolysis by-product (Figure S5).

Lastly, we observe a significant amount of cadmium metal in the precipitate (Figure 2C). If we use a different quencher tripropylamine, as expected we no longer see the DIPAB salt, but we still observe unambiguous formation of cadmium metal. This tells us that the quencher is not solely responsible for forming metallic cadmium. When we image the reaction mixture after catalysis by transmission electron microscopy (TEM), we observe faceted microcrystals that primarily co-localize with cadmium by energy-dispersive X-ray spectroscopy (EDS) (Figure 3C). We, therefore, hypothesize a degradation mechanism where the surface passivating layer of $Cd(oleate)_2$ etches off during catalysis and leads to loss of CdS colloidal stability, followed by either surface cadmium atoms or $Cd(oleate)_2$ being reduced to Cd^0.

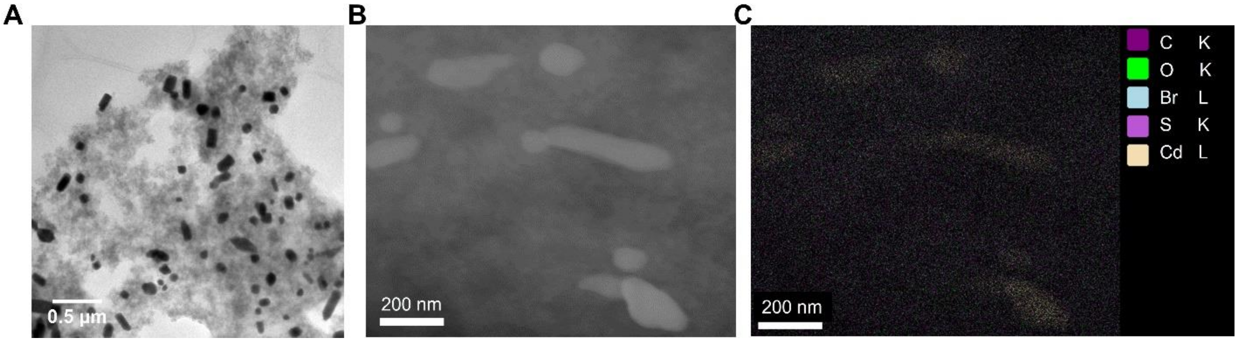


Figure 3. TEM images of the reaction mixture after catalysis. (A) Bright-field image of faceted microcrystals formed during catalysis. (B) STEM image of microcrystals. (C) EDS elemental mapping of microcrystals showing primarily Cd co-localization.

This mechanism was proposed to occur on the surfaces of QDs that were n-doped by external reductants.[11] The authors doped CdSe QDs with excess electrons using a strong chemical reductant, sodium naphthalenide ($Na[C_{10}H_8]$), and saw the dissociation of ligands by NMR and FTIR spectroscopy. They proposed that this occurred via the reduction of surface Cd^{2+} sites to form Cd^0 deposits with dissociation of the anionic oleate ligands. Cd^0 formation has also been invoked during photocatalysis but only observed by color change.[12,13]

Metal deposits are commonly used as electron sinks for reduction reactions.[14] Therefore, it is possible that as more metallic cadmium is formed, it can rapidly extract electrons and become the active site for reduction. This can also explain why we do not observe a decrease in product formation rate despite chemical changes to the catalyst. Looking at the shape of the curve in Figure 1A, there may be two regimes – 1) catalysis by colloidal CdS (up to ~3 hours) followed by 2) catalysis by Cd^0 and heterogeneous CdS. This finding adds to our atomic-level understanding of the processes occurring on QD surfaces during catalysis.

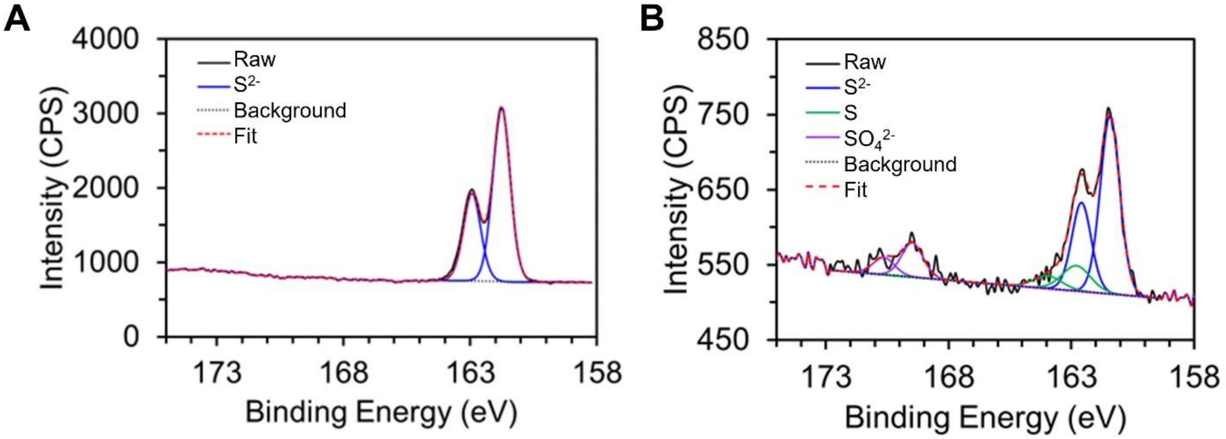


Figure 4. Sulfur XPS measurements referenced to carbon. (A) CdS before catalysis and (B) Precipitate after catalysis.

We also observe mild sulfur oxidation by X-ray photoelectron spectroscopy (XPS) of our precipitate after catalysis (Figure 4). Since XPS is a surface technique, we hypothesise that these changes also occur on the QD surface. Since our experimental setup is under inert conditions, possible sources of oxidation could be accumulated photo-induced holes, the DIPAB salt by-product, or the oxygen atoms of the ligand binding groups.

Notably, these degradation phenomena do not occur in the absence of product formation. If CdS QDs are illuminated with any singular reagent (DIPEA, ammonium bromide salt, or 2-bromobenzonitrile), there are slight changes in the absorption spectra, but they are reversible and the QDs remain intact (Figure S6A). We used tetrabutylammonium bromide (TBABr) as a proxy for bromide salts formed during the reaction. There are slight changes to the second and third optical transitions in the presence of DIPEA and TBABr, with a slight increase in scattering (blue and green). This has previously been seen with surface ligand etching.[15] There is also a slight decrease in absorption in the presence of 2-bromobenzonitrile. These results indicate that the reagents themselves could slightly interact with the surface of the QDs during catalysis. When CdS QDs are illuminated in the presence of DIPEA and a classic reversible electron acceptor, methyl viologen MV^{2+}, complete degradation of the QDs is also observed (Figure S6B). This tells us that a complete turnover cycle of hole quenching and electron extraction is necessary to observe these effects, although this exact degradation product in this case was not characterized.

We propose the degradation that we observe is due to the unbalanced accumulation of charge carriers in the QD during catalysis.[16] When CdS is illuminated with only DIPEA or 2-bromobenzonitrile, the QD becomes doped,[17] but the system reaches an equilibrium where back electron transfer or Auger recombination occurs with minimal chemical change. However, when both DIPEA and 2-bromobenzonitrile are present and the cycle is complete, the generation of product shifts the equilibrium toward a continuous flux of charges being transferred, leading to charge accumulation and reactivity to the QD surface. It is also possible that reaction by-products such as DIPAB or other transient radical species play a role in interacting with / degrading the QD.

For our specific system, we primarily observe the effects of electron accumulation that results in ligand etching and cadmium metal formation. However, we also observe slight photo-oxidation effects as S^{2-} becomes S and SO_4^{2-} at the QD surface. This work highlights that many chemical reactions can occur on the surface of QDs during catalysis, so charge carriers involved in charge transfer are not necessarily excitonic or band-edge. A growing amount of evidence shows that photo-excited charges localize at surface states before being extracted.[18–20] This is extremely plausible given the poor luminescence of our material, the abundance of trap states, and the fast rates of charge trapping observed in CdS QDs.[21]

We also highlight the need for more rigorous benchmarking of QD catalysts and demonstrate that QD photocatalysis is often a “black box” with many side reactions that are not well understood. Given our results, it is consistent that the addition of excess ligand can re-passivate the surface and prevent degradation, but a more atom economic method is still desired.

In terms of designing better catalysts, a thin shell that does not impede extraction of either electron or hole may be beneficial, but the shell may still be subject to the same degradation pathways as a core-only QD. One method of designing QDs that is potentially beneficial for catalysis and stability is the “ligand locking” method reported by several groups.[22,23] If the catalyst can withstand the flux of charge transfer and maintain its structure, then we can achieve a recyclable and scalable system. Alternatively, preventing charge accumulation in the QDs through the use of appropriate redox mediators or redox-active ligands may provide a path forward.[24,25]

This work demonstrates QD photocatalyst degradation pathways that remain under-reported. We show that a complete catalytic cycle leads to the etching of the CdS QD surface, loss of colloidal stability, and the formation of micro-crystalline cadmium metal that may serve as electron sinks for substrate reduction. We also demonstrate surface sulfide oxidation to sulfur and sulfates. This work pushes the community toward a more atomistic understanding of the processes that can occur on the QD surface during photocatalysis and can help us design more stable catalysts that are highly active and scalable.

Supplementary Material

Details of the experimental methods, characterization tools, and additional supporting data may be found in the Supporting Information document accompanying this manuscript.

Acknowledgements

We gratefully acknowledge support from the Department of Energy Office of Basic Energy Sciences under grant DE-SC0021232. Part of this work was conducted at the Molecular Analysis Facility, a National Nanotechnology Coordinated Infrastructure site at the University of

Washington, which is supported, in part, by the National Science Foundation (Grant No. NNCI-1542101).

References

(1) Yuan, Y.; Jin, N.; Saghy, P.; Dube, L.; Zhu, H.; Chen, O. Quantum Dot Photocatalysts for Organic Transformations. *J. Phys. Chem. Lett.* **2021**, *12* (30), 7180–7193. https://doi.org/10.1021/acs.jpclett.1c01717.

(2) Widness, J. K.; Enny, D. G.; McFarlane-Connelly, K. S.; Miedenbauer, M. T.; Krauss, T. D.; Weix, D. J. CdS Quantum Dots as Potent Photoreductants for Organic Chemistry Enabled by Auger Processes. *J. Am. Chem. Soc.* **2022**, *144* (27), 12229–12246. https://doi.org/10.1021/jacs.2c03235.

(3) Sha, Y.; Lin, X.-M.; Niklas, J.; Poluektov, O. G.; Diroll, B. T.; Lin, Y.; Wen, J.; Hood, Z. D.; Lei, A.; Shevchenko, E. V. Insights into the Extraction of Photogenerated Holes from CdSe/CdS Nanorods for Oxidative Organic Catalysis. *J. Mater. Chem. A* **2021**, *9* (21), 12690–12699. https://doi.org/10.1039/D1TA01124C.

(4) Weng, B.; Qi, M.-Y.; Han, C.; Tang, Z.-R.; Xu, Y.-J. Photocorrosion Inhibition of Semiconductor-Based Photocatalysts: Basic Principle, Current Development, and Future Perspective. *ACS Catal.* **2019**, *9* (5), 4642–4687. https://doi.org/10.1021/acscatal.9b00313.

(5) Ning, X.; Lu, G. Photocorrosion Inhibition of CdS-Based Catalysts for Photocatalytic Overall Water Splitting. *Nanoscale* **2020**, *12* (3), 1213–1223. https://doi.org/10.1039/C9NR09183A.

(6) Cheng, L.; Xiang, Q.; Liao, Y.; Zhang, H. CdS-Based Photocatalysts. *Energy Environ. Sci.* **2018**, *11* (6), 1362–1391. https://doi.org/10.1039/C7EE03640J.

(7) Caputo, J. A.; Frenette, L. C.; Zhao, N.; Sowers, K. L.; Krauss, T. D.; Weix, D. J. General and Efficient C–C Bond Forming Photoredox Catalysis with Semiconductor Quantum Dots. *J. Am. Chem. Soc.* **2017**, *139* (12), 4250–4253. https://doi.org/10.1021/jacs.6b13379.

(8) Pal, A.; Ghosh, I.; Sapra, S.; König, B. Quantum Dots in Visible-Light Photoredox Catalysis: Reductive Dehalogenations and C–H Arylation Reactions Using Aryl Bromides. *Chem. Mater.* **2017**, *29* (12), 5225–5231. https://doi.org/10.1021/acs.chemmater.7b01109.

(9) DiMeglio, J. L.; Bartlett, B. M. Interplay of Corrosion and Photocatalysis During Nonaqueous Benzylamine Oxidation on Cadmium Sulfide. *Chem. Mater.* **2017**, *29* (17), 7579–7586. https://doi.org/10.1021/acs.chemmater.7b02899.

(10) Yue, W.-J.; Day, C. S.; Brenes Rucinski, A. J.; Martin, R. Catalytic Hydrodifluoroalkylation of Unactivated Olefins. *Org. Lett.* **2022**, *24* (28), 5109–5114. https://doi.org/10.1021/acs.orglett.2c01941.

(11) Hartley, C. L.; Dempsey, J. L. Electron-Promoted X-Type Ligand Displacement at CdSe Quantum Dot Surfaces. *Nano Lett.* **2019**, *19* (2), 1151–1157. https://doi.org/10.1021/acs.nanolett.8b04544.

(12) Zhao, J.; Holmes, M. A.; Osterloh, F. E. Quantum Confinement Controls Photocatalysis: A Free Energy Analysis for Photocatalytic Proton Reduction at CdSe Nanocrystals. *ACS Nano* **2013**, *7* (5), 4316–4325. https://doi.org/10.1021/nn400826h.

(13) McClelland, K. P.; Weiss, E. A. Selective Photocatalytic Oxidation of Benzyl Alcohol to Benzaldehyde or C–C Coupled Products by Visible-Light-Absorbing Quantum Dots. *ACS Appl. Energy Mater.* **2019**, *2* (1), 92–96. https://doi.org/10.1021/acsaem.8b01652.

(14) Wu, K.; Chen, Z.; Lv, H.; Zhu, H.; Hill, C. L.; Lian, T. Hole Removal Rate Limits Photodriven H2 Generation Efficiency in CdS-Pt and CdSe/CdS-Pt Semiconductor Nanorod–Metal Tip Heterostructures. *J. Am. Chem. Soc.* **2014**, *136* (21), 7708–7716. https://doi.org/10.1021/ja5023893.

(15) Anderson, N. C.; Hendricks, M. P.; Choi, J. J.; Owen, J. S. Ligand Exchange and the Stoichiometry of Metal Chalcogenide Nanocrystals: Spectroscopic Observation of Facile Metal-Carboxylate Displacement and Binding. *J. Am. Chem. Soc.* **2013**, *135* (49), 18536–18548. https://doi.org/10.1021/ja4086758.

(16) Wang, J.; Ding, T.; Wu, K. Electron Transfer into Electron-Accumulated Nanocrystals: Mimicking Intermediate Events in Multielectron Photocatalysis II. *J. Am. Chem. Soc.* **2018**, *140* (32), 10117–10120. https://doi.org/10.1021/jacs.8b05942.

(17) Shulenberger, K. E.; Keller, H. R.; Pellows, L. M.; Brown, N. L.; Dukovic, G. Photocharging of Colloidal CdS Nanocrystals. *J. Phys. Chem. C* **2021**. https://doi.org/10.1021/acs.jpcc.1c06491.

(18) Prather, K. V.; Stoffel, J. T.; Tsui, E. Y. Redox Reactions at Colloidal Semiconductor Nanocrystal Surfaces. *Chem. Mater.* **2023**, *35* (9), 3386–3403. https://doi.org/10.1021/acs.chemmater.3c00481.

(19) Wu, K.; Du, Y.; Tang, H.; Chen, Z.; Lian, T. Efficient Extraction of Trapped Holes from Colloidal CdS Nanorods. *J. Am. Chem. Soc.* **2015**, *137* (32), 10224–10230. https://doi.org/10.1021/jacs.5b04564.

(20) Olshansky, J. H.; Balan, A. D.; Ding, T. X.; Fu, X.; Lee, Y. V.; Alivisatos, A. P. Temperature-Dependent Hole Transfer from Photoexcited Quantum Dots to Molecular Species: Evidence for Trap-Mediated Transfer. *ACS Nano* **2017**, *11* (8), 8346–8355. https://doi.org/10.1021/acsnano.7b03580.

(21) Shulenberger, K. E.; Jilek, M. R.; Sherman, S. J.; Hohman, B. T.; Dukovic, G. Electronic Structure and Excited State Dynamics of Cadmium Chalcogenide Nanorods. *Chem. Rev.* **2023**, *123* (7), 3852–3903. https://doi.org/10.1021/acs.chemrev.2c00676.

(22) Loiudice, A.; Segura Lecina, O.; Bornet, A.; Luther, J. M.; Buonsanti, R. Ligand Locking on Quantum Dot Surfaces via a Mild Reactive Surface Treatment. *J. Am. Chem. Soc.* **2021**, *143* (33), 13418–13427. https://doi.org/10.1021/jacs.1c06777.

(23) Wang, D.; Sheridan, M. V.; Shan, B.; Farnum, B. H.; Marquard, S. L.; Sherman, B. D.; Eberhart, M. S.; Nayak, A.; Dares, C. J.; Das, A. K.; Bullock, R. M.; Meyer, T. J. Layer-by-Layer Molecular Assemblies for Dye-Sensitized Photoelectrosynthesis Cells Prepared by Atomic Layer Deposition. *J. Am. Chem. Soc.* **2017**, *139* (41), 14518–14525. https://doi.org/10.1021/jacs.7b07216.

(24) Lowe, G. A. Enabling Artificial Photosynthesis Systems with Molecular Recycling: A Review of Photo- and Electrochemical Methods for Regenerating Organic Sacrificial Electron Donors. *Beilstein J. Org. Chem.* **2023**, *19* (1), 1198–1215. https://doi.org/10.3762/bjoc.19.88.

(25) Dou, F. Y.; Harvey, S. M.; Mason, K. G.; Homer, M. K.; Gamelin, D. R.; Cossairt, B. M. Effect of a Redox-Mediating Ligand Shell on Photocatalysis by CdS Quantum Dots. *The Journal of Chemical Physics* **2023**, *158* (18), 184705. https://doi.org/10.1063/5.0144896.

TOC Graphic