

PRF Number: 58220-UNI6

Title: The Effects of Surface Chemistry on the Generation of Redox Equivalents in Lead Sulfide Quantum Dots for Heterogeneous Catalysis

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Research Results

The outlined objectives of this project are: (1) investigate the chemical factors controlling the replacement of native oleate ligands in ultrathin lead sulfide quantum dot (PbS QD) films suspended at a liquid-air interface and (2) track the effects of this surface chemistry on the generation of trapped charge carriers in PbS QD films under applied DC bias. In Year 1 of this project we verified a method of tracking the rate and yield of oleate displacement from a PbS QD film suspended on a liquid subphase by measuring the contraction of the film as a function of time. During Year 2 we were able to use this method in combination with NMR spectroscopy to systematically investigate the factors affecting this ligand exchange for two important classes of ligand exchange targets: short, aliphatic organic molecules and halide ions. Both ligand classes promise to alter the trapping dynamics in PbS QD films by altering the average interdot separation and the energy and occupation of QD surface states.

Film contraction kinetics were analyzed using plots of the percent change in film surface area as a function of time fit to a single exponential decay function. Data was collected on carboxylic acids, thiols, amines, and tetraalkylammonium halides. For these ligands, the rate of PbS QD film contraction increased with the concentration of the entering ligand. Figure 1a shows an example of these kinetics for formic acid. NMR spectroscopy of the liquid subphase indicates that this contraction occurs on the same timescale as the native oleate displacement. This data is consistent with the exchange of sterically demanding oleates for smaller ligands via an associative rate-determining step. For exchange with tetraalkylammonium halides, altering the cation from tetramethylammonium to tetrahexylammonium increases both the rate and degree of film contraction (Figure 1b). This result is also explicable in terms of an associative exchange mechanism where the strong ion-pairing of the tetramethylammonium salts reduces the free halide concentration.

The mechanism of this exchange was further elucidated by comparing the rates of film contraction across differing ligand chemistries. Both carboxylic acids and thiols produced faster film contraction than either amines or tetraalkylammonium halides at the same concentration. From this information we proposed that carboxylic acids and thiols were able to stabilize the associative transition state through either hydrogen bonding with the outgoing oleate or transfer of a proton to the oleate (Figure 2). ¹H-NMR spectroscopy of ligand exchange on colloidal samples of quantum dots helped to support this mechanism. Oleates are displaced from the QD surface as protonated oleic acid in the presence of carboxylic acids and thiols, but they are displaced as deprotonated oleate in the presence of amines and tetraalkylammonium halides. The formation of free oleic acid during exchange with thiols is particularly suggestive of proton transfer during an associative ligand exchange; the polarization of the S–H bond induced by S bonding to Pb²⁺ would explain how an otherwise extremely weak proton donor is able to protonate a weak base like oleate.

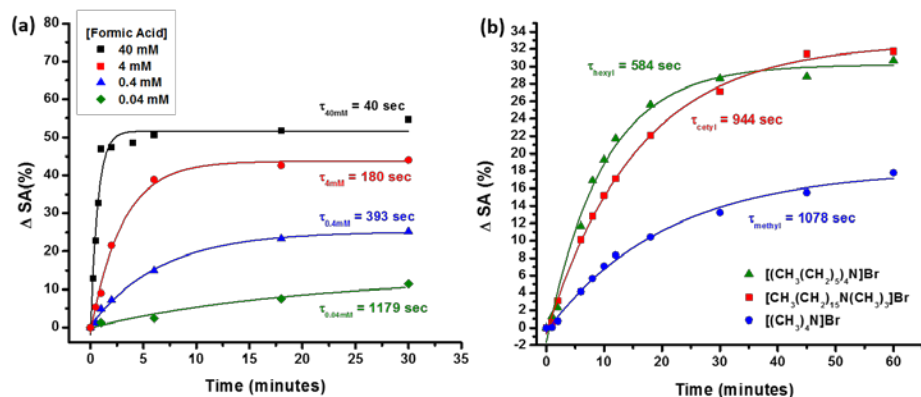


Figure 1. Plots show the % change in QD film area as a function of time. Solid lines represent single-exponential fits with the listed lifetimes. **(a)** Four trials where formic acid at various concentrations is injected into the liquid subphase below the QD film. **(b)** Exchange data for bromide salts with various tetraalkylammonium counterions.

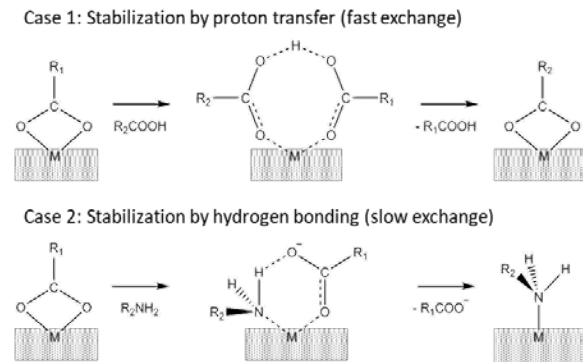


Figure 2. Illustration of an associative exchange mechanism to explain the differing rates of ligand exchange for carboxylic acids, thiols, amines, and halides. Carboxylic acids and thiols are able to stabilize the associative transition state through proton transfer (Case 1). Amines may partially stabilize the transition state through hydrogen bonding (Case 2) whereas halides would be unable to stabilize the departing oleate. In an associative rate-determining step, stabilization of the departing oleate increases the rate of oleate displacement.

As a result of our work to-date, we have developed a toolbox for systematically introducing carboxylic acid, thiol, amine, and halide ligands to the surfaces of PbS QDs self-assembled at a liquid-air interface. The resulting films are compact and mechanically robust such that they can be transferred to various substrates for imaging and electrical analysis. Our group is currently using a photoelectrical testing station to screen candidate ligand preparations for conductivities suitable for bias-stress analysis. In the coming year these bias-stress measurements will be carried out to compare the yield and rate of generation of trapped charge carriers in ultrathin PbS QD films.

Products

Results of thin-film ligand exchange studies using short, aliphatic ligands and tetraalkylammonium halides were collected into two oral presentations given by undergraduate students Adam Milam and Mary Salyards at the 2018 Southeastern Regional Meeting of the American Chemical Society (SERMACS). Initial results of $^1\text{H-NMR}$ studies of the solution-phase exchange using tetraalkylammonium halide ligands was presented by an undergraduate student, Perry Wasdin, as a poster at the 2018 SERMACS. Further work extending the $^1\text{H-NMR}$ studies to aliphatic ligands were incorporated into oral presentations given by Perry at the 2019 National Conference on Undergraduate Research at Kennesaw State University and the 2019 World Congress on Undergraduate Research at the University of Oldenburg, Germany. Two manuscripts are in preparation that will describe the results of organic and halide ligand exchange. These manuscripts will be submitted for publication by the end of the academic year.

Impact on PI Career

The PI is a pre-tenure faculty member at a PUI, and this project has had a substantial impact on activities that will ensure a successful reception of tenure and development of an active, undergraduate research program. The award of this PRF grant fulfilled the PI's tenure requirement of one externally-funded research grant. Results generated by this grant motivated further grants submitted to the National Science Foundation, including an MRI grant for a fluorescence lifetime spectrometer and a CAREER grant for a comprehensive quantum dot research program involving synthetic, surface functionalization, and charge transport studies. The publications currently in preparation for submission will fulfill the PI's tenure requirements for peer-reviewed publications prior to tenure application. The materials and capital equipment purchased through this grant allowed for the PI to build an onsite apparatus for measuring thin film photocurrents, which will enable future studies of excitonic nanomaterials.

Impact on Students

This grant covered the wages for a total of six undergraduate research students over the course of Year 2. The students involved included one sophomore (Amberly Rogers), two junior (Perry Wasdin and Adam Milam), and two senior (Mary Salyards and Zachary Nofs) chemistry majors as well as one sophomore biology major (Amanda Clay). Travel funds allowed four students to attend the 2018 SERMACS to give poster and oral presentations. The performance of substantive undergraduate research experiences led to significant recognition of these students' accomplishments; Mary Salyards was awarded the 2018 ACS Georgia Section Women in Chemistry Scholarship and Perry Wasdin was awarded the 2018 UWG Beheruz N. Sethna Undergraduate Research Award. During Year 2 both supported senior students completed the research requirements for their ACS-certified B.S. degree and presented their senior theses. Mary Salyards has since enrolled in the doctoral program at the University of Arizona, and Zachary Nofs has been offered a position with the functional films company Kimoto Tech. Zachary is currently applying to the Department of Defense's Science Mathematics and Research for Transformation Scholarship to continue pursuing applied chemical research in the public sector. Perry Wasdin and Adam Milam are currently applying to graduate programs and planning to prepare senior theses to present in the Spring of 2020 based on their work on this project.