

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 goals for Year 1 of this research project focused on a study of the chemical factors controlling the rate and yield of displacement of oleate ligands from the surfaces of as-synthesized lead sulfide quantum dots (PbS QDs) and their replacement with new ligands that show promise in controlling the exciton dynamics at QD-electrode interfaces. Ligand exchanges were performed on freestanding, ultrathin PbS QD films supported on an acetonitrile subphase by injecting an incoming ligand into this subphase. QD films supported on a liquid surface contract when the native oleate ligands are exchanged for shorter ligands and the nearest-neighbor separation is reduced. The change in film area was measured as a function of time using a Thorlabs CMOS camera capturing ten high-definition images per second (Figure 1a). Plots of the change in film area as a function of time fit well to single exponential decay functions for all ligands tested, which supports the interpretation that QD reorganization is associated with a single

process with a single, rate-determining step. The timescales for film contraction, loss of incoming ligand from the subphase, and the partitioning of oleate into the subphase are all similar. As laid out below, the timescale of film reorganization is also sensitive to the nature of the incoming ligand. Taken together, these results demonstrate that video imaging of QD film contraction can be used to measure the rate and yield of ligand exchange within a QD film. This is the first quantitative demonstration of the utility of this technique; it will be of great practical interest as a simple, cheap, and efficient method for tracking nanoparticle reorganization on the benchtop.

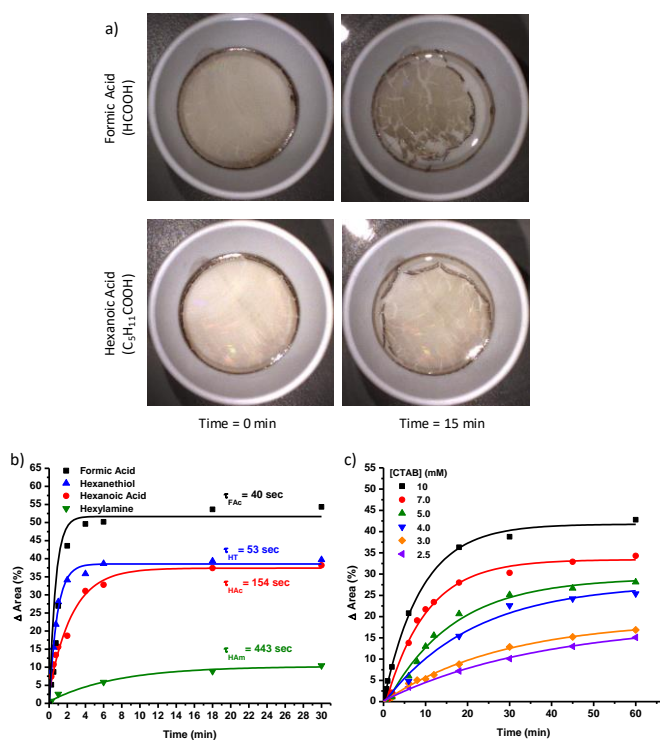


Figure 1. a) PbS QD monolayers suspended on acetonitrile undergoing ligand exchange for formic acid (top) and hexanoic acid (bottom). The shorter ligand produces greater film contraction. b) Plot of the percent change in film area versus time for PbS QD monolayers ligand-exchanged with formic acid (black squares), hexanethiol (blue upright triangles), hexanoic acid (red circles), and hexylamine (green downward triangles). Lines are single exponential fits with the indicated lifetimes. c) Plot of the percent change in film area versus time for PbS QD monolayers ligand-exchanged with different concentrations of CTAB. Lines represent single-exponential fits of each data set.

Initial ligand exchange studies concentrated on primary, aliphatic carboxylic acids, thiols, and amines as entering ligands. The systematic exchange of ligands with different tail lengths and binding groups was used to distinguish the likely mechanisms of ligand exchange in ultrathin films of PbS QDs. The rate of film contraction was shown to be dependent upon both the concentration of the entering ligand and the nature of its binding group (Figure 1b). This information suggests an associative rate-determining step for ligand exchange whereby the incoming ligand first coordinates to the QD surface and the oleate subsequently leaves. Experiments comparing the exchange rates for incoming carboxylic acid ligands showed that exchange rate increased with the acid dissociation constant of the acid. These results have informed the current working hypothesis of an associative interchange mechanism whereby the incoming ligand's

ability to stabilize the transition state through either hydrogen bonding with the outgoing oleate or transfer of a proton to the oleate has a significant effect on the activation energy for ligand exchange. Further efforts to validate this mechanism using computational modeling of ligand exchange transition states are ongoing.

During the Summer of 2018, a second avenue of ligand exchange studies was pursued to determine the ability of halides to replace surface-bound oleate from ultrathin PbS QD films. These experiments were motivated by reports showing improvements in QD-sensitized solar cell performance following halide-passivation of the QD surface. Cetyltrimethylammonium bromide (CTAB) was found to effectively produce film contraction, which indicates that surface-bound oleate ligands were replaced by bromide. The rate of film contraction generally increased with the concentration of CTAB present in the subphase (Figure 1c), which indicates an associative rate-determining step like that found for organic ligand exchange. The rate of bromide exchange was slower than the rates of carboxylic acid, thiol, or amine exchange. This slower halide exchange is consistent with the current hypothesis of an exchange transition state that is stabilized in the case of organic ligands by hydrogen bonding and proton transfer. Preliminary results of bromide ligand exchanges performed using alternative quaternary ammonium cations (i.e. tetramethylammonium and tetrahexylammonium) show that the nature of the cation affects the rate of ligand exchange. The role of the cation in this exchange is currently under investigation—particularly whether it exists as an ion-pair with the halide and whether it can assist in stabilizing the associative exchange transition state.

Products

Initial results acquired during the Fall of 2017 for ligand exchange studies using organic ligands were presented as a poster at the 2017 Southeastern Regional Meeting of the American Chemical Society (SERMACS). Two oral presentations are scheduled for the 2018 SERMCAS to present results on organic ligand exchange and halide exchange gathered during the Spring and Summer of 2018. Two manuscripts are currently in preparation that will describe the results of organic and halide ligand exchange. These manuscripts will be submitted to ACS journals for publication in the coming 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 five undergraduate research students over the course of Year 1. The students involved included one freshman, one sophomore, one junior, and two senior chemistry majors. These majors are all on the department's ACS-certified degree track, which requires the completion and presentation of a senior thesis project. During this time, both supported senior students completed experiments that they will present as senior theses in the Fall of 2018 and in the Spring of 2019. All supported students are graduate-school bound, and the performance of substantive undergraduate research experiences is critical for their preparation for graduate study. Travel funds allowed four undergraduate research students to attend the 2017 SERMACS to present posters, and a further four students are scheduled to attend the 2018 SERMACS to give one poster and three oral presentations.

Students engaged in this project gained a series of valuable skill sets that will prepare them for graduate studies. All students were trained in air free synthetic techniques that included the use of a Schlenk line and glovebox. Students learned to synthesize colloidal nanocrystals using standard hot injection methods and to purify them via solvent extraction, centrifugation, and rotary evaporation. Students were trained in UV-vis-NIR absorption spectroscopy and NMR spectroscopy to quantify QD size, concentration, and surface chemistry. Electron microscopy of students' QD samples was performed offsite at Georgia Tech's Materials Characterization Facility to train students in nanocrystal imaging techniques. All research students attended weekly group meetings wherein they presented their results to other group members and explained their experimental plans. Problems of experimental design were discussed and solved as a group with group members being assigned literature readings where appropriate. In this manner, undergraduates practiced developing experimental strategies in the manner of graduate students.