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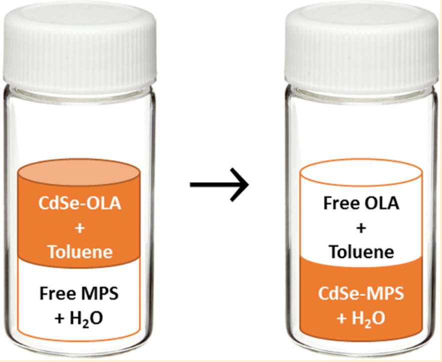
A Biphasic Ligand Exchange Reaction on CdSe Nanoparticles: Introducing Undergraduates to Functionalizing Nanoparticles for Solar Cells

Jennifer M. Zemke* and Justin Franz[†]

Department of Chemistry, Winona State University, 175 West Mark Street, Winona, Minnesota 55987, United States

Ⓢ *Supporting Information*

ABSTRACT: Semiconductor nanoparticles, including cadmium selenide (CdSe) particles, are attractive as light harvesting materials for solar cells. In the undergraduate laboratory, the size-tunable optical and electronic properties can be easily investigated; however, these nanoparticles (NPs) offer another platform for application-based tunability—the NP surface. In the interest of exploiting these particles for solar applications, the surface can be tuned to facilitate charge transfer out of the nanoparticles to maximize photocurrent for high-efficiency, low-cost solar cells. This multiweek undergraduate laboratory experiment introduces students to semiconducting nanomaterials and to taking steps to ensure functionality of these materials for solar applications. The experiment includes the synthesis of oleic acid-capped (OLA) CdSe particles and a biphasic ligand exchange reaction to afford ionically functionalized CdSe nanoparticles capped with sodium 3-mercaptopropane-1-sulfonate (MPS). Both the CdSe-OLA and CdSe-MPS materials in this experiment are characterized for ligand binding and relative particle size distribution by FTIR, ^{1}H NMR, and UV−visible spectroscopies.



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■ INTRODUCTION

The purpose of this laboratory experiment is to introduce the applicability of nanochemistry into the undergraduate laboratory curriculum through student synthesis and surface manipulation of semiconductor nanoparticles (NPs). Furthermore, this laboratory activity allows students to reintroduce themselves to techniques previously presented in organic chemistry for characterization of inorganic nanomaterials. Finally, through the development of and assessment of student laboratory reports, students are encouraged to connect the applicability of their synthesized products to current energy concerns and research problems regarding solar energy conversion.

According to the International Energy Agency, only 3.5% of the world's total primary energy supply in 2012 came from what could be considered renewable energy sources (hydro, wind, solar, geothermal), whereas 81.7% of that energy supply came from burning fossil fuels (oil, coal, and natural gas).[1] To meet the ever increasing energy demands of today's world, it only seems reasonable to place more emphasis on renewable energy sources like solar power. One avenue of research involves the creation of thin-film polymer solar cells. These cells are typically cost-effective devices but suffer from low conversion efficiencies (3−10%).[2] Semiconductor NPs have received plentiful attention as candidates to increase the efficiency of solar cells.[3−8] The addition of semiconductor NPs to the aforementioned polymeric solar cells could prove to enhance the efficiency of these cells while maintaining low cost and ease of processing.[6,9]

A popular explanation of this possible increase in efficiency is due to the possibility of multiple exciton generation (MEG, also called carrier multiplication, CM). In these processes for low band gap (E_g) semiconductor nanoparticles, one high energy photon ($h\upsilon \geq 2E_g$) could produce more than one electron−hole pair, or exciton as seen in Figure 1. Due to strong confinement and the lack of lattice phonon coupling, MEG has been observed for many types of nanoparticles including lead and cadmium chalcogenides such as PbS, PbSe, PbTe, CdS, and CdSe.[3,10−13] Other instances of MEG have been reported for InAs, InGaAs, and silicon NP samples to name a few.[3,14−16] While there has been some controversy over the extent of reported MEG in NP systems,[17,18] any overproduction of charge carriers per photon absorbed could lead to improvements in efficiency of well-engineered NP-based photovoltaic cells.

While MEG has been most studied and most pronounced in the lead chalcogenide samples, these samples often have exciton absorbance peaks in the NIR region of the electromagnetic

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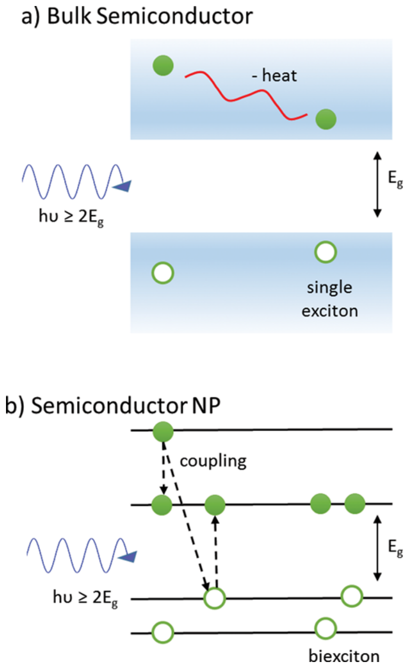

Figure 1. Photon energy lost as heat to lattice phonon coupling in bulk semiconductors (a) and multiple exciton generation (MEG) for semiconductor nanoparticles (b).

spectrum. A typical undergraduate laboratory may not be equipped with a spectrometer capable of measuring absorbance between 1000 and 3000 nm; thus, cadmium selenide NPs were chosen for this laboratory experiment (typical CdSe exciton absorbance peaks between 400 and 700 nm). Additionally, undergraduate experiments have previously been developed to safely synthesize batches of CdSe particles and to investigate their size-tunable optical and electronic properties.[19,20] It is important to note that while the likelihood of using CdSe in solar cells for MEG purposes is unlikely in practice due to the necessity of near-UV photons to induce the MEG process,[4] this laboratory exercise still serves as an important platform to introduce MEG and practical manipulations of semiconducting NPs for solar applications.

While the observation of MEG is itself an interesting research endeavor, the realization of successfully collecting multiexcitons in a working device is dependent on the many interfaces these excitons must traverse, including the nanoparticle surface ligands as seen in Figure 2. The typical synthesis of many Pb or Cd chalcogenide nanoparticles employ oleic acid (OLA) as an initial capping ligand.[19,21] OLA provides an excellent buffer to potential NP aggregation and eventual precipitation of these nanoparticles while also making the NPs readily dispersible in organic solvents; however, it is also an electrically insulating ligand and not viable for working solar devices. Instead, short-chain ligands with good stability are highly desired for these devices.[10,22] While many ligands have been used in these types of devices (e.g., 1,2-ethanedithiol and 1,2-ethanediamine), many of these device observations have employed solid-state ligand exchanges[10] where the use of traditional characterization (NMR, FTIR, absorbance spectra) becomes more complicated. For this reason, a suitable, solution-phase biphasic ligand exchange reaction was chosen in this experiment. The synthesized CdSe-OLA NPs are converted to water-soluble, ionically charged CdSe-MPS NPs while maintaining the ability to be solution processed and easily characterized via ^{1}H NMR and FTIR and UV–visible absorption studies. The MPS ligand is closely related to dimercaptopropanesulfonate (DMPS), a ligand previously shown to increase the photoresponse in analogous lead sulfide materials.[22]

■ EXPERIMENTAL METHODS

This experiment has been performed for three years in two different courses. It is a three week module as proposed and is designed for groups of 3–4 students; however, given the time frame of this experiment and adequate hood space, it may be possible to have students work in pairs. Six groups in a materials chemistry course (3 groups per year) and seven groups in a traditional upper-level inorganic chemistry course have successfully completed this laboratory experiment.

Synthesis of CdSe-OLA (Week 1)

Synthesis of the parent CdSe-OLA nanoparticles is accomplished using a modified procedure from Nordell et al.[19] A batch of relatively monodisperse nanoparticles can be achieved in the same manner by heating a precursor solution of 134 mg of CdO and 1.20 mL of oleic acid in 8 mL of octadecene. Once the requisite temperature has been reached (225 °C), 5 mL of selenium precursor solution (12 mg/mL elemental Se and 0.14 mg/mL trioctylphosphine in octadecene) is quickly injected into the heated flask. Students quench the reaction by carefully transferring all of the reaction mixture to a room temperature beaker after their desired color is obtained. In a typical reaction, orange to red particles are formed within 5 min after injection.

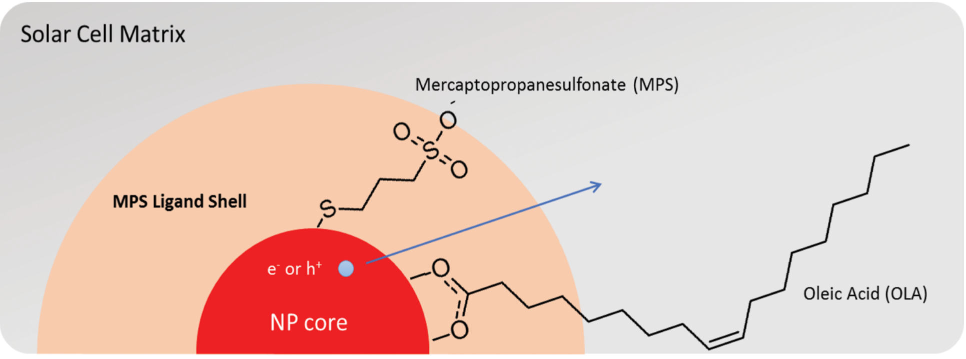

Figure 2. Depiction of the nanoparticle core and ligand shell showing the length and insulating nature of the organic soluble oleic acid versus ionic mercaptopropanesulfonate. To perceive photocurrent, charge carriers (electrons, e$^-$ or holes, h$^+$) must be extracted from the nanoparticle through the ligand shell, into the device matrix.

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The nanoparticles are cleaned of excess ligand and octadecene by precipitating in acetone (~35 mL) in a 50 mL centrifuge tube. The contents are centrifuged at 4000−6000 rpm and 20 °C for 10 min. This results in either a concentrated layer of nanoparticle solution or a nanoparticle pellet at the bottom of the centrifuge tube. At this stage, the supernatant liquid is carefully removed via pipet to minimally disturb the particles. If the students have a concentrated liquid layer, they may add acetone again to reprecipitate their particles and repeat the centrifugation process. If the students obtained a pellet after the first centrifugation step, they should dissolve their pellet into a small amount of toluene (added dropwise until the NPs are fully suspended). Acetone is then added to precipitate the NPs. The particles are typically fairly clean after two rounds of precipitation, but a third precipitation cycle is suggested to remove any residual 1-octadecene and unbound oleic acid. Once a final pellet of nanoparticles has been obtained, it is dried to obtain a yield. Typical student reactions yield 150 mg of cleaned CdSe-OLA particles.

Biphasic Ligand Exchange (Week 2)

The synthesized NPs at this point are coated with oleic acid. These oleic acid ligands must be exchanged because oleic acid is a fatty insulator that is undesirable for electron transport in solar cells. The desired ligand, sodium 3-mercaptopropanesulfonate (MPS) is a short, ionic ligand that should improve conductivity in a solar cell. MPS is also soluble in water making a biphasic reaction a possibility. To conduct the ligand exchange from oleic acid to sodium 3-mercaptopropanesulfonate, each student group suspends half of their CdSe-OLA NPs in toluene at a concentration of ~50 mg/mL. Separately, an equal volume solution of 250 mM MPS is prepared in deionized water. The two solutions are then combined and either shaken manually or with a vortexer at low speed until after the bottom layer becomes highly colored and the top layer becomes colorless indicating the NPs have migrated into the water phase.

Students are instructed to shake samples for 30 min, but can choose to continue mixing for up to an hour to improve NP migration. The ideal result of this reaction is shown in Figure 3; however, with low volumes, it may be hard to distinguish two phases due to emulsions. Centrifugation is employed to try to break formed emulsions in the process. Upon centrifugation, the bottom layer should be highly colored and the top layer should be colorless. The CdSe-MPS particles are cleaned of excess MPS ligand by the same precipitation and centrifugation cycle mentioned above. In this case, however, acetonitrile is an appropriate antisolvent and the particles are readily dispersed in water. Once a pellet of CdSe-MPS particles is obtained, it is dried for characterization.

Characterization (Week 3)

While some characterization may be performed prior to the third week of experimentation, students must collect enough spectra to discuss size redistribution of the NPs through the ligand exchange process, successful synthesis of CdSe-OLA NPs, and successful ligand exchange to CdSe-MPS. To discuss size distributions of their NP samples, students collect UV−visible spectra before and after ligand exchange. To determine ligand binding to the NPs, students utilize ^{1}H NMR and FTIR spectroscopy. Again, students do this before and after ligand exchange.

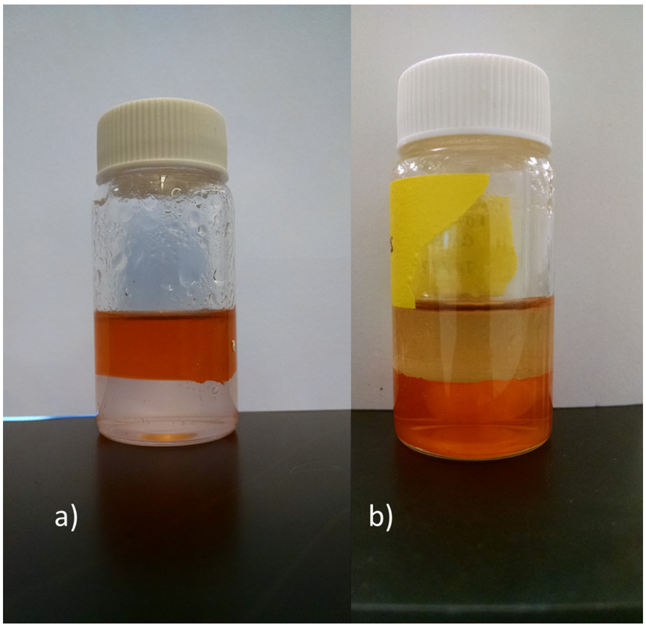

Figure 3. Photo of ligand exchange reaction: (a) at the beginning of the reaction period with CdSe-OLA NPs in toluene over MPS in H_2O and (b) an almost completed reaction of toluene over CdSe-MPS NPs. After the reaction is completed, the bottom layer should be highly colored and the top layer should be colorless. Emulsions formed during the reaction may make this indiscernible.

■ HAZARDS

In the synthesis of CdSe-OLA particles, students must quench their reaction mixture while it is at 225 °C. Extreme caution should be taken during this process. Students have effectively used an insulated glove and have adopted the use of a clamp to quench their particles. Both Se and CdO are hazardous via ingestion and inhalation and are skin and eye irritants. CdO is a suspected carcinogen and is classified as a possible developmental toxin. Trioctylphosphine may cause burns through all routes of exposure and should be handled with care while under a fume hood. MPS is a skin and eye irritant as well and may cause respiratory irritation if inhaled. Oleic acid, acetone, acetonitrile, chloroform, and toluene are flammable. Deuterated chloroform is a skin irritant and is potentially carcinogenic. All solid and liquid waste should be disposed of in properly labeled containers. Proper personal protective equipment including gloves, goggles, and a lab coat should be worn. The procedures outlined herein should be performed in a fume hood whenever possible. Although hazards associated with the CdSe-MPS particles are unknown, all NPs should be handled with care to avoid exposure.

■ RESULTS AND DISCUSSION

To monitor the approximate size distributions of the particles through the ligand exchange process, students obtain UV−visible spectra. Spectra recorded of the OLA-capped particles and the MPS-capped particles typically show little difference in excitonic absorption through the biphasic ligand exchange process as evidenced by the nearly identical absorption profiles in Figure 4. This indicates that there is typically little redistribution of nanoparticle size through the ligand exchange process. In the case shown, the full width at half-maximum (fwhm) for the exciton absorption peak for CdSe-OLA sample was ~36 nm, whereas the fwhm of the CdSe-MPS sample was

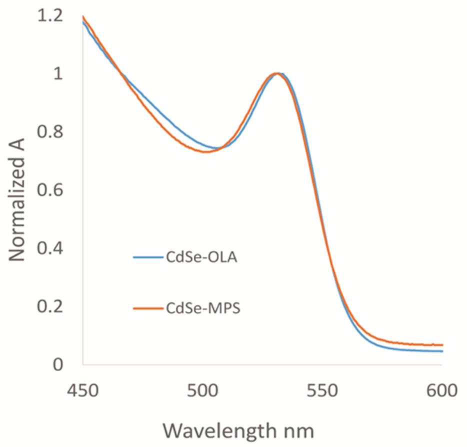

Figure 4. UV−visible absorption spectra of CdSe-OLA NPs in chloroform (blue) and CdSe-MPS NPs in water (red). Note that the OLA NPs can be dispersed in several organic solvents including toluene, hexanes, and chloroform.

~40 nm. Students are encouraged to estimate the sizes of the NP batches from the absorption spectra.[23,24] The approximation put forth by Yu et al. indicates the batches in Figure 4 have a diameter of ~2.7 nm.[23]

While it is important to note that the relative size distribution of the nanoparticles remains relatively unchanged through this ligand exchange process, the major focus of this laboratory experiment lies in proof of ligand binding to the nanocrystal core. Students are able to use ^{1}H NMR and FTIR spectra to discuss this aspect of the experiment. Figure 5 shows an overlay of student-obtained FTIR spectra for free OLA and CdSe-OLA. FTIR signatures that point to OLA attachment to the CdSe NPs include the disappearance of the characteristic strong stretch near 1700 cm^{-1}. For free OLA, this corresponds to the C═O stretch of the carboxylic acid. The disappearance of this stretch indicates that the carboxylate headgroup appears to be attached to the NP in a bridged or bidentate fashion. Other FTIR signatures that appear in free OLA are apparent in bound OLA lending further credence that OLA exists on the NP surface. Additionally, as is seen in Figure 6, when oleic acid is bound to the nanoparticles, the ligand ^{1}H NMR resonances appear broadened and in some cases seem to disappear. This is due to being tethered to a large object that rotates slowly on the NMR time scale.[22] Resonances close to the ligating atom(s) appear most broadened, while those further away tend to retain some fine structure.

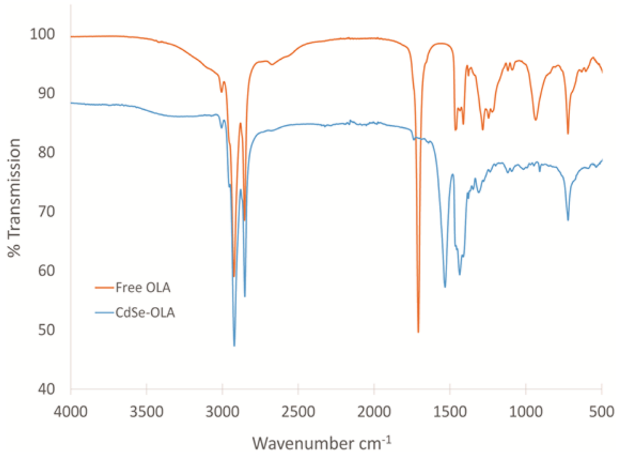

Figure 5. Student FTIR spectra of free OLA and CdSe-OLA. Note the near disappearance of the band at 1708 cm^{-1} indicating that the oleic acid is bound to the nanoparticle likely through a bidentate or bridged motif.

During the biphasic ligand exchange reaction, the strength of the Cd−S bond and high concentrations of MPS at the toluene/water interface drive the reaction forward. As with the characterization of CdSe-OLA, ligand binding is investigated via ^{1}H NMR and FTIR spectroscopy. In addition to the change in solubility of the NPs indicating the short, ionic MPS ligand has attached to the particles, evidence for successful ligand exchange lies in the disappearance of the thiol stretch near 2260 cm^{-1} indicating binding of MPS to the NPs through a thiolate linkage. Additionally, the CdSe-MPS nanoparticles show a strong S−O stretch near 1040 cm^{-1} indicating MPS has been successfully added to the NPs (Figure 7). The ^{1}H NMR spectra shown in Figure 8 also indicate successful ligand exchange as signals in the CdSe-MPS particles again appear broadened from the respective free MPS resonances.

Students were assessed by way of laboratory reports and a lab quiz. Students successfully demonstrated the ability to connect spectral data obtained to prove NP−ligand binding for the CdSe systems and for an analogous PbS system (see the lab quiz in Supporting Information). Students also demonstrated the ability to discuss the relation of their UV−visible spectra to potential size redistribution through the ligand exchange process. Finally, students were encouraged to emphasize the connection of postsynthetic modification of CdSe nanoparticles to current applications in solar energy. Prompts for the discussion of these topics is included in the Supporting Information.

■ TROUBLESHOOTING COMMON ISSUES

There are a few common complications that may arise during the course of this laboratory experiment. The most typical issue deals with precipitation of the CdSe NPs. Students often add too much initial solvent to their NP pellets thereby diluting the NP samples. In this instance, upon addition of the proper antisolvent, the NPs will no longer precipitate. If samples appear transparent before or after centrifugation, excess solvent can be easily removed via rotary evaporation to reconcentrate the NP sample, and the precipitation may be reattempted. In addition to complications arising due to dilute NP samples, in some instances gels have formed during centrifugation. In these circumstances, excess solvent can typically be removed and additional antisolvent can be added to afford significant precipitation.

Other complications that may arise are typically results of an overestimation of NP yield. In the case of overestimating the CdSe-MPS yield, the problem lies with obtaining the ^{1}H NMR spectrum for CdSe-MPS particles. Because all of the hydrogen atoms exist on carbon atoms very close to the CdSe core, the signals are significantly broadened and in dilute circumstances will be almost completely unapparent. To circumvent this issue and to resolve the signals, students must use a fairly concentrated solution of CdSe-MPS. This is a minor issue, however, due to the fact that the absence of free MPS in the NMR spectrum, the confirmation of a sulfonate in the FTIR, and the ease of particle dispersion in water all indicate that a successful ligand exchange has occurred.

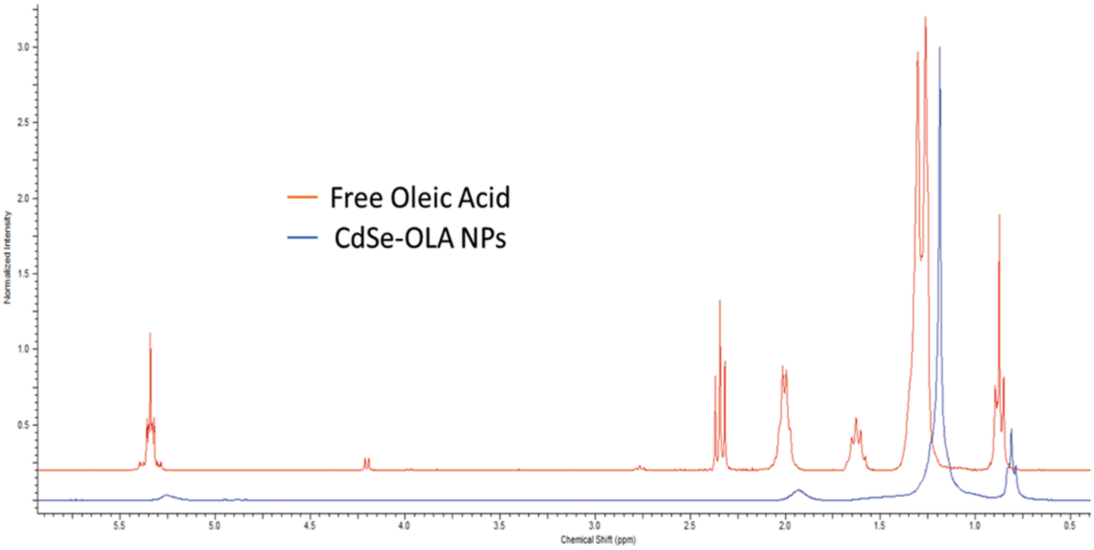

Figure 6. ^{1}H NMR spectra of unbound (free) oleic acid and CdSe-OLA nanoparticles.

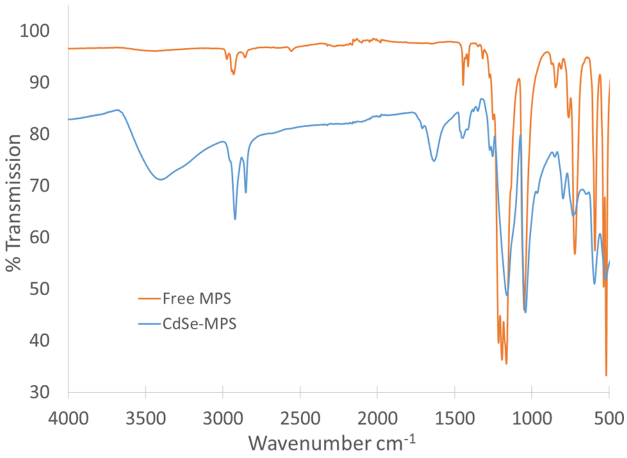

Figure 7. Representative student FTIR spectra of free MPS and CdSe-MPS NPs.

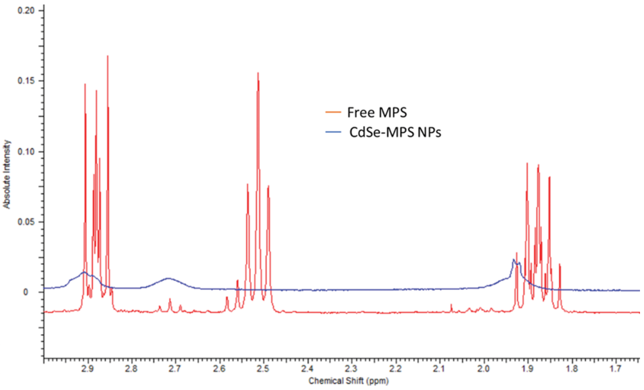

Figure 8. Representative student ^{1}H NMR spectrum of CdSe-MPS NPs in D_2O. Note that there are broad resonances near those of free-MPS indicating binding of MPS to the CdSe NPs.

Overestimation of the CdSe-OLA yield can lead to frustration in the ligand exchange reaction. Overestimation of the amount of CdSe-OLA in the ligand exchange reaction results in decreased concentrations of nanoparticles. This results in decreased kinetics of the exchange reaction as fewer NPs reach the biphasic interface.

■ CONCLUSION

While the synthesis of semiconducting nanomaterials has been reported for undergraduate laboratory exercises, by performing this experiment, students gain experience tailoring these nanomaterials toward a specific application. Synthesis and subsequent surface manipulation of semiconducting CdSe nanoparticles is accomplished in this multiweek experimental layout. Students synthesize CdSe-OLA via established procedures and perform a biphasic ligand exchange reaction to afford CdSe-MPS nanoparticles. These MPS-coated particles provide short-chain, ionically functionalized materials for possible future incorporation in solar cells. The use of NMR, FTIR, and UV−vis spectroscopy techniques allows students to prove ligand binding to the nanoparticle surface and to discuss possible size redistribution through the ligand exchange process. Finally, through the creation of student laboratory reports, students have the opportunity to connect their in-lab experience to global concerns regarding energy.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

The Supporting Information is available on the ACS Publications website at DOI: 10.1021/acs.jchemed.5b00847.

> Document containing laboratory handouts, a materials list, instructor notes, and other sample student NMR spectra (PDF, DOCX)

■ AUTHOR INFORMATION

Corresponding Author

*E-mail: jzemke@winona.edu.

Present Address

[†](J.F.) Cotter High School, Winona, Minnesota 55987, United States

Notes

The authors declare no competing financial interest.

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