Preparation of CdS Nanoparticles by First-Year Undergraduates

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Interest in nanotechnology is due to the unique properties of materials with dimensions less than 100 nm *(1)*. Educators and funding programs, such as the National Science Foundation's Nanotechnology in Undergraduate Education program, recognize that the incorporation of nanotechnology early in the college curriculum exposes students to cutting-edge research and prepares them for future careers in nanotechnology-related fields *(2–4)*.

This article describes a simple method for students to synthesize 5-nm CdS particles in a water-in-oil microemulsion during a three-hour general chemistry laboratory session. Quantum-size effects are observed through an obvious difference in colors of bulk and nanoparticle samples. Students gain an understanding of nanoscience and the use of surfactants—subjects that are not traditionally addressed in the general chemistry laboratory.

Students prepare two water-in-oil, or reverse, microemulsions in a hexane/1-propanol solution. Each contains micelles formed by hexadecyltrimethylammonium bromide (CTAB) surfactant molecules that surround droplets of aqueous $CdCl_2$ or Na_2S solutions. The chemical reaction of Cd^{2+}(aq) and S^{2-}(aq) to produce CdS(s) occurs when the two solutions are mixed and the micelles collide with each other. The small size of the micelles limits the growth of the CdS particles. Students prepare bulk CdS for comparison. This experiment is based on work by Agostiano et al. *(5)*.

Many excellent chemical education articles describe the synthesis and characterization of semiconductor nanoparticles, such as CdSe *(6, 7)*, CdS *(8, 9)*, PbS *(8)*, ZnS *(10)*, and ZnO *(11)*. Owing to their experimental techniques (inert atmosphere, H_2S gas, or elevated temperature) or the method of analysis (fluorescence, kinetic modeling), these experiments are more appropriate for upper-level laboratory courses. The synthesis method in this procedure is simple and analysis of CdS particles requires one UV–vis spectroscopy measurement for each lab group. The vivid color difference between bulk (orange) and nano-sized (yellow) particles makes the quantum effects easy to measure and visually appealing to first-year students.

Theory

Articles by Rosenthal et al. *(7)* and Hale et al. *(11)* contain useful information regarding the applications, synthesis, and theory of semiconductor nanoparticles. A brief synopsis is provided here but these articles should be consulted for a more complete description of nanomaterials.

Nanometer-sized CdS particles have a wider band gap than the bulk material owing to the quantum confinement of the electron–hole pair that forms upon absorption of a sufficiently energetic photon. The larger energy difference causes a shift in the visible absorbance spectrum of CdS with a corresponding color change from orange to yellow. Particle size can be calculated by the effective mass model that relates the change in band-gap energy to the radius of the particle *(12)*

$$E_g^{\text{nano}} \cong E_g^{\text{bulk}} + \frac{h^2}{8r^2}\left(\frac{1}{m_e^*} + \frac{1}{m_h^*}\right) - \frac{1.8e^2}{4\pi\varepsilon\varepsilon_0 r} \quad (1)$$

where E_g^{nano} is the band-gap energy of the nanoparticle as determined from the UV–vis absorbance spectrum; E_g^{bulk} is the band-gap energy of bulk CdS at room temperature; h is Planck's constant; r is the particle radius; m_e^* is the effective mass of conduction-band electron in CdS; m_h^* is the effective mass of valence-band hole in CdS; e is the elementary charge; ε is the relative permittivity of CdS; and ε_0 is the permittivity of a vacuum. A derivation of this equation is presented elsewhere *(7, 8)* and numerical values of all terms in eq 1 are provided in the Supplemental Material.W The band gap of nanoparticles can be calculated using the cutoff wavelength obtained from the absorbance spectrum of a translucent CdS solution, as shown in Figure 1.

A typical twenty-minute briefing limits the instructor to discussing only the basic information about energy bands and how a change in the band-gap energy affects the color and absorbance spectrum of CdS particles. The instructor notes in the Supplemental MaterialW suggests how to present these topics. Although short, this introduction was adequate for students to learn some of the differences between bulk and nanometer-sized materials. First-year students at this university had already prepared ferrofluids *(13)*, so they understood how surfactants restrict particle growth. For students without this background, a short explanation of micelles is

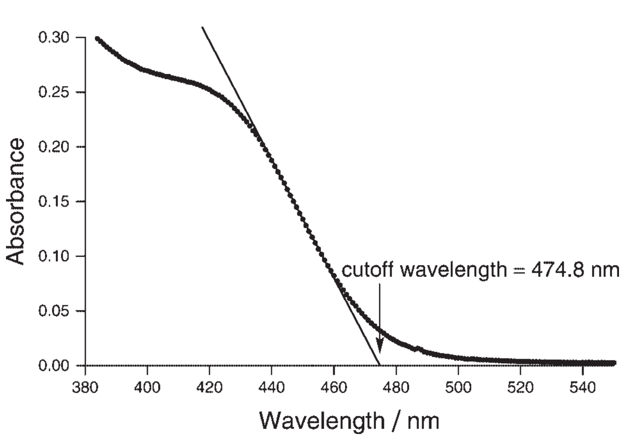

Figure 1. Absorbance vs wavelength spectrum of a CdS microemulsion with particle diameter of 5.2 nm. The cutoff wavelength is the *x* intercept of the linear portion of the spectrum.

provided in the Supplemental Material.[W] Many general chemistry textbooks describe micelles and an article has been published in this *Journal (14).*

Experimental

Chemicals were used as received from Fisher or Sigma Aldrich. 1-Pentanol was HPLC grade and other chemicals were reagent grade. Hexane consisted of a mixture of isomers with 55% 1-hexane. Deionized water was used to prepare aqueous solutions. For best results, the Na_2S solution should be prepared immediately prior to the laboratory session.

Students prepared bulk CdS particles by mixing 1 mL of 0.012 M $CdCl_2$ and 0.012 M Na_2S aqueous solutions together. Orange CdS crystals precipitated immediately. Observant students noted that upon mixing, the precipitate was briefly yellow colored before it turned orange. The appearance of this solution was compared to that of the CdS nanoparticle microemulsion prepared next.

Nanoparticles formed by mixing two microemulsions containing $CdCl_2$ (solution A) or Na_2S (solution B). Students prepared solutions A and B by combining 12.0 mL of hexane, 3.0 mL of 1-pentanol, and 0.60 g of CTAB in separate beakers. These mixtures were cloudy owing to the low solubility of CTAB. Students added 0.6 mL of 0.012 M $CdCl_2$ stock solution to solution A and 0.6 mL of 0.012 M Na_2S stock solution to solution B. Upon the addition of the aqueous component, the cloudy mixtures became colorless and transparent. Occasionally, Solution B remained slightly cloudy but this did not affect results. Students mixed solutions A and B to form a slightly cloudy yellow solution C that became translucent within a few minutes. The yellow color indicated the formation of CdS nanoparticles. A reference solution, D, used for spectrophotometric analysis was prepared in the same manner as solutions A and B except that water was substituted for the stock solution. Solutions A, B, C, and D were continuously stirred during preparation using a magnetic stir bar and stirring plate. Students analyzed their microemulsions using a UV–vis spectrophotometer. Each student received the absorbance versus wavelength data in an Excel spreadsheet similar to the data-analysis template included in the Supplemental Materials.[W]

Hazards

Cadmium compounds, sodium sulfide, pentanol, and hexane are toxic and should be handled with extreme care. Cadmium sulfide and cadmium chloride are carcinogens. Hexane and pentanol are flammable liquids. Owing to the presence of organic vapors and the odor of the Na_2S solution, students should perform this experiment in a fume hood. Students should wear gloves, goggles, and lab aprons or lab coats. All solutions and precipitates should be disposed of properly.

Results

Working in pairs, students prepared bulk and nanoparticle CdS samples and then recorded the absorbance spectrum of the microemulsion during a three-hour lab session. Figure 1 shows a typical absorbance spectrum for a microemulsion. Students can calculate the particle size using eq 1 and answer questions such as those provided in the Supplemental Materials.[W]

Conclusions

This experiment introduces students to quantum size effects—an important concept in nanotechnology. Students learn the relationships between colors, optical absorbance, and band-gap energy. Additionally, students are exposed to micelles and can see how their formation affects the CdS particles. First-year students learn the basics of quantum-size effects and are introduced to nanotechnology.

[W]Supplemental Material

The student laboratory handout, microemulsion parameters template, instructor notes, and a data-analysis template are available in this issue of *JCE Online.*

Acknowledgments

A grant from the National Science Foundation (award #0303986) provided funding for Florida Tech's Nanotechnology Laboratory for First-Year Undergraduates. Reviewers of this manuscript provided useful suggestions.

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