Synthesis and Optical Properties of Quantum-Size Metal Sulfide Particles in Aqueous Solution

J. M. Nedeljković,[1] R. C. Patel,[2] P. Kaufman, C. Joyce–Pruden, and N. O'Leary
Clarkson University, Potsdam, New York 13699-5810

During the past decade, "small-particle" research has become quite popular in various fields of chemistry and physics (*1*). The recognition of quantum-size effects in very small colloidal particles has led to renewed interest in this area (*2*). "Small particles" are clusters of atoms or molecules ranging in size from 1 nm to almost 10 nm or having agglomeration numbers from 10 up to a few hundred. In other words, small particles fall in size between single atoms or molecules and bulk materials. The agglomeration number specifies the number of individual atoms or molecules in a given cluster.

The research in this area is interdisciplinary, and it links colloidal science and molecular chemistry. The symbiosis of these two areas of research has revealed some intriguing characteristics of small particles. Colloidal science teaches us how to prepare very small semiconductor particles and how to stabilize these aggregates with respect to coagulation and formation of bulk material. The electronic properties of the particles, on the other hand, are related to their solid-state physics:

- band structures and band gap
- charge-carrier mobilities and lifetimes
- the electrochemical positioning of the band edge potential with respect to that of the solution

Of particular importance are quantum effects that arise when the size of the semiconductor particles becomes smaller than the Bohr radius of the first exciton state. Numerous important properties of the semiconductor, such as its optical absorption and luminescence emission, undergo drastic changes in this size domain.

Describing the States

The band gap of a semiconductor is by definition the energy necessary to create an electron (e^-) and hole (h^+) that are at rest with respect to the lattice and far enough apart that their Coulombic attraction is negligible.

The Confined Wannier Exciton

If one carrier approaches the other, they may form a bound state (Wannier exciton) approximately described by a hydrogenic Hamiltonian:

$$\hat{H} = -\frac{\hbar^2}{2m_h}\nabla_h^2 - \frac{\hbar^2}{2m_e}\nabla_e^2 - \frac{e^2}{\varepsilon|r_e - r_h|} \tag{1}$$

where m_h and m_e are the effective masses of the hole and electron; ε is the semiconductor dielectric constant; and r_e and r_h are the positions of the hole and the electron.

The Electronic Energy Levels

Several attempts have been made to calculate the electronic energy levels in quantum-size particles. Brus and associates (*3, 4*) have used the elementary electron–hole in a box model to account for the optical properties of small colloidal particles and thin films. The confined Wannier exciton Hamiltonian (eq 1) is used in the Schroedinger equation for the crystallite excited state.

$$\left(-\frac{\hbar^2}{2m_h}\nabla_h^2 - \frac{\hbar^2}{2m_e}\nabla_e^2 + V(r_e, r_h)\right)\Psi = E\Psi \tag{2}$$

For the inside R,

$$V(r) = -\frac{e^2}{\varepsilon r} + \text{polarization terms}$$

For the outside R, we get

$$V(r) = \infty$$

where R is the radius of the particle.

An Approximate Solution

The polarization terms are generally small (*4*) and can be neglected here. Since V depends on the relative position of the electron and hole, this problem cannot be transformed to the center of mass coordinate. Thus, it cannot be solved exactly. An approximate solution can be obtained by taking the solution for the first excited state of the particle in a box problem when assuming that the electron and hole are uncorrelated.

We seek an approximate solution for the lowest S eigenfunction of a particle in a spherical well of infinite depth. Following Flugge (*5*), these functions are

$$\Psi_n(r) = \left(\frac{C_n}{r}\right)\sin\left(\frac{n\pi r}{R}\right) \tag{3}$$

in spherical coordinates. This yields (see the appendix)

$$\Delta E = \frac{\pi^2\hbar^2}{2R^2}\left(\frac{1}{m_e} + \frac{1}{m_h}\right) - \frac{1.8e^2}{\varepsilon R} \tag{4}$$

where ΔE is the energy of the first excited state.

The first term in eq 4 corresponds to the sum of the confinement energies for the electron and the hole, while the second expression is their Coulomb interaction energy. The quantum confinement term dominates as R decreases, and the lowest excited state shifts to an energy that is greater than the band gap of the bulk semiconductor. This model is quite elementary and ignores two important effects in real crystallites: the coupling of electronic states to vibrations, and the structure of the crystallite surface.

Bulk Solids in Analogy with Polymers

It is easier to understand the transition from molecular to bulk properties from the point of view of MO theory. For example, the relationship between bulk silicon and the silicon atom is similar to the relationship between organic polymers and their constituent monomers. A piece of bulk

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[1] On leave from Boris Kidric Institute of Nuclear Sciences, Vinca, 11001 Belgrade, Yugoslavia.

[2] Author to whom correspondence should be addressed.

silicon is simply a normal, albeit extremely large, inorganic molecule.

Consider a small silicon crystallite growing from Si atoms. The Si atom has four sp hybrid orbitals which, in combination with neighboring orbitals, form doubly occupied bonding and empty antibonding orbitals. Each new atom adds one orbital to the bonding set and to the antibonding set for each bond formed. A spread of orbital energies develops within each orbital set, and the HOMO–LUMO separation in the molecule becomes the band gap of the solid. The electronic properties of quantum-size semiconductor clusters have led to remarkable discoveries: enhanced photoredox chemistry (*6*) and large nonlinear optical effects (*7*).

Quantum-size semiconductor particles have been prepared from many materials. Particularly well-studied examples are sulfides (*8–11*) and selenides (*6, 12*). The preparation often involves chemical methods. Care must be taken to arrest the precipitation to prevent the formation of large agglomerates. Thus, the synthesis is usually carried out in the presence of a suitable protective agent. In analogy with polymerization, the interaction of protective agents with clusters corresponds to termination of the polymerization reaction.

Due to its use in solar energy conversion and enhanced nonlinear optical properties, CdS is one of the most studied semiconductor materials. Bulk CdS is a direct band-gap semiconductor ($E_g = 2.53$ eV), with a relative dielectric constant of 5.7. Bulk PbS is a small band-gap semiconductor ($E_g = 0.41$ eV), and consequently the absorption onset occurs in the infrared range, at about 3,020 nm.

Experimental

All the experiments described here can be readily completed in a 3-h period, and they require commonly available chemicals.

Preparation of Colloidal Lead Sulfide

- ***Caution***: Hydrogen sulfide is toxic. The entire preparation must be carried out in a hood.

Materials

- a 3-neck 250-mL round-bottom flask
- 10 mL of 1% (w/w) of 10000–30000 molecular weight polyvinylalcohol (PVA)
- 2 mL of 1×10^{-2} M lead acetate
- 88 mL of distilled water
- 1 mL of H_2S gas, N_2, or Ar gas for purging
- a 5-mL syringe

The H_2S gas may be prepared by dissolving a small amount (approximately 0.2 g) of sodium sulfide in 5 mL of water contained in a 20-mL Erlenmeyer flask capped with a rubber serum cap and a vent needle. This solution is acidified by injecting 2 mL of 2 M hydrochloric acid. Enough H_2S can be safely generated by this procedure to serve over ten students or groups.

We have found it satisfactory for the instructor to demonstrate the sample preparation described below to the students, and then provide each student group with enough material for a spectral scan. This procedure eliminates the handling of H_2S by students. A detailed description of gas transfer by this syringe technique can be found in the literature (*13*).

Procedure

Combine 10 mL of 1% (w/w) of PVA, 88 mL of water, and 2 mL of 1×10^{-2} M lead acetate in the 250-mL round-bottom flask. Bubble $N_2(g)$ through the solution for 30 min. A disposable pipet connected to tygon tubing can be used. Then close the system to the atmosphere. Inject 1 mL of H_2S with a syringe through a rubber septum mounted on one neck of the flask. Immediately shake the flask vigorously for 3 to 5 min.

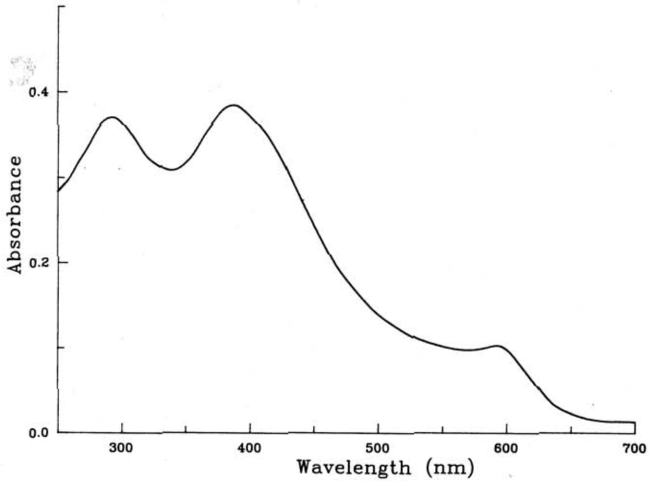

Figure 1. Optical absorption spectrum of 2×10^{-4} M PbS.

A wine-red color should be seen when the flask is held against a light source. Measure the absorption spectrum between the wavelengths of 250 and 700 nm (Fig. 1). This characteristic spectrum is associated with relatively uniform 4-nm PbS particles (*14–16*).

Repeat the experiment in the absence of PVA, and note the nearly black color due to the formation of bulk PbS. It will also become immediately apparent that suspensions of quantum-size particles are quite transparent. This is due to the low scattering of light. The turbidity is caused by the very small particle size. The bulk PbS sample is very different in this respect.

Preparation of Colloidal Cadmium Sulfide

Materials

- 0.8 mL of 1×10^{-2} M cadmium perchlorate
- 3 mL of 1% (w/w) polybrene (Sigma)
- 1 mL of freshly prepared 8×10^{-3} M sodium sulfide
- 15.2 mL of distilled water
- N_2 or Ar gas for purging
- ice bath
- stirplate and stirbar
- syringe
- two beakers, 50-mL and 1-L

Procedure

Combine 0.8 mL of 1×10^{-2} M cadmium perchlorate, 3 mL of 1% (w/w) of polybrene, and 15.2 mL of distilled water in a 50-mL beaker placed in an ice bath. Stir the solution on a stir plate while purging the solution with argon or nitrogen gas for 20 min. Adjust the gas flow rate to avoid excess foaming. When the purging is completed, very quickly inject 1 mL of 8×10^{-3} sodium sulfide solution.

The final solution should be a clear and pale yellow. Measure the absorption spectrum between the wavelengths of 250 and 550 nm (Fig. 2).

Calculating the Radius of Q-CdS

The blue shift in absorption due to confinement of charge carriers can be observed for both semiconductors. The band-gap energy of quantum-size CdS particles can be determined by substituting the experimentally determined absorption onset into the following equation. (See the intersection of the tangent with the wavelength axis in Figure 2.)

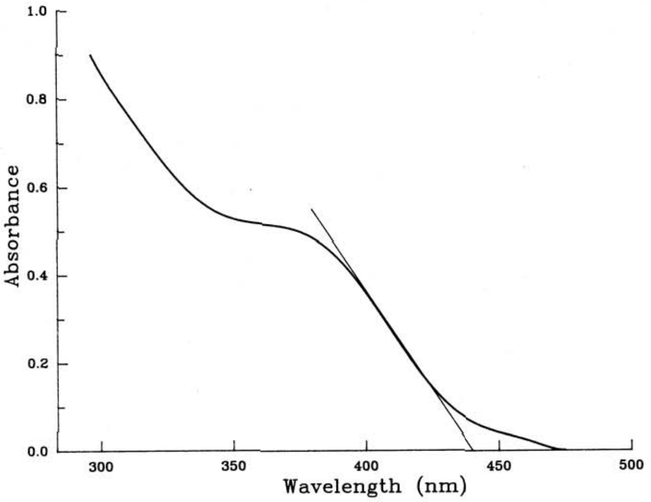

Figure 2. Optical absorption spectrum of 4×10^{-4} M CdS. The intercept at 439 nm corresponds to the absorption onset.

$$E_g = h\nu_g = h\frac{c}{\lambda_g} = \frac{(4.14 \times 10^{-15}\ \text{eVs})(2.99 \times 10^{8}\ \text{m/s})(10^{9}\ \text{nm/m})}{439\ \text{nm}} \tag{5}$$

It is easy to find the corresponding band-gap value (E_g = 2.83 eV) and the increase in band-gap energy due to quantum-size effects (see eq 4).

$$\Delta E_g = E_g(R) - E_g(\infty) = 0.3\ \text{eV}$$

In the quantum-size region, band-gap energies are extremely sensitive to the particle size and thus can be used for fairly accurate particle sizing. Effective masses of electrons and holes are known ($m_e = 0.19$ m, $m_h = 0.8$ m, where m is the free-electron mass), so substitution into eq 4 yields:

$$\begin{aligned}\Delta E_g &= 0.3\ \text{eV}\\ &= \left(\frac{1}{0.19} + \frac{1}{0.8}\right)\left(\frac{1.60 \times 10^{-19}\ \text{J/eV}}{9.11 \times 10^{-31}\ \text{kg}}\right)\left(\frac{\pi^2}{2R^2}\right)(6.58 \times 10^{-16}\ \text{eVs})^2\\ &\quad - \frac{1.8(1.60 \times 10^{-19}\ \text{A}^2\text{s}^2)^2\,(6.24 \times 10^{18}\ \text{eV/J})}{5.7(R)(4\pi)(8.85 \times 10^{-12}\ \text{A}^2\text{s}^2)}\end{aligned}$$

Rearranging, we get

$$[\text{R}]^2 + 1.5 \times 10^{-9}\ \text{m}\ [\text{R}] - 8.1 \times 10^{-18}\ \text{m}^2 = 0 \tag{6}$$

Solving eq 6, we get

$$R = 2.2\ \text{nm}$$

Thus,

$$D = 2R = 44\ \text{Å}$$

Summary

This experiment illustrates

- simple colloidal techniques for the preparation of two different types of quantum-size metal sulfide particles
- the blue shift of the measured optical absorption sectra when the particle size is decreased in the quantum-size regime
- use of a simple quantum mechanical model to calculate the particle size from the absorption onset measured for CdS

Literature Cited

1. Henglein, A. *Top. Curr. Chem.* **1988**, *143*, 113–180.
2. Henglein, A. *Chem. Rev.* **1989**, *89*, 1861–1873.
3. Brus, L. E. *J. Chem. Phys.* **1983**, *79*, 5566–5571.
4. Brus, L. E. *J. Chem. Phys.* **1984**, *80*, 4403–4409.
5. Flugge, S. *Practical Quantum Mechanics*; Springer: Berlin, 1971; Volume 1, p 155.
6. Nedeljković, J. M.; Nenadovic, M. T.; Micic, O. I.; Nozik, A. J. *J. Phys. Chem.* **1986**, *90*, 12–13.
7. Shmitt-Rink, S.; Miller, D. A. B.; Chemla, D. S. *Phys. Rev. B* **1987**, *35*, 8113–8125.
8. Fojtik, A.; Weller, H.; Koch, U.; Henglein, A. *Ber. Bunsenges. Phys. Chem.* **1984**, *88*, 969–977.
9. Nozik, A. J.; Williams, F.; Nenadovic, M. T.; Rajh, T.; Micic, O. I. *J. Phys. Chem.* **1985**, *89*, 397–399.
10. Lianos, P.; Thomas, J. K. *Chem. Phys. Lett.* **1986**, *125*, 299–302.
11. Herron, N.; Wang, Y.; Eckert, H. *J. Am. Chem. Soc.* **1990**, *112*, 1322–1326.
12. Steigerwald, M. C.; Alivisatos, A. P.; Gibson, J. M.; Harris, T. D.; Kortan, R.; Muller, A. J.; Thayer, A. M.; Duncan, T. M. Douglass, D. C.; Brus, L. E. *J. Am. Chem. Soc.* **1988**, *110*, 3046–3050.
13. McNally, J. P.; Leong, V. S.; Cooper, N. J. "Cannula Techniques for the Manipulation of Air-Sensitive Materials" In *Experimental Organometallic Chemistry: A Practicum in Synthesis and Characterization*, ACS Symposium Series No. 357; A. L. Wayda; M. Y. Darensbourg, Eds.; American Chemical Society, Washington, DC, 1987; p 6.
14. Gallardo, S.; Gutierrez, M.; Henglein, A.; Janata, E. *Ber. Bunsenges. Phys. Chem.* **1989**, *93*, 1080–1090.
15. Nenadovic, M. T.; Comor, M. I.; Vasic, V.; Micic, O. I. *J. Phys. Chem.* **1990**, *94*, 6390–6399.
16. Micic, O. I.; Rajh, T.; Comor, M. I.; Zec, S.; Nedeljković, J. M.; Patel, R. C. *Mat. Res. Soc. Symp. Proc.* **1991**, *206*, 127–132.

Appendix

Derivation of the Equation for the First Excited State

The Hamiltonian of the Wannier exciton can be written as

$$-\frac{\hbar^2}{2m_e}\nabla_e^2\Psi - \frac{\hbar^2}{2m_h}\nabla_h^2 - \frac{e^2}{\varepsilon\,|\mathbf{r}_e - \mathbf{r}_h|}\Psi + E_g\Psi = E\Psi$$

Assuming that the hole is in the center of the sphere,

$$-\frac{\hbar^2}{2m^*}\nabla^2\Psi - \frac{e^2}{4\pi\varepsilon_o\varepsilon R}\Psi = (E - E_g)\Psi$$

where

$$\frac{1}{m^*} = \frac{1}{m_e} + \frac{1}{m_h}$$

The Schrödinger equation in spherical coordinates is

$$\begin{aligned}&-\frac{\hbar^2}{2m^*}\left(\frac{1}{r^2}\frac{\partial}{\partial r}\left(r^2\frac{\partial\Psi}{\partial r}\right) + \frac{1}{r^2\sin\theta}\frac{\partial}{\partial\theta}\left(\sin\theta\frac{\partial\Psi}{\partial\theta}\right) + \frac{1}{r^2\sin^2\theta}\frac{\partial^2\Psi}{\partial\varphi^2}\right)\\ &\quad - \frac{e^2}{4\pi\varepsilon_o\varepsilon R}\Psi = (E - E_g)\Psi\end{aligned}$$

The solution given by the wave function for S orbitals is

$$\Psi_n = \frac{C_n}{r}\sin\frac{n\pi r}{R}$$

It follows for the Schrödinger equation

$$\frac{1}{r^2}\frac{\partial}{\partial r}\left(r^2\frac{\partial\Psi}{\partial r}\right) + \frac{8\pi^2 m^*}{h}\left(E - E_g + \frac{e^2}{4\pi\varepsilon_o\varepsilon R}\right)\Psi = 0$$

$$\frac{\partial\Psi}{\partial r} = \left(\frac{rC_n\frac{n\pi}{R}\cos\frac{n\pi r}{R} - C_n\sin\frac{n\pi r}{R}}{r^2}\right)r^2$$

$$r^2\frac{\partial\Psi}{\partial r} = C_n\frac{n\pi}{R}r\cos\frac{n\pi r}{R} - C_n\sin\frac{n\pi r}{R}$$

$$\begin{aligned}\frac{\partial}{\partial r}\left(r^2\frac{\partial\Psi}{\partial r}\right) &= C_n\frac{n\pi}{R}\left(\cos\frac{n\pi r}{R} - r\frac{n\pi}{R}\sin\frac{n\pi r}{R}\right) - C_n\frac{n\pi}{R}\cos\frac{n\pi r}{R}\\ &= -C_n r\left(\frac{n\pi}{R}\right)^2\sin\frac{n\pi r}{R}\end{aligned}$$

$$\frac{1}{r^2}\frac{\partial}{\partial r}\left(r^2\frac{\partial\Psi}{\partial r}\right) = -\frac{Cn}{r}\sin\frac{n\pi r}{R}\left(\frac{n\pi}{R}\right)^2 = -\Psi\left(\frac{n\pi}{R}\right)^2$$

$$-\left(\frac{n\pi}{R}\right)^2\Psi = -\frac{8\pi^2 m^*}{h}\left(E - E_g + \frac{e^2}{4\pi\varepsilon_o\varepsilon R}\right)\Psi$$

$$E = E_g + \frac{n^2\pi^2\hbar^2}{2R^2 m^*} - \frac{e^2}{4\pi\varepsilon_o\varepsilon R}$$

For $n = 1$, and conversion to SI units,

$$\Delta E = E - E_g = \frac{\pi^2\hbar^2}{2R^2}\left(\frac{1}{m_e}+\frac{1}{m_h}\right) - \frac{1.8e^2}{\varepsilon R}$$