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Enhanced Photoredox Chemistry in Quantized Semiconductor Colloids

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Optical effects due to size quantization have been observed for HgSe, PbSe, and CdSe colloids in water and acetonitrile with particle diameters of 20–100 Å. For diameters less than 50 Å, the optical absorption edge of HgSe and PbSe is blue shifted by several volts. The results are consistent with perturbation of the semiconductor band structure due to carrier confinement in very small particles resulting in an increase in the effective band gap. The redox potential of photogenerated carriers is greatly enhanced in such quantized semiconductor particles; reduction reactions that cannot occur in bulk materials can occur in sufficiently small particles. This has been demonstrated with H₂ evolution in 50-Å PbSe and HgSe colloids and CO₂ reduction in 50-Å CdSe colloids.

Quantization effects that arise from the confinement of charge carriers in small semiconductor particles are under active investigation.¹⁻⁸ These effects lead to a series of discrete states in the conduction and valence bands and to an increase of the effective band gap.

This, in turn, leads to enhanced redox potentials for photoexcited electrons and holes in very small semiconductor particles. In this Letter, we present both photochemical and photophysical evidence for large quantization effects in small-sized HgSe, PbSe, and CdSe colloids. To a first approximation, the energy of the quantized levels is inversely proportional to the effective mass and the square of the particle diameter. In our study, HgSe and PbSe colloids were used because they have very small electron effective masses (~ 0.05). Since the band gaps of HgSe and PbSe are both 0.3 eV, colloids consisting of large particle sizes (> 500 Å) are black and opaque; colloids with small particle sizes exhibit different colors depending on the size. CdSe, with an effective mass of 0.1 and a band gap of 1.7 eV, was studied for CO₂ reduction since it has a greater stability against photocorrosion compared to HgSe and PbSe.

Colloids with extremely small particle sizes were made by controlled precipitation of metal selenide in water or acetonitrile in the presence of stabilizers, such as (NaPO₃)₆, SiO₂, Nafion, styrene/maleic anhydride copolymer, and polyethylene glycol. All these colloids show large blue shifts in their absorption edge and in their emission spectra. All the stabilizers were checked for their resistance against reduction processes. For this purpose, Ti⁰ colloids were used as the reducing agent; its standard redox potential is -1.9 V vs. NHE. We found that only SiO₂ and Nafion are very stable in the presence of Ti⁰, and therefore only these stabilizers were used to study photoredox chemistry.

SiO₂ colloids⁹ with a particle diameter of 50 Å were used for the preparation of selenide colloids in water. The colloids were prepared in water-alcohol mixtures at -20 °C, and the sols were then filtered through membrane filters with a pore size of 100 Å. For HgSe, 20 mL of solution containing 2×10^{-4} M HgCl₂, 6×10^{-3} M SiO₂, and 2×10^{-4} M CH₃COONH₄ (buffer) were

bubbled with argon for 30 min. The argon stream was stopped and 0.1 mL of H₂Se gas was injected into the solution which was vigorously stirred. Argon was then bubbled again to remove excess H₂Se from the solution.

HgSe colloids were stable for weeks; they become brown-black upon warming to 95 °C. For aqueous PbSe and CdSe colloids, Pb(CH₃COO)₂ and Cd(ClO₄)₂ were the starting salts. These colloids were stable for days.

HgSe and PbSe colloids in acetonitrile were prepared by injecting 0.1 mL of H₂Se into 20 mL of a deaerated solution containing 0.1% Nafion (Solution Technology, Inc.) and 2×10^{-4} M HgCl₂ or Pb(CH₃COO)₂; the solution of Pb(CH₃COO)₂ contained 2% water. Excess H₂Se was removed by bubbling with argon. The particle size was smaller in acetonitrile than in water prepared with the same stabilizer. It is important to exclude light and air during the preparation of these colloids. The particle sizes of the colloids were determined by diluting and then drying the sols, and examining them with transmission electron microscopy. The particle sizes in acetonitrile were typically 20–30 Å; the colloids were prepared just before they were studied. For photochemical experiments the colloids were illuminated with an Osram XBO 150-W xenon lamp.

Absorption and emission spectra of HgSe colloids are shown in Figure 1. In Figure 1a, the absorption spectrum is of HgSe in water with particle diameters of about 50–100 Å and 1000 Å; in Figure 1b the absorption and emission spectra are shown for HgSe in acetonitrile with particle diameters of about 20–30 Å. The spectra show large shifts in the fundamental absorption edge reflecting an increase in the effective band gap. For HgSe with 20–30-Å particles the band edge shift is about 2.8 eV (bulk band gap = 0.35 eV). The photoluminescence emission spectrum of the HgSe colloid shows an emission peak at 430 nm (2.88 eV) with excitation ranging from 270 to 360 nm; the emission spectrum is not dependent on the wavelength of the exciting light which indicates a rather uniform particle size distribution. These emission spectra support the conclusion that the absorption shift is due to an increased effective band gap.

Absorption spectra of PbSe colloids with large and small particles in acetonitrile are shown in Figure 2. Again, the effects of size quantization are clearly seen. The photoluminescence emission spectrum of PbSe/Nafion in acetonitrile shows the same features as that for HgSe except the intensity for the same concentration of colloids is ten times less than for HgSe.

Radiation chemical processes provide a method for determining the redox potentials of colloids.^{10,11} A transient, strongly negative redox potential can be created in the solution by pulse radiolysis,

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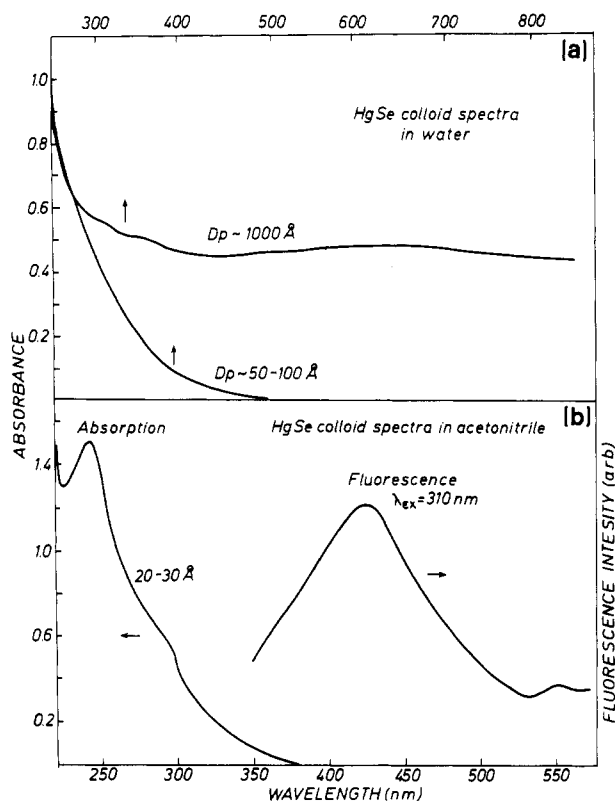


Figure 1. (a) Optical absorption spectra of HgSe colloids in water (2×10^{-4} M) with SiO_2 stabilizer (6×10^{-3} M, 50 Å) with 1000-Å and 50-100-Å particle sizes; (b) optical absorption and fluorescence spectra of HgSe (2×10^{-4} M)-Nafion (0.025%) in acetonitrile prepared with 20-30-Å particle sizes.

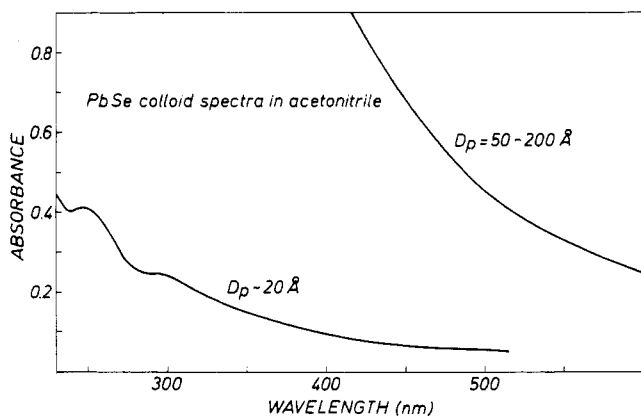
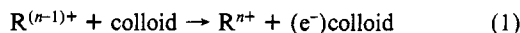


Figure 2. Comparison of optical absorption spectra of PbSe colloids with particle sizes 50-200 Å and 20 Å.

resulting in charge transfer between the redox couple $[\text{R}^{n+}/\text{R}^{(n-1)+}]$ and the semiconductor particles:



Experiments were performed wherein various redox couples generated by pulse radiolysis were produced in the presence of PbSe and HgSe colloids with 50-Å particle size. The position of the lowest empty electronic state of these colloids was determined by observing which redox couples could inject electrons into the semiconductor particles. The results are summarized in Figure 3, which shows the redox couples studied and the deduced positions of the empty electronic states for 50-Å-diameter PbSe and HgSe. In this figure, only redox couples above the indicated energy levels for the two semiconductors could inject electrons into the respective colloids; the uncertainty in the electronic energy positions of the semiconductors is also indicated in the figure. Thus, for example, for PbSe, MV^+ could not inject electrons into 50-Å particles but could do so for large particles ($D_p > 1000$ Å). This again reflects

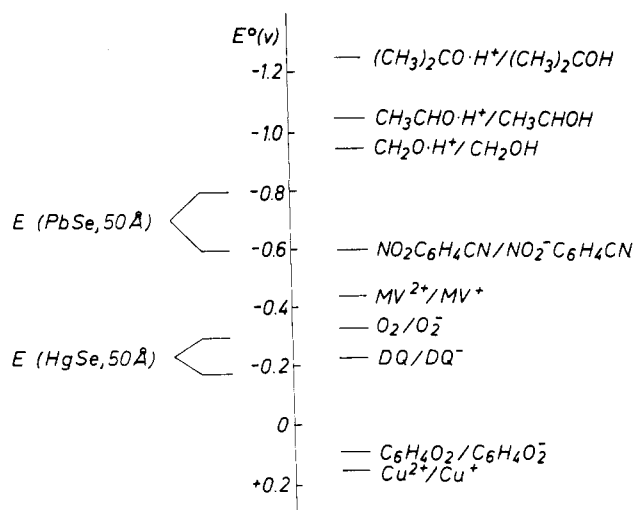


Figure 3. Energy level diagram for equilibration of 50-Å HgSe and PbSe semiconductor particles with redox couple potentials in aqueous solution.

the effects of size quantization in the 50-Å particles.

Since quantization in small particles creates energy levels that can accommodate high-energy electrons with enhanced reduction potentials the probability is enhanced for cathodic corrosion processes to occur when these energy levels are populated, either through photon absorption or via electron injection from highly reducing radicals produced during pulse radiolysis. Such cathodic corrosion would be in competition with other electron-transfer reactions. For example, for PbSe colloids we see clear evidence for Pb^0 formation in a two-step process in the presence of $\dot{\text{C}}\text{H}_2\text{OH}$ or $\dot{\text{C}}\text{H}_3\text{OH}$ radicals. The first step involves electron injection and storage in PbSe, followed by reduction of PbSe to Pb^0 .

Although the cathodic corrosions of HgSe and PbSe colloids are important processes during illumination of colloids in water or acetonitrile, corrosion can be suppressed if a fast electron acceptor is present. For example, we found that MV^{2+} is preferentially reduced to MV^+ in UV illuminated aqueous solutions (pH 9) of PbSe/ SiO_2 colloids in the presence of triethanolamine as a hole scavenger. This reduction does not occur with large PbSe particles ($D_p > 1000$ Å).

More important examples of photoreduction processes that could only be achieved with small particles of a given semiconductor were also obtained. These involved H_2 evolution with aqueous colloids of HgSe ($D_p < 50$ Å) and PbSe ($D_p < 50$ Å) and CO_2 reduction to formic acid from CO_2 -saturated aqueous solutions with CdSe colloids ($D_p < 50$ Å). In the former two cases, the initial quantum efficiency is about 1-2% in the presence of EDTA (pH 6) or S^{2-} (pH 8.5) as hole scavengers. It is to be noted that for these hydrogen evolution reactions a metal catalyst was not present. Hydrogen was detected by gas chromatography using a 154D Perkin-Elmer instrument. In the latter case, the efficiency of CO_2 reduction was not determined, but the formation of formic acid was positively detected by the Grant analytical method.¹² Large-particle-sized CdSe colloids did not yield formic acid under the same experimental conditions.

We believe these results represent the first demonstration of enhanced photoredox chemistry produced by size quantization effects in very small semiconductor particles. Enhanced power conversion efficiencies may also be feasible with these types of particles.¹³

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