16

PHOTOCHEMISTRY OF SEMICONDUCTOR COLLOIDS:
PROPERTIES OF EXTREMELY SMALL PARTICLES OF Cd_3P_2 AND Zn_3P_2 ☆

H. WELLER, A. FOJTIK [1] and A. HENGLEIN

Hahn-Meitner-Institut für Kernforschung Berlin,
D-1000 Berlin 39, Federal Republic of Germany

Extremely small particles of Zn_3P_2 and Cd_3P_2 were prepared as colloids in aqueous solution and in the solid state. The onset of absorption and the fluorescence band, which lie in the infrared for the macrocrystalline materials, can be shifted through the whole range of the visible by changing the particle size. Fluorescence quantum yields of 15% were obtained. The optical effects are due to the strong perturbations in the electronic energy levels as a consequence of carrier confinement (Q-type materials). The solid particles, which fluoresce strongly, can be redissolved without changes in size. Methylviologen quenches the fluorescence and promotes the photoanodic dissolution.

PHOTOCHEMISTRY OF SEMICONDUCTOR COLLOIDS:
PROPERTIES OF EXTREMELY SMALL PARTICLES OF Cd_3P_2 AND Zn_3P_2 [☆]

H. WELLER, A. FOJTIK [1] and A. HENGLEIN

Hahn-Meitner-Institut für Kernforschung Berlin,
D-1000 Berlin 39, Federal Republic of Germany

Extremely small particles of Zn_3P_2 and Cd_3P_2 were prepared as colloids in aqueous solution and in the solid state. The onset of absorption and the fluorescence band, which lie in the infrared for the macrocrystalline materials, can be shifted through the whole range of the visible by changing the particle size. Fluorescence quantum yields of 15% were obtained. The optical effects are due to the strong perturbations in the electronic energy levels as a consequence of carrier confinement (Q-type materials). The solid particles, which fluoresce strongly, can be redissolved without changes in size. Methylviologen quenches the fluorescence and promotes the photoanodic dissolution.

1. Introduction

Semiconductors experience large changes in the position of their electronic energy levels when they are made in the form of small colloidal particles [1–9]. The perturbations are due to carrier confinement resulting in an increase in the energies of the exciton and the band gap. In this "Q state", where a gradual transition from semiconductor to molecular material takes place, the optical and photocatalytic properties of the material are significantly different from those of the macrocrystal. The new phenomena which can be observed have been demonstrated recently for Q-CdS [6]. The color of the luminescence can be varied from red to blue. As particles of different size can be distinguished by their absorptions, magic agglomeration numbers in a size distribution of small colloidal particles may be recognized. Q-CdS was also prepared in the solid state as a strongly fluorescing material which could be redissolved in water without changes in particle size. Similar effects have been de-

scribed for ZnS [5]. More recently, Q materials of $ZnSe_2$, $CdSe_2$, In_2S_3 and In_2Se_3 have also been prepared in this laboratory [10].

In the present paper, we report some properties of Q-type cadmium phosphide and zinc phosphide. In the macro state, these materials are black semiconductors with band gaps of 1.3 eV (Zn_3P_2) and 0.5 eV (Cd_3P_2) [11]. Enormous perturbations are observed when these materials are prepared as small particles in solution or in the solid state. Most important is the fact that the fluorescence of the Q materials is much stronger than that of the macro-crystals and that of Q-CdS. Practical application of such materials in electro-optical devices may become possible.

The colloids were prepared in aqueous solution as described for CdS [6], using hexametaphosphate as complexing agent and phosphine instead of hydrogen sulphide. Various particle sizes were obtained by controlled growth from extremely small nuclei at different phosphine concentrations and temperatures. The color of the various Cd_3P_2 colloids prepared was black, brown-red, deep red, orange, yellow, and almost white (with decreasing particle size).

The solid materials were obtained by removal of 80% of the solvent in a rotary evaporator at 40°C as described for CdS [6]. The colloids flocculated in the form of light flakes (larger particles) or almost liquid

---

flakes (small particles) which had a remarkable tendency to stick to the glass walls. Centrifugation, washing and drying of the precipitate led to powders of the above colors. The details of the preparations will be described elsewhere [10].

2. Results

Figs. 1 and 2 show absorption and fluorescence spectra of colloidal solutions of Zn_3P_2 and Cd_3P_2. The Zn_3P_2 solution in fig. 1 had a yellow tinge. The absorption spectrum contained a maximum at 360 nm, and the fluorescence spectrum had a sharp band at wavelengths where the steep increase in absorption occurs. In the case of Cd_3P_2, a maximum in the absorption spectrum was present for the smaller particles (fig. 2a). With increasing particle size, the onset of absorption shifted towards longer wavelengths. Some structure was still observed in spectrum b. The fluorescence band was also shifted towards longer wavelengths with increasing particle size. It often had a shoulder (for example at 600 nm, curve a'). The decay time of fluorescence was shorter than 2 ns. These effects are quite similar to those observed for CdS solutions of different particle size [6]. However, the quantum yields of fluorescence were much greater. They amounted to 15% for the smaller particles a, b, c, and became smaller for particles of larger size (10% for particle d).

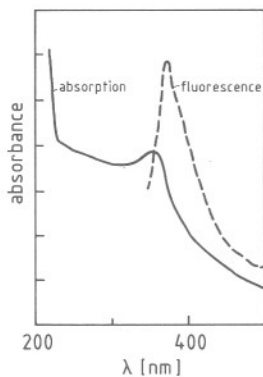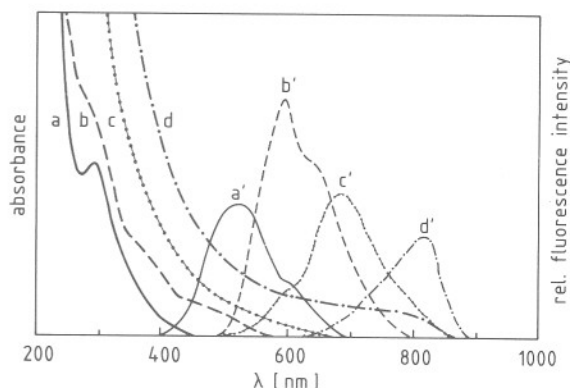Gram amounts of the solid Q materials in fig. 2

Fig. 2. Absorption (a, b, c, d) and fluorescence (a', b', c', d') spectra of colloidal solutions of cadmium phosphide of different particle size. Color of solutions: (a) colorless; (b) yellow-green; (c) orange; (d) red. Excitation of fluorescence at 300 nm.

were obtained from 1–2 ℓ of solution as described above. The powders were stabilized by 30% hexametaphosphate as described for CdS [6]. The stabilizing material is necessary to keep the small particles from coming into close contact, as otherwise the quantum-mechanical effects due to the confinement of charge carriers disappear (in other words, the particles form black materials in the absence of the stabilizer). The solid powders showed strong fluorescence in all colors through the visible depending on particle size. The quantum efficiency of fluorescence of the solid particles was close to one. They could be redissolved to yield colloidal solutions, the absorption and fluorescence spectra of which were practically identical to the spectra before separation of the particles. They also dissolved in small concentrations in styrene to yield fluorescencing solutions.

No changes in absorption were observed when Q-Cd_3P_2 was illuminated in a deaerated solution. However, in the presence of air, the colloid was decomposed. This process, which leads to Cd^{2+} and phosphate ions, could be followed readily by measuring the optical absorption spectrum at various times of illumination. Fig. 3 shows the absorbance of an illuminated sol as a function of time. Fig. 3 also contains the results obtained from illumination of an aerated solution of 3×10^{-4} M methylviologen (1,1'-dimethyl-4,4'-bispyridinium dichloride, MV^{2+}). It is seen that the rate of decomposition of the colloid is

Fig. 1. Absorption and fluorescence spectrum of extremely small particles of zinc phosphide; excitation of fluorescence at 300 nm.
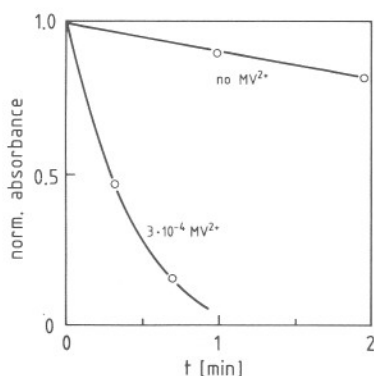
Fig. 3. Optical absorption of a Cd_3P_2 colloid as a function of time of illumination ($\lambda = 366$ nm) in the absence and presence of MV^{2+}. Aerated solution.
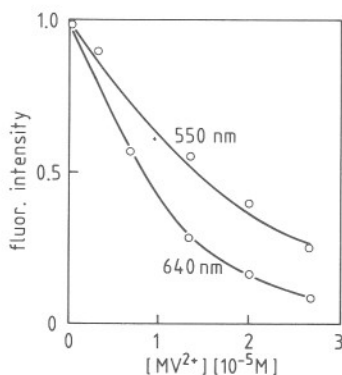

Fig. 4. Normalized intensity of fluorescence of two Cd_3P_2 samples (with the fluorescence maximum at 550 and 640 nm) as a function of the concentration of added methylviologen.

strongly enhanced by this additive. Similar observations have previously been made with sols of cadmium sulfide [12]. MV^{2+} also quenches the fluorescence of Cd_3P_2. Fig. 4 shows typical quenching curves (fluorescence intensity as a function of MV^{2+} concentration). The smaller the particle size, the greater the MV^{2+} concentration required to achieve the same degree of quenching.

3. Discussion

As in the case of CdS [6], we ascribe the maxima in the absorption spectra of Zn_3P_2 and Cd_3P_2 to

transitions from the valence band to the ground state of a strongly distorted exciton. In solutions of larger particles, the broad distribution in particle size does not allow one to resolve the absorption maximum for these transitions. Structure in the absorption spectrum may be due to preferential agglomeration numbers in the size distribution. Such "magic" numbers may arise if the colloid is formed under conditions where Ostwald ripening of the particles is slow as compared to particle association [6]. The size of the particles in figs. 1 and 2 is in the 1−2 nm range as inferred from filtration experiments and electron microscopic observations. Unfortunately, the latter experiments did not yield pictures of good contrast which would allow one to obtain a histogram.

A rough calculation of the particle size was carried out using the method described in ref. [10]. The electronic energy of an exciton was calculated assuming that a positive hole is in the center of a spherical particle, and assuming that the potential energy of the electron is infinite at distances greater than the radius of the particle. Using a band gap energy of 0.55 eV for macrocrystalline Cd_3P_2, a reduced effective mass of the exciton of 0.0454 and a high-frequency dielectric constant of 15.5 [11], one finds that strong optical effects occur in Cd_3P_2 at much greater particle sizes than in CdS. The range of particle sizes corresponding to the colloids in fig. 2 is rather narrow as the energy of the excitonic state considerably changes with particle size in this range. A radius of 1.1 nm was obtained for the colorless particles (fig. 2a) and 2.1 nm for the red particles (fig. 2d). An undisturbed exciton in macrocrystalline Cd_3P_2 has a radius of about 18 nm.

The quenching of the fluorescence by MV^{2+} is attributed to the transfer of an electron from the excited colloidal particle to form MV^+. Infact, when a deaerated solution of yellow Cd_3P_2 was illuminated in the presence of MV^{2+}, the blue color of half reduced methylviologen developed. This electron transfer to MV^{2+} was observed for all the colloids in fig. 2. It is concluded that the potential of the lowest electronic level in these particles is more negative than −0.4 V (i.e. more negative than the reduction potential for MV^{2+}). In aerated Cd_3P_2 solution, the photoanodic dissolution takes place

$$Cd_3P_2 + 4O_2 \xrightarrow{\text{light}} 3Cd^{2+} + 2PO_4^{3-} .$$
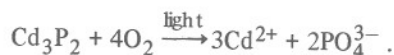
We explain this by the mechanism already discussed for CdS particles [7]. Oxygen removes electrons, thus giving the positive holes a chance to oxidize phosphide anions partially. Further oxidation of the damaged phosphide anions occurs either by O_2 or O_2^- (the latter being formed in the electron pick-up). In the presence of MV^{2+} the removal of electrons occurs more efficiently, thus preventing the holes from recombining and in this way increasing the rate of dissolution.

References

[1] R. Rossetti, S. Nakahara and L.E. Brus, J. Chem. Phys. 79 (1983) 1086.

[2] L.E. Brus, J. Chem. Phys. 79 (1983) 5566.

[3] R. Rossetti, J.L. Ellison, J.M. Gibson and L.E. Brus, J. Chem. Phys. 80 (1984) 4464.

[4] L.E. Brus, J. Chem. Phys. 80 (1984) 4403.

[5] H. Weller, U. Koch, M. Gutiérrez and A. Henglein, Ber. Bunsenges. Physik. Chem. 88 (1984) 649.

[6] A. Fojtik, H. Weller, U. Koch and A. Henglein, Ber. Bunsenges. Physik. Chem. 88 (1984) 969.

[7] A. Henglein, Pure Appl. Chem. 56 (1984) 1215; in: Modern trends of colloid science in chemistry and biology, ed. H.-F. Eicke (Birkhäuser, Basel, 1985).

[8] F. Williams and A.J. Nozik, Nature 311 (1984) 4821.

[9] A.J. Nozik, F. Williams, M.T. Nenadović, T. Rajh and O.I. Mićić, J. Phys. Chem. 89 (1985) 397.

[10] A. Fojtik, A. Henglein and H. Weller, Ber. Bunsenges. Physik. Chem., to be published.

[11] Landolt–Börnstein, numerical data and functional relationships in science and technology, New Series, Vol. 17f, (Springer, Berlin, 1983) pp. 183, 193.

[12] A. Henglein, J. Phys. Chem. 86 (1982) 2291.