



**PHOTOCHEMISTRY OF SEMICONDUCTOR COLLOIDS.  
SIZE QUANTIZATION EFFECTS IN Q-CADMIUM ARSENIDE <sup>☆</sup>**

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Extremely small particles of  $\text{Cd}_3\text{As}_2$  were prepared as colloids in aqueous solution and in the solid state. While macrocrystalline  $\text{Cd}_3\text{As}_2$  is almost a metal absorbing in the far-infrared (band gap = 0.1 eV), the small particles have absorptions and fluorescences in the visible or near-infrared depending on the particle size. The solid particles can be redissolved without change in size, and are photoanodically decomposed in the presence of air. Methyl viologen is reduced by visible light in the presence of small (few nm diameter) particles of  $\text{Cd}_3\text{As}_2$ , this reduction being enhanced by excess arsine. Methyl viologen quenches the fluorescence and promotes the photoanodic dissolution of the particles.

## PHOTOCHEMISTRY OF SEMICONDUCTOR COLLOIDS. SIZE QUANTIZATION EFFECTS IN Q-CADMIUM ARSENIDE<sup>\*</sup>

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### 1. Introduction

It has been reported that cadmium phosphide,  $\text{Cd}_3\text{P}_2$ , can be prepared as a colloid in aqueous solution in the form of extremely small particles and that these particles can also be obtained in the solid state by careful evaporation of the solvent [1]. These small semiconductor particles have unusual optical properties, which are caused by the strong perturbations of the electronic energy levels due to carrier confinement [2,3]. In fact, the conduction band in these particles degenerates into a system of rather widely spaced electronic levels; these particles represent a transition from semiconductor to molecular properties. We designate compounds showing such size quantization effects as "Q-materials". They generally fluoresce strongly and have photocatalytic properties.

After the preparation and investigation of cadmium phosphide, it was a natural step to synthesize the homologous cadmium arsenide. The procedure which was first described for CdS [3] was applied. Hydrogen arsenide was injected into a deaerated solution of

$\text{Cd}(\text{ClO}_4)_2$  in the presence of metaphosphate. The solution has to be alkaline as arsenides decompose in acidic media. Moreover, the alkalinity determines the rate of the precipitation reaction and therefore the size of the colloidal particles formed. The metaphosphate complexes cadmium ions and prevents them from being precipitated as hydroxide in alkaline solution.

$\text{Cd}_3\text{As}_2$  is a black material in the macrocrystalline state. Its energy gap is only 0.1 eV [4], i.e.  $\text{Cd}_3\text{As}_2$  is almost a metal. It is shown here that the size quantization effects in this material are very pronounced as the band gap can be shifted by many electron volts through the whole range of the visible spectrum, i.e. samples absorbing anywhere – as desired – in the visible or in the infrared can be made by changing the size of the particles. As already found for  $\text{Cd}_3\text{P}_2$ , the small  $\text{Cd}_3\text{As}_2$  particles luminesce with the colour of the emitted light depending on the size of the particles.

### 2. Results and discussion

A colorless sample of  $\text{Cd}_3\text{As}_2$  was prepared by injecting half the stoichiometric amount of arsine into a deaerated  $2 \times 10^{-4}$  M  $\text{Cd}(\text{ClO}_4)_2$  solution at  $\text{pH} = 11.5$ . The solution also contained  $3 \times 10^{-4}$  M sodium hexametaphosphate. The reaction was allowed to pro-

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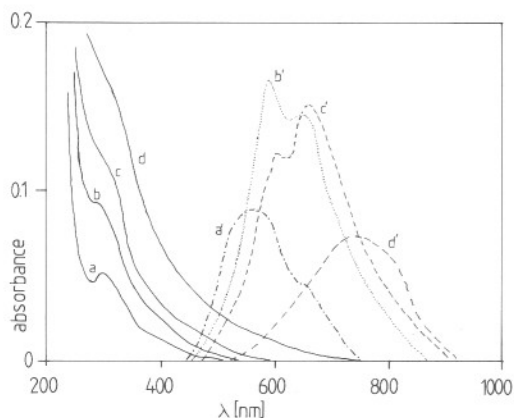


Fig. 1. Absorption (full line) and fluorescence (dashed) spectra of  $\text{Cd}_3\text{As}_2$  particles of different size. (a) Fresh solution; (b) after 1 h; (c) after 4 h; (d) after 1 day.

ceed for 10 min. The unreacted arsine was then removed by evacuation with a water pump. The amount of  $\text{Cd}_3\text{As}_2$  formed was determined iodometrically. It corresponded to 40% conversion of the arsine added originally.

The absorption spectrum (fig. 1) contains a maximum at 300 nm which is attributed to an exciton transition band. The fluorescence spectrum contains a maximum at 560 nm and a shoulder at 660 nm.

At  $\text{pH} = 11.5$ , the absorption spectrum does not change substantially over several hours, i.e. the particles do not grow rapidly. The evaporation procedure could therefore be applied to obtain the particles in the solid state in the form of a pale powder. This powder luminesced green-yellow upon illumination with UV light. The powder could be redissolved in water to yield a solution with the original spectrum in fig. 1a. The powder was stable for months. The small  $\text{Cd}_3\text{As}_2$  particles are prevented from getting into close contact by the hexametaphosphate matrix which was formed upon the evaporation of the solvent. Boiling of a solution resulted in a black precipitate.

Using different amounts of arsine and different temperatures during precipitation at  $\text{pH} = 11.5$ ,  $\text{Cd}_3\text{As}_2$  samples of yellow, orange, red and grey color (increasing particle size) were prepared in solution as well as in the solid state. All these materials fluoresced, the wavelengths of the emitted light being red-shifted with increasing particle size. The quantum yields of fluorescence in solution were about 10%.

Using  $\text{pH} = 12.0$  in the precipitation procedure, solutions were obtained which changed their color within a few hours. The particles grew more rapidly in these solutions. At first the spectrum of the solution resembled that of a solution prepared at  $\text{pH} = 11.5$ , as described above, see curve a in fig. 1. The spectra at various times of aging are also shown in fig. 1. It is seen that the intensity of fluorescence increases up to a maximum at 1 to 4 h. The lower intensity recorded at longer times is probably due to the decreased sensitivity of the detection system at longer wavelength. The shoulder at 660 nm present in spectrum 1a' grows into a maximum upon aging and becomes stronger than the first maximum. The absorption spectrum is unstructured at longer times. The fluorescence is suggested to be emitted upon the recombination of charge carriers trapped at defect sites. The fact that two maxima are present may be taken as an indication for the existence of two types of defect states.

The Q- $\text{Cd}_3\text{As}_2$  colloids undergo many of the typical photoreactions which have been found previously in our laboratory for other semiconductor colloids with band gaps in the visible such as CdS [5–7]. They are photoanodically dissolved upon illumination in the presence of air, the quantum yields being 0.01 to 0.025 molecules  $\text{Cd}_3\text{As}_2$  decomposed per photon absorbed. The products of the photoanodic dissolution are  $\text{Cd}^{2+}$  and  $\text{AsO}_4^{3-}$  ions. In the presence of  $3 \times 10^{-4}$  M methyl viologen,  $\text{MV}^{2+}$ , the rate of this photo-dissolution is enhanced by a factor of 15. As in the case of CdS [6], a mechanism is suggested with the following steps: (1) formation of electrons and positive holes by light absorption; (2) reaction of the electrons with adsorbed  $\text{MV}^{2+}$ ; (3) reoxidation of semi-reduced methyl viologen,  $\text{MV}^+$ , by oxygen; (4) oxidation of arsenide by positive holes to yield  $\text{As}^{2-}$  radicals; (5) further oxidation of  $\text{As}^{2-}$  by oxygen to yield  $\text{AsO}_4^{3-}$ .

The fluorescence of  $\text{Cd}_3\text{As}_2$  is quenched by methyl viologen at all wavelengths. However,  $\text{MV}^{2+}$  is more efficient in quenching the fluorescence of the second maximum at longer wavelengths than that of the first maximum. In the case of a  $3 \times 10^{-5}$  M solution of orange  $\text{Cd}_3\text{As}_2$ , for example,  $3.0 \times 10^{-6}$  and  $4.5 \times 10^{-6}$  M  $\text{MV}^{2+}$  was required to decrease the fluorescence intensities by 50% in the first and second maximum, respectively. This finding corroborates the

above conclusions according to which different fluorescence centres exist in the small particles.

When a deaerated solution of orange  $\text{Cd}_3\text{As}_2$  is illuminated no decomposition of the colloid takes place. In the presence of  $\text{MV}^{2+}$ , the blue color of  $\text{MV}^+$  appears and the colloid is degraded. The rate of reduction of  $\text{MV}^{2+}$  is increased when excess arsine is present. We attribute this to the scavenging of positive holes by arsine. The recombination of charge carriers is diminished in this way, i.e. more electrons succeed in reacting with  $\text{MV}^{2+}$  molecules. In addition, the rate of corrosion of the colloid is decreased.

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