



**PHOTOCHEMISTRY OF SEMICONDUCTOR COLLOIDS;  
PREPARATION OF CdO AND In<sub>2</sub>O<sub>3</sub> SOLS AND SOME PHOTO-REACTIONS ☆**

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## PHOTOCHEMISTRY OF SEMICONDUCTOR COLLOIDS; PREPARATION OF CdO AND In<sub>2</sub>O<sub>3</sub> SOLS AND SOME PHOTO-REACTIONS ☆

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### 1. Introduction

Colloidal solutions of metal oxides are often prepared by hydrolysis of their chlorides or alcoholates. For example, colloidal TiO<sub>2</sub> is obtained by hydrolyzing TiCl<sub>4</sub> or Ti[OCH(CH<sub>3</sub>)<sub>2</sub>]. The hydrolysis method is applicable to cases where the intermediate hydroxides rapidly lose water. In other cases, such as in the hydrolysis of Zn<sup>2+</sup> in alkaline solution, the hydroxides are the final products and are not photo-active. However, it has recently been shown that the hydrolysis of Zn<sup>2+</sup> with NaOH in alcohol solution yields a photo-active colloid of ZnO [1]. This was explained by the dehydrating action of the alcohol. The colloid could even be recovered from the solution in the form of a powder of high specific surface area which could in turn be redissolved in alcohol or water.

Attempts were made to prepare colloids of CdO and In<sub>2</sub>O<sub>3</sub> by precipitating Cd<sup>2+</sup> and In<sup>3+</sup> with NaOH in alcohol but this procedure yielded only the hydroxides. However, the latter were formed in a state where they could be dehydrated to an appre-

ciable extent to yield soluble and photo-active powders of the oxides. We describe here the procedure of colloid preparation and the changes in the optical absorption spectra of the colloids on exposure to light. Such changes have recently been observed for ZnO [1] and are due to the deposition of excess electrons on the colloidal particles [2].

### 2. Experimental

Colloidal In<sub>2</sub>O<sub>3</sub> was prepared as follows: To 250 ml methanol were added 0.1 ml 0.1 M sodium hexametaphosphate (Riedel de Haen) followed by 2 g In(ClO<sub>4</sub>)<sub>3</sub>·8H<sub>2</sub>O. After the indium perchlorate had dissolved, four pellets of NaOH were added with stirring. As the sodium hydroxide dissolved the solution became turbid and In(OH)<sub>3</sub> was precipitated. 5 ml water was added 30 min after the sodium hydroxide addition to ensure complete precipitation. After a further 15 min stirring the precipitate was recovered by centrifugation, washed twice with acetone, twice with diethyl ether and finally allowed to dry for 30 min.

The dry, white powder of indium hydroxide was heated carefully in an open ampule using a Bunsen burner until no more water evolved and the powder was uniformly pale yellow. Vacuum was then applied

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to draw off the water condensed on the upper part of the ampule and the powder was strongly heated under air for 5 min. A typical sample of the powder had a specific surface of  $18 \text{ m}^2/\text{g}$  as determined by single point BET.

200 mg of the powder were added to 50 ml methanol, sonicated for 15 min and centrifuged for 30 min to remove a small insoluble fraction. Dissolution occurred only when  $30 \mu\text{l}$  of concentrated  $\text{HClO}_4$  were added before sonication. Addition of  $\text{NaOH}$  instead of  $\text{HClO}_4$  dissolved only a small portion of the colloid. It seems that the isoelectric point of the colloid is close to  $\text{pH } 7$ . The slightly opaque very pale yellow solution was finally diluted as required. The solution was stable for several months. The  $\text{In}_2\text{O}_3$  powder could also be dissolved in water, the resulting solution being stable for a few days as a slow hydration to form  $\text{In}(\text{OH})_3$  took place.

Colloidal  $\text{CdO}$  was prepared in the same way using 2 g  $\text{Cd}(\text{ClO}_4)_2 \cdot 8\text{H}_2\text{O}$ . The yellow-brown powder obtained could be dissolved upon sonication in methanol to yield a long-lived yellow sol. Hydration in aqueous solution took place within one day. A typical sample of the powder had a specific surface of  $53 \text{ m}^2/\text{g}$ .

Concentrations were determined by adding  $\text{HClO}_4$  to the sols until the oxides were decomposed. The  $\text{Cd}^{2+}$  and  $\text{In}^{3+}$  content of the resulting solutions were determined polarographically. Absorption coefficients of the sols were calculated from the measured absorbancies and the polarographically determined concentrations.

The crucial point in the preparation is the duration and strength of heating. Different batches gave colloids of more or less different composition and solubility. A certain content of  $\text{OH}^-$  or water in the powders is necessary for them to be soluble. Glowing of the powders led to a loss in weight ranging from 2% to 20% depending on the batch, and the remaining powders were insoluble. On the other hand, the  $\text{OH}^-$  or water content of the samples should be low to assure a good photo-response of the colloidal particles. It should also be mentioned that the absorption coefficients given in figs. 1 and 2 can vary depending on the content of hydrate in the samples.

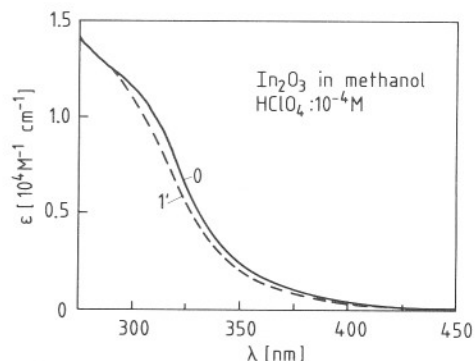


Fig. 1. Absorption spectrum of  $\text{In}_2\text{O}_3$  in methanol before and after illumination with the monochromatic light ( $\lambda = 366 \text{ nm}$ ) of a xenon-mercury lamp.

### 3. Results and discussion

Examination of the  $\text{In}_2\text{O}_3$  powder under an electron microscope revealed that it contained a very wide spectrum of particle size between 30 and 300 Å. X-ray diffraction studies gave reflexes due to cubic  $\text{In}_2\text{O}_3$ . From the shape and width of the lines a mean particle size could be calculated using Scherrer's equation. This mean size ranged between 50 and 300 Å in agreement with the electron microscopic observations. The  $\text{CdO}$  powder also had a wide spectrum of particle size. The X-ray diffraction signals were relatively broad which indicates that smaller particles were more abundant than in the  $\text{In}_2\text{O}_3$  powder. Again, the signals corresponded to cubic  $\text{CdO}$ .

The spectra of  $\text{In}_2\text{O}_3$  and  $\text{CdO}$  in methanol are shown in figs. 1 and 2 (curves 0). In both cases, the

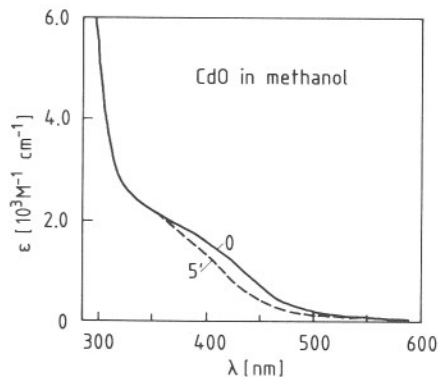


Fig. 2. Absorption spectrum of  $\text{CdO}$  in methanol before and after illumination with monochromatic light ( $\lambda = 366 \text{ nm}$ ).

long tail in the spectrum begins close to the wavelength corresponding to the band gap energy of the macrocrystalline materials (2.6 eV for  $\text{In}_2\text{O}_3$ ; 2.2 eV for CdO). However, the main rise in absorption occurs at much shorter wavelengths. This may be due to a contribution from smaller particles having a larger band gap, or due to the fact that the optical transitions in  $\text{In}_2\text{O}_3$  and CdO are indirect [3].

The two figures also show that the spectra experience on illumination a blue-shift in a wavelength range below the onset. The shifts shown in the figure became only slightly stronger on further illumination. The two colloids thus show the same behavior as ZnO [1], although the effects are less pronounced. Upon admission of air the blue-shifts partially recovered, while in the case of ZnO a full recovery was observed [1]. Addition of  $10^{-3}$  M  $\text{H}_2\text{O}_2$ , however, led to a complete recovery of the absorption spectra.

These effects are explained by the generation of excess electrons on the colloidal particles following illumination, the positive holes simultaneously formed being scavenged by methanol. This explanation is based on observations which have been made in experiments on excess electron deposition on CdS particles [2], and, more recently, on ZnO particles using radiation chemical methods [4]. In both cases, the transfer of an electron from a reducing radical to a colloidal particle led to bleaching below the absorption edge. The excess electrons on the semiconductor particles cause a change in the energy of the localized exciton produced by light absorption near the edge.

The excess electrons are long-lived. They react only partially with oxygen. Addition of methyl viologen to the illuminated solutes did not lead to a reversal of the absorption shifts. However, hydrogen peroxide, which is a more powerful oxidizing agent, removed the excess electrons and restored the original absorption spectra. It is concluded from these experiments that the electrons stored on CdO and  $\text{In}_2\text{O}_3$  are at less negative potentials than in ZnO.

In the case of alkaline  $\text{In}_2\text{O}_3$  solutions, an unexpected effect was observed on illumination. As can be seen from fig. 3, the absorption increases at all wavelengths. Further illumination did not lead to additional changes. It is supposed that only that fraction of  $\text{In}_2\text{O}_3$  powder containing a large percentage of OH groups is soluble in alkaline solution. It seems

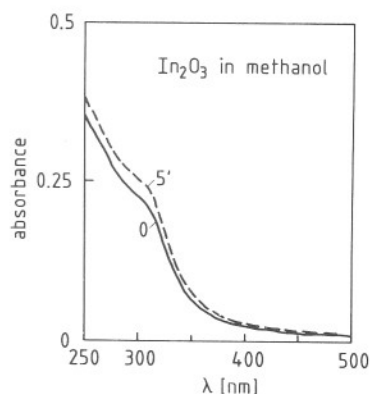


Fig. 3. Absorption spectrum of CdO in alkaline solution ( $pH \approx 8$ ) before and after illumination ( $\lambda = 366$  nm).

that illumination has a similar effect to heating of the powder, i.e. dehydration to yield additional oxide.

Photochemical reactions on suspended  $\text{In}_2\text{O}_3$  and CdO, such as the formation of oxygen and reduction of  $\text{Ag}^+$  ions, have been reported in the literature [5,6], the yields being rather low. We found that  $\text{Ag}^+$  ions are also reduced to form colloidal silver when deaerated colloidal solutions of  $\text{In}_2\text{O}_3$  and CdO containing  $10^{-3}$  M  $\text{AgClO}_4$  and 20 vol% propanol-2 were illuminated with the 366 nm light of a xenon-mercury lamp. Methyl viologen, which has a one-electron reduction potential of  $-0.4$  V, could not be reduced under these conditions. Thus it seems that the conduction band in  $\text{In}_2\text{O}_3$  and CdO is more positive than  $-0.4$  V. This would also explain why oxygen was rather inefficient in removing stored electrons as described above. Macrocrystalline CdO is known to have its conduction band at about  $-0.1$  V [7].

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