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SEMICONDUCTING AND PHOTOCATALYTIC PROPERTIES OF MERCURIC THIOCYANATE

K. TENNAKONE

Department of Physics, University of Ruhuna, Matara, Sri Lanka, and
Instiute of Fundamental Studies, Bauddhaloka Mawatha, Colombo 7, Sri Lanka

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Mercuric thiocyanate is found to be a p-type semiconductor with a band gap of about 3.2 eV. The microcrystals of this material easily absorb several dyes from aqueous solutions. Experimental data on photoreduction of carbonic acid to formaldehyde by dye sensitized $Hg(CNS)_2$ and semiconductors are presented showing that the photocatalytic activity is enhanced when the dye is strongly adsorbed.

1. Introduction

Solid state photovoltaic cells and other promising solar energy conversion systems, such as photoelectrochemical cells [1–5] and particulate dispersions of photocatalysts [6–9], depend on the use of semiconductor materials. The type of semiconductor adaptable, is highly restrictive in the case of dry solid state cells. In wet cells, a larger variety of semiconductor materials, polycrystalline or amorphous, can be used and for this reason wet cells continue to attract much attention, in spite of the frustrating problem of photocorrosion [1–8]. Photostability, a band gap appropriate to the solar spectrum, high carrier mobility and easily available methods for preparation of surface coatings are essential requirements for a material for photoelectrochemical use (the location of the band edges with respect to the redox level in the electrolyte is also important, but these parameters are adjustable to a certain extent). In the case of a photocatalyst the above requirements can be further relaxed since there is no necessity for preparation of surface coatings and the carrier mobilities become less important as the particle size decreases. Thus photostability and band gap are the major factors that decide the suitability of a photocatalyst. Low band gap materials sensitive to the visible region generally undergo photocorrosion. High band gap semiconductors can be sensitized with dyes [10–13], but unfortunately, the dye sensitization presents additional problems, that is, the sensitizer must remain firmly adsorbed to the semiconductor substrate and should not photodegrade [10–13]. As the variety of sensitizers and the number of high band gap semiconductor materials, not necessarily of high carrier mobility, that can be prepared in microcrystalline form are practically infinite, it is conceivable that some of the best systems for solar energy conversion are dye sensitized particulate dispersions.

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Over the past two years the author was searching for semiconducting materials easily adsorbing cationic dyes. Motivated by the fact that CNS is a ligand which enhances chemiadsorption when present in a solid substrate, a number of inorganic, water insoluble thiocyanates were tested for semiconduction. In this work we report our observations on semiconducting, dye adsorbtion and photocatalytic properties of mercuric thiocyanate.

2. Experimental

Mercuric thiocyanate $Hg(CNS)_2$ was made by mixing equimolar solutions of potassium thiocyanate and mercuric nitrate (mercuric chloride cannot be used as it yields HgClCNS instead of $Hg(CNS)_2$). The white precipitate of $Hg(CNS)_2$ was washed with deionized water and dried in vacuum at 80°C. Polycrystalline powder pressed into a fibre glass disc was used to measure the diffuse reflectance spectrum with a Unicamp SP 500 Series II spectrophotometer. The temperature variation of the conductivity was studied using compressed pellets as well as single crystals (sizeable single crystals can be made by diffusing solutions of mercuric nitrate and potassium thiocyanate into a chamber of water through capillary tubes).

The dyes used as sensitizer were chlorides and thiocynates of methyl violet (MV), rosaniline (R) and rodamine 6 G (RO). The thiocyanates of the dyes were made by boiling the respective chlorides with KCNS, and the product was separated and purified by recrystallization. The absorbtion isotherms were obtained by agitating the $Hg(CNS)_2$ powder with an aqueous solution of the dye at different concentrations. Equilibrium concentrations in the solutions were estimated colorimetrically. The dye adsorbed into the solid was extracted with warm alcohol and again estimated colorimetrically. The peak absorbtion wavelengths of the sensitized powders were determined from diffuse reflectance measurements.

The photocatalytic activity was tested by examining the ability of the dye absorbed powder to reduce carbonic acid to formaldehyde. 2 g of $Hg(CNS)_2$, 1 mg of the dye and 200 ml of water were stirred magnetically in a 250 ml pyrex flask (the pH of the solution was kept at ~ 5 by addition of HCl or Na_2CO_3 depending on the dye). Purified carbon dioxide was bubbled and the flask was irradiated with a medium pressure 200 W mercury lamp. A major portion of the UV component ($\lambda < 300$ nm) was removed by filtering with pyrex glass sheets. After 30 min the contents of the flask were distilled and the distillate was tested for formaldehyde by the following method.

50 ml of the distillate was mixed with 1 ml of Tollen's reagent and the optical density of the mixture at 550 nm was noted every half minute until the saturation value was reached. From a calibration experiment with distilled water containing known amounts of formaldehyde and the same amount of Tollen's reagent [14], $H \cdot CHO$ can be estimated up to concentrations $> 10^{-5}$ mol l^{-1}.

When any one of the above components, i.e., $Hg(CNS)_2$, dye, CO_2 or the light was removed, $H \cdot CHO$ was not detectable (in absence of the dye, $Hg(CNS)_2$ yields detectable quantities of $H \cdot CHO$ if the light is unfiltered for UV).

Several other chemical tests showed that the dye or $Hg(CNS)_2$ does not introduce a substance, sensitive to the Tollen's reagent into the distillate. For comparison, the experiment was repeated by replacing $Hg(CNS)_2$ with other familiar semiconducting powders, e.g. TiO_2 and ZnO_2 (BDH). The light intensities were measured using an International Light IL 700 research radiometer.

3. Results and discussion

The diffuse reflectance spectrum of the solid $Hg(CNS)_2$ is shown in fig. 1. An absorbtion edge is seen at $\lambda \simeq 390$ nm, indicating that the band gap of the material is about 3.2 eV. The plot of log σ vs. T^{-1} is a straight line (fig. 2) showing that the conductivity varies with the temperature according to the law

$$\sigma = \sigma_0 \, e^{-E/2kT}, \qquad (1)$$

where $E = 2.96$ eV, which is consistent with the value obtained for the band gap. As the conductivity of the material is very small ($\sigma_{30} \sim 3 \times 10^{-8}\ \Omega^{-1}\ \text{cm}^{-1}$) accurate measurements of the carrier mobilities are very difficult. However, thermoelectric tests show that the material is p-type.

The absorbtion isotherms at 30°C of several cationic dyes on $Hg(CNS)_2$ and TiO_2 are given in fig. 3. It is clear that $Hg(CNS)_2$ adsorbs dyes more easily than TiO_2. Again the absorption is greater when the anionic ligand in the dye is CNS^-.

The yield of $H \cdot CHO$ for sensitized catalysts (30 min exposure at an absorbtion

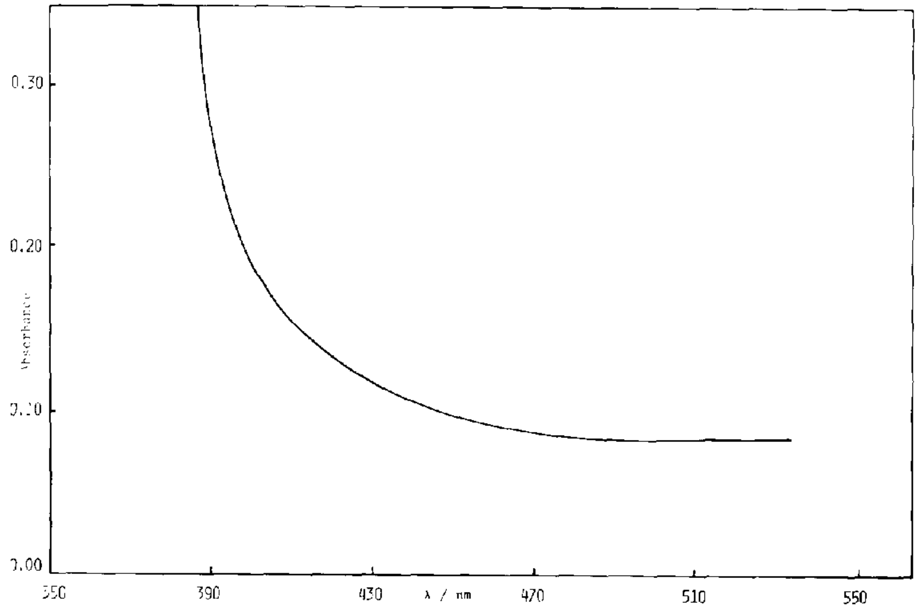

Fig. 1. Diffuse reflectance spectrum of solid mercuric thiocyanate.

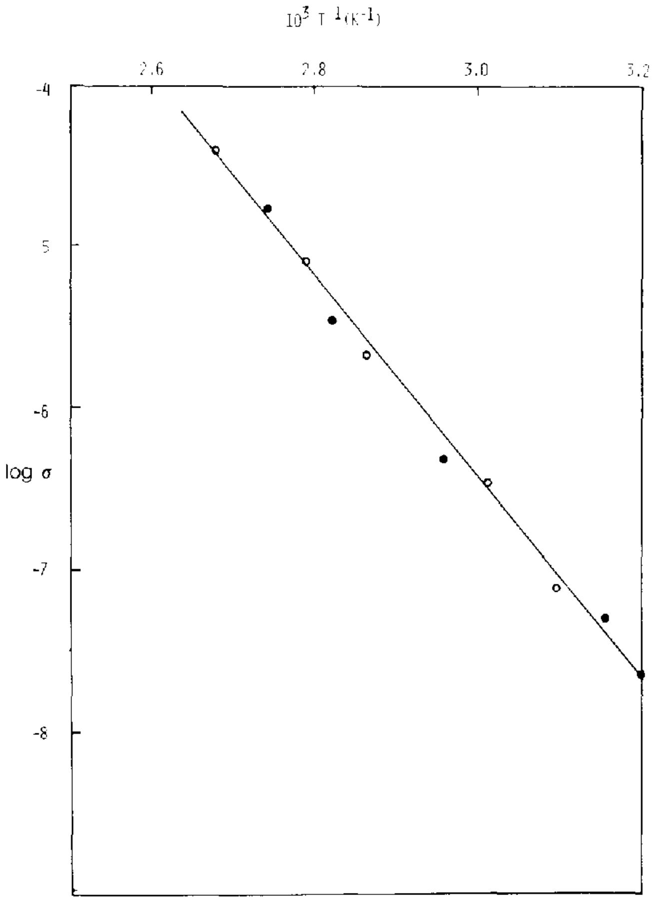

Fig. 2. Plot of log σ vs. T^{-1} (σ in Ω^{-1} cm^{-1}). ○ – compressed pellets, ● – single crystals.

Table 1

The yield of H·CHO (mol l^{-1} h^{-1}) for different sensitized powders (light source as described in the experimental section). λ_{max} (nm) is the absorption peak in the sensitized powder. A_{max} is the peak absorbance in arbitary units

Powder	Yield $\times 10^4$	A_{max}	λ_{max} (nm)
$Hg(CNS)_2$/MV thiocyanate	5.3	10	587
$Hg(CNS)_2$/MV chloride	4.8	9	587
$Hg(CNS)_2$/R thiocyanate	3.7	6.0	546
$Hg(CNS)_2$/R chloride	3.0	4.5	546
$Hg(CNS)_2$/RO chloride	2.1	3.4	528
TiO_2/MV thiocyanate	0.8	2.5	587
TiO_2/MV chloride	0.8	2.0	587
ZnO_2/MV chloride	~ 0.0	3.0	587
$Hg(CNS)_2$ unsensitized	~ 0.0	–	–
TiO_2 unsensitized	~ 0.0		–

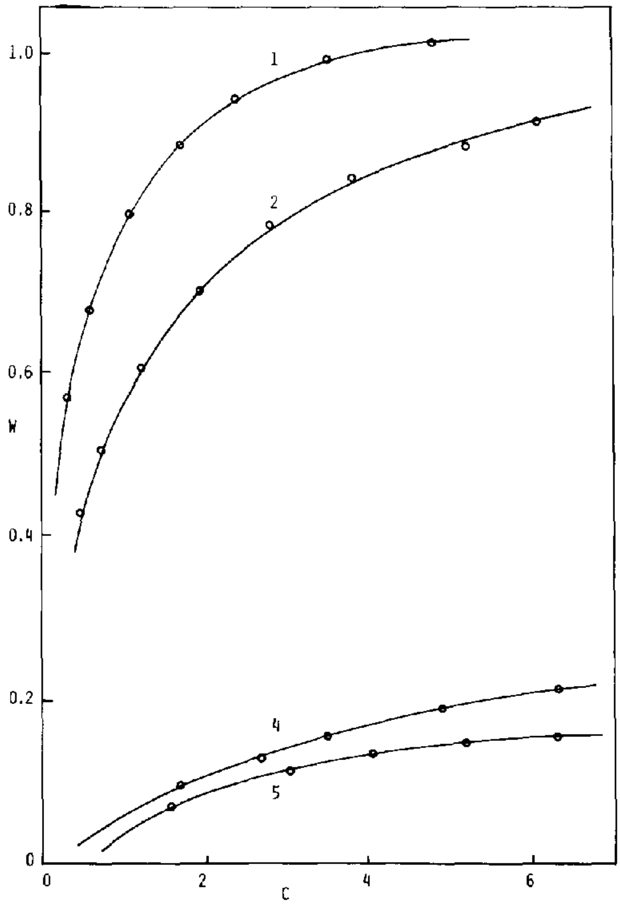

Fig. 3. The absorbtion of the isotherm at 30°C of methyl violet on photocatalysts, i.e., the plot of w (wt. of dye in mg absorbed per g of powder) vs. C (concentration of the dye in aqueous solution in equilibrium); pH ~ 5. 1: $Hg(CNS)_2$ on MV thiocyanate; 2: $Hg(CNS)_2$ on MV chloride; 3: TiO_2 on MV thiocyanate, and 4: TiO_2 on MV chloride.

rate of light of about 0.5 W per ml from a mercury lamp with UV ($\lambda < 300$ nm) filtered off) is given in table 1. Due to the presence of back reactions (i.e., oxidation of the reduction products of CO_2), $H \cdot CHO$ is not produced at a constant rate: a saturation is reached in about 30 min at the above intensity of light. For each dye the highest conversion rate is obtained with $Hg(CNS)_2$. We attribute this to a high absorption power of dyes on $Hg(CNS)_2$.

The reactions occurring at the surface of the sensitized catalyst can be pictured as

$$D + h\nu \rightarrow D^*, \qquad D^* \rightarrow D^- + \text{hole},$$

where D denotes a dye molecule, D* an excited dye molecule and D^- a dye molecule that has gained an electron. D^- and the hole participate in redox reactions leading to reduction of CO_2 with oxygen evolution. Another possibility is that photons absorbed by the dye molecules generate excitations which migrate into the semiconductor and decompose into electron–hole pairs, bringing about the redox reactions.

4. Conclusion

The purpose of the above investigation is to search for semiconductor materials that could be used in the particulate form and are suitable for dye sensitization. Obviously the system has no practical value; the back reactions prevent generation of significant quantities of reduction products. Again, the dyes photodegrade, because the oxidation of dye molecules is a process alternative to oxygen liberation. However, $Hg(CNS)_2$ is completely photostable.

The thiocyanates of copper and silver are also p-type semiconductors [15–16] (with band gaps of 3.3 and 3.4 eV, respectively) that quite easily adsorbs dyes. But dye sensitized AgCNS and CuCNS do not photoreduce carbonic acid possibly because the redox levels in these materials lies beyond the valence and conduction bands. CuCNS can be coated on copper substrates, and dye sensitized photoelectrochemical cells made with this material have reasonably high conversion efficients [17]. $Hg(CNS)_2$ has a tetragonal layered structure. In addition to a high band gap the layered structure adds to stability [18].

Sensitized or unsensitized $Hg(CNS)_2$ gives a higher yield of $H \cdot CHO$ ($\sim 8 \times 10^{-4}$ mol l^{-1} h^{-1}) if UV ($\lambda < 300$ nm) is not filtered from the 200 W mercury lamp. However, with the unsensitized powder no conversion is detectable if UV ($\lambda < 300$ nm) is filtered off. The sensitized $Hg(CNS)_2$ possibly has some capacity to photodecompose H_2O. Unfortunately we could not carry out this investigation due to the lack of analytical facilities for detecting trace quantities of H_2. The pyrex filters we have used transmit a fair amount of UV radiation that can activate TiO_2 or ZnO_2. However, our detection technique is not sufficiently sensitive to detect this effect. Again the possibility remains that synergetic effects complicate the reaction when dye sensitized catalysts are used.

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