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Preparation of New Organosols of CdS and CuS and their Utilization in Preparing MS-poly(acrylonitrile) Composites (M = Cd, Cu); the Semiconducting Properties of the Composites

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Some semiconducting metal sulfides are now used as photoconductors, phosphors, electrodes of photogalvanic cells, catalysts, etc. [1]. Exploration of the chemistry and physics of the metal sulfides is now becoming more important in view of the recent rapid development in the practical uses of compound semiconductors [1, 2]. The preparation of metal sulfides by reaction of metal compounds with H_2S in aqueous media has been studied for more than 100 years, and its chemistry is well established. However, the reaction of metal compounds with H_2S in organic solvents, as well as properties of metal sulfides formed in organic solvents, have been explored much less. We have examined reactions of CdX_2 (X = I, Cl) and $Cu(OCOCH_3)_2$ with H_2S in DMF (N,N-dimethylformamide) and DMSO (dimethyl sulfoxide) and found that the reactions give new organosols of CdS and CuS.

Cadmium(II) and copper(II) sulfides are especially useful materials among the metal sulfides, since they show semiconductivity, photoconductivity, fluorescence and other interesting properties. However, their practical uses are sometimes restricted due to their non-miscibility in solvents. Therefore, obtaining the new organosols may expand the use of cadmium(II) and copper(II) sulfides in various practical applications.

When dry H_2S (20 mmol) was introduced into a DMF (50 cm^3) solution of CdI_2 (10 mmol) at 15 ℃, the colorless solution rapidly turned yellow or yellowish-orange showing the formation of CdS. The solution looked homogeneous by visual observation, and this homogeneous state was maintained for more than 2 days at 15 ℃ and more than 2 months at −15 ℃. Irradiation of light seems to facilitate precipitation of CdS. Addition of acetone (50 cm^3) to the DMF solution gave a yellow precipitate of CdS (confirmed by elemental analysis and comparison of its X-ray diffraction pattern with that of an authentic sample, yield = 95%). CdS once precipitated was no longer soluble in DMF under any conditions tested, indicating that the cadmium(II) sulfide was soluble only in a metastable state. Similar solutions containing CdS were obtained by using $CDCl_2$ as the starting material, $(NH_4)_2S$ as the sulfur compound, or DMSO as the solvent.

Addition of excess dry H_2S to a DMSO solution of $Cu(OCOCH_3)_2$ afforded a dark green solution and a small amount of precipitate. Filtration of the reaction mixture gave a solution which appeared homogeneous by visual observation. By addition of acetone or methanol to the solution, CuS (confirmed by elemental analysis and X-ray diffractometry, yield = 50%) was recovered. The copper(II) sulfide once precipitated was not soluble in DMSO. Use of DMF as the solvent gave a similar solution.

Although the DMF or DMSO solution of CdS and CuS looked homogeneous, light scattering studies by an Ar laser scattering technique [3] indicated that CdS and CuS existed in the form of small particles with a radii of r = 40–150 Å and r = about 670 Å, respectively. The radius of the CdS particle depended on the preparative conditions and history of the solution. For example, the DMF solution prepared as described above and stored for 2 weeks at −15 ℃ contained CdS particles with an average radius of 50 Å. Monitoring of this solution by the laser scattering technique at 16.6 ℃ indicated that the radius of the CdS particle increased with time, reaching about 80 Å after 7 h and about 150 Å after 22 and 27 h (Fig. 1). On further standing at 16.6 ℃ under irradiation from an Ar laser, precipitation of CdS started after about 30 h. The organosol of CuS in DMSO was stable at room temperature. The formation of the organosol seems

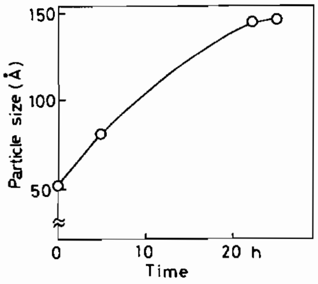

Fig. 1. Increase in particle size (radius) of CdS with time on standing of DMF-sol of CdS at 16.6 ℃ under irradiation of Ar laser.

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to be related to the large surface energy of metal sulfide particles in the solvents. Coordination of DMF and DMSO to the metal sulfide may account for the large surface energy. Coordination of DMF and DMSO to metal compounds is known [4].

One of the uses of the organosols is preparation of composites of the metal sulfides with polymers. In such composites the metal sulfides are highly dispersed and the composites are expected to be useful in the manufacture of electric devices. For example, addition of poly(acrylonitrile) (PAN) to the DMF solution of CdS and evaporation of the resulting solution gave a yellow transparent film (PAN:CdS = 7:10 wt/wt) which had an electrical conductivity (σ) of 4×10^{-6} S cm^{-1}. Increase in the wt – % of CdS in the composite to 74 gave a material (film) with σ value of 2×10^{-5} S cm^{-1}. The values are much larger than the electrical conductivity of PAN and 10^2–10^3 times larger than that of the CdS which was recovered from the organosol. Analogously, PAN–CuS composite (film) was obtained and its electrical conductivity depended on its composition, steeply increasing with increase in the content of CuS (Fig. 2). Formation of an electrical conducting channel by contact of highly dispersed copper(II) sulfide explains this result. Mixing of commercially available powdery CuS and a DMSO solution of PAN and drying the mixture gave a composite of CuS and PAN (wt – % of CuS = 44). However the composite had considerably (10^2–10^3 times) lower electrical conductivity ($\sigma = 10^{-5}$ S cm^{-1}) than did the composite prepared by using the organosol.

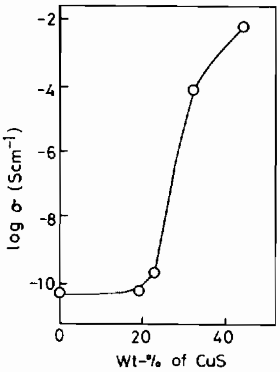

Fig. 2. Dependence of electrical conductivity (σ) of CuS–PAN composite on wt – % of CuS in the composite. Measured at 25 °C.

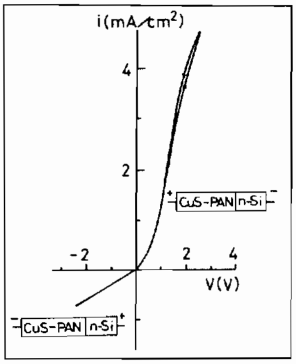

Fig. 3. i-V curve of p–n junction consisted of the CuS–PAN composite (wt – % of CuS = 44, $\sigma = 1.9 \times 10^{-2}$ S cm^{-1}, thickness = 0.07 mm) and n-type silicon semiconductor (R = 1.1–1.6 Ω, n = 5×10^{15} cm^{-3}, thickness = 0.625 mm). At 25 °C. Scanning rate = 4 mV/sec.

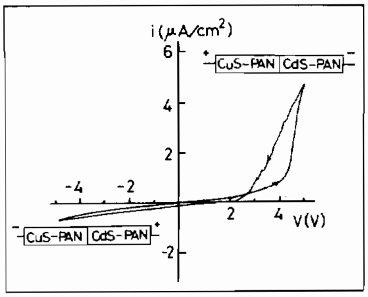

Fig. 4. i-V curve of p–n junction consisted of the CuS–PAN composite (as in Fig. 3) and CdS–PAN composite (wt – % of CdS = 0.74, $\sigma = 2.1 \times 10^{-5}$ S cm^{-1}, thicknesss = 0.05 mm). At 25 °C. Scanning rate = 4 mV/sec.

Recently it has been reported that CuS–treated PAN film or fiber, which contains dispersed CuS only in the surface area, shows electrical conductivity [5] and the CuS–treated PAN fiber is now commercially produced. The electrical conductivity of this CuS treated PAN is apparently based on CuS in the surface area of the fiber or film and, for example, the electrical conductivity between the two surfaces of the film is very low. On the contrary, the CuS–PAN composite prepared in this study contains CuS dispersed uniformly in the polymer, and consequently is useful to form electric devices. Figures 3 and 4 show i-V curves of p–n junctions consisted of the CuS–PAN composite (p-type) and n-type silicon (Fig. 3) and the CuS–PAN composite (p-type) and CdS–PAN composite (n-type) (Fig. 4). The p–n junctions show rectification. Measurement of the Hall effect of the CuS–PAN composite (wt – % of CuS = 44) shows that the composite is a p-type semiconductor with hole mobility of 41 cm^2 V^{-1} s^{-1} and carrier density of 1.8×10^{16} cm^{-3}. Preliminary experiments revealed that these devices are usable as photogalvanic cells. Since a variety of polymers can be dissolved in DMF and DMSO, various semiconducting MS (M = Cd, Cu)–polymer composites could be obtained by using the organosols described above.

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