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Preparation of Electrical-Conducting CdS-Polymer Composites Using Organosols of CdS. Dependence of Electrical Conductivity on Kind of Polymer

Takakazu YAMAMOTO,* Etsuo KUBOTA, and Atsushi TANIGUCHI
Research Laboratory of Resources Utilization, Tokyo Institute of Technology, 4259 Nagatsuta, Midori-ku, Yokohama 227

Cadmium sulfide-polymer (poly(acrylonitrile), poly(vinylidene fluoride), etc.) composites containing cadmium sulfide in 16-73 wt-% are prepared by using organosols of cadmium sulfide. The composites are n-type semiconductors and show electrical conductivity ranging 10^{-9}-$10^{-2.5}$ S cm^{-1}.

Although cadmium sulfide is a useful material to prepare electric devices such as photovoltaic cells and photodetectors,[1)] its practical use is sometimes restricted because of its low mechanical strength and difficulties in molding it. On this basis, many efforts have been made to prepare CdS films by special techniques such as electrochemical deposition and sputtering,[2)] and sometimes cadmium sulfide is used with polymer binders.[3)]

Previously we reported preparation of new organosols of cadmium sulfide (radius of CdS particles = 50-150 Å) in N,N-dimethylformamide (DMF) and dimethylsulfoxide (DMSO).[4)] Since DMF and DMSO dissolve various kinds of polymers, the organosols are suitable to prepare various kinds of CdS-polymer composites containing highly dispersed cadmium sulfide particles. Some of the composites have relatively high electrical conductivity and seem to have practical use to make electric devices. We now report preparation and electrical-conducting properties of the composites of cadmium sulfide and various polymers.

Figure 1 shows dependence of the electrical conductivity (measured in the dark) of the CdS-polymer composites on wt-% of CdS at 25 °C. The yellowish orange composites (films) were prepared by dissolution of the polymer into the organosol of CdS in DMF, spreading the solution on a glass plate, and removing the solvent under vacuum. A CdS-poly(acrylonitrile) film with about 60 wt-% of CdS had transparency. Use of DMSO, instead of DMF, as a solvent afforded similar composites. The electrical conductivity of the films thus obtained was measured by a two point method. Following features of the present CdS-polymer composites are seen from Fig. 1. 1) Although CdS is dispersed in insulating polymers, some of the composites show electrical conductivity (σ) of 10^{-4}-$10^{-2.5}$ S cm^{-1}. The value is much larger than electrical conductivity of pure polymers and 10^{3}-10^{4} times larger than that of CdS pellet which was prepared by pressing CdS powder recovered from the organosol at 400 kg/cm^2. Previously reported polymer-CdS composites prepared by mixing polymers and CdS powder had much lower electrical conductivity.[3)] We also prepared CdS-polymer composites (films) by mixing commercially available CdS powder and DMF solutions of polymers, spreading the mixture on a glass plate, and remove of DMF under vacuum. The electrical conductivity of CdS-poly(acrylonitrile) composites thus obtained (data are shown

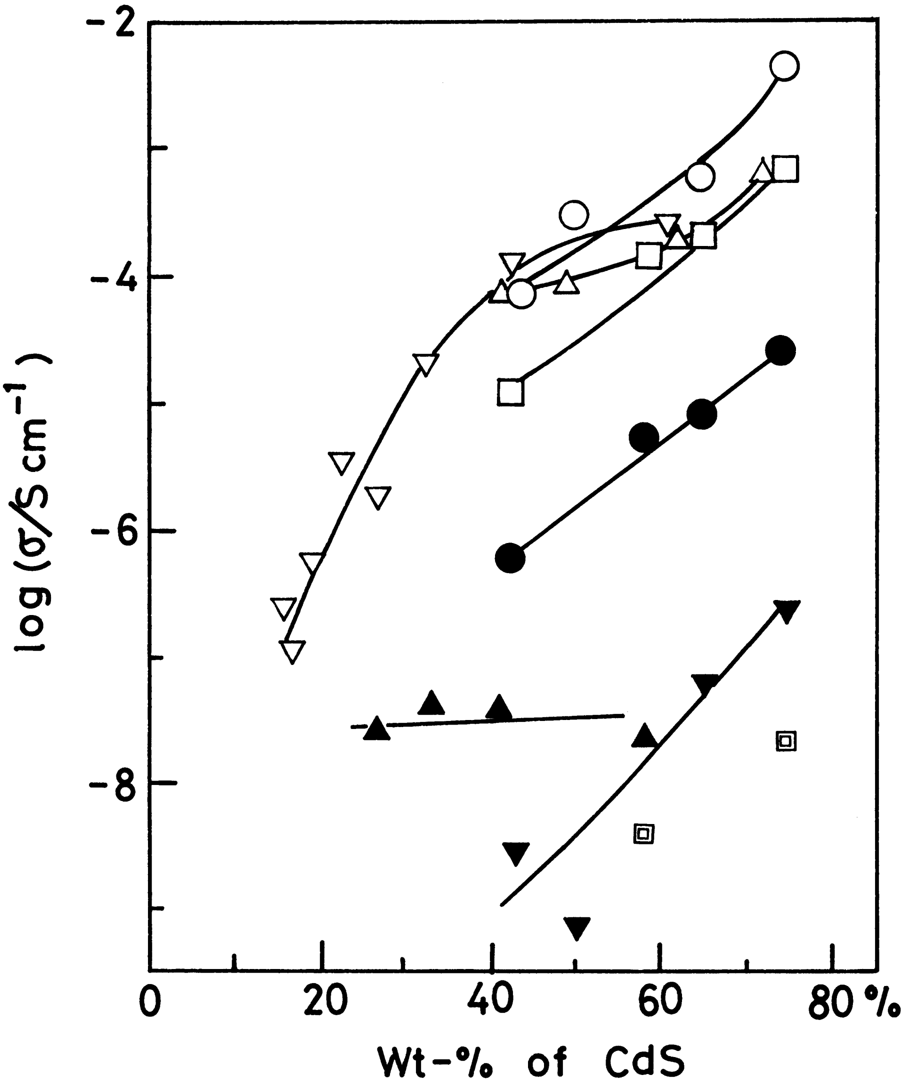

Fig. 1. Electrical conductivity of CdS-polymer composites at 25 °C. Polymer: poly(vinylidene fluoride) (○), copolymer of methyl vinyl ether and maleic anhydride (50:50) (△), copolymer of vinyl chloride and vinyl acetate (90:10) (▽), poly(acrylonitrile) (□), poly(vinyl butyral) (●), poly(vinyl formal) (▲), and poly(N-vinyl-2-pyrrolidone) (▼). ⧈ : Data for CdS-poly(acrylonitrile) composites prepared by using commercial CdS powder (see the text).

by ⊡ in Fig. 1) is much lower than that of the CdS-poly(acrylonitrile) composites prepared by using the organosol of CdS. Use of a copolymer of vinyl chloride and vinyl acetate (90:10) gave similar results. These results show merits to use the organosol to prepare electrically conducting CdS-polymer composites.

2) The electrical conductivity of the CdS-polymer composite strongly depends on the kind of polymer. For example, poly(vinylidene fluoride) and a copolymer of vinyl chloride and vinyl acetate (90:10) give the composites which show 10^3-10^4 times larger electrical conductivity than that of the composites prepared by using poly(vinyl formal) and poly(N-vinyl-2-pyrrolidone). If the electrical current flows through chains formed by CdS particles, the strong dependence of the electrical conductivity on the kind of polymer may be related to difference in ease of the formation of the CdS chains in the polymers.

Hall effect of the composites indicates that the composites are n-type semiconductors, suggesting that the electrical current flows through chains formed by the CdS particles. CdS is usually an n-type semiconductor. Electron mobility for the copolymer of vinyl chloride and vinyl acetate (90:10)-CdS composite (wt-% of CdS = 50-60) is about 10 $cm^2\ V^{-1}\ s^{-1}$. A CdS-poly(vinyl chloride) composite (wt-% of CdS = 64), which has electrical conductivity comparable to that of the copolymer of vinyl chloride and vinyl acetate-CdS composite, also shows similar electron mobility.

Temperature dependence of the electrical conductivity roughly obeys Arrhenius type equation (temperature range: -35 - +70 °C),

$$\sigma = \sigma_0 \exp(-E_a/RT) \qquad (1)$$

and the E_a values are shown in Table 1.

Table 1. Activation energy, E_a, for the electrical conduction

Polymer	wt-% of CdS	E_a/eV
poly(vinylidene fluoride)	43	0.32
	51	0.31
copolymer of vinyl chloride and vinyl acetate (90:10)	32	0.33
	42	0.29
poly(acrylonitrile)	59	0.47
poly(vinyl butyral)	44	0.44

Most of the CdS-polymer composites are stable under air. Among the CdS-polymer composites, those obtained by using the copolymer of vinyl chloride and vinyl acetate, poly(vinyl chloride), and poly(acrylonitrile) show some mechanical strength. Although a number of electrically conducting polymers are recently reported,[5)] most of them are p-type conductors. The present semiconducting films are, on the other hand, n-type, and may be useful to make electrical devices in combination with the p-type polymers. Actually a p-n junction prepared by using the CdS-poly(acrylonitrile) film and a p-type CuS-poly(acrylonitrile) film shows rectification of electrical current (Fig. 2).

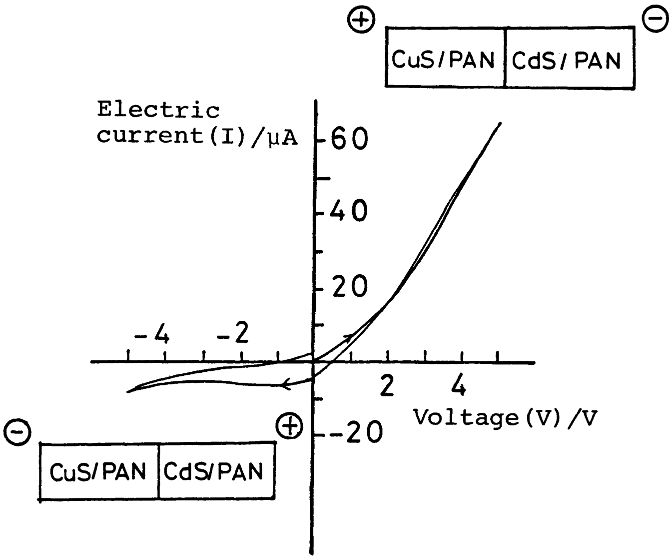

Fig. 2. I-V curve of p-n junction between p-type CuS-poly(acrylonitrile) and n-type CdS-poly(acrylonitrile) composites at room temperature in the dark. PAN = poly(acrylonitrile). Area = 1 cm^2. Two composites (films) were pressed mechanically to make the junction.

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