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An Improved Method for Preparation of CdS Particle-Dispersing Film with Excellent Light-Induced Current Generation

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A homogeneously CdS particle-dispersing film was obtained according to the counter-current method by which Cd^{2+} and H_2S were incorporated into Nafion film from an opposite side in a counter-current diffusion way. The resulting film had a light-induced current in an order of $\mu A\ cm^{-2}$ with a ratio of current in light to dark around 430.

Metal chalcogenides such as CdS, PbS and ZnS are useful as semiconductor applicable to solar cell, photodetector, photoreceptor of xerography and photocatalyst. It is generally pointed out that single crystals of semiconductors have an advantage of excellent electronic properties but a disadvantage of high production cost compared with those of semiconductive particle-dispersing films. Recently, Yamamoto and his colleagues[1] reported that excellent electronic properties were achieved in ultrafine particle-dispersing films of CdS and CuSx which were prepared by casting of organosols of those semiconductors dispersed in organic solvent with stabilizing polymer additives. On the other hand, Bard and his coworkers[2] reported of the in situ method to obtain CdS particle-dispersing film by solid-phase reduction of Cd^{2+} with H_2S in perfluorinated cation exchange membrane of Nafion (Nf). This has an advantage of convenience with no need of solvent evaporation that is required in a conventional screen printing method. It was, however, found by the present authors that the resulting film of CdS particle-dispersing Nafion prepared by Bard's method had such a "caved structure" that has a vacant domain in the film with no CdS particle precipitated. Then, it was examined to improve the method in order to get a homogeneously particle-dispersing film with excellent electronic properties.

Nafion 117 purchased from Aldrich Chemical Co. Ltd. was cleaned by boiling in concentrated nitric acid and then in distilled water for a couple of hours, respectively. Nf film thus cleaned was set in a separable two-compartment cell and a 0.1 M (M=mol dm^{-3}) $Cd(CH_3COO)_2$ aqueous solution was placed in one of the two compartments, placing distilled water saturated with H_2S in the other. The

film colored pale yellow immediately after bubbling H_2S gas into the distilled water and gradually turned to orange with time. The content of CdS precipitated in Nf was calculated by measuring an increment in weight of film before and after the reaction. Furthermore, morphological structures of the resulting films were observed in their cross-sections under an optical microscope. Light-induced current was measured under illumination of a sample sandwiched between two plates of ITO (indium tin oxide)-coated glass electrode at 0.5 V applied and ca. 200 mW cm^{-2} of light intensity using 650 W tungsten-halogen lamp with a 5 cm-thick water filter.

Bard's method described the stepwise procedures consisting of dipping Nf into Cd^{2+}-containing aqueous solution and dipping the resultant film into H_2S-saturated water. The reason why the caved structure was formed in these procedures is considered as follows: If a diffusion rate of Cd^{2+} were faster than that of H_2S in the solid matrix of Nf, Cd^{2+} ion could diffuse toward an interface of Nf and H_2S-saturated solution before H_2S gets deeply into the solid matrix so that the reactants, Cd^{2+} and H_2S, could encounter with each other in an outer region of the matrix. Balancing of diffusion rates of the reactants in Nf is thus relevant to a homogeneous precipitation of CdS in Nf and also important as well in the counter-current method as described below. That is, CdS particle was formed in a solution containing Cd^{2+} when a concentration of $Cd(CH_3COO)_2$ was less than 0.01 M, while CdS precipitated in a solution containing H_2S when that concentration was higher than 1.0 M. The concentration of H_2S at a saturation in water is approximately 0.1 M. This could also be

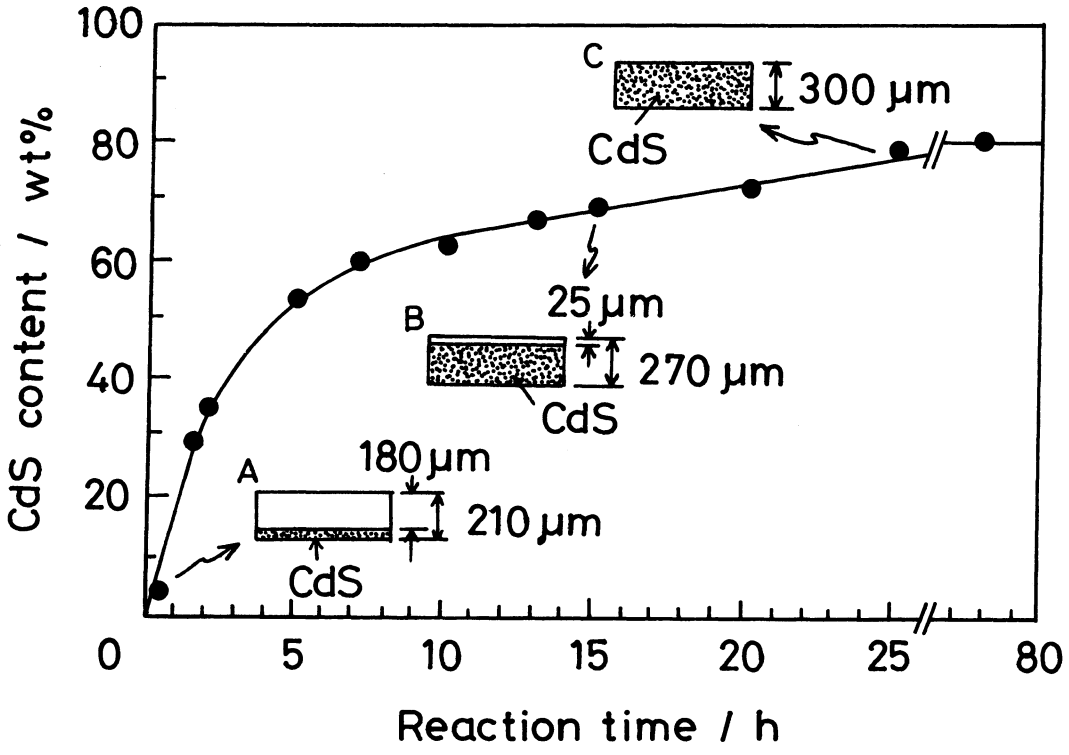

Fig. 1. Correlation of CdS content to the reaction time with H_2S and the membrane structures of the CdS-Nf composite film.

explained by imbalance of the diffusion rate in Nf between Cd^{2+} and H_2S in the counter-current precipitation. From the above-described results, it was an appropriate condition of the counter-current method that both of the concentrations of $Cd(CH_3COO)_2$ and H_2S were evenly 0.1 M.

Figure 1 indicates a correlation of CdS content to reaction time with membrane structures of resulting CdS-dispersing Nf. The CdS precipitation started to occur in an outermost region of the matrix film facing a H_2S-saturated solution and was gradually growing with time toward the other interface of the film. It was recognized under microscope that CdS particles were homogeneously dispersed in Nf as shown in Fig. 1-C after 25 hours of the reduction. A thickness of the CdS-containing Nf film increased with increasing the CdS content and up to 150% of the initial one after 25 hours when the thickness reached 300 μm and the CdS content was 80 wt%. Figure 2 shows SEM pictures of a cross-section of the CdS-containing Nf film which was

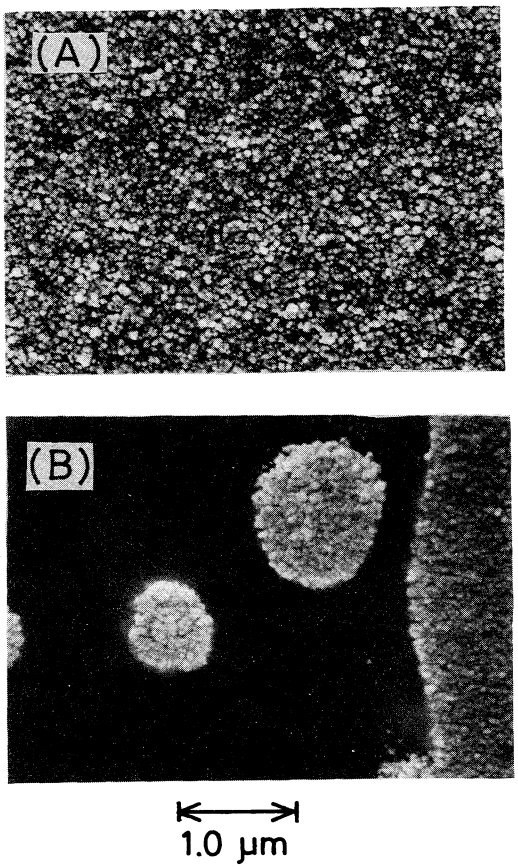

Fig. 2. SEM pictures of a cross-section of the CdS-Nf composite film. A middle region (A) and a boundary domain (B) of the particle-dispersing film are represented.

Table 1. Photo-current of the CdS-Nf composite films under illumination of 650 W tungsten-halogen lamp at 200 mW cm^{-2}

Sample[a]	CdS content[b] / wt%	i_{ph}[c] / nA cm^{-2}	i_{ph}/i_d[d]	σ_{ph}(25°C) / S cm^{-1}
1	10	20	2	1.0×10^{-9}
2 A	5	10	1	0.5×10^{-9}
3 B	70	370	37	1.5×10^{-8}
4 C	80	4300	430	2.5×10^{-7}

a) The symbols given here are the same as in Fig. 1. b) (CdS/(CdS+Nf))x100.
c) Photo-current at 0.5 V bias applied. d) Ratio of photo-current to dark-current.

obtained after 15 hours of the reduction. These photographs indicate that an average size of CdS particles in Nf is approximately 0.05 - 0.10 μm in diameter and further that some of them aggregate into a larger particle of 1 - 2 μm in diameter in a boundary domain of the particle-dispersing area in Nf, as shown in Fig. 2-B, which tended to fuse with each other to form a homogeneous region as shown in Fig. 2-A. A visible absorption spectrum of the composite film had an offset wavelength of absorption at 515 nm which is almost the same as that of CdS prepared by a conventional method.

Table 1 indicates the results of light-induced current of the CdS-dispersing films with various membrane structures. Sample 1 is the film prepared according to Bard and Samples 2-4 correspond to the films A-C described in Fig. 1. In the case that the vacant domain was extended as seen with Samples 1 and 2, a light-induced current passed across the film was neglegible. On the other hand, a high current passed under illumination when CdS particle was homogeneously dispersed in the film like Sample 4. A particle-to-particle distance of CdS in Nf is considered to have a great influence upon the photo-induced electron transfer across the solid matrix. A mechanical strength of the film #4 was so much weakened due to a full incorporation of CdS particles to Nf film. Ideally, a photo-current would be increased up to around 10^3 nA cm^{-2} keeping a mechanical strength at an appropriate level. We have done the following experiment to meet this requirement. The vacant domain of Sample 3 was modified with polypyrrole according to Iyoda et al.[3] in order to increase an electronic conductivity of the film. The resulting film had a layered structure of CdS-dispersing domain overlaid with a conductive polypyrrole-deposited domain. It had a good mechanical strength as well as a high photo-current in an order of μA cm^{-2}.

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