CHEMISTRY LETTERS, pp. 605-608, 1988.

Preparation of Size-Controlled CdS Colloids in Water and Their Optical Properties[1)]

Yoshio NOSAKA, Katsuhiko YAMAGUCHI, Hajime MIYAMA, and Hisaharu HAYASHI[+]
Department of Chemistry, Technological University of Nagaoka,
Nagaoka 940-21
[+]Institute of Physical and Chemical Research, Wako 351

Size of colloidal CdS particles in aqueous medium was controlled by adding thiols in the procedure of the preparation. The change in optical absorption spectra and the quantum yield of photoinduced electron transfer were measured for these size-controlled CdS colloids.

Colloidal semiconductors are used as photocatalysts and studied to clarify the interfacial chemical kinetics by means of techniques of photochemistry.[2,3)] When the particle diameter decreases the following effects are expected: (a) increase of reaction site because of the increase of surface area per weight of the particles. (b) increase of reducing and oxidizing abilities caused with the shift of the conduction band and valence band energy levels. (c) decrease of the chance of recombination for photoinduced electron-hole pairs because of their faster arrival to reaction site at the surface. Of all colloidal semiconductors, CdS has been reported most frequently from a viewpoint of the small size effect.[4-15)] Several researchers used non-aqueous medium such as acetonitrile,[5-8)] methanol,[5,7)] 2-propanol[9)] to make a ultrafine colloidal CdS. Micro-heterogeneous medium such as inner sphere of reversed micell,[10,11)] surface of lipid vesicle,[12)] and solid medium such as silicate glass,[13)] synthetic clay,[14)] and zeolite[15)] have been used to prepare small-size CdS particles. However, no report has been published so far about the formation of size-controlled colloidal particles in aqueous solution, in which the kinetics at solid-water interface can be studied. In this letter we will show that the size of colloidal CdS particle in aqueous solution is controlled by adding some reagent in the procedure of the colloid preparation. Some optical and photochemical properties were examined for these size-controlled colloidal particles.

Cadmium chloride ($CdCl_2$), sodium sulfide ($Na_2S,9H_2O$), methylviologen, ethyleneglycol (from Nakarai Chemical Co. Ltd.), sodium hexametaphosphate (HMP), mercaptoethanol (RSH), methanethiol sodium salt (15% in water) and ethanethiol (from Tokyo Kasei Kogyo Co. Ltd.) were used without further purification. Colloidal CdS was prepared at room temperature by adding Na_2S aqueous solution into the $CdCl_2$ aqueous solution containing a stabilizing agent. As a stabilizing agent, HMP, polymeric viologen (PV4(4)),[16,17)] and α-dimethylamiono-6-Nylon (AQN, from Toray Co. Ltd.) were used.

When additives such as RSH were present in $CdCl_2$ solution, the obtained CdS colloids showed absorption as in Fig. 1. These spectra are different from that for the colloidal CdS obtained without additives which has absorption edge at about 520 nm. The shift of the absorption edge to shorter wavelength was well documented as the shift of energy levels with the decrease of diameter.[18,19] Then, the absorption spectra depend on diameter distribution of particles.[13,19] By adding RSH, an absorption peak was observed at 340 nm which is attributable to the transitions between discrete energy levels. Thus, the difference in the spectra in Fig. 1 are explained as various distributions of particle diameter. From the spectra one may qualitatively describe the particle size distribution as follows: Diameter of colloidal CdS obtained with RSH is smaller than that with ethanol and has narrower distribution than that with ethyleneglycol. When ethylenethiol is used as an additive, the very fine colloidal CdS is obtained, but no particle is formed with methanethiol. These differences may be caused by a different interaction between additives and Cd^{2+} in the formation process of CdS particles. Figure 2 shows the spectra of CdS colloids which were obtained in the presence of RSH additive and some stabilizer. Rather large CdS colloidal particles were obtained for HMP-stabilized colloid. This observation indicates that anionic HMP prevents the effect of additives compared with neutral AQN and cationic PV4(4) stabilizers.

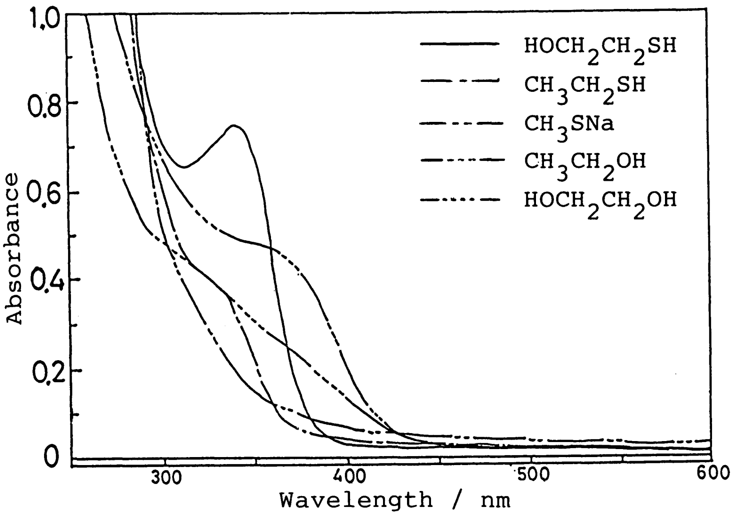

Fig. 1. Absorption spectra for AQN-stabilized CdS colloids prepared with various additives. [additives] = 0.24 M, [CdS] = 0.2 mM, [AQN] = 0.1 g/L.

In the presence of various amount of RSH, CdS colloids showing absorption spectra as in Fig. 3 were obtained. With the increase of the RSH concentration the absorption edge shifted gradually to the shorter wavelength, indicating the decrease of particle diameter. The spectra were fairly reproducible from preparation to preparation and did not change for several months under dark or deaerated condition. A similar series of the spectra is also

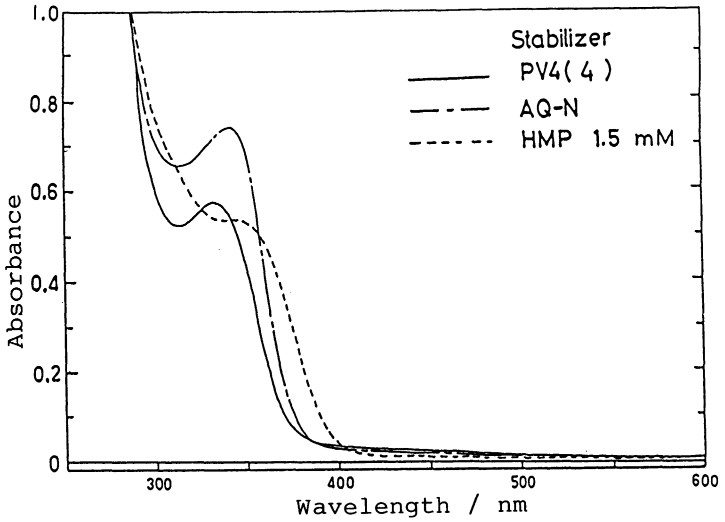

Fig. 2. Absorption spectra for CdS colloids prepared with 0.24 M mercaptoethanol and various stabilizers.

obtained for 0.5 mM CdS colloids. The wavelength of the absorption edge of the two series of spectra was plotted in Fig. 4 as a function of the concentration ratio of RSH to CdS. Figure 4 shows the absorption edge, or the particle, changes with the concentration ratio of RSH and S^{2-}. Since thiols such as RSH are adsorbed tightly on CdS surface,[20)] formation of CdS is probably a competing reaction with thiols. Thus, the size of colloidal CdS can be controlled by varying the concentration of additives.

Furthermore, when ionic thiols, such as mercaptopropionic acid and mercaptoethylamine (cysteamine), were used as additives, the obtained CdS colloids were stable without polymeric stabilizers.[21)] Presumably, these ionic additives are adsorbed tightly on the surface of CdS fine particles and prevent aggregation of the particles.

When polymeric viologen PV4(4) was used as a stabilizer, absorption of viologen cation radicals was observed with laser pulse irradiation on colloidal CdS. The formation of cation radical indicates that photoinduced conduction band electrons transfer to viologen group in polymeric stabilizer. The quantum yield of the electron transfer immediately after the laser pulse was measured for colloidal CdS particles having various diameters. Where the laser light was at 337 nm from a Molectron UV-24 N_2 laser. In Fig. 5, the

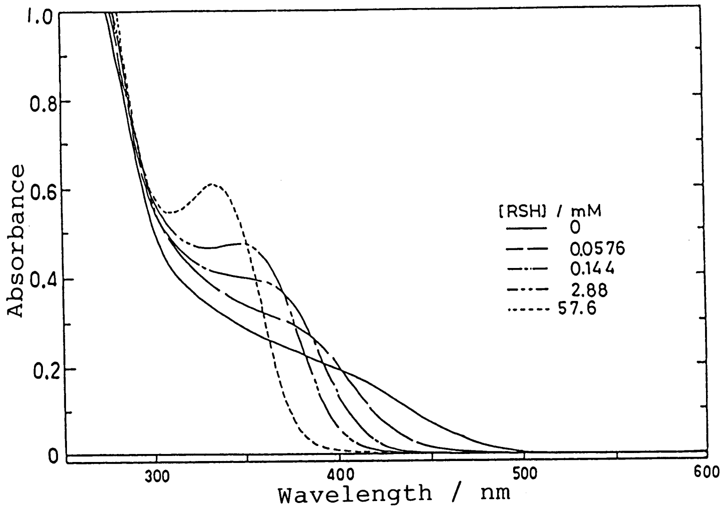

Fig. 3. Absorption spectra for AQN-stabilized CdS colloids prepared with various amounts of mercaptoethanol. [CdS] = 0.2 mM.

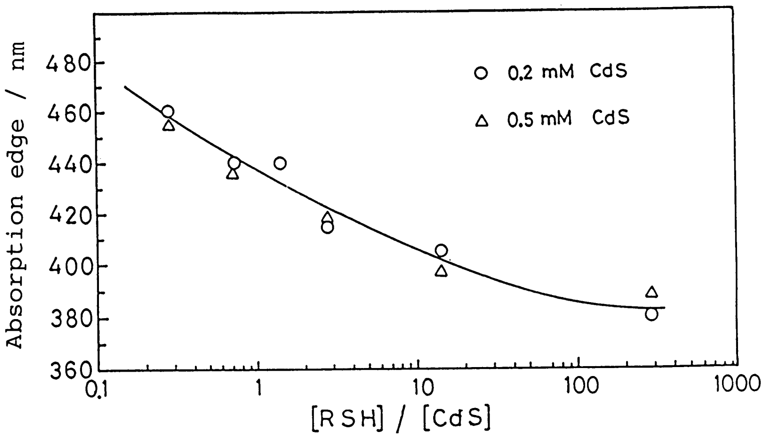

Fig. 4. Relationship between absorption edge and the concentration ratio of mercaptoethanol to CdS.

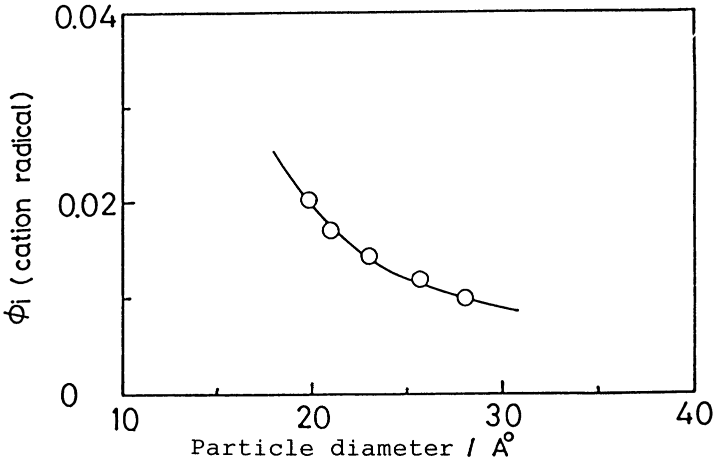

Fig. 5. Relationship between particle diameter and quantum yield of cation radical of pendant viologen of PV4(4)-stabilized CdS colloid.

obtained quantum yield was plotted against particle diameter which is estimated from the absorption edge according to the reported relationship.18) The quantum yield was almost inversely proportional to the diameter. When total weight of particles is constant, the sum of surface area of the particles is in inverse proportion to the diameter of each particle. Therefore, Fig. 5 indicates that the quantum yield is almost proportional to the total surface area. Provided that the number of trapping site for photoinduced conduction-band electron is proportional to the surface area, this observation consists with the result that the electron transfer occurs via surface trapped electron.22)

The present work was partially supported by the Iwatani Foundation and by a Grant-in-Aid for Scientific Research No. 61040040 from the Ministry of Education, Science and Culture.

References

1) Presented partly at the National Meeting of the Chemical Society of Japan, Tokyo, April, 1987.
2) "Homogenous and Heterogeneous Photocatalysis," ed by E. Pelizzetti and N. Serpone, NATO ASI Ser. C, Vol. 174, Reidel Publ. Co., Dordrecht (1986).
3) K. Kalyanasundaram, M. Graetzel, and E. Pelizzetti, Coord. Chem. Rev., 69, 57 (1986).
4) R. Rossetti, S. Nakahara, and L.E. Brus, J. Chem. Phys.,79, 1086 (1983).
5) R. Rossetti, J.L. Ellison, J.M. Gibson, and L.E. Brus, J. Chem. Phys., 80, 4464 (1984).
6) J.J. Ramsden, S.E. Webber, and M. Graetzel, J. Phys. Chem., 89, 2740 (1985).
7) A.J. Nozik, F. Williams, M.T. Nenadovic, T. Rajh, and O.I. Micic, J. Phys. Chem., 89, 397 (1985).
8) P.V. Kamat, N.M. Dimitrijevic, and R.W. Fessenden, J. Phys. Chem., 91, 396 (1987).
9) A. Fojtik, H. Weller, U. Koch, and A. Henglein, Ber. Bunsenges. Phys. Chem., 88, 969 (1984).
10) P. Lianos and J.K. Thomas, Chem. Phys. Lett., 125, 299 (1986).
11) T. Dannhauser, M. O'Neil, K. Johansson, D. White, and G. McLendon, J. Phys. Chem., 90, 6074 (1986).
12) H.J. Watzke and J.H. Fendler, J. Phys. Chem., 91, 854 (1987).
13) A.I. Ekimov and A.A. Onushchenko, JETP Lett., 40, 1136 (1985).
14) R.D. Stramel, T. Nakamura, and J.K. Thomas, Chem. Phys. Lett., 130, 423 (1986).
15) Y. Wang and N. Herron, J. Phys. Chem., 91, 257 (1987).
16) H. Miyama, Y. Nosaka, T. Kobayashi, and A. Kuwabara, J. Polym. Sci., Polym. Lett. Ed., 21, 945 (1983).
17) Y. Nosaka, A. Kuwabara, and H. Miyama, J. Phys. Chem., 90, 1465 (1986).
18) H. Weller, H.M. Schmidt, U. Koch, A. Fojtik, S. Baral, A. Henglein, W. Kunath, K. Weiss, and E. Dieman, Chem. Phys. Lett., 124, 557 (1986).
19) L. Brus, J. Phys. Chem., 90, 2555 (1986); New J. Chem. 11, 123 (1987).
20) M.J. Natan, J.W. Thackeray, and M.S. Wrighton, J. Phys. Chem., 90, 4089 (1986).
21) Y. Nosaka, N. Ohta, K. Yamaguchi, and H. Miyama, submitted for publication.
22) Y. Nosaka, and M.A. Fox, J. Phys. Chem., in press.

(Received December 24, 1987)