

Synthesis of cadmium sulfide nanoparticles *in situ* using γ -radiation

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Cadmium sulfide nanoparticles have been produced *in situ* in aqueous solution at room temperature by precipitating Cd^{2+} ions with homogeneously released S^{2-} ions, which were generated from the decomposition of $\text{Na}_2\text{S}_2\text{O}_3$ by γ -irradiation.

Semiconductor particles in the nanometric range with dimensions comparable to the Bohr radius exhibit strongly size dependent optical and electrical properties. Such particles may lead to quantum dot lasers, single electron transistors and a host of other applications.¹ It is important to synthesize such particles at the desired size with a narrow size distribution and in an easy-to-handle condition. Many of the studies have focused on group II–VI semiconductor nanoparticles, in particular cadmium sulfide, because of their technological importance. Nanosized CdS particles are often prepared by precipitating Cd^{2+} ions with gaseous H_2S ^{2,3} as the source of S^{2-} ions. Because Cd^{2+} ions and H_2S are in separate phases and mix unevenly, the formation and aggregation of CdS particles is inevitably uneven. Other reports are of efforts in preparing CdS nanometer particles by mixing Cd^{2+} ions with Na_2S in aqueous solutions, water/oil microemulsions or other media.^{4–6} As the precipitation of Cd^{2+} with S^{2-} is quicker than their homogeneous mixing, the inhomogeneity at early stages results in a broadening of the size distribution. Also, deoxygenation and fresh Na_2S aqueous stock solutions are necessary in these methods to avoid the formation of colloidal sulfur and other species because of the instability of Na_2S . On the other hand, some reports have utilized other S^{2-} reservoirs, such as P_2S_5 or thioacetamide (TAA), to provide a homogeneous and rapid release of S^{2-} ions.^{7,8} However, it is difficult to control the decomposition rate of P_2S_5 and TAA because non-aqueous or other complex manipulations are required.

Here we report a novel method for synthesis of the CdS nanoparticles at room temperature by utilizing homogeneous release of S^{2-} from the decomposition of sodium thiosulfate ($\text{Na}_2\text{S}_2\text{O}_3$) upon γ -irradiation.^{9,10} In the presence of metal cations such as Cd^{2+} in solution, sulfide particles are formed by precipitation. To prevent the small CdS particles from coming into close contact and undergoing further aggregation, a surfactant, sodium dodecyl sulfate (SDS), is also needed in the system. Isopropyl alcohol, which is a scavenger of oxidative radicals such as $\cdot\text{OH}$, is thus added to improve the yield of nanoparticles.

Analytically pure $\text{Na}_2\text{S}_2\text{O}_3$, $3\text{CdSO}_4 \cdot 8\text{H}_2\text{O}$, isopropyl alcohol and SDS were mixed in appropriate proportions in distilled water. The solutions were irradiated by a ^{60}Co γ -ray source. After irradiation, the pale yellow product was collected and washed with distilled water. Finally, the product was dried in vacuum at 50 °C for 3 h.

X-Ray powder diffraction (XRD) was carried out on a Rigaku Dmax γ_{A} X-ray diffractometer with $\text{Cu-K}\alpha$ radiation ($\lambda = 0.154178$ nm). The absorption spectrum was recorded on a UV-2100 Shimadzu UV–VIS spectrophotometer using quartz cells. Transition electron microscopy (TEM) micrographs were taken with a Hitachi Model H-800 transmission electron microscope, using an accelerating voltage of 200 kV.

Fig. 1 shows the XRD pattern of a sample of CdS produced by γ -irradiation and is compared with the data of the JCPDS

file.¹¹ The CdS particles were identified as β -CdS which belongs to the cubic crystal system. The broad peaks indicate that the dimensions of the CdS nanoparticles are very small. Employing Scherrer's equation,¹² the mean size of the CdS nanoparticles was estimated to be 2.3 nm.

The TEM image of the CdS sample of Fig. 1 is shown in Fig. 2, which reveals that small particles aggregate into secondary particles because of their extremely small dimensions and high surface energy. Therefore the size and the size distribution of the nanoparticles is difficult to determine precisely by simply viewing the TEM image.

The influence of the absorbed dose on the CdS nanoparticle size was studied by recording the absorption spectra of solutions irradiated with different absorbed doses, using aqueous solutions containing the same concentration of SDS as reference. Fig. 3 shows that the absorption spectra are structured and their absorption onset is in the violet wavelength range. It has been established that for relatively small semiconductor particles, the absorption spectrum provides a direct measure of the size of the crystallites.^{2,13–15} By comparing the position of shoulders with the results of ref. 2, the particles are estimated to be *ca.* 1.5 nm in diameter. Fig. 3 also shows the progressive shift of the

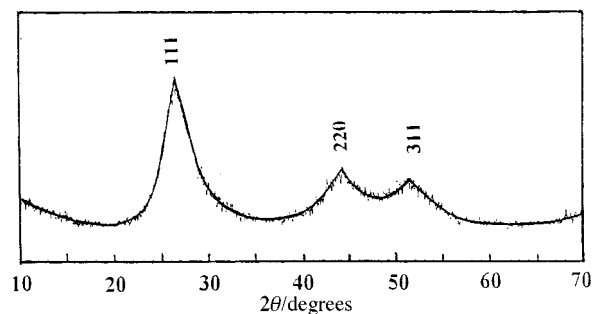


Fig. 1 XRD pattern of a CdS sample produced by γ -irradiation



Fig. 2 TEM image of the CdS sample shown in Fig. 1

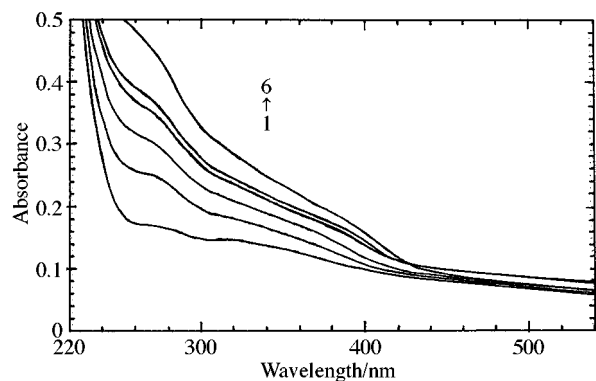


Fig. 3 Absorption spectra of irradiated CdS solutions with various absorbed doses: (1) 1000 Gy, (2) 1500 Gy, (3) 2000 Gy, (4) 2500 Gy, (5) 3000 Gy, (6) 4000 Gy. Solution: 2×10^{-4} M $\text{CdSO}_4 \cdot 8/3\text{H}_2\text{O}$, 2×10^{-4} M $\text{Na}_2\text{S}_2\text{O}_3$, 0.3 M Pr^iOH , 0.05 M SDS. Reference: aqueous solution containing the same concentration of SDS.

absorption onset with increasing irradiation dose, indicating that CdS particles gradually grow larger. The difference (in nm) between the position of the onset and the mean position of the shoulders characterizes the size polydispersity.¹⁶ Fig. 3 reveals that the size polydispersity of the particles increases as the absorbed dose increases but does not change distinctly. It seems that the observed homogeneity is a direct consequence of the homogeneous mixing of $\text{S}_2\text{O}_3^{2-}$ and Cd^{2+} , and the even production of S^{2-} upon γ -irradiation.

Upon standing for ten days, the irradiated solutions show almost no change in absorption spectra. The system in the absence of SDS displays a weaker absorption, which shifts to longer wavelength and decays quickly upon aging. The surfactant layer around the small particles provides a microenvironment without water and other ions and inhibits the reverse

(corrosion) reaction as well as coalescence; this favors the stabilization of small colloidal semiconductor particles.

In summary, γ -irradiation of the mixture provides promptly released and evenly dispersed S^{2-} ions, which then rapidly precipitate with Cd^{2+} ions and aggregate *in situ*. The surfactant prevents the small particles from coming into close contact and growing larger. A detailed study of the mechanism of the γ -irradiation route is underway and will be reported elsewhere.

Notes and References

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Received in Cambridge, UK, 20th April 1998; 8/02910E