Crystallographic and Spectroscopic Investigations of the Effect of Preparation Procedure on CdS Nanoparticles Made in Reversed Micelles

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Nanoparticles, due to their small size and unusual electronic and optical properties, have received a considerable amount of scientific attention. Of the many materials investigated, CdS may be considered a model compound. Numerous methods for the preparation of CdS nanoparticles have been demonstrated.[1-3] Reverse micelles have shown great versatility in the ability to control particle size through manipulation of the internal water-core dimensions of the micelle or nanoreactor. Optical characterization of CdS particles prepared in reverse micelles of different sizes shows a strong correlation between the absorption-edge onset or absorption-band maximum vs. particle size.[4,5] The phenomenon is attributed to the quantum-confinement effect. Recently it has been shown that the quantum efficiency of trap-state emission from CdS nanoparticles prepared with diameters on the order of 2-3 nm in reverse micelles can be significantly increased through a photoirradiation procedure.[5] The result is highly-luminescent (~18% quantum yield) CdS nanoparticles that display trap-state emissions. Such particles have potential applications to the development of gas sensors and electro-optical devices.[6] A detailed investigation of the quantum-efficiency-enhancement phenomenon has revealed a strong dependence of the optical characteristics on preparation procedure.[1] The dependence correlates with an interesting finding that the initial crystal structure of the CdS nanoparticles is an apparent function of the mixing dynamics of two precursor solutions for the reverse-micelle method. Rapid mixing of two solutions of small volume (5 mL each of $CdNO_3$ in AOT/heptane and Na_2S in AOT/heptane) resulted in CdS nanoparticles with cubic structure (Figure 1, top). Rapid mixing of two solutions of larger volume (15 mL of each solution), thus changing the mixing characteristics, resulted in CdS nanoparticles with a different structure, possibly hexagonal or a mixture of cubic and hexagonal (Figure 1, bottom). In both preparations, the water to AOT ratio was held constant (w = 4) and the $CdNO_3$ and Na_2S bulk concentrations were kept at $2x10^{-4}$ M. Particle sizes were not affected by the change in procedure, being ~2-3 nm for both methods; however, the UV-VIS spectra were very different for the two procedures (Figure 2). The CdS nanoparticles from small volume have an absorption-band onset and band maximum significantly blue shifted from that of the CdS nanoparticles prepared from large volume.

The ability to alter crystal structure through simple changes in preparation procedure (inadvertently or by design) can clearly play an important role, in addition to the quantum-confinement effect, in determining the optical and electronic properties of nanoparticles.[1] In this paper, we present data for the systematic investigation of the effects preparation procedure have on the crystal structure of CdS nanoparticles prepared using the reverse-micelle method. The results will be discussed within the context of the observed optical properties and the quantum-yield-enhancement phenomenon.

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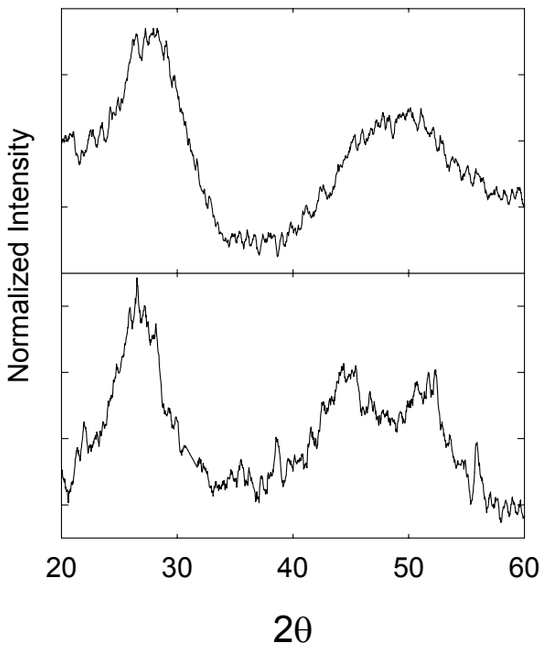

Figure 1. X-ray powder diffraction results for CdS nanoparticles prepared by the small-volume (top) and large-volume (bottom) methods.

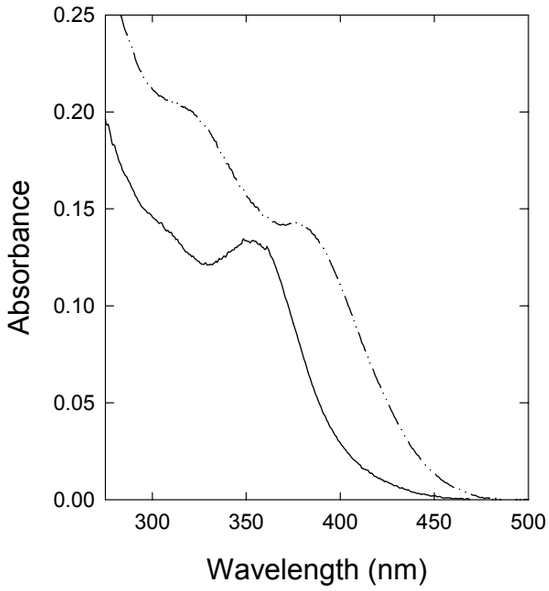

Figure 2. UV-VIS absorption spectra of the CdS nanoparticles prepared by the small-volume (—) and large-volume (-·-·-) methods.