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Synthesis of CdS quantum dots by mechanochemical reaction

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Abstract. The synthesis of ultrafine cadmium sulphide quantum dots by mechanochemical reaction has been studied using X-ray diffraction, transmission electron microscopy and UV-VIS absorption spectroscopy. The solid-state displacement reaction of $CdCl_2 + Na_2S \rightarrow CdS + 2NaCl$ induced by mechanical milling resulted in the formation of CdS particles with an average diameter of < 8 nm. The average particle size was controlled within the range of 4 to 8 nm by varying the size of the grinding media. The onset energy of optical absorption showed a blue shift with decreasing particle size.

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During the last decade semiconductor quantum dots have attracted considerable attention in many fields of Physics, Chemistry and Engineering [1–3]. When the dimensions of semiconductor particles approach the exciton Bohr diameter, dramatic changes in optical and electrical properties are expected due to the quantum confinement effect [4]. These properties are controllable to a certain degree, making semiconductor quantum dots very promising for a number of device applications in microelectronics, non-linear optics and other fields.

CdS is a II-VI semiconductor with a direct band-gap of about 2.4 eV and has a wide range of applications including phosphors and photovoltaic cells. The exciton Bohr diameter in CdS is 8 nm and quantum size effects are expected for smaller particle sizes. Many synthesis methods for producing CdS quantum dots have been previously studied [5–10]. Recently, Ding et al. [11–16] have shown that nanoparticles of a number of metals and oxides including Fe, Cu, Ni, Co, Al_2O_3, Fe_2O_3 and ZrO_2 can be synthesised by a novel method involving the mechanical activation of solid-state displacement reactions, either during ball milling or during subsequent heat treatment. Tsuzuki et al. [17] have synthesised ZnS nano particles of 7–9 nm in size in a salt matrix by mechanochemical processing via the reaction $ZnCl_2 + CaS \rightarrow ZnS + CaCl_2$. In this paper we report the synthesis of CdS quantum dots of 4 to 8 nm in diameter by the mechanochemical displacement reaction $CdCl_2 + Na_2S \rightarrow CdS + 2NaCl$.

The starting materials used in this study were anhydrous $CdCl_2$ powder (99.99%), Na pieces (99.9%), S powder (99.998%) and NaCl powder (99.9%) as a diluent. The $CdCl_2$ and NaCl powders were dried under vacuum at 200 °C prior to use. The reactants were sealed in a hardened steel vial with steel balls under a high-purity Ar-gas atmosphere. Milling was performed with a Spex 8000 mixer/mill using a ball-to-powder mass ratio of 10 : 1 and ball sizes of 4.8 to 12.6 mm. Following the milling, the NaCl was removed by washing the as-milled powder 5 times with deionised, deoxygenated water and dried under vacuum at room temperature.

The structure of the powder was studied under an Ar gas atmosphere with a Siemens D5000 X-ray diffractometer with Cu K_α radiation. The average crystallite diameter was determined from the linewidth of the X-ray diffraction spectra using the Scherrer formula [18]. The morphology and particle size were studied using a Philips 430 transmission electron microscope (TEM) equipped with an energy dispersive spectrometer for composition analysis. UV-VIS optical absorption spectra were recorded with a Milton Roy Spectronic 3000 Array.

The starting Na_2S powder was prepared by milling stoichiometric amounts of Na and S, together with NaCl as a diluent to prevent combustion and enable well separated particles of Na_2S to form [17]. The volume ratio of NaCl to Na_2S was 10 : 1. It was found that milling for 1 hour with 12.6 mm diameter grinding balls resulted in the formation of Na_2S having a crystallite size of $\sim$ 30 nm.

$CdCl_2$ was added to the mechanically alloyed mixture of Na_2S and NaCl in the stoichiometric amount to form CdS. The volume ratio of NaCl to CdS in the product phase was 16 : 1. The NaCl diluent was left in the starting powder to facilitate the formation of separate CdS nanoparticles in the NaCl matrix during milling [17]. X-ray diffraction patterns showed that milling for 1 hour with 12.6 mm diameter balls was sufficient to complete the reaction. The colour of the

powder was found to change with milling, becoming more yellow as the milling time increased. No changes in the diffraction patterns or powder colour were found after milling for longer than 1 hour.

Figure 1 shows the X-ray diffraction patterns of washed samples, which were milled to completion of the reaction, with ball sizes varying from 4.8 to 12.6 mm. The corresponding line spectra of bulk hexagonal (wurtzite) and cubic (zinc blende) structures [19] of CdS are shown for comparison. The diffraction pattern of the sample milled with 12.6 mm diameter balls consisted of peaks associated with both the cubic and hexagonal phases. The peaks associated with the hexagonal phase diminished with decreasing ball size and only the cubic zinc-blende phase was evident in the diffraction pattern of the sample milled with 4.8 mm balls.

The diffraction peak at 44° was used for determining particle sizes to avoid convolution of the peaks from hexagonal and cubic phases. As shown in Fig. 2, the CdS particle size decreased with decreasing ball size, reaching 4.3 nm in samples milled with 4.8 mm balls. The effect of ball size on the CdS particle size appears to be due to the decrease in the energy of ball powder collisions with decreasing ball size. Previous measurements in Spex mills have shown that changes in milling parameters which decrease the collision energy result in a decrease in the crystallite size of milled powders [20].

TEM measurements showed that the milled powder consisted of unagglomerated, nanosized particles. Figure 3 shows a transmission electron micrograph of the sample milled with 4.8 mm balls and subsequently washed. Using dark field imaging, the individual particles are found to be single crystals. The particle sizes are in the range of 3–7 nm, and more than 50% of particles have sizes between 4 and 5 nm, in good agreement with the X-ray diffraction measurements of particle size.

Figure 4 shows the absorption spectra of the samples milled with 4.8 mm and 12.7 mm balls at room temperature. The powders were washed and dispersed in a $(NaPO_3)_6$ aqueous solution. The absorption onset for the sample milled with 12.7 mm balls was 510 nm, which is nearly the same as that for bulk CdS (515 nm) [5]. This is consistent with the fact that the average particle size in this sample is 8.3 nm, just above the exciton Bohr diameter. On the other hand, the absorption onset for the sample milled with 4.8 mm balls was shifted toward lower wavelength. Since the cubic and hexagonal CdS have virtually the same band gap energy [21], this blue shift

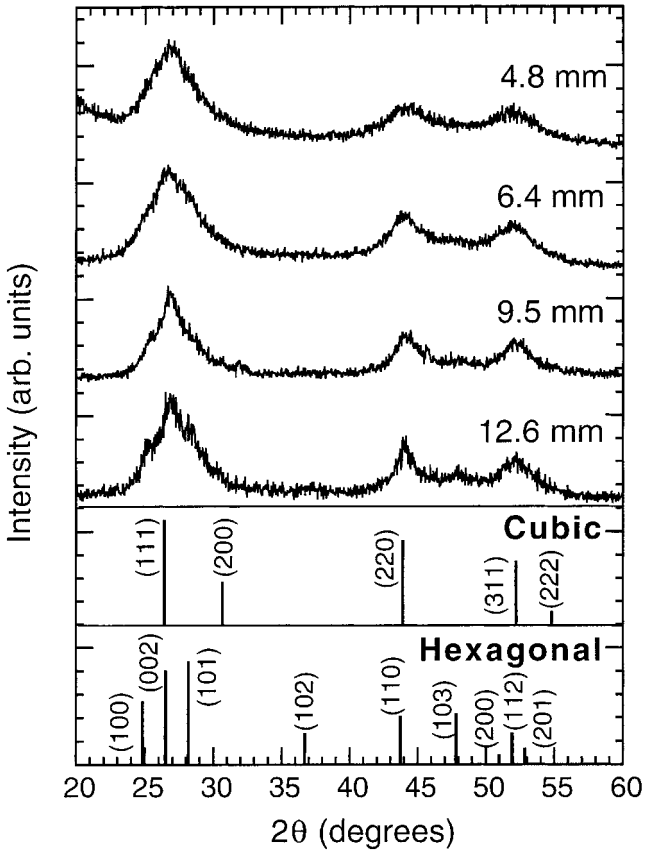

Fig. 1. X-ray diffraction patterns of milled and washed powders. The ball sizes are indicated in the figure. The corresponding line spectra of hexagonal (wurtzite) and cubic (zinc blende) structures of CdS are also shown for comparison

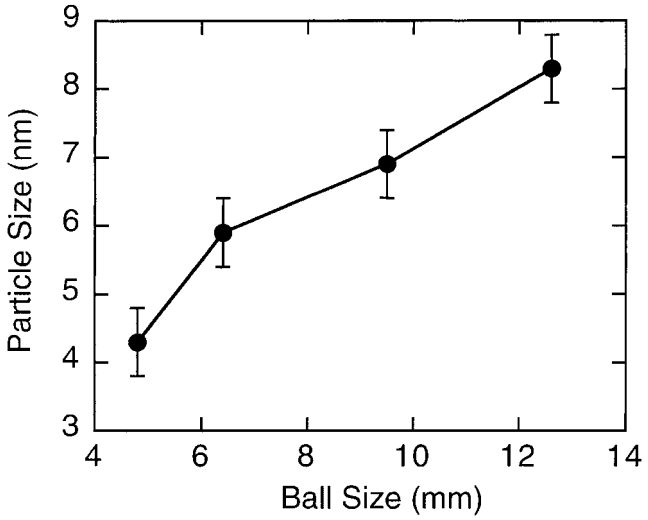

Fig. 2. Effect of ball size on the average CdS particle size determined from X-ray diffraction peak widths

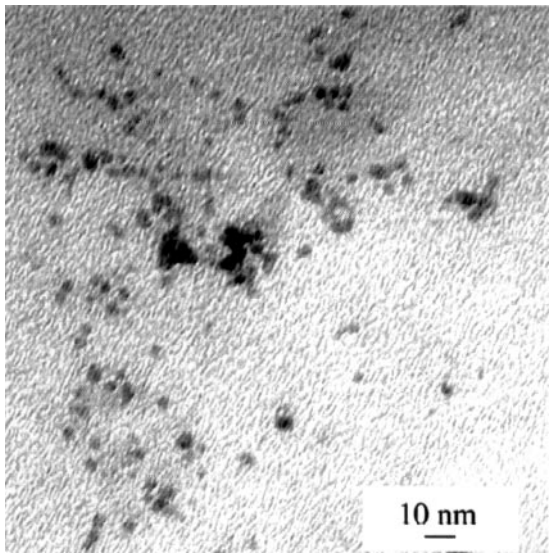

Fig. 3. Transmission electron micrograph of CdS particles synthesised by milling with 4.8 mm balls

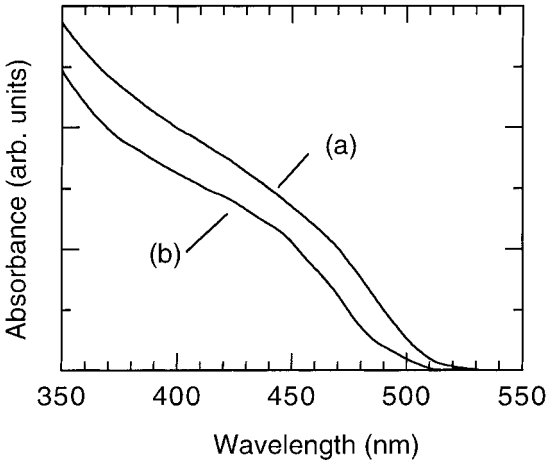

Fig. 4. Optical absorption spectra of the sample milled with (a) 12.7 mm, and (b) 4.8 mm balls

is attributed to the quantum confinement effect. Spanhel et al. [22] have measured the wavelength of optical-absorption threshold for CdS quantum dots as a function of particle size. The absorption threshold of the sample milled with 4.8 mm balls, which was determined as the wavelength of the inflection point of the absorption spectrum [22], was 470 nm. According to their results, an absorption threshold of 470 nm corresponds to a particle size of $\sim$ 4 nm, which agrees well with the size estimated from the X-ray diffraction measurements. The absorption shoulder around 450 nm may represent a 1s-1s exciton state [1, 23].

In conclusion, CdS quantum dots were synthesized by mechanochemical processing via the solid-state displacement reaction of $CdCl_2 + Na_2S \rightarrow CdS + 2NaCl$. The average particle size was controlled within the range of 4–8 nm by using different milling-ball size. This novel synthesis method has a wide range of applications for the synthesis of II-VI and III-V semiconductor quantum dots in an economical and efficient way.

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