Ultrasonic-mediated Preparation of Mesoporous Crystalline CdS Nanoparticle

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Cubic mesoporous CdS crystalline nanoparticles (4–6 nm) have been prepared by template-free ultrasonic-mediated precipitation, employing simple inorganic precursors at room temperature. The N_2 adsorption–desorption isotherm reveals that the as-prepared CdS nanoparticle has an average pore size of ≈5.4 nm.

Inorganic metal chalcogenides (CdS, PbS, and ZnS) have received considerable attention owing to their wide range application in solar cells, photocatalysis, sensors, luminescent devices, optical filters,[1–3] etc. It is well known that semiconductor nanoparticles show higher photocatalytic activity compared to the bulk materials because of changes in surface area, band gap, morphology, and generation of surface defects.[4] In general, the semiconductor metal oxides or chalcogenides have tunable band gap as a function of its particle size,[5] which creates adequate interests to the research in this field. Various methods have been adopted for the preparation of CdS nanoparticles.[6–9] Recently, the mesoporous materials have attracted much attention owing to their higher surface area, and application in selective catalysis and separation of large molecules. The preparation of mesoporous CdS with untainted cubic crystalline phase has little complication. The CdS has two stable crystalline phases, such as cubic and hexagonal; among them the hexagonal crystalline phase is more stable one. Because of effortless conversion of cubic to more stable hexagonal crystalline phase, preparation of pure cubic CdS has been a tricky issue.

Recently, sonochemistry has been demonstrated to be an excellent method for the preparation of mesoporous materials.[10–12] It arises from acoustic activation, the formation, growth, and implosive collapse of bubbles in a liquid. The collapse of bubbles generates localized hot spots with transient temperatures around 5000 K, pressure of about 20 MPa, and heating and cooling rates greater than 109 K s^{-1}.[13,14] These conditions are conducive for effectively perturbing the cations and the anions present in the solution faster and thereby alter the rate of the precipitation reaction. In the recent literature, few attempts have been made to fabricate cubic and hexagonal CdS nanoparticles by the ultrasonication precipitation route.[15–17] Indeed, mesoporous crystalline CdS nanoparticles have not been observed. Herein, we report a simple route to prepare mesoporous cubic crystalline CdS nanoparticles by ultrasonic-mediated precipitation using Na_2S and $Cd(NO_3)_2$ as the precursors at room temperature.

In the typical synthesis, 250 mL of 5 mM Na_2S solution was taken in a 1000-mL glass beaker and kept in an ultrasonicator water bath. Then, 250 mL of 1 mM $Cd(NO_3)_2$ was slowly added into the Na_2S solution using a peristaltic pump (Miclins) at the rate of 20 mL/h. The resulting precipitate was filtered and washed until the solution is free form S^{2-} ions. For the sake of comparison, bulk CdS particle was prepared by conventional precipitation method. In this method, an equimolar amount of Na_2S solution was added dropwise to a stirred solution of 1 M $Cd(NO_3)_2$, and the resulting CdS precipitate was washed and dried. The CdS particles prepared from ultrasonic method and usual precipitation method are designated as CdS-U and CdS-B, respectively, in subsequent discussions.

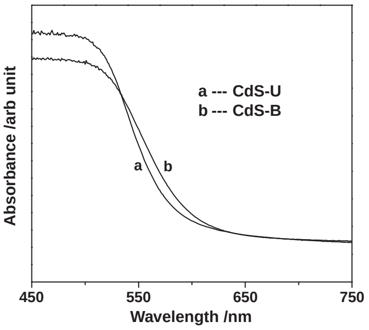

Figure 1. UV–vis absorbance spectra of as-prepared (a) CdS-U, (b) CdS-B.

Figure 1 shows UV–vis absorption spectra (CARY 5E UV–vis–NIR) of the as-prepared mesoporous CdS-U nanoparticle and as-prepared CdS-B. The onset absorption of CdS-U particle shows blue shift when compared to onset absorption of CdS-B. Meanwhile, owing to the relatively larger in the size CdS-U when compared to exciton radius, the quantum size effect may not account the observed blue shift. However, the CdS is a direct band gap semiconductor; the band gap energy has good correspondence with its particle size,[5] and the observed shift can be explained on the basis of smaller size of CdS-U nanoparticles when compared to CdS-B.

X-ray diffraction pattern (Figure 2) of as-prepared CdS-U nanoparticle reveals that the d values of 1.75, 2.04, and 3.32 correspond to the (311), (220), and (111) planes with the lattice constant $a = 5.818$, confirms the presence of cubic crystalline phase of CdS (JCPDS No. 10-0454). Peak broadening has also been observed in the as-prepared CdS-U nanoparticle and attributed to the smaller particle size. The particle size has been calculated using the Debye–Scherrer equation[18] and the value obtained is 4–6 nm. The as-prepared CdS-B shows no definite X-ray diffraction pattern indicating the amorphous nature of the material. Whereas, the calcination of CdS-B (300 °C, 2 h in air) yields the hexagonal crystalline CdS rather than cubic crystalline CdS because of more stability of hexagonal structure.

The N_2 adsorption and desorption isotherms of as-prepared CdS-U sample are shown in Figure 3. It can be seen from the figure that the hysteresis found in this material is of type IV and can be attributed to the mesoporous nature of the as-prepared CdS-U nanoparticle. However, in addition to mesopores, the as-prepared CdS-U shows the less microporosity, which can be clearly seen from the presence of Type-I isotherm[19] feature in N_2 sorption isotherm (Figure 3).

The pore size distribution has been studied using B. J. H.

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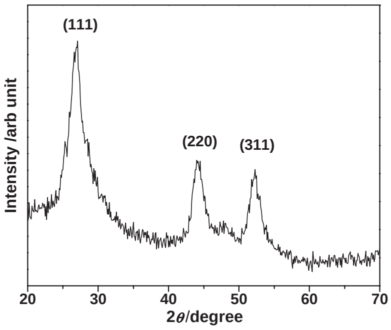

Figure 2. X-ray diffraction patterns of CdS-U.

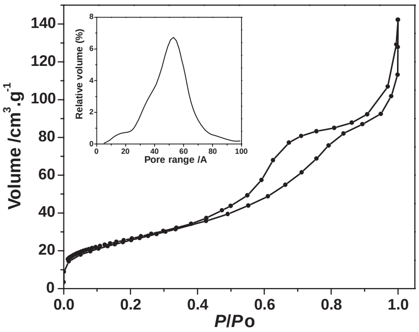

Figure 3. N_2 adsorption–desorption isotherm and pore size distribution (inset) of as-prepared CdS-U sample.

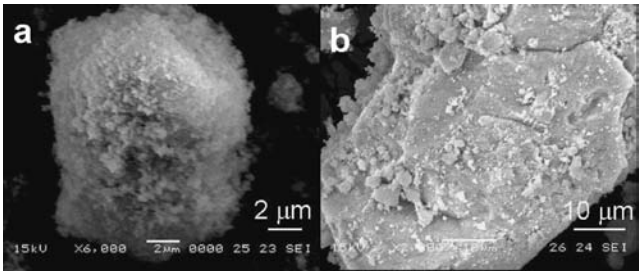

Figure 4. SEM photographs of (a) as-prepared CdS-U, (b) CdS-B.

method and is shown in Figure 3 (inset). The CdS-B has a specific surface area of $\approx 14\,m^2/g$. The specific surface area and pore volume of as-prepared CdS-U sample are $95\,m^2/g$ and $0.157\,cm^3/g$, respectively. It can be stated that maximum pore volume is contributed by the pores with an average size of 5.4 nm. It is particularly noteworthy to state that this method yields the low range mesoporous materials with less microporosity.

Surface morphology of CdS nanoparticles has been studied by scanning electron microscopy (SEM). The SEM pictures of the as-prepared CdS and CdS-B samples are presented in Figures 4a and 4b. The growth of fine spongy particles is observed on the surface of the CdS-U even at higher magnification (Figure 4a), whereas in case of the bulk sample in Figure 4b, the surface was found with large outgrowth of CdS particles.

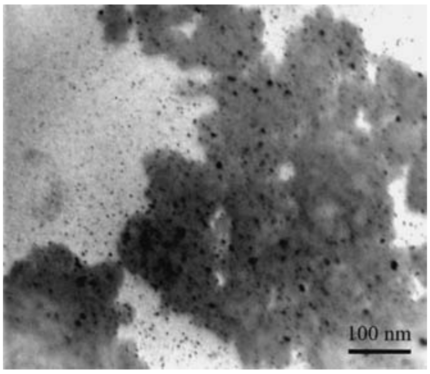

Figure 5. TEM image of as-prepared CdS-U particles.

The transmission electron micrograph (TEM) of the CdS-U sample is shown in Figure 5. The fine mesoporous CdS particles in the nanosize range (4–6 nm) both in well-dispersed and agglomerated forms are clearly observed. This mesoporous CdS particle is being investigated for photocatalytic water splitting.

In summary, we have demonstrated a simple route for the preparation of mesoporous CdS nanoparticles by simple template-free ultrasonic-mediated precipitation at room temperature. The most significant feature of this method is preparation of mesoporous cubic crystalline CdS nanoparticles in the range of 4–6 nm in size, which does not need a stabilizing agent and organic precursor. As no template material has been used, calcination is not needed. Using this method, other inorganic metal chalcogenide nanocrystallite porous in nature can also be prepared.

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