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Micro-emulsion under ultrasound facilitates the fast synthesis of quantum dots of CdS at low temperature

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ABSTRACT

Semiconductor nano-particles of CdS (about 2 nm) with a hexagonal phase have been prepared at a relatively low temperature (60 °C) and short time in micro-emulsion (O/W) under ultrasound. This study presents the effects of ultrasonic irradiation on the formation of CdS nano-particles in micro-emulsion and compares the results with samples prepared without sonication. The nano-particles have been characterized by high-resolution transmission electron microscopy (HRTEM), X-ray diffraction (XRD), energy dispersed analysis of X-ray (EDAX), UV–visible spectroscopy, and surface area measurements (BET). The effect of some important factors such as sonication time, intensity of ultrasound, temperature, and oil fraction was studied on the prepared nano-particles. The particle size can be controlled by applying the ultrasonic waves on the micro-emulsion under proper conditions. It has been postulated that bubble collapse generates high temperature and many nucleation sites which lead to the uniform spherical particles with small size and fast transition phase. Further evidence was obtained by UV–visible absorption and a photoluminescence spectrum. The study of optical properties reveals that the band-gap of the CdS nano-particle decreases with increase of sonication time and reach an approximate constant value. It was also observed that nano-particles grew faster at the beginning of sonication and then reached an almost constant value. The growth of nano-particles at different intervals during sonication was followed by UV–visible spectroscopy.

1. Introduction

Semiconductor nano-crystals have been widely studied in recent years owing to their unusual physical properties and the wide range of potential applications [1–3]. One of the important properties is the optoelectronic behavior of the semiconductors which is often strongly dependent on their particle size, morphology and crystal phases. In semiconductors with very small size, quantum confinement modulates the band structure of nano-particles and increases the band-gap [4]. The control of nano-particles' properties is significant for many technological applications such as light-emitting diodes [5], photocatalysts [6], biological labels [7], electrochemical cells [8], lasers [9], and microcavities [10]. Among the II–VI semiconductors, CdS is of special interest because it exhibits high photosensitivity and its band-gap energy (2.4 eV) appears in the visible spectrum [11]. Cadmium sulfide as a semiconductor is useful in applications such as optoelectronics [12], photocatalysis [7], and photo-degradation of water pollutants [13,14]. Various techniques have been successfully developed for the synthesis of CdS nano-crystals. The important methods used are electrochemical methods [15], gamma-irradiation [16], solvo-hydrothermal [17], thermal evaporation [18,11], microwave [19], micro-emulsion [20–22] and ultrasonic method [23].

Micro-emulsion processing has been proven to be an effective way for the controlled growth of inorganic nano-particles [24,25] with narrow size distribution and good mono-dispersity. This is due to its ability to stabilize the clusters and thus inhibit their indefinite growth. In addition, it is a gentle technique and does not require special instruments or extreme conditions [26]. The products of micro-emulsion process are particles with poor crystallinity. Therefore, to improve the crystal phase of the products it is necessary to use relatively high temperatures and long reaction times (above 300–400 °C) [17]. Hence, it seems that the combination of ultrasound and micro-emulsion is very suitable for synthesis of CdS nano-particles. This combination could be useful for controlling of crystal phase, morphology, and the size of the nano-particles.

In the present work, we have used a combined method of ultrasound and micro-emulsion which is called sono-micro-emulsion method for the synthesis of CdS nano-particles. Sonochemical processing has an important role in this kind of research which is due to the fact that this approach can in principle generate novel materials with unusual properties [23] such as metals [27], metal carbides [28], metal oxides [29], and metal chalcogenides [30,31]. Acoustic cavitation produced by ultrasonic waves can strongly

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increase the surface area and mass transfer between two phases, both of which enhance the diffusion coefficient on the interface mixing better than conventional agitation [32,33].

There are relatively few reports on the formation of nano-particles using the combination of ultrasound and micro-emulsion [34]. The sonochemical formation of CdS nano-particles have been reported with a hexagonal structure in the range of 80–120 nm in CS_2–water–ethylenediamine micro-emulsion [35]. Wang et al. have prepared CdS nano-particles with a cubic structure by a sonochemical method in an O/W micro-emulsion [36]. De et al. have synthesized semiconductor nano-particles (CdS and ZnS) in W/O media and reported that the photo-absorption threshold of semiconductors increases as the H_2O content of reverse micelles increases [37].

2. Experimental section

2.1. Materials

Ethylenediamine, sulfur, *p*-xylen, CTAB and 1-butanol from Merck and $CdCl_2$, $2H_2O$ from Fluka have been used without further purification. De-ionized water was used for the sample preparation.

2.2. Synthesis of nano-particles

First, 1000 mg of sulfur was dissolved in 50 ml of *p*-xylen at about 313 K. Then, a quaternary oil-in-water micro-emulsion formed by CTAB/1-butanol/*p*-xylen/water with a proper ratio and used as a reaction medium for CdS nano-particles preparation. The composite of micro-emulsion was set with weight ratio between oil and CTAB, water and oil, co-surfactant and surfactant at 0.6, 44, and 2, respectively. The micro-emulsion was prepared in two separate parts (A = 80% and B = 20% w/w). The A portion contained sulfur (37.8 mg) in oil phase and the B portion contained cadmium chloride (0.025 M) and ethylenediamine (0.41 M) in the aqueous phase of the micro-emulsion. The clear micro-emulsion of B was added slowly into the clear micro-emulsion of A. The mixed micro-emulsion was stirred by stirring and Heidolph homogenizer DIAX 900 separately and it was heated to about 60 °C for 30 min without sonication. In another experiment, the above-mentioned mixture of micro-emulsion was irradiated with ultrasound (20 kHz Sonifier W-450, output acoustic power 45.5 W (amplitude 75%), horn with 1.9 cm diameter) for 30 min (Fig. 1). During sonication, the temperature was increased from 30 to 60 °C by stopping the circulating bath. Nucleation processes began immediately and after 5 min a large amount of nuclei was formed. The precipitate was separated by centrifugation, washed with distilled water and then 2–3 times with absolute ethanol for removing the excess surfactant, and then dried in dessicator at room temperature.

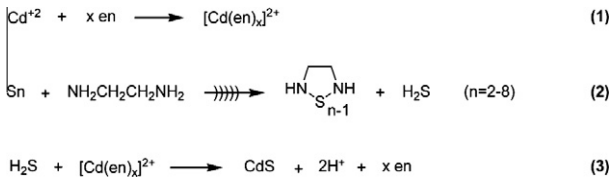
2.3. Characterization of CdS nano-particles

The structure and morphology of the final products has been studied by transmission electron microscopy (HRTEM), Hi-TEM is Hitachi 300 kV H-9500 TEM with accelerate voltage 300–100 kV and resolution 0.1 nm for the crystal lattice and 0.18 for point to point, X-ray diffraction (XRD) patterns were recorded in a wide angle range (2θ = 10–70°) by Bruker-axs, D8 Advance in scanning step of 0.02°/s, with monochromatized Cu Kα radiation (λ = 1.5406 Å). The energy dispersed analysis of X-ray (EDAX) was carried out using a Philips, XL30 model, and the surface area measurement (BET) was done by MONOSORB and the out-gassing of the samples were carried out at 100 °C for 3 h. The optical properties of the nano-particles were studied by UV–visible spectroscopy (Unico 2800).

3. Results and discussion

In the present study, it is confirmed that ultrasonic irradiation would favor the formation of the hexagonal phase of CdS and facilitates the phase transition at relatively low temperature. The effect of important factors such as sonication time, intensity of ultrasound, oil fraction, and temperature was studied on the CdS nano-particles.

The nature and morphology of the metal sulfides depend on the preparation conditions [17,38]. In the present work, sulfur



Scheme 1. Suggested reaction steps.

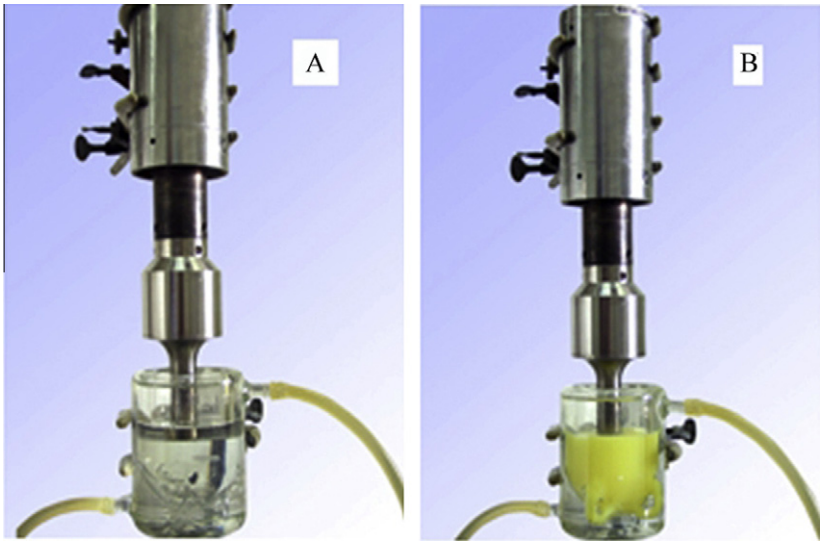


Fig. 1. Showing the experimental set up: (A) 0 min and (B) 30 min.