Available online at www.sciencedirect.com

SCIENCE DIRECT

Materials Letters 59 (2005) 2689 – 2692

materials letters

www.elsevier.com/locate/matlet

# Solution precipitation of CdS micro-spheres built up from wurtzite CdS crystals

Xin-Yong Tao[a,b], Xiao-Bin Zhang[a,b,*], Ji-Peng Cheng[b], Wan-Zhen Huang[a,b]

[a]*State Key Laboratory of Silicon Materials, Zhejiang University, Hangzhou 310027, China*
[b]*Department of Materials Science and Engineering, Zhejiang University, Hangzhou 310027, China*

Received 21 December 2004; accepted 18 April 2005
Available online 11 May 2005

**Abstract**

CdS micro-spheres built up from wurtzite CdS crystals have been synthesized via a simple chemical bath deposition method. X-ray diffraction (XRD) shows that the as-prepared CdS micro-spheres have a high crystallinity. TEM, SAED, and FE-SEM are used to investigate the micro-structure and the formation mechanism of the CdS micro-spheres is discussed.


*Keywords:* CdS; Micro-sphere; Chemical bath deposition

## 1. Introduction

There is increasing scientific interest in the synthesis of ordered two-dimensional (2D) and three-dimensional (3D) structures assembled by nanoparticles. Much work in this direction is stimulated by the potential use of ordered 2D and 3D nano/microstructures in advanced technologies, such as photonics and plasmonics [1]. Semiconductor nanocrystals have received more attentions for both fundamental research and technical application, owing to their strong size-dependent properties and excellent chemical processibility [1]. As CdS is one of the most important II–VI group semiconductors, having vital optoelectronic applications for laser light-emitting diodes and optical devices based on nonlinear properties [2], many routes have been exploited to synthesize CdS semiconductor particles and particle arrays [3,4].

Bioorganic molecules, such as DNA, have been successfully utilized as stabilizers and templates in the synthesis and assembly of CdS nanoparticles [5,6]. CdS nanoparticles have been also synthesized using inorganic templates such as mesoporous silica (MCM-41 [7] and SBA-15 [8]), porous alumina [9], and reverse micelles [10] and hyperbranched conjugated polymers as well [11].

Here we report that novel CdS micro-spheres with the aspects of soccer, built up from wurtzite CdS crystals, can be successfully synthesized via a simple chemical bath deposition method. In addition, the formation mechanism of CdS micro-spheres with especial shape is also discussed.

## 2. Experiment

Chemical bath deposition (CBD) [12] was used to synthesize CdS micro-spheres in the present work. In a typical procedure, 10 ml of 1 M thioacetamide (TAA) aqueous solution was injected into a mixture of 1 ml 0.5 M HCl and 10 ml 0.5M $CdCl_2$ under ultrasonic vibration until a transparent solution was formed (the ultrasonic treatment is just for more effective mixing). The resulting solution was kept in a chemical bath at different temperatures (40–90 °C) for 24 h. After it cooled down to room temperature, the precipitated products were filtered and washed with adequate ethanol and distilled water several times. Finally, they were dried in air at room temperature. To explore the formation process of CdS micro-spheres, some intermediate products were collected at different reacting times.

* Corresponding author. Department of Materials Science and Engineering, Zhejiang University, Hangzhou 310027, China.

0167-577X/$ - see front matter © 2005 Elsevier B.V. All rights reserved.
doi:10.1016/j.matlet.2005.04.022

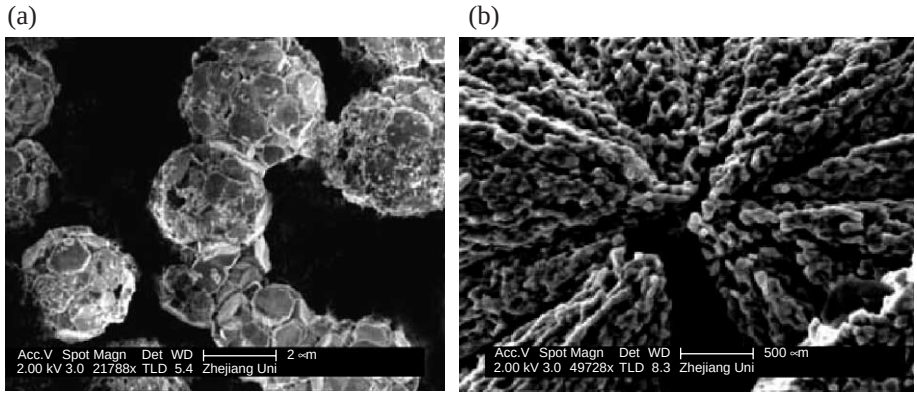


Fig. 1. Typical FESEM images of the as-prepared CdS spheres (a) and the inner surface of a cracked one (b) synthesized at 50 °C for 24 h.

The samples were characterized by X-ray diffraction (XRD, Rigaku D/Max 2550/ PC) using Cu-Kα radiation, field emission scanning electron microscope (FESEM, Sirion, FEI) and transmission electron microscope (TEM, JEM-200 CX, 160 kV).

## 3. Results and discussion

FESEM images (Fig. 1a) show the morphology of the as-prepared products (50 °C, 24 h), revealing that they are all spherical with a diameter distribution from 2 to 3 μm. These CdS spheres look like soccers, whose exterior surface is made up of several hexagonal facets. This particular morphology is rather different from the conventional CdS spheres reported previously [3–9]. In order to examine the inner texture of the CdS micro-spheres, intensively ultrasonic vibration was applied to split the CdS micro-spheres. Fig. 1b presents a typical cross-sectional FESEM image of a cracked CdS sphere, showing that it is actually composed of a large number of closely packed nanoparticles.

TEM observations indicate that only a few colloid spheres formed for a short aging time (e.g. 30 min, see Fig. 2a), which are in nanometer size with a narrow diameter distribution. The typical SAED pattern of the colloid sphere (Fig. 2a inset) exhibits widened rings feature, revealing the polycrystalline nature of the sample composed of nanoparticles. However, when the aging time was increased to 300 min, micro-spheres with the flat facets were observed, as shown in Fig. 2b. The appearance of discrete reflections in the SAED pattern (Fig. 2b inset) approves that the spheres consist of many nanocrystals with good crystallinity.

XRD analysis (Fig. 3) shows that the finally as-synthesized micro-spheres are the wurtzite (hexagonal) structure CdS with a lattice constant of $a = 0.4132$ nm and $c = 0.6710$ nm, which are very close to the ideal values of the perfect wurtzite structure as reported in the literature (JCPDS Card, File No.75-1545). No other diffraction peaks, e.g. CdO, Cd, S, in addition to CdS have been found. It is interesting to note that the well-crystallized wurtzite CdS spheres were obtained at such a low temperature (50 °C) in our simple CBD method. Rhee et al. have reported that the starting transit temperature of CdS nanoparticles from an amorphous phase to the crystalline one with hexagonal structure was as high as 160 °C in their synthesis process using hydrothermal method and that the temperature to get a nearly perfect hexagonal phase was to be above 240 °C [13]. A rough estimate of the particle size was obtained by application of the Scherrer equation [14,15]. The crystal size obtained by applying Scherrer equation is interpreted as an average crystal dimension, perpendicular to the reflecting planes [14]. The obtained values of the crystallite size are 9, 20 and 31 nm for samples prepared at 50 °C for 8, 16 and 24 h, respectively. The results indicate that the average particle sizes and the crystallinity gradually increase with the reaction time.

Based on the above results, a descriptive mechanism is proposed for the precipitation of CdS spheres and the growth

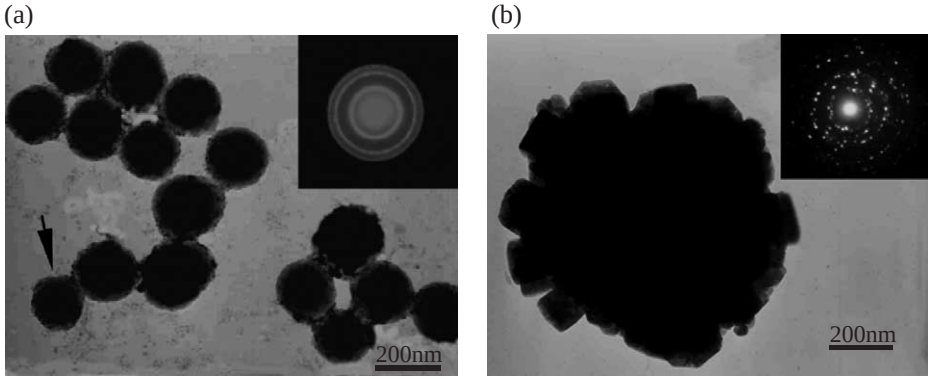


Fig. 2. Typical TEM images and the selected area electron diffraction patterns (SAED) of the products synthesized at 50 °C in different aging times: (a) 30 min and (b) 300 min.