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Morphological control of cadmium sulfide nanostructures by electrophoretic deposition

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ABSTRACT

Thin films and one-dimensional CdS nanostructures were formed by electrophoretic deposition of nanoparticles with morphological control. Particles less than 10 nm in diameter were prepared by a microwave assisted synthesis using trisodium citrate as capping agent. The particles were characterized by UV–Vis spectrophotometry, dynamic light scattering, and X-ray diffraction. Nanoparticles in the resulting aqueous dispersion were electrodeposited without any further treatment on aluminum plates. The nanostructures consisted of thin films with surface roughness being tuned with the applied voltage. One-dimensional nanostructures were formed by varying the applied voltage and by changing the molar ratio of the precursors in the nanocrystal synthesis. These results illustrate two different mechanisms of electrophoretic deposition that lead to the formation of different nanostructures.

Introduction

The last few decades have seen increasing research activity related to the synthesis of semiconductor nanocrystals and the construction of various nanostructures such as nanorods (Sitt, Hadar, & Banin, 2013), nanowires (Zhao, Hua, & Yao, 2013), thin films (Su et al., 2013), needles (Sun et al., 2011), ribbons (Jie et al., 2006), belts (Li et al., 2014), tetrapods (Zhao, Pang, Yang, Ge, & Wang, 2009), and other more unusual nanostructures (Kharisov, Kharissova, & Jose-Yacaman, 2010; Shen, Bando, & Lee, 2005). The potential of these materials has been demonstrated in applications including optoelectronics devices (Li, Jia, & Cao, 2010; Mora-Seró & Bisquert, 2010), photocatalysis (Hernández-Torres, Ojeda-Carrera, Sánchez-Cantú, Silva-González, & Gracia-Jiménez, 2014; Shen, Meng, & Xin, 2011), and biotechnology (Kenry Lim, 2013; Rakovich et al., 2014).

II–VI semiconductors such as CdS, CdSe, ZnS, and ZnSe are promising materials because of their unique optical and electronic properties, which can be tuned by changing the particle size (Segets et al., 2012), morphology (Buhro & Colvin, 2003), and capping agents (Shen et al., 2012). CdS is a wide direct band gap (E_g) semiconductor, which normally occurs in either cubic or hexagonal polymorphs (Subba Ramaiah, Pilkington, Hill, Tomlinson, & Bhatnagar, 2001).

CdS nanoparticles have been synthesized by wet chemical techniques including coprecipitation (Mishra, Srivastava, Prakash, Yadav, & Panday, 2011), solvothermal (Dalvand, Mohammadi, & Fray, 2011), and microwave-assisted synthesis (Kundu, Lee, & Liang, 2009). The use of microwaves to synthesize semiconducting nanocrystals allows for narrow particle size distributions by avoiding thermal gradients in reaction mixtures to give better control over the nucleation and crystal growth processes (Gerbec, Magana, Washington, & Strouse, 2005).

Many nanostructures have been produced by different physical vapor deposition techniques such as thermal evaporation (Grover et al., 2012), pulsed laser deposition (Acharya, Skuza, Lukaszew, Liyanage, & Ullrich, 2007), and sputtering (Islam et al., 2013). However, the high operating costs of these techniques have aroused interest in deposition techniques from aqueous media such as chemical bath deposition (Kwon, Ahn, & Yang, 2013) and electrophoretic deposition (EPD) (Hasan, Kavich, Mahajan, & Dickerson, 2009; Islam, Xia, Telesca, Steigerwald, & Herman, 2004; Salant et al., 2010).

EPD is deposition technique that is becoming more widely used and has been applied to the production of various nanostructures of different materials (Besra & Liu, 2007). This technique is based on the migration of charged particles under an external applied voltage. Suspended charged particles migrate toward the corresponding electrode and agglomerate to form a deposit (Boccaccini et al., 2006; Corni, Ryan, & Boccaccini, 2008). Thin films (Liepina, Bajars, Lusis, Mezinskis, & Vanags, 2013; Mahajan & Dickerson, 2010), one-dimensional nanostructures (Bai et al., 2009; Cao,

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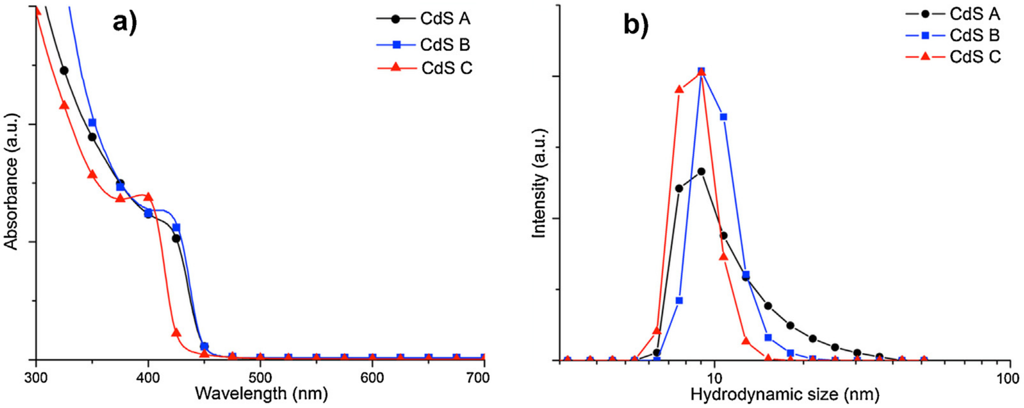

Fig. 1. (a) UV–Vis spectra and (b) particle size distribution of CdS A, B, and C nanoparticles.

2004; Sandoval, Marin, Real, Comedi, & Tirado, 2014), monolayers (Gonzalo-Juan, Krejci, & Dickerson, 2012; Krejci, Gonzalo-Juan, & Dickerson, 2011), and other nanostructures (Choi & Park, 2006; He, Cai, Lin, & Chen, 2010) have been produced by EPD techniques.

In this work we present the morphological control of CdS nanostructures using EPD in aqueous media. CdS thin films and one-dimensional nanostructures were successfully formed by depositing CdS nanoparticles that were prepared by a microwave-assisted synthesis.

Materials and methods

All chemical reagents were used as received without any further purification. The dispersions obtained were characterized by means of UV–Vis spectroscopy and dynamic light scattering using a Perkin Elmer Lamba 12, spectrophotometer (Perkin Elmer, Waltham, Massachusetts, USA) and a Microtrac Zetatrac (Nikkiso, San Diego, CA, USA), respectively. For X-ray diffraction (XRD) analysis, the solvent was evaporated at room temperature and the XRD patterns of the resulting solid were measured using a Siemens D5000 ($\lambda = 1.5418$ Å) (Siemmens, Munich, Germany). The CdS nanoparticle dispersions and the deposited CdS nanostructures were characterized by scanning electron microscopy (SEM) using a field emission-SEM (JSM 6701F, JEOL, Tokyo, Japan). The topographic and roughness analysis of the CdS films were performed by atomic force microscopy (AFM) (Angstrom Advanced Inc., Braintree, MA, USA), using a scanning probe microscope AA300 in contact mode.

The CdS nanoparticles were prepared following a previously reported procedure (López, Vázquez, & Gómez, 2013). A trisodium citrate solution (2 mmol/L) containing $CdCl_2$ and thioacetamide (TAA), at one of the following Cd/TAA molar ratios: 1:1 (CdS A), 1:2 (CdS B), and 2:1 mmol (CdS C), was heated for 60 s in a conventional microwave oven (LG-intelowave) at 2.45 GHz and 1650 W of nominal power. The formation of CdS nanoparticles was apparent as the reaction mixture color changed from transparent to yellow.

The CdS nanoparticles were deposited on aluminum (AA 1100 alloy >99% Al) electrode plates (dimensions 0.8 cm × 4 cm) in an electrophoretic cell with the vertically aligned electrodes separated by 1 cm. The plates were polished and cleaned with deionized water and acetone prior to use. To evaluate the effect of applied voltage on the morphological characteristics of the CdS films, the particle sample CdS A was deposited under different constant applied voltages of 300, 600, and 900 mV for 24 h. After deposition, the electrodes were extracted from the colloidal suspension and maintained at the same voltage for a further 15 min. The effect of the ionic environment on the morphological characteristics of the CdS films was evaluated by depositing all the CdS particle types, CdS A, B, and C, at 600 mV for 24 h.

Results and discussion

The solution UV–Vis spectra of the CdS nanoparticles synthesized at the different Cd/TAA molar ratios are shown in Fig. 1(a). An absorption peak around 412 nm is visible for the CdS A and B nanoparticles, whereas the UV–Vis spectrum of CdS C is clearly blue-shifted, indicating a smaller particle size. This absorption is related to the band gap (E_g). The calculated E_g values were 3.00 eV for both the CdS A and B particles. For the CdS C particles, E_g was determined as 3.10 eV. These values are larger than the E_g reported for bulk CdS (2.42 eV) owing to quantum confinement in the nano-sized CdS particles. The E_g values were then used to estimate the particle size by an empirical formula Eq. (1) reported by Yu, Qu, Guo, and Peng (2003), where D (nm) is the particle's diameter and λ (nm) is the wavelength of the first excitonic absorption peak.

$$D = -6.6521 \times 10^{-8}\lambda^3 + 1.9557 \times 10^{-4}\lambda^2 - 9.2352 \times 10^{-2}\lambda + 13.29 \quad (1)$$

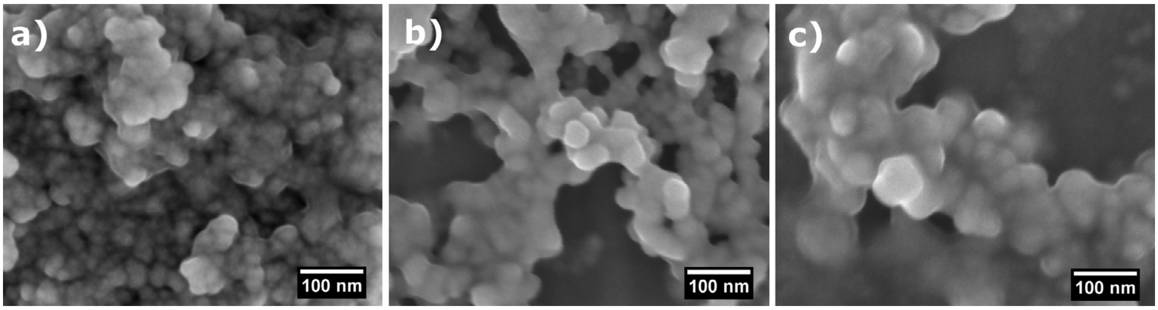

Fig. 2. SEM images of (a) CdS A, (b) CdS B, and (c) CdS C nanoparticles.

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