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Ultrasound-assisted preparation of CdSe nanocrystals in the presence of Polyvinyl alcohol as a capping agent

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ABSTRACT

Nanosized Polyvinyl alcohol-capped CdSe particles were prepared via a simple and fast ultrasound-assisted technique through the reaction between aqueous solutions of cadmium acetate and sodium selenosulfate. The nanoparticles are characterized using X-ray diffraction (XRD), UV–Visible spectrophotometer, Scanning electron microscope (SEM), Energy dispersive X-ray (EDAX) analysis and Fourier transform infrared (FTIR) spectrometer. XRD pattern reveals that the nanoparticles are in well-crystalline cubic phase. The broadening of diffraction peaks indicated the formation of particles in the nanometer size regime. A shift in absorption peak is observed in the spectra near 544 nm due to quantum confinement effect. Particle sizes calculated from the X-ray diffraction studies agree fairly well with those estimated from optical absorption studies. The homogeneity of the sample could be controlled by adjusting the concentration of Polyvinyl alcohol. SEM images of a specific concentration of Polyvinyl alcohol for as-prepared CdSe nanocrystals show uniform particles distribution. The particle size is found to be less than 100 nm based on the observed SEM images and the reason of this mismatch is discussed. The calculated result from XRD and optical characterizations shows that the particles size is smaller than those observed in SEM images. The elemental analysis from EDAX shows that the average atomic percentage of Cd:Se was 50:50 showing that the prepared samples are exactly stoichiometric.

1. Introduction

Research on nanomaterials increased remarkably in the past years due to their unique characteristics such as quantum confinement effects and their potential applications. The term, quantum confinement effect, was introduced to explain a wide range of physical and chemical properties of nanostructured materials in response to changes in dimensions or shapes within nanoscales [1–6]. The reasons for this behavior can be reduced to two fundamental phenomena. First is the high dispersity of nanocrystalline systems; i.e. the number of atoms at the surface is comparable to the number of those which are located in the crystalline lattice [7]. The second phenomenon arises from quantum mechanics where it is well known that electrons and holes, confined by potential barriers to a space comparable or smaller than the De Broglie wavelength of the particles, have discretely allowed energy states rather than a continuum [8–10]. The size dependent emission property, particularly for CdSe nanocrystals, renders its significance in modern technologies such as large screen liquid crystal display [11], light-emitting diodes [12], thin film transistors [13], fluorescent probes in biological imaging [14], photovoltaic devices [15] gamma ray detectors [16], lasers [17], biomedical tags [18], photoconductors [19,20], etc. There are several methods for the preparation of selenides including solid-state reactions [21], electrochemical methods [22,23],

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microwave-assisted preparation [24,25], chemical bath deposition [26–29], high temperature pyrolysis of single source precursors [30,31], vacuum deposition [32], gas-phase reaction between elements or its compounds and gaseous H_2Se [33–35], photochemical methods [36] and reaction of an organocadmium precursor with an Se source in a high temperature solvent[37]. Polymers are considered to be a good choice as capping agents for such purposes. Polyvinyl alcohol (PVA) is an important water-soluble, transparent, tasteless and nontoxic polymer and it has been successfully applied in nanofabrication [38–46].

Generally selenosulfate and selenourea are the main selenium sources to provide Se^{2-} ions for the preparation of selenides through reactive solution growth. However, when compared to selenosulfate, selenourea is expensive and not readily available. Thus, selenosulfate is a better Se^{2-} source for solution preparation of selenides. Cubic CdSe semiconductor thin films have been prepared based on the chemical reaction of complexed cadmium salts, with sodium selenosulphate (Na_2SeSO_3) in aqueous alkaline medium [47–50].

Until now, a lot of research has been done on the synthesis of CdSe nanomaterials with wideuse of the reaction between cadmium salt and sodium selenosulfate being widely used to prepare CdSe nanoparticles and CdSe nanowires [51–54]. Most of these above-mentioned methods need long reaction times and/or special instrument to synthesize CdSe nanoparticles because of the presence of a complexant in the reaction media. However, the reaction between uncomplexed Cd salts and selenosulfate can be reasonably fast [55]. In this paper we report the synthesis of CdSe nanocrystals in PVA solution that acts as a stabilizing agent; they have been grown via an ultrasound-assisted process. We have chosen the ultrasound-assisted process because of its many advantages, such as easier composition control, better homogeneity, lower processing temperature, easier fabrication of plenty of nanoparticles, lower cost, and possibility of using high purity starting materials [56–58]. In this paper we also report the structural, optical and structural properties of CdSe nanocrystals.

2. Experimental section

2.1. Chemicals

Cadmium acetate dihydrate ($C_4H_6CdO_4 \cdot 2H_2O$ extra pure), Se powder (purity ≥ 99%), sodium hydroxide (NaOH extra pure), sodium sulfite (Na_2SO_3 extra pure), Polyvinyl alcohol (PVA $(C_2H_4O)_x$) powder and absolute ethanol were obtained from Merck and directly employed without purification.

2.2. Instruments

Optical absorption studies were carried out using a UV–vis spectrophotometer (Lambda-40 Perkin Elmer). The structural characterization of nanocrystals was carried out by analyzing X-ray diffraction (XRD) patterns, obtained using a Philips X Pert, X-ray diffractometer using Cu Kα radiation (wavelength = 1.54056 A°). The surface morphology of samples was analyzed using a scanning electron microscope (SEM), LEO, 1430VP at 14 and 15 kV accelerating voltage. Quantitative analyses were obtained by an energy dispersive X-ray analysis (EDAX) model LEO, 1430VP with accelerating voltage 15 kV. The samples used for SEM and EDAX observations, which at first bounded to SEM stage, the sample on the stage was coated with a thin layer of gold and palladium. The Fourier transform infrared spectra were obtained using a Varian-3600 FTIR spectrometer.

2.3. Preparation of polyvinyl alcohol (PVA) stabilized CdSe nanoparticles

PVA-Capped CdSe nanocrystals were prepared using the following typical procedure. An aqueous solution of cadmium acetate complexed with tartaric acid was mixed with an aqueous solution of sodium selenosulfate (Na_2SSeO_3). This solution was prepared via dissolution of 0.25 g of elemental selenium powder in 50 ml of 1.1 M aqueous solution of Na_2SO_3 by magnetical stirring for 2 h at 80 °C applying reflux column system. All of the selenium powder

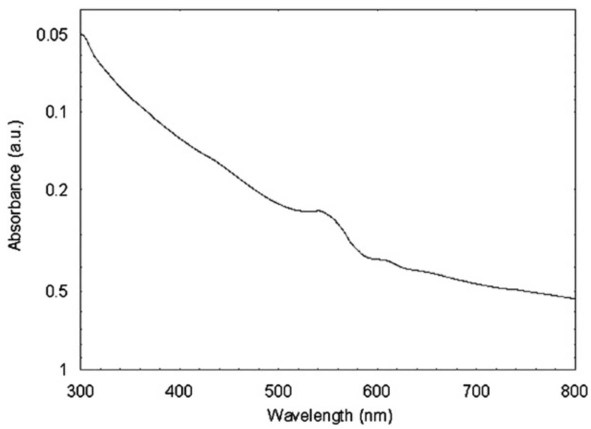

Fig. 1. UV–vis spectra of PVA-capped CdSe nanocrystals prepared by ultrasound-assisted technique.

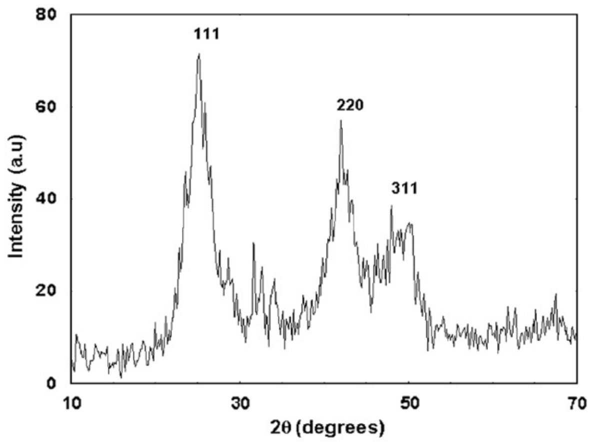

Fig. 2. XRD pattern of PVA-capped CdSe nanocrystals prepared by ultrasound-assisted technique.