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Investigation on a two-pot solvothermal route for preparing high quality CdSe QDs

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High quality zinc-blende CdSe quantum dots (QDs) have been synthesized through a novel two-pot solvothermal route employing non toxic and low cost materials without the use of inert atmosphere. The temperature is varied by maintaining the precursor amount a constant in all experiments. The X-ray powder diffraction (XRD) and high resolution transmission electron microscope (HRTEM) measurements indicate the occurrence of zinc-blende CdSe quantum dots (QDs) with the size ranging from 3.5 to 7 nm. The absorption spectra of the CdSe nanoparticles exhibit a blue shift, as an indication of the quantum confinement effect. The photoluminescence (PL) spectra of the CdSe nanoparticles confirm that the particles are monodisperse, size-tunable and possess enhanced luminescent property.

1. Introduction

The synthesis of II–VI semiconductor quantum dots, in particular CdSe, has become well-established, and the interest in these materials has been fueled by the ability to synthetically adjust their size-dependent electronic and optical properties [1]. In CdSe, the conduction or lowest unoccupied band is composed of Cd 5s orbitals. The valence or highest occupied band formed from Se 4p orbitals is more complex due to the 3-fold spatial degeneracy. Quantum confinement occurs when the radius of the nanocrystals becomes comparable to the bulk exciton Bohr radius ($\sim$56 Å for CdSe) [2]. Through quantum confinement of photocreated electron-hole pair, the optical properties of the nanocrystal can be tuned by its size. For example, a 1.2 nm nanocrystal will have 88% of its atom on the surface and absorb light at 420 nm, while an 8.5 nm nanocrystal consists of 20% surface atoms and absorbs light at 650 nm [3]. The applications, primarily involving CdSe NCs include the photostable luminescent biological labels [4], solar cells [5] and light-emitting devices (LEDs) [6]. To realize these wide ranges of potential applications, the luminescent properties of semiconductor nanocrystals must be strictly controlled. The development of a number of colloidal synthetic routes over the last years, particularly for CdSe, has yielded a remarkable degree of control over the size and shape of the nanocrystals [7]. The synthesis of CdSe nanocrystals has improved considerably over the past decade. Among the various methods used for preparing CdSe, the TOPO method permits the production of highly monodisperse nanoparticles in quantities of hundreds of milligrams in a single experiment. However, a great hindrance for its development on a large scale is represented by the high temperatures employed and by the toxicity of the starting materials. In particular, alkyl metals such as $(CH_3)_2Cd$ and $(CH_3)_2Zn$ are pyrophoric, explosive at high temperatures and liberate highly toxic gases of metal oxide so that all the reactions involving these chemicals must be carried out with extreme precautions under an inert atmosphere. Hence, efforts have been made to modify the TOPO method with more stable and less toxic cadmium sources. A series of experiments led to the conclusion that $(CH_3)_2Cd$ is not a necessary raw material for producing high quality CdSe QDs and it can be replaced by other cadmium salts, for example CdO and cadmium salts with an anion of a weak acid, such as $Cd(Ac)_2$ and $CdCO_3$ are proved to be excellent substitutes [8,9]. This new synthetic scheme works significantly better than $(CH_3)_2Cd$ related ones and can be readily scaled up for the industrial production. The use of alternative ligands and precursors for the synthesis of CdSe nanocrystals at elevated temperatures provided a decent database to design a synthetic system that generates CdSe nanocrystals with acceptable emission properties. Among all the ligands reported, primary amines have shown the most promising results for achieving high PL efficiency for a variety of semiconductor nanocrystals. Especially the presence of stearic acid was proven to be helpful for the formation

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of CdSe nanocrystals in the orange-red window. In addition, cadmium stearate in amines can bear significantly high temperatures, which is required for the formation of semiconductor nanocrystals with high structural quality. The preparations of soluble 3 nm thiol-capped CdSe nanoparticles have been reported using cadmium stearate under similar solvothermal conditions. The use of stearates instead of toxic and flammable organometallic precursors is worthy of note [10,11].

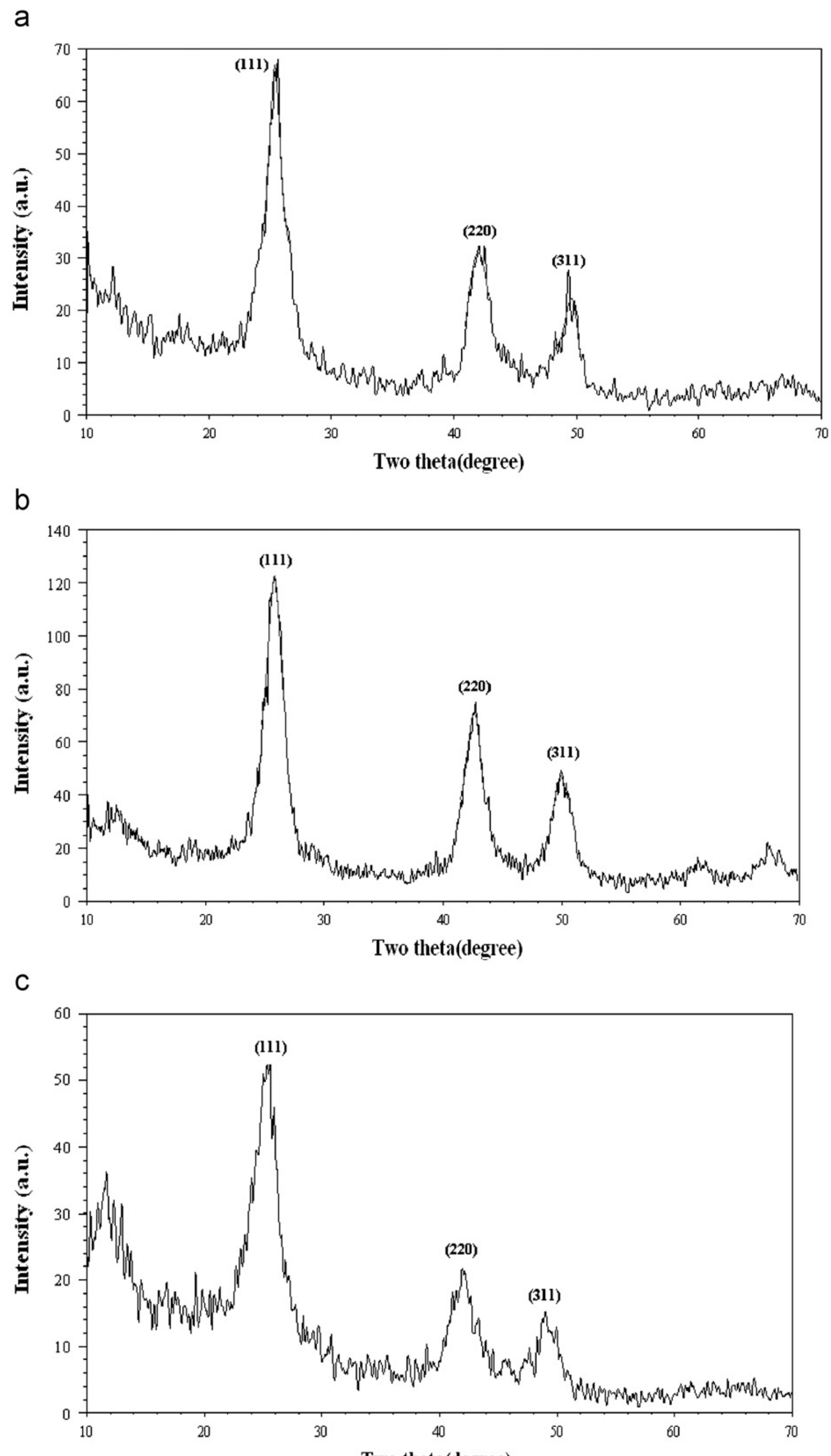

Fig. 1. XRD patterns of the CdSe nanoparticles prepared at (a) 200 °C (b) 220 °C and (c) 240 °C.