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Optical characterization of CdS semiconductor nanoparticles capped with starch

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ABSTRACT

Starch capped cadmium sulfide (CdS) nanoparticles were synthesized by aqueous solution precipitation. Starch added during the synthesis of nanoparticles resulted in cadmium-rich nanoparticles forming a stable complex with starch. The size of the CdS quantum dots was measured using high resolution transmission electron microscopy (HRTEM) and X-ray diffraction (XRD). The average diameter (d) of nanoparticles spanned the range 4.8 ± 0.4 to 5.7 ± 0.2 nm when the pH of the solution was varied within the range 10–14. The main Raman phonon of CdS, the longitudinal optical mode located around 300 cm^{-1}, softens as diameter decreases, in accordance with theoretical predictions. In addition, the largest Raman response of starch, near 478 cm^{-1}, related with the important skeletal vibration modes of the starch pyranose ring, dominates the spectra of the CdS capped nanoparticles and also softens as the size decreases. This fact indicates a strain variation on CdS as a function of d which increases as the pH increases.

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1. Introduction

Due to the wide range of possible applications, the development of metal and semiconductor–polymer nanocomposites presents new challenges and opportunities for future technologies. As an intermediate between molecular and bulk states, inorganic nanoparticles often exhibit unique properties (e.g., electrical, optical, magnetic, and catalytic), which are, in addition, dependent on their size. This also makes them perfect building blocks for preparation of composite nanostructures with adjustable performances. A polymer is a good choice for a matrix material since it enables an easy processing of the obtained nanocomposites into technologically useful forms. Furthermore, depending on the preparation procedures, polymer matrices can be used to control the size and shape of the inorganic nanofiller.

Semiconducting nanoparticles research is one of the most investigated subjects due to their wide field of applications. The physical properties of nanoparticles are strongly dependent on their size, essentially due to quantum confinement effects. In semiconductors, quantum confinement modulates the band structure of nanoparticles and hence, many properties can be tuned by changing the nanoparticles size. Lately, the surface modification of fluorescent semiconductor nanoparticles by biomolecules and nucleic acids has added a new dimension to nanoparticle research with respect to their biological applications [1]. These recent developments have increased the need for characterization techniques that can provide molecular level information about the electronic and optical properties of nanocrystalline semiconductors. Resonance Raman spectroscopy is an excellent probe of molecular or solid-state vibrations that are coupled to electronic transitions. Quite detailed information about the energies of the ground and excited states of the system can be obtained from steady-state Raman measurements. Raman scattering in polar semiconductors depends on the interaction of lattice vibrations (phonons) and electrons; since phonons are very sensitive to their local environment, resonant Raman spectroscopy can, in principle, provide more reliable information about the electronic structure of nanostructured materials. Resonant Raman spectroscopy has been used to probe the nature of CdS ultrathin films grown onto Au substrates using electrochemical atomic layer deposition [2]. In addition, there is a report on Raman spectroscopy measurements performed on nanostructured CdS prepared by a chemical route [3,4]. The nanoparticles, synthesized using aqueous solution precipitation, are small enough to show effects due to quantum confinement. It is well known that in a crystalline CdS semiconductor the observed Raman shifts usually correspond to longitudinal optical (LO) phonons, transverse optical (TO) modes [5], and LO-multiphonon processes [6]. But in the case of nanostructured materials the quantum size effects come into play due to the enhancement of the surface to volume ratio which makes it plausible for observation,

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besides the LO phonon, the surface phonon (SP) mode [3] and the second harmonic LO phonon [4] by Raman scattering.

The purpose of the present work is to study the optical characterization of starch capped CdS quantum dots as a function of the nanoparticle size by using X-ray diffraction, HRTEM, photoacoustic spectroscopy, and Raman spectroscopy, which would eventually allow for the biocompatible capping of semiconductor nanocrystals. Previously, we have reported [7] an effective one-step method for the preparation of well-controlled CdS nanoparticles of uniform size using starch as capping agent in an aqueous solution. The synthesis of cadmium sulfide nanoparticles by aqueous solution precipitation consists of preparing a chemical bath of a salt which contains cadmium cations, and anions of either, sulfates, nitrates, chlorides or acetates, and sulfur contained in thiourea. Here, we report the dependence of the CdS nanoparticles size on the pH of the growing solution, and study the vibrational properties as a function of the diameter in the interval 4.8–5.7 nm.

2. Experimental

CdS nanoparticles were prepared by aqueous solution precipitation. The chemicals used for CdS synthesis are cadmium chloride ($CdCl_2$), potassium hydroxide (KOH), ammonium nitrate (NH_4NO_3) and thiourea ($CS(NH_2)_2$) (all of them from Sigma–Aldrich). Native starch (Sigma–Aldrich) was used as the capping agent. A dilute aqueous solution of sodium hydroxide (NaOH) was used to control the pH and deionized water was used as the solvent. The CdS nanoparticles were obtained by controlling the pH in the range 10–14. The temperature of the aqueous solution precipitation was raised up to 80 °C and maintained at this temperature for 15 min for all the samples. The details of the preparation procedure are published elsewhere [7].

The structure and phase of the powder sample were determined with a Siemens D5000 X-ray Diffractometer using the *CuKα* radiation. The optical absorption of the nanoparticles was recorded by photoacoustic (PAS) spectroscopy. The PAS spectra were measured using a home-made spectrometer consisting of a 1000 W xenon lamp (Oriel), a mechanical chopper locked at 17 Hz, a monochromator and an air-filled brass cell equipped with an electret microphone. The sample was placed inside the closed PAS cell and illuminated with chopped light from the xenon lamp passing through the monochromator. The acoustic signal was detected by the electret microphone and amplified by a lock-in amplifier (Princeton Applied Research 5210). The experimental set-up has been described in detail elsewhere [8]. The particle size and morphology of the CdS nanoparticles were characterized using a FEI Tecnai G2 F30 TWIN 300 kV transmission electron microscope equipped with an energy dispersive spectroscopy (EDS) coupled module. Raman spectra of the powder nanoparticles were recorded using a Dilor-Jobin Yvon-Spex spectrometer employing the 632.8 nm line of a He–Ne laser.

3. Results and discussions

X-ray diffraction (XRD) patterns provided information about the crystalline structure and grain size of the nanoparticles. Fig. 1 shows the typical X-ray diffraction pattern of starch capped CdS nanoparticles for pH = 11. The XRD peaks are found at 2θ values of 26.5°, 43.44°, and 52.13°, corresponding to diffraction from the (1 1 1), (2 2 0) and (3 1 1) scattering planes, respectively, of the zinc-blende CdS rather than amorphous or hexagonal phase (JCPDS file No. 10-454). The broadening of diffraction peak provides information about the crystallite size. As the width increases, the particle size decreases and vice versa. The crystallite size was calculated using the Debye–Scherrer formula $d = 0.9\lambda/\beta\cos\theta$, where d is the crystallite size, λ is the wavelength of X-rays, β is the full-width at half-maximum (FWHM) in radians and θ is the diffraction angle. Corresponding to the maximum intensity peak, the crystallite size was determined to be 5.2 nm. Fig. 2 shows the particle size of starch capped CdS nanoparticles as a function of the pH value indicating that the nanoparticle diameter increases with increasing pH. A similar behavior has been observed by other authors in CdS nanoparticles capped with a polymer [9] and with thioglycerol [10]. Fig. 3 displays a representative TEM image of the nanoparticles prepared with a pH of 11, which is in accordance with the diameter calculated by Debye–Scherrer formula. In Fig. 3 the amorphous matrix of the starch after gelatinization is also clearly showed.

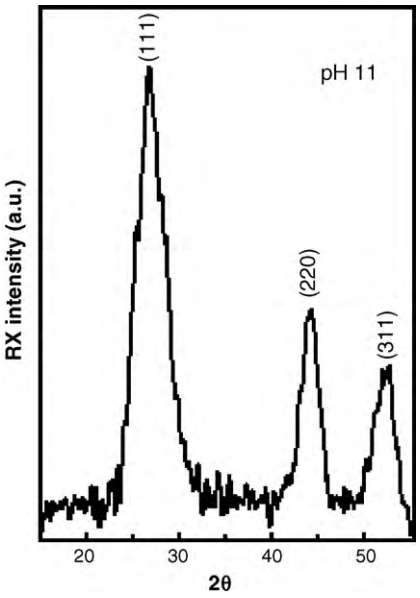

Fig. 1. XRD pattern of starch capped CdS nanoparticles for pH = 11.

For a direct band gap semiconductor, such as CdS, the band gap energy is obtained from the expression $[\alpha(h\nu)^* h\nu]^2 = C(h\nu - E^*)$, where α is the optical absorption coefficient, C is a constant, $h\nu$ is the photon energy of the incident radiation, h is the Planck's constant, ν is the photon frequency, and E^* is the band gap energy of the CdS nanoparticle. The absorption spectra for the CdS nanoparticle samples were obtained by photoacoustic spectroscopy (PAS). This technique and the theoretical model have been described in

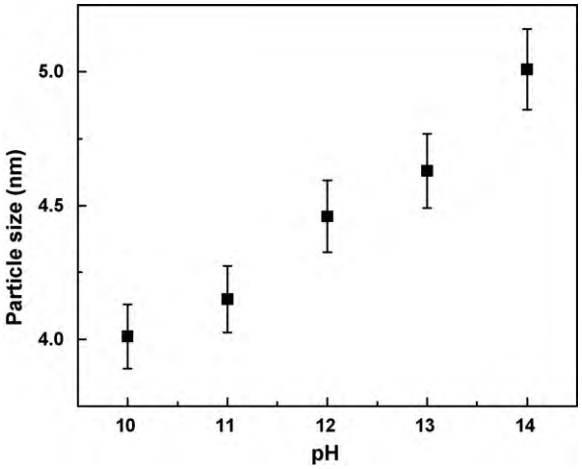

Fig. 2. Plot of the particle size of starch capped CdS nanoparticles as a function of pH.