

NEW ROUTE FOR THE SYNTHESIS OF AMMONIA-FREE CdS TETRAPODS NANOPARTICLES AT ROOM TEMPERATURE BY CHEMICAL BATH DEPOSITION

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At this work, it is presented a new route to produce ammonia-free cadmium sulfide tetrapod nanoparticles at room temperature using three precursors, cadmium nitrate, polyethyleneimine and thioacetamide by chemical bath deposition method. The tetrapod cadmium sulfide nanoparticles were characterized by UV-Vis spectrum, transmission electronic microscope and Raman analysis. The optical band gap of tetrapod nanoparticles was 2.78 eV, the length of the arms was 39.45 nm and its width was 3.27 nm. From TEM was found an orthorhombic crystallographic structure of the nanoparticles and vibration modes ($1LO = 272.79$ nm and $1LO = 292.79$ nm).

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1. Introduction

Cadmium sulphide (CdS) is one of the semiconductor material more studied because of photoconducting nature, large band gap ($E_g = 2.42$ eV, 515 nm) [1] and their optoelectronic potential applications [2-4] and specifically in the heterojunction solar cells with high efficiency [5, 6]. Synthesized in the form of thin film they have been reported by various methods: successive ionic layer adsorption and reaction, chemical bath deposition (CBD), molecular beam epitaxy, physical vapor deposition and more [7]. In the nanometric scale, the semiconductor particles are known as quantum dots, nanocrystals or nanoparticles and have been reported different methods of synthesis of semiconductor nanoparticles (SNPs): sol-gel, solvothermal, chemical precipitation, hydrothermal, vapor deposition and others [8-11]. Due to their size, the NPs have a optical, electrical, physical and chemical novel properties [12-13], which a very different to the bulk material, and make them good candidates for applications in the fields of composite materials [14], chemical sensing [15], optoelectronics [16], and so on [17-19]. Between the shapes of SNPs have been synthesized are monopod [20-22], bipod [7, 9, 23], tetrapod [24-27], among others [28-31]. However, recently the possibility of using the morphology of the SNPs to create self-assembled nanostructures and especially the tetrapod morphology in SNPs of CdSe, ZnO, CdTe and CdS has been of interest [27, 32-36]. Phuruangrart et al [37] synthesized CdS tetrapod nanoparticles (TCdS-NPs), and other forms, using the thermal method at 200°C; while Du et al [38] using a phosphine-free method (precursors: CdCl₂ and sulphurous) at 90°C obtained TCdS-NPs and Vaneski et al obtained CdSe/CdS tetrapod nanoparticles synthesized in a mixture of water/ethylenediamine [27].

In this paper, we report the synthesis of CdS tetrapod nanoparticles utilizing cadmium nitrate, polyethyleneimine and thioacetamide that eliminates the problems of the high temperature of growth and more environmental friendly by chemical bath deposition (CBD) technique.

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2. Experimental and characterization

The typical synthesis of TCdS-NPs was: 0.1 M tetrahydrate cadmium nitrate (0.25 ml), 0.5 ml polyethyleneimine: water (3.5:50 vol.), ultrasonic vibration by 2 minutes, 0.1 M thioacetamide (0.05 ml), ultrasonic vibration by 2 minutes and posteriorly is heated at 70 °C during 5 minutes. The obtained nanoparticles in suspension, have the typical yellow of the cadmium sulfide and being observed for several weeks keeping the stability without precipitation.

The UV-Vis TCdS-NPs spectrum was obtained with an Ocean Optics USB4000 spectrometer. For the TEM micrographs were used a JEOL JEM – 2010F, the Raman dispersion measurement was carried out by using a micro Raman X'plora BXT40 with a resolution of 2400T.

3. Results and discussions

The TCdS-NPs optical properties were investigated with the UV-Vis spectroscopy. The Fig. 1 shows the absorbance spectrum of the TCdS-NPs and the insert the direct bandgap calculated by x-intercept of the first linear portion of the plot of the $[(OD)(h\nu)]^2$ vs energy. The bandgap calculated was 2.78 eV (446 nm) higher than bulk CdS (2.42 eV, 515 nm). It is observed that the absorption starts at approximately 480 nm, implying the absorption blue-shift (0.38 eV) with respect to bulk CdS which agrees with previous investigations [39, 20, 40]. The above is referred to quantum confinement in the CdS nanoparticles [41].

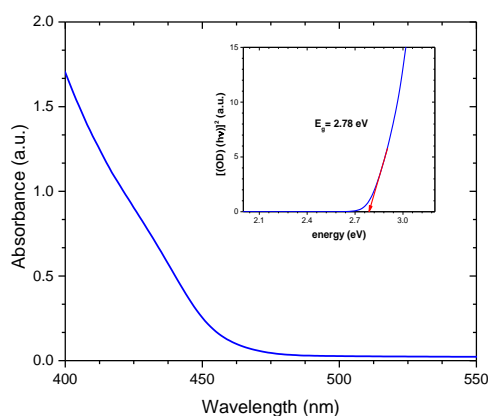


Fig. 1. Absorbance spectra of the TCdS-NPs and the insert the direct bandgap calculated.

The Fig. 2 shows the images of the structural CdS-TNPs obtained with TEM and High-resolution TEM (HRTEM). In the Fig. 2a shows a typical CdS nanoparticles image obtained with TEM, observing that shape is tetrapod. The length and width of the arms were different as the diameter of the center, one example is the observed in the Fig. 2b (length: 39.45 nm and width: 3.27 nm of the arm). The lattice fringes were observed in the arms and the center of the tetrapods using HRTEM (see Fig. 2c) and the insert the ED pattern of the one arm. The Fig. 2d show the IFFT of from the insert of the Fig. 2c, where is appreciated two main interplanar distances corresponding to (412) and (053) directions for the TCdS-NPs (0.312 nm and 0.242 nm)

The HRTEM characterization shows CdS polypoid nanoparticles corresponding with a orthorhombic crystallographic structure referred to PDF# 47-1179 database.

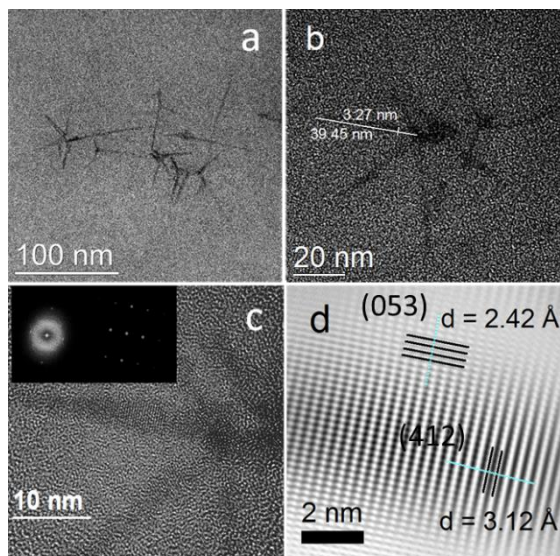


Fig. 2. HRTEM micrographies in the upper case with the same region but with two different scales, in the next row the interplanar distance measured and the Laue pattern is shown and in the last figure is the reproduction of using like a mask of the micrograph program and after that the FFT.

The Fig. 3 show the spectra Raman of tetrapod CdS nanoparticles, showing a fundamental width band centered on 3378 nm

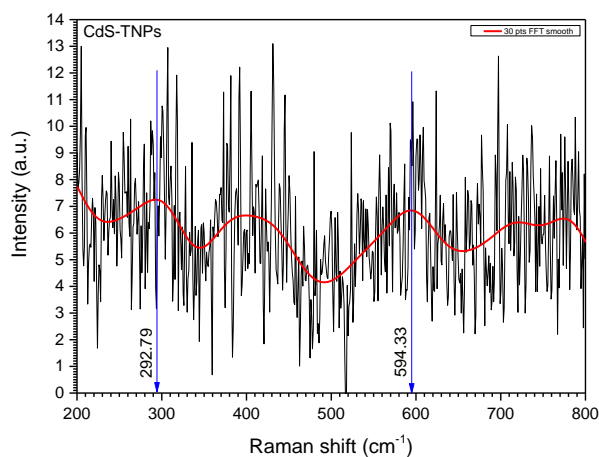


Fig. 3. Raman spectra of tetrapod CdS nanoparticles excited by polarized 633 nm laser.

4. Conclusions

CdS tetrapods nanocrystals were synthesized utilizing tetrahydrate cadmium nitrate, thioacetamide and polyethyleneimine as chelating agent at room temperature by CBD method.

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