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J.A. ASCENCIO[1,✉]
P. SANTIAGO[2]
L. RENDÓN[2]
U. PAL[1,3]

Structural basis for homogeneous CdS nanorods: synthesis and HREM characterization

[1] Instituto Mexicano del Petroleo, Apartado Postal 14-805, C.P. 07730, Mexico D.F., Mexico
[2] Instituto de Física, Universidad Nacional Autónoma de Mexico, Apartado Postal 20-364, 01000 Mexico D.F., Mexico
[3] Instituto de Física, Universidad Autónoma de Puebla, Apartado Postal J-48, Puebla, Pue. 72570, Mexico

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ABSTRACT Since the devolution of multiple efforts for producing semiconductor nanorods, the control of size and structure become critical for their applications in nanotechnology. The use of distinct methods has allowed a partial control of the size of the nanorods; however, the internal structure has been reported to be very varied, requiring the consideration of defects and twins in the interpretation of the analytical data. With the help of a solvothermal method, we report the synthesis of a homogeneous sample of CdS nanorods, with size around 50 nm in length and 7 nm in diameter. The structure of these rods was characterized by high-resolution transmission electron microcopy (HREM) and simulation tools for producing models and simulated images for different orientations. From the experimental and theoretical results we report the preferential axis for growing nanorods and the necessity of CdS fcc-like structures to explain all the nanorods produced in this work and in general those reported in the literature. The use of the calculated images, reported in this paper, opens an easy way to understand HREM images even for a non-specialist.

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1 Introduction

The application of nanostructured materials in alternative energy is clearly rich, especially in solar-cell development, where the use of one-dimensional structures has attracted the attention of many researchers recently [1–7]. Control of the size of the nanorods and the study of properties governed by their size and structure are of immense importance for their applications [4]. These materials are based on structures with important local electronic properties, which have been associated with the size effects [5, 6]. Theoretical and experimental studies of these materials relate directly the electronic structure, particularly the band gap, to their small size and shape [5]. In this way, the perspective to obtain small-diameter nanostructures, with length several times bigger than their radius, allows the understanding of the behavior as a function of the geometry of the nanorods. These systems fundamentally have important conditions to prefer a specific path for the transportation of charge on the axis of the structures. Among the II–VI semiconductors, nanostructured CdS is of particular importance for its applications in optoelectronics.

When the size becomes close to the critical dimensions, where the charge confinement is evident and the quantum effects are important, it is well known that not only the external structure but also the internal atomistic distribution affects the properties of a material [8]. This last parameter is very important for nanoparticles and it must also be characterized for the case of nanorods. Furthermore, as much of the evidence denotes, the growth process of nanorods involves a coalescence behavior along a preferential growth axis, as the function of an internal twin or a particular crystallographic face [9–11]. In both the cases, the system searches for a way to minimize its energy and grows along a preferential axis. This behavior has two main variables: the internal structure and the external passivating agents. The consideration of both the variables should allow a better control over the growth parameters.

In this work, an effort is made to show that, for the nanorods synthesized by a simple method with very homogeneous distribution of size and structure, it is possible to identify the effect of possible defects or contrasts in high-resolution transmission electron microscopy (HREM). This allows determining the crystalline structure and the structural growth parameters. The use of experimental HREM, as well as simulation of HREM images and fast Fourier transforms (FFTs) together, allows a well-sustained structure determination of semiconductor nanorods. Previous reports have demonstrated the benefits of this calculation for the structural studies and the dynamics analysis of nanostructures [12, 13].

2 Methods

CdS nanorods were synthesized using a solvothermal route [14]. Cadmium chloride ($CdCl_2$, 2.5 H_2O, Fermont, 99.9%) and S (Aldrich, 99.5%) powder were stoichiometrically added in a 100-ml two-neck round-bottom flask. Then the flask was filled with ethylenediamine (Merck) up to about 80% of its volume. The solution was

✉ Fax: +52-553003-6429, E-mail: ascencio@imp.mx

heated slowly to 135 °C and kept at this temperature for 5 h. The solution was neither shaken nor stirred during heating. The solution-containing flask was then allowed to cool to room temperature. A yellow-colored precipitate was formed at the bottom of the flask. The precipitate was washed with deionized water to remove residue of the organic solvent and collected by filtration. The filtered material was then dried in vacuum at room temperature.

A Shimadzu UV-vis 310 PC double-beam spectrophotometer was used for absorption measurement. For the electron-microscopic observation, a drop of the colloidal solution of the material was dispersed on copper microgrids and dried in vacuum. The sample was characterized by high-resolution electron microscopy using a Schottky field-emission Jeol JEM 2010-F microscope with analytical equipment attached. High-resolution images were obtained at the optimum focus condition (Scherzer) and processed by a Gatan image filter system.

Based on the unit cell for CdS, nanorod models were built in order to compare the experimental results with an atomistic structure. The models were used to calculate HREM images based on the multislice method. The parameters were fixed to the corresponding conditions of the experimental observations.

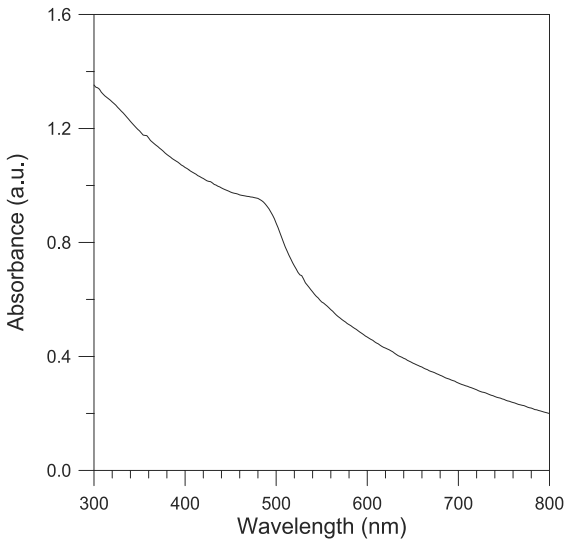
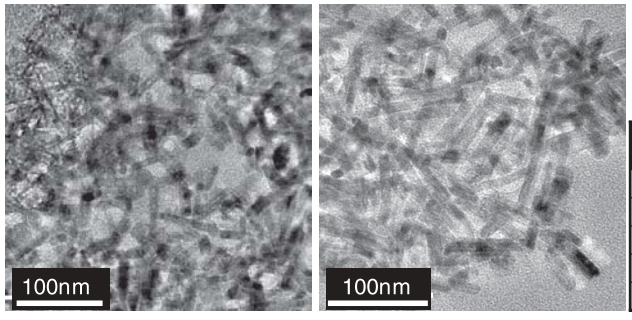


FIGURE 1 The UV-vis absorption spectrum of CdS nanorods



Diameter (nm)	%	Lengt h (10 nm)	%
0 – 5	5	0 – 3	3
5 – 6	8	3 – 4	11
6 – 7	19	4 – 5	47
7 – 8	58	5 – 6	34
8 – …	10	7 – …	5

FIGURE 2 Low-magnification images of nanorod samples. We can see the formation of homogeneous CdS nanorods. The statistical variation of length and width of the nanorods is given in the *table*

3 Results and discussion

A typical UV-vis optical absorption spectrum of the CdS nanorods is shown in Fig. 1. The absorption band revealed a peak at about 482 nm with an onset near 520 nm. The peak position of the absorption band coincides exactly with the characteristic absorption of bulk CdS.

In order to identify the size distribution in length and radius, the obtained nanorods were studied at low magnification of the transmission electron microscope (TEM). In Fig. 2, two typical TEM images of the grown nanorods are shown. The images revealed highly non-dispersed nanorods with good structural homogeneity with no nanoparticle formation. The sizes of the nanostructures are around 7 nm in diameter and over 50 nm in length (81% and 77% of the observed ones respectively). The statistical variation of the dimensions of the nanorods is given in the table in Fig. 2.

From the low-magnification images, the use of HREM for a deeper analysis is indispensable. The use of higher magnification allows identifying the internal structure, which can be associated with the growth parameters during the synthesis. As in the case of semiconductor materials the contrast is more complicated compared to one-atom-based materials; the use of molecular simulation becomes very important in order to recognize the different possible contrasts produced.

In Fig. 3, a series of simulated HREM images is shown for the case of a fcc-based CdS nanorod, at the conditions of the microscope used experimentally. The series of images corresponds to the rotation of each 5-degree step over the two main crystallographic axes ([100] and [010]). It is clear how the different orientations induce contrast that can be associated with apparent defects but produced just by the atomistic overlapping, at different orientations. In fact, one of the most relevant items of data obtained from this series is that, besides the expected hexagonal and square contrasts, a kind of detail is observed that can be associated with twins in the growth direction. Several sections with apparently amorphous structures were also revealed. However, in both cases they correspond to special orientations of the fcc structure.

In order to identify the structure of our nanorods, the HREM images were obtained in local areas of the samples. In Fig. 4, examples of the characteristic contrast for the nanorods are shown. The three different images shown in the figure correspond to the fcc-based structures (with their corresponding FFTs), which show characteristics identified in the calculated images. In this way, the borders are formed by faces {001} and {111}, with small sections of {011} faces that are present just in the more energetic regions. In the model beside the experi-

FIGURE 3 Series of HREM images calculated for a CdS nanorod model (fcc-like structure), with rotation steps for each 5 degrees

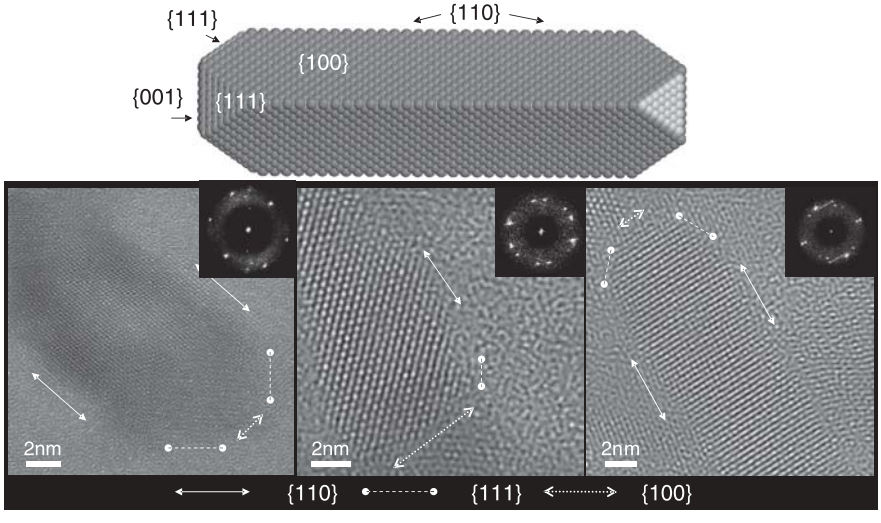


FIGURE 4 Experimental HREM images of synthesized nanorods and a model (*top*) that shows the different {110}, {111} and {100} faces, which are also observed in the structure profiles

mental images, the corresponding faces are explained. It is also clear that, apart from the internal contrast, the nanorod profiles change when the orientation varies, forming more rounded or flat corners depending on the length of the {111} faces.

This evidence denotes that the nanorods based on fcc crystal symmetry grow preferentially following the [001] axis. These results also demonstrate the energetic conditions for growing this kind of material.

4 Conclusions

From the experimental results we can conclude that the solvothermal method, as the method for producing CdS (and several other chalcogenides) nanorods, is very good. This allows obtaining homogeneous nanorods of around 50 nm and 7 nm of length and diameter respectively. The structure of the nanorods determined from all the studied images is fcc-like. The simulation tools can be used to determine the internal details and corresponding profiles of the nanorods. The simulated HREM images for the different orientations allows us to conclude that all the reported images in the literature can be associated with the contrast obtained in the calculated mosaic, which include effects in the contrast that could be confused with twinned or multiple-defect structures.

The exhaustive theoretical study of HREM images and the shape of the CdS nanorods also helps us to conclude that the preferential growth axis is parallel to [001] of the fcc crystal, forming longitudinal {010} faces and limited by corners of {111} faces. These considerations allow establishing the preferential growing axis and the produced atomistic structure.

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