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Synthesis of ZnO_2 Nanocrystals Produced by Hydrothermal Process

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ABSTRACT

Zinc peroxide (ZnO_2) nanocrystals were directly produced by hydrothermal process. The nanocrystals were synthesized using zinc acetate as precursor and hydrogen peroxide as oxidant agent. The ZnO_2 powders were characterized by X-ray powder diffraction and transmission electron microscopy. The results of transmission electron microscopy indicated that the ZnO_2 powders consisted of nanocrystals with diameters below to 20 nm and a faceted morphology. High resolution electron microscopy observations have been used in order to the structural characterization. ZnO_2 nanocrystals exhibit a well-crystallized structure.

INTRODUCTION

Nanocrystals with diameter less than 100 nm show novel physical and chemical properties, differing from those of the corresponding bulk materials [1,2]. Recently, there has been increasing interest in zinc oxide (ZnO) and zinc peroxide (ZnO_2) semiconductor materials. The direct wide band gap of ZnO makes it one of the most promising candidates for application in optoelectronics devices [3], solar cells [4], light emitting diodes (LEDs) [5], transistors, etc. On the other hand, ZnO_2 powder is widely used as padding in rubber industry, plastic processing, cosmetics, pharmaceutical industries, therapeutic applications, and pyrotechnic mixtures [6]. Furthermore, nanoparticulated ZnO_2 powder can additionally be used as precursor for preparation of ZnO nanoparticles [7]. A large number of methods are known for the preparation of ZnO_2 [6]. While most of the physical methods to growth zinc peroxide often require special equipment, high temperature and pressure conditions, chemical methods are simple and do not require those extreme growing conditions. Also they provide a facile way for low cost and large-scale production, which does not need expensive raw materials and complicated equipments [8]. ZnO_2 is chemically grown by adding a zinc precursor to a solution of hydrogen peroxide [9,6], sometimes applying additional sources of energy, such as light or heat. Typical methods used to obtain ZnO_2 samples have been electrodeposition [10], sol-gel [11], hydrothermal process [12], and chemical precipitation [13]. Here we report the structural properties of ZnO_2 nanocrystals grown through a hydrothermal process without the assistance of molecular stabilizer. The crystallite size of synthesized powder was below 20 nm. Structural properties of nanocrystals were studied through X-ray diffraction and transmission electron microscopy.

EXPERIMENTAL PROCEDURE

Zinc acetate dehydrate [$Zn(CH_3COO)_2·2H_2O$, 99.6%, Baker] and hydrogen peroxide [H_2O_2, sol. 30%, Baker] were purchased and used without further purification. All the reagents are of analytical grade. In a three-neck round-bottom flask equipped with a thermometer, 585.4 mg of zinc acetate dihydrate was dissolved in 80 ml of deionized water (E-pure Barnstead system, 18 MΩ cm). After, 4 ml of hydrogen peroxide was added as oxidant agent, then the solution was heated up to 100 °C and the hydrothermal reaction was conducted during 10 h. Finally, the solution was cooled to room temperature, and the ZnO_2 powders were extracted from the liquid medium by centrifugation and washed with deionized water several times. The material was dried in an air chamber by 24 hours to obtain ZnO_2 powders.

Structural and morphological characterization of ZnO_2 nanocrystals was performed by X-ray diffraction (XRD; Bruker Advance D-8) and transmission electron microscopy (TEM; Philips Tecnai F20, 200 kV, point resolution of 2.3 Å). TEM specimens were prepared by dispersing and subsequent drying a drop of solution on a copper grid (3 mm in diameter) covered with an amorphous carbon film. The transmission electron microscopy images have been digitally processed.

RESULTS AND DISCUSSION

The hydrothermal method is a simple route to obtain ZnO_2 nanocrystals. Figure 1a shows the experimental X-Ray diffraction pattern obtained from the ZnO_2 powders. It is important to mention that the product of the hydrothermal process is a colloidal solution; therefore it was dried in an air chamber by 24 hours. X-Ray diffraction pattern reveals that although Bragg peaks are broad, the whole XRD pattern can be well fitted using a single phase. All observed diffraction peaks match with such reported for cubic zinc peroxide (JCPDS card No. 13-0311). From the XRD pattern the calculated lattice parameter and average crystal size were 0.4871 nm and 15 nm, respectively. The Scherer's equation was applied to determine the crystal size, using the (200) reflection peak. No additional diffraction peaks attributed to secondary phases were found; therefore the synthesis method is effective to obtain single phase ZnO_2 nanopowders. On using the ZnO_2 cubic structure (Space group: *Pa-3*, No. 205) and a crystal size of 15 nm for peak broadening a theoretical X-Ray diffraction pattern was generated, it is shown in Figure 1b. The features of simulated XRD pattern are in agreement with the experimental X-Ray diffraction pattern (Figure 1a). Both, theoretical and experimental diffraction patterns show a well defined crystalline structure. Figure 1c shows an atomic model of the ZnO_2 crystal. This atomic model was using to performance the simulated XRD pattern. Some works have reported the formation of ZnO_2 from the photochemical reaction of H_2O_2 and $Zn(CH_3COO_2)_2$ [9]. These results indicated that photochemical reactions finish after 5 h and the corresponding average particle size of ZnO_2 reaches about 70 nm. ZnO_2 powders were found to be highly crystalline without any impurity or second phase. In our case, the crystal size is smaller (15 nm) and the synthesis process is simple. Is interesting to mention that in both cases, highly crystalline powders were synthesized.

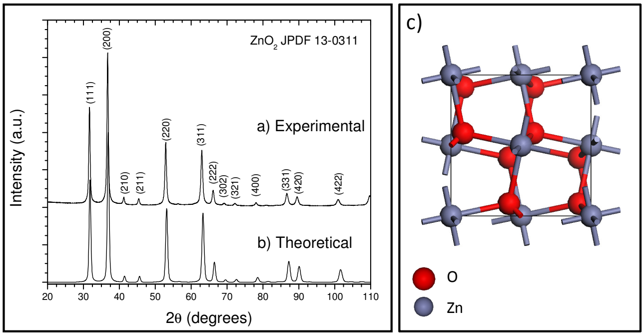

Figure 1. a) Experimental X-ray diffraction pattern from zinc peroxide sample. b) Theoretical X-ray diffraction pattern of cubic-ZnO_2 nanocrystals. c) Atomic model of the ZnO_2 crystal.

Transmission electron microscopy (TEM) is a powerful tool used to structural characterization at nearly atomistic resolution. In this paper, TEM was using to analyze the crystal structure of the ZnO_2 nanocrystals. Figure 2 shows a series of TEM images obtained from the ZnO_2 powders. Figure 2a shows a dark field transmission electron microscopy (DF-TEM) image. The image shows small crystals. The crystal size cannot be determined accurately from this image; however it is possible to observe some crystals with diameter length from 10 to 20 nm. Figure 2b shows a DF-TEM image with high resolution. In this image crystal size is clear (indicated with white circles) also, it is possible to observe a contrast consisting of periodic arrays or features whose dimensions are bigger than the atomic dimensions of the sample under observation (ZnO_2). Without experience in TEM, the interpretation of such image could be mistaken as the direct image of the atomic structure. This is the result of interference phenomena well-known "Moiré patterns" [14]. This phenomenon is commonly observed in layered structures, but is also observed in small particles. In dark field images, frequently very narrow fringes occur down to a nanometric scale [15].

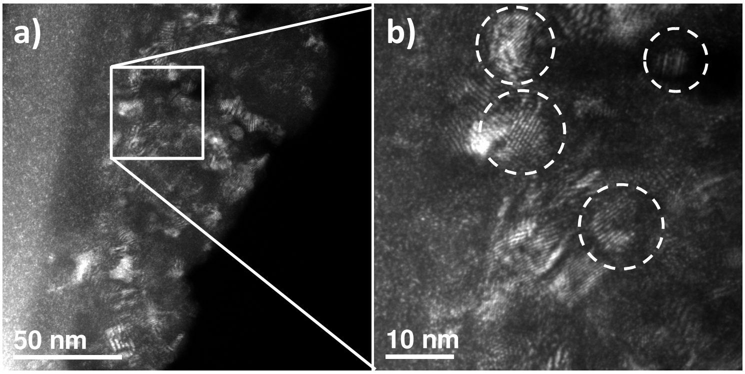

Figure 2. a) and b) DF-TEM micrographs of the zinc peroxide nanocrystals. The images are dominated by the contrast of Moiré fringes.

The crystal quality, besides lattice defects, has strong influence on the resulting physical and chemical properties of materials, such influence is more predominant in the nanomaterials with high surface/volume ratio, and therefore it is important to study them carefully. To analyze the atomic arrangement of ZnO_2 nanocrystals, high resolution transmission electron microscopy (HR-TEM) was used. Figure 3a shows a HR-TEM image from the ZnO_2 sample. The image shows a polycrystalline material composed by faceted nanocrystals. Figure 3b shows a magnified image of a nanocrystal along with its corresponding Fast Fourier Transform (FFT). The interplanar spacing 0.244 nm correspond to the (200) plane. It is worth to note that the lattice fringes are not lineal, which it is also reflected on the FFT as irregular reflection spots, such feature is attributed to the presence of lattice defects. Figure 3c shows a filtered image from the FFT. The black circle indicates a lineal dislocation. This 1D crystal defect is was found repeatedly in the synthesized nanocrystals. These dislocations may stimulate growing of ZnO nanocrystals at high temperatures, acting as dissociation sites.

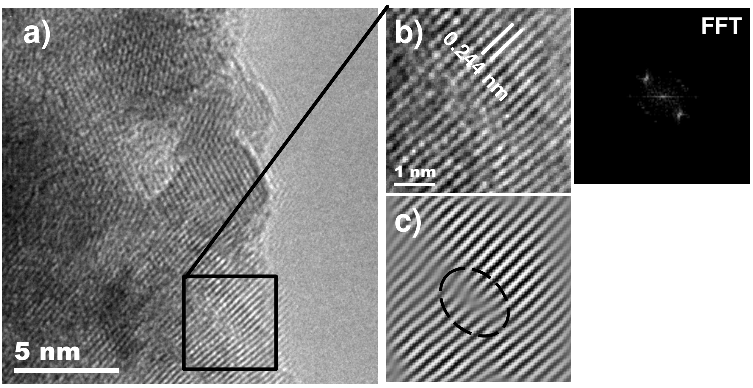

Figure 3. a) HR-TEM image of the as-grown ZnO_2 nanocrystal. b) Atomic arrangement of cubic-ZnO_2 nanocyrstal showing the lattice fringe related to (200) planes. c) Linear dislocation exposed by filtered image technique selecting specific frequencies of FFT pattern.

Figure 4a shows a typical HR-TEM image of a ZnO_2 nanocrystal. The crystal size is about 10 nm. The interplanar spacings 0.246 and 0.282 nm could be measured, corresponding to the (200) and (111) planes of the cubic-ZnO_2 structure, respectively. Figure 4b shows the FFT pattern obtained from the nanocrystal. FFT exhibits the expected form cubic-ZnO_2 viewed along the crystallographic [101] direction, revealing the well crystalline structure of the nanocrystal. Figure 4c shows the filtered images from the contribution of the different reflection spots. While the reflection spots labeled as 1, 2 and 3 are produced by a single nanocrystals (indexed reflections on the FFT), the reflection 4 (indicated by a white arrow on the FFT) is produced by an adjacent crystal with different orientation, and hence exposing other crystallographic planes. On using the filtered image technique it is possible to distinguish among single crystals (or phases) found in a polycrystalline sample, this technique is also adequate to analyze lattice defects, like dislocations, moiré fringes, etc.

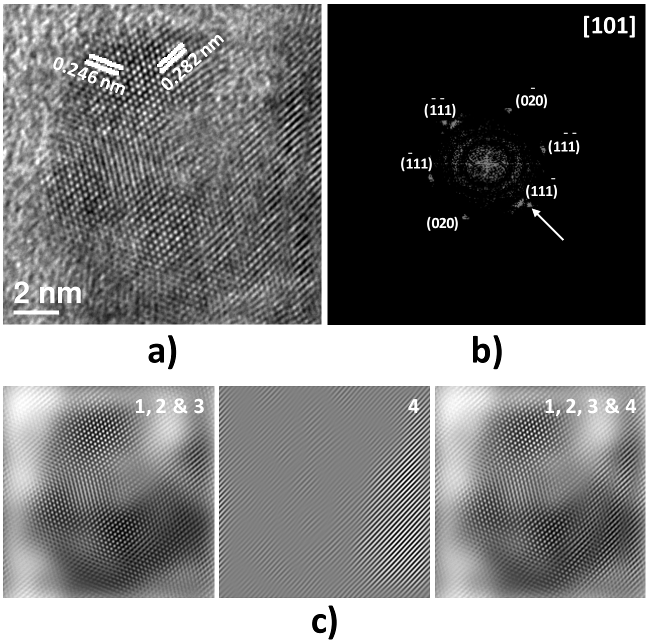

Figure 3. a) HR-TEM image of the as-grown ZnO_2 nanocrystals showing the interplanar spacing corresponding to (200) and (111) planes. b) FFT of the image shows the [101] zone axis of the nanocrystal. c) Filtered images based in the selection of the main frequencies of the FFT pattern.

CONCLUSIONS

Cubic-ZnO_2 nanocrystals were synthesized by a facile hydrothermal technique, without the assistance of any molecular surfactant. The process is spontaneous, and neither extreme growing conditions nor expensive equipment is required. XRD reveals well crystallized nanocrystals with average diameter of about 15 nm, in agreement with HR-TEM measurements. Transmission electron microscopy reveals that the material is polycrystalline with faceted crystals. The as-synthesized ZnO_2 nanocrystals commonly exhibit linear dislocations, which can be revealed by filtered image technique.

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