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Facile synthetic route for producing one-dimensional zinc oxide nanoflowers and characterization of their optical properties

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ABSTRACT

The morphologies and unique properties of zinc oxide nanoflowers make the nanoflowers promising candidates for use in wide range of future technological device applications. This paper describes the use of a versatile single-step synthetic route for producing ZnO nanoflowers under hydrothermal conditions at various reaction times. High-quality ZnO crystal was obtained after only 4 h by using this synthetic route. The morphology evolution and the length of rods that compose the flowers were monitored using SEM and ImageJ software. From the SEM images, it was possible to identify the formation of pure ZnO nanoflowers after 15 min under hydrothermal conditions. The length of the nanoflowers and the presence of defects in their morphology directly affected their optical properties, as examined using UV–visible and photoluminescence spectrophotometry. For samples kept at 5 and 10 min under similar conditions the time was not enough to form nanoflowers of pure ZnO materials. Actually, the samples are composed by two phases with zinc hydroxide being majority (>95%) and morphology like-rods.

1. Introduction

Over the last decade, the one-dimensional (1D) zinc oxide nanostructures have received considerable attention of the scientific and industrial communities because of their potential application in optics, optoelectronics, electronic, catalysis, photocatalysis, solar cells and biological devices [1–10]. ZnO is a wide band gap (3.37 eV) semiconductor whose high excitation binding energy (60 mV) that ensures efficient excitation emissions at room temperature. Several chemical and physical synthetic routes have previously been developed to fully explore the properties of (1D) ZnO nanostructures used in the aforementioned applications [11–20]. An aqueous chemical solution, first reported by Vayssieres [21–23], for preparing metal oxide nanorod arrays on different substrates at low temperature is now widely used to synthesize ZnO nanostructure in solution [24,25]. Since this seminal work, the chemical solution route has become a versatile approach to synthesizing ZnO nanowires, hexagonal disks [26], nanorods [27–34], well-aligned whiskers [35] and flowers [36] by adjusting the pH of aqueous reaction solution. Nowadays, several efforts are being dedicated to understanding the ZnO growth mechanisms for different (1D) nanostructures obtained by changing the alkaline complexes (such as NH_4OH [24,25], hexamethylenetetramine [37], $NaOH^{31}$) that are mixed with the soluble zinc salts [24,25,37–39]. In addition, the effects that different morphology [40–44], size [45], and the presence of defects or dopants [46,47] have on the fundamental properties of nanostructures have also extensively investigated and are the subject of many reviews [27,48,49]. This paper describes the synthesis of (1D) ZnO nanoflowers obtained under hydrothermal conditions for different reaction times. The morphology evolution and nanostructure size (estimated using ImageJ software) were monitored using scanning and transmission electron microscopy (SEM and TEM). Structural properties of the nanostructures were evaluated using X-ray diffraction (XRD). The prime novelty of this manuscript is related to the zinc oxide nanoflowers synthesized by a single-step at low temperature and controllable morphology formation. In addition, the visible band present on the PL spectra is linked to the presence of defect easily manipulate by the synthesis time. This means that the presence of the defect on the nanostructure formation is attributed to the time that the solution remains under hydrothermal conditions and the complete formation of 1D nanostructure is reached.

2. Experimental section

All commercial chemical reagents were used without any further purification. A 50 mmol L^{-1} solution of zinc chloride ($ZnCl_2$, Carlo Erba, 97%) was prepared to synthesize the nanostructures. Ammonium hydroxide (NH_4OH, Vetec, 28–30%) was then added, and the mixture was continuously stirred until it reached the required pH (~10.5). The pH was determined by titration in order to guarantee the formation of zinc hydroxide and provide enough concentration of OH^- ions to fast produce ZnO 1D nanostructure. The mixture was then transferred to an autoclave flask and heated in a conventional oven at 90 °C for different reaction times. After heating, the flask was rapidly cooled, and the obtained precipitates were centrifuged

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and cleaned using distilled water for several times. Table 1 summarizes all the zinc oxide nanostructure powders synthesized at different heating times in the current work.

The quality, purity, and structural parameters of the obtained powder samples were examined using powder X-ray diffraction (XRD, Bruker D8 Focus) with Cu Kα radiation (λ = 1.5405 Å) 2θ = 25–140° in steps of 0.02°. The nanostructure-morphology evolution was monitored using SEM (FEI Inspect F50) and TEM (Tecnai F20 FEI, operating at 200 kV). Optical properties were evaluated using a Varian Cary 50 Scan UV–Visible Spectrophotometer with a tungsten lamp. Deionized water was used as the baseline for the spectroscopic analysis. The photoluminescence (PL) analysis was performed using a Varian Cary Eclipse Fluorescence Spectrophotometer with a xenon flash. The PL spectra were obtained at room temperature with an excitation wavelength λ_{ex} = 300 nm (4.13 eV). For comparison, the intensities of all emissions were normalized to that of the UV emission. The spectrofluorometer was set to work with automatic filters in order to prevent secondary and tertiary emissions. The spectra were smoothed using the averaging adjacent method (for 20 data points). For optical analysis of the samples, a fixed concentration (158 mg/L) of nanoparticles was dispersed in deionized water and was maintained in an ultrasound bath. PL spectra of the deionized water was performed and the peak at 333 nm associated with water emission was removed from all the spectra.

3. Results and discussion

3.1. Synthesis

The hydrothermal synthetic route by using $ZnCl_2$ and NH_4OH as reactants has been widely studied to produce ZnO nanorods in solution and also those vertically oriented on substrates [50–52]. Moreover, many other synthetic routes involving alkaline complexes, such as hexamethylenetetramine [37] and NaOH [53–55], have been used to synthesize ZnO nanorods in solution. Once NH_4OH is added as a source of OH^- to an aqueous Zinc chloride solution, the first reaction occurring can be described by the following equations:

$$Zn^{2+} + 2OH^- \rightleftharpoons Zn(OH)_2 \quad K_{SP} = 3.10^{-16} \tag{1}$$

$$Zn(OH)_2 + 2OH^- \rightarrow [Zn(OH)_4]^{2-} \tag{2}$$

$$Zn(OH)_2 \xrightarrow{\Delta H} ZnO + H_2O \tag{3}$$

$$[Zn(OH)_4]^{2-} \xrightarrow{\Delta H} ZnO + 2OH^- + H_2O \tag{4}$$

The above reactions can be summarized in a global equation as below [37,56].

$$Zn_{2+} + 2OH^- \rightleftharpoons Zn(OH)_2 \rightarrow 2H_2O \tag{5}$$

There is also a contribution from the ammonia complexes after the hydrothermal reaction begins, as described by the following equation:

$$[Zn(NH_3)_4]^{2+} + 2OH^- \xrightarrow{\Delta H} ZnO + 4NH_3 + H_2O \tag{6}$$

The complexes in the solution originated from the addition of concentrated NH_4OH, which generates many $Zn(OH)^2$ nuclei that can be stabilized by $[Zn(OH)_4]^{2-}$ and $[Zn(NH_3)_4]^{2+}$ in the double layer. Before the hydrothermal reaction starts, the $[Zn(OH)_4]^{2-}$ complex is stabler in solution than $[Zn(NH_3)_4]^{2+}$. Because the formation constant of the former is larger than that of the latter, the $[Zn(OH)_4]^{2-}$ becomes the predominant species in solution. However, after the initial stage of the hydrothermal reaction begins, the first ZnO nuclei (from $[Zn(OH)_4]^{2-}$, Eq. (4)) are generated, releasing OH^- in the region around the nuclei. The OH^- reacts with $[Zn(NH_3)_4]^{2+}$ also acting as the ZnO nuclei. In fact, both of these generated complexes (Eqs. (4) and (6)) are responsible for ZnO nanorod formation in different steps of the synthetic reaction [57].

Table 1
Samples codes and its respective time under hydrothermal conditions.

Sample	Time of heating (h)
$Zn(OH)_2$	1/12
$Zn(OH)_2$-0	1/6
ZnO-1	0.25
ZnO-2	0.5
ZnO-3	2
ZnO-4	4
ZnO-5	6
ZnO-6	32
ZnO-7	48
ZnO-8	72

These results are consistent with those in recent studies found in the literature which synthesis of ZnO in solution could be explained by two steps: (1) low temperatures favor the growth of long rods, and (2) high temperatures induce a competition between growth and nucleation [58–60]. For instance, Zhou and Deng [37] reported a detailed analysis of the synthesis and the growth of ZnO nanorods at 55–85 °C and proposed a growth method based on the reaction rate constants. They concluded that at temperature lower than 85 °C, the Zn^{2+} concentration can be fitted by the first-order reaction model if the nucleations are ignored when compared to crystal growth. At temperatures higher than 85 °C, on the other hand, the supersaturation level increases in solution because of faster alkaline decomposition, making the environment favorable for nucleation. Our results corroborate the model proposed by Zhou and Deng, since for higher temperatures (90 °C) the nanorods tends to grow faster, reaching their maximum length in a shorter time.

3.2. Morphology and structural properties

The quality of the hydrothermal produced powders was evaluated using XRD. For samples kept during 5 and 10 min under hydrothermal conditions the zinc hydroxide phase was found to be majority (Fig. S1). To better understanding this both sample the Rietveld refinement was performed using a similar crystallographic parameters reported by Chakradharg and co-workers [61]. From Rietveld refinement data the samples obtained at 5 and 10 min are composed by two phases indexed as being zinc hydroxide and zinc oxide, respectively (Fig. S1). The percentage of zinc oxide phase increase with the synthesis times from 3.5 to 5.04%, as illustrated in Fig. S1. In addition, the indexed peaks and calculated lattice parameters from Rietveld refinement, summarized in Table S1, corresponding to the zinc hydroxide phase (β-$Zn(OH)_2$, compared with JCPDS #89-0138) and hexagonal wurtzite crystal structure of zinc oxide (JCPDS #36-1451).

On the other hand, samples synthesized for a period longer than 15 min had the diffraction peaks indexed to the wurtzite (hexagonal) crystallographic arrangement of ZnO (JCPDS No. 36-1451). No peaks associated with impurities or other phases were observed in the XRD data, indicating that the synthetic route used to produce the powders was versatile and that it efficiently produced highly pure crystalline ZnO nanostructures in a single step. The lattice parameters for all powder samples were estimated from the position of the peaks assuming hexagonal crystallographic arrangement. The values obtained for lattice parameters and cell volumes are consistent with those in the literature [62] and in the Joint Committee on Powder Diffraction Standards® (JCPDS) catalog, as summarized in Table 2.

The structural parameters remained practically unchanged for powder samples synthesized at different reaction times, as better depicted in Fig. 1. This result was expected once the unique wurtzite phase was indexed for all samples produced in this study. From the XRD data (Fig. 1), the orientation degree was calculated using a relation first proposed by Lotgering [63]: