Synthesis and characterization of ZnO flower-like structures

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ABSTRACT

The flower-like ZnO nanorods have been successfully synthesized by a surfactant-assisted hydrothermal method. The nanostructures formed by ZnO nanorods were synthesized and deposited without seeding in glass flask by a hexamethylenetetramine (HMTA)-assisted hydrothermal method at low temperature with NaOH as surfactant and catalyst. The synthesized ZnO flowers comprise of several spike structures that have hexagonal cross section and taper toward the end. The structures are investigated using X-ray diffraction, scanning electron microscope and transmission microscope. The optical properties are studied with UV-VIS, FTIR, and Raman spectroscopy. The process of synthesis is simple and highly reproducible. The synthesized flower-like structures are suitable for use as sensors applications.

1. Introduction

Over the last few decades, zinc oxide (ZnO) has become an important semiconductor for versatile applications in various application areas such as UV and optoelectronic sensor, chemical vapor sensor, optical, and photonic devices. The ZnO has two allotropies: Wurtzite and Zincblende of which Wurtzite is the most stable form. The wurtzite ZnO is a semiconductor having wide direct band gap of 3.37 eV and high exciton binding energy ~60 meV. That makes it a competing material for use in various types of sensors such as optoelectronic, UV, and gas sensors.[1–9] In addition to one-dimensional ZnO structures, several types of morphologies, such as flowers, needles, hollow and solid rods [8–11] are of interest for their high surface to volume ratio, nanometer order thickness, excellent permeation, and optical properties make it suitable for devices applications.[2,12] A lot of attention has been paid over the past few years to the synthesis techniques of this material using different methods. ZnO nanorods and flowers are the promising materials for various types of sensor applications due to their ultra-high surface-to-volume ratios. Some workers [13–21] have carefully studied the gas sensing characteristics of ZnO nanowires. ZnO nanorod photodetectors with Mg doping have been reported.[1] The ZnO nanosheets on glass substrate with a length of ~1.2 μm have been reported [4] at room temperatures using the solution method. Many other methods like CVD [7] are also reported to grow nanowires of ZnO for photodetector applications. In addition, gas sensors based on ZnO nanowires fabricated with a micro-electromechanical system exhibited a very high sensitivity to ethanol gas and a fast response time (within 10 s) at 300 °C, showing a promising application for ZnO nanowire humidity sensors. Due to this property, ZnO nanostructures have attracted a lot of attention in the past few years for use as humidity and gas sensors.[22] Some workers have demonstrated the use of ZnO nanorod sensors for detection of biological molecules.[23] They functionalized ZnO nanorod surfaces with biotin and developed nanosensors for real time detection of biological molecules using surface-modified ZnO nanorods as a conducting channel. Some metal oxides also form a hetero-junction with unique sensing properties that make it suitable for humidity sensor. Several methods such as electro-deposition, evaporation, vapor-liquid-solid (VLS) growth,[29] metallo-organic catalyst-assisted vapor-phase epitaxy, aqueous thermal decomposition, microwave-activated chemical-bath deposition (MW-CBD), chemical bath deposition (CBD),[23] hydrothermal-assisted method, etc. [10,23–29] have been reported for the synthesis of these nanomaterials.
However, hydrothermal-assisted (HTA) method is most convenient over others as it is less expensive with easier composition control, large area deposition and works at lower temperatures [29]. Besides, the hydrothermal method is better than other dry methods due to low cost, simple process and high yield, and consistency of the product just by regulating the ingredients and process. In our present process of synthesis, very nice flower-like ZnO structures are grown that are highly reproducible under identical conditions making them suitable for commercial use.

2. Method of synthesis

The flower-like ZnO nanostructures are synthesized by the simple hydrothermal method.[11,19] The chemical reagents used in this study were analytical reagent grade procured from CDH Chemicals and used as received without further purification. Zinc nitrate (Zn(NO3)2.6H2O) was used as a precursor and hexamethylenetetramine, also called methenamine ((CH3)6N4) as a surfactant and catalyst. The precursor solution was prepared by dissolving 3.0 g of zinc nitrate and 2.8 g of methenamine in deionized water with a resistivity of 18 MΩ cm−1 under vigorous stirring by a magnetic stirrer at room temperature (27°C) for half an hour to form a 0.01 M equimolar solution. It was observed that a white ZnO powder precipitated at the bottom of the flask. Finally, the substrates were thoroughly washed with deionized water and ethyl alcohol and then allowed to dry in air at room temperature. The prepared sample was then placed at 60°C in an oven to remove the remaining moisture and then collected and stored in an air-tight vial for further characterization. The morphology of the samples formed is shown in SEM micrographs (Figure 5) indicating that the ZnO nanorods are arranged in a flower-like assembly with well-defined hexagonal rod-like structures. The detailed characterization of the sample was done using UV-vis spectrometer, SEM, FTIR, Raman, XRD and TEM, and SAED. The details of characterization are discussed in the following section.

3. Characterization

UV–vis

The samples were characterized for the absorbance at room temperature with unpolarized light at normal incidence in the wavelength range of 200–900 nm using the PG Instruments T90 UV/VIS Double Beam Scanning Spectrophotometer. Ethyl alcohol was used as a solvent and particle solutions were sonicated before use. The typical absorption spectrum of one of the grown sample is shown in Figure 1.

FTIR

Thereafter, its FTIR spectra were recorded at room temperature and the results are shown in Figure 2.

FT-Raman

The FT-Raman scattering experiment was performed at room temperature using Varian FT Raman model 600 UMA. The Raman spectrum of the grown ZnO structure is shown in Figure 3. The peak observed at 435 cm−1 indicates the nonpolar E2- high mode of active Raman [22]. The broadness of the peak can be explained by the assorted sizes of rods/spikes in the flower structures in the sample. The higher baseline indicates that a high percentage of hexagonal phase of ZnO is present in the grown sample. The multiplicity of many small peaks may be due to many vibrational modes.

XRD spectrum

The X-ray diffraction (XRD) pattern of the ZnO nanorods was obtained with a X-ray diffractometer (Panalytical Xpert-PRO) using the CuKα (1.5406Å)
radiation, with a scanning speed of 1.2 per min at 40 kV and 30 mA. The sample was mounted at 2.5° and scanned from 20° to 90° with a scan rate of 2° per minute. The XRD spectrum is shown in Figure 4. All diffraction peaks can be indexed as hexagonal ZnO without any impurity peaks. The X-ray diffraction pattern in Figure 4 shows that (101) is the strongest like in a polycrystalline ZnO. The quite prominent 002 peak indicates that the rods are normal to their base. All diffraction peaks are indexed with lattice constant \( a = 3.248 \) Å and \( c = 5.206 \) Å which are consistent with the standards. No other peak is observed confirming the absence of any other structural impurity in the sample.

The 2θ values of XRD pattern of the grown ZnO flow- ers perfectly match with the standard values of hexagonal ZnO for the peaks occurring at 31.766, 34.419, 36.250, 47.435, 56.590, 62.851, and 67.941.

**SEM**

Morphology of the sample was studied using a Zeiss EVO40 scanning electron microscope. The SEM imaging was done at 20 kV. The Figure 5 shows the SEM micrograph of the samples at different magnification (a) at 6.63 K, (b) 25 K (c) 35 K, and d, e, and f at 50 K magnifications. It is clear that the structure comprises several rods of about 1–3 μm lengths and about 100–300 nm thickness. There is a uniformity of the growth pattern of the flowers as seen in Figure 5(a).

The flower structures are in a ball shape with approximately 150–200 spikes emanating from the center of the ball Figure 5(b)–(f). The hexagonal morphology is clearly visible in most of the spikes. A few rods end up with broad hexagonal cross sections Figure 5(f). Others also have the same cross sections but with smaller size and appear like a spike.

The typical structure of such spikes of the grown flow- ers are shown in Figure 6. The dumbbell-like structure is formed by cementing of the two spikes as shown in the Figure 6.

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**Figure 3.** The Raman spectrum of the sample recorded with Varian. The peak is observed at 435 cm\(^{-1}\).

**Figure 4.** The XRD spectrum of ZnO flowers recorded by Panalytical XpertPro.
Figure 5. SEM micrographs of ZnO flowers. The hexagonal cross-section structure is clearly visible.

Figure 6. The typical structure of ZnO rods/Spikes that constitute the flowers.

**TEM**

The TEM of the sample was performed using the JEOL FE2100t TEM electron microscope with a 2.1 Å resolution (point to point) at 200KV. An excellent crystallinity of the spikes in the flower-like structure of ZnO is observed that are grown by cementing mechanism. The TEM images (Figure 7) indicate that the spikes of these flowers are not hollow but solid structures with almost uniform density. The selected area electron diffraction (SAED) pattern were also obtained on TEM with an accelerating voltage of 200 kV. The SEAD pattern of the sample is shown in Figure 6. The fringe widths of ~0.157 nm were observed that are close to the known wurtzite structure of ZnO.
4. Conclusion

The flower-like ZnO nanorods are successfully synthesized via a surfactant-assisted hydrothermal method without seeding using hexamethylenetetramine (HMTA) with 

NaOH as a surfactant and catalyst at low temperature. The grown ZnO flowers have several rod-like structures that are emanating from the center. The rods are hexagonal in shape and taper toward the end and vary in length from 500 nm to 3 μm and thickness is in the range of 100–350 nm. With the change in temperature and processing time, the morphology of the grown structures also changes. The process of synthesis is simple and highly reproducible. The length and diameter of the spikes of the flower can be controlled by changing the time of reaction and the concentration of the surfactant. The large surface area of flower-like structures make these suitable for use as sensors. This method can be used to grow ZnO flower-like structures in different sizes with promising use as sensors for different gases and chemicals. The size and density of flowers can be easily controlled by the chemical properties of the solution such as pH, concentration of precursor, growth temperature, and the time of reaction. The current hydrothermal method provides a reliable and cost-effective method of manufacturing functional ZnO nanoflowers for sensor applications at a large scale.

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Disclosure statement

No potential conflict of interest was reported by the authors.

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