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A Simple Hydrothermal Protocol for the Synthesis of Zinc Oxide Nanorods

Research Article

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Abstract : Herein we report the hydrothermal preparation and characterization of zinc oxide nanorods (ZnONRs). The hydrothermal protocol in the synthesis of ZnONRs uses zinc acetate dihydrate [$Zn(CH_3COO)_2.2H_2O$] as a precursor and sodium hydroxide (NaOH) as a reducing agent. ZnONRs, thus synthesized then characterized using different techniques such as ultraviolet-visible (UV–vis) spectroscopy, X-ray diffraction (XRD), transmission electron microscopy (TEM) and energy dispersive X-ray diffraction (EDX) spectroscopy. A prominent characteristic UV-vis peak at 376 nm$\lambda_{(max)}$ of the nanorods indicated primarily the formation of ZnONRs. XRD pattern of the sample confirmed the hexagonal wurtzite phase of ZnO. The rod shape nature of synthesized ZnO with an average aspect ratio (length/diameter of ZnONRs) of 2.20 was estimated from TEM analysis, and thus indicated single particles and aggregation of ZnONRs. EDX spectroscopic analysis indicated the presence of Zn and O elements. These results support the successful synthesis of rod-shaped nanoscale ZnO.

Keywords : *Zinc oxide nanorod • Hydrothermal • XRD • TEM • Aspect ratio • EDX*

1. Introduction

ZnO, an active *n*-type semiconducting metal oxide received considerable attention in the area of nanomaterials because of its unique properties such as large exciton energy (~60 meV), a wide bandgap (~3.37 eV), and a variety of applications like gas sensors, near-UV light emitters, spin electronics, field-effect transistors, short-wavelength lasers, piezoelectric devices, ultrasensitive, transparent conductor, and photovoltaic. As mentioned earlier, ZnO has unique chemical, physical, and effective biological properties (Mohammadi *et al*., 2018). All these characteristics features and wide applications window make ZnO an intensively studied material in recent times.

Nano-sized ZnO, one of the dimensions is between 1 nm and 100 nm, have a higher surface area to volume ratio compared to micron sized ZnO, and hence their uses are superior to micron-sized ZnO for many applications (Doolittle *et al*., 2003). Generally, nanomaterials possess high surface areas to volume ratios, quanta confinements, and various shape and size-dependent properties and therefore attracted huge demand due to their large possibility of applications in electronics, catalysis, dye degradation, nanomedicine including many areas of nanotechnology (Augustine *et al*., 2017), (Gebre & Sendeku, 2019), (Chavali & Nikolova, 2019). Notably, ZnO nanopowders have been, other than semiconductor materials, showed antimicrobial activity against some bacterial strains (Judith & Espitia, 2012) against Gram-negative and Gram-positive bacteria (Dadi *et al*., 2019), (Elumalai *et al*., 2015). ZnO is suitable for pathogenic treatment. Also, ZnO has been proven of showing dye degradation properties on various dyes (Prabakaran & Pillay, 2019), (Ajmal *et al*., 2014), (Balcha *et al*., 2016)

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which is cost-effective alternative for large scale treatment of dye polluted water. ZnO can also be used in solar photocatalysts and food applications (Ong *et al*., 2018), (Shi *et al*., 2014). From the above discussion it is clear that due to its unique chemical, physical, and effective biological properties, ZnO can play role as an antibacterial agent and photocatalyst for dye degradation. Therefore, synthesizing ZnO by a simple and cost-effective method is essential.

Preparation of ZnO at the nanoscale with different shapes like spheres, needles, flowers, flakes, pills, pencils, rods are possible (Moulahi & Sediri, 2014), (Moulahi & Sediri, 2014), (Mohan *et al*., 2020), (Elen *et al*., 2009), (Akhoon *et al*., 2015), (Vasireddi *et al*., 2017). The shape of nanomaterials affects greatly on many applications since the specific surface area varies with the shape of nanomaterials. Therefore, controlling shape is one of the keys focuses to produce desired shape ZnO at the nanoscale.

The synthesis of ZnO nanomaterials has different methods like physical, chemical, and biological (Qi *et al*., 2018), (Singh *et al*., 2011), (Agarwal *et al*., 2017). Chemical synthesis is widely used as this route offers a high percentage of product conversion from a precursor with a short reaction time. Some of such type of synthesis methods are chemical precipitation, chemical vapor deposition, sol-gel, spray pyrolysis, sputtering, microwave-assisted, hydrothermal, etc. (Naveed Ul Haq *et al*., 2017), (Ocakoglu *et al*., 2015), (Aneesh *et al*., 2007). Amongst these methods, hydrothermal one is very advantageous over other synthetic methods as it uses cheap water as the solvent, one-step synthesis and no need of ball milling of the product, low aggregation, high purity, and excellent control of particles' shape, morphology, and size. In a hydrothermal method, heat treatment is applied in the aqueous precursor to obtaining the target product. The synthesis and growth mechanism of ZnO were also studied to obtain small sizes particles (Meulenkamp, 1998), (Vasireddi *et al*., 2017). However, a further demonstration of the hydrothermal method for preparing ZnONRs is needed again to verify the growth. Considering the advantages of the hydrothermal method, in this article, synthesis of ZnONRs through the hydrothermal method using a simple laboratory oven and their characterization is reported which may be useful for many applications against bacterial pathogens and dye degradation.

2. Experimental

2.1 Materials

Zinc acetate dihydrate [$Zn(CH_3COO)_2.2H_2O$] as a precursor was purchased from Scharlau, Spain. Sodium hydroxide (NaOH) as a reducing agent was purchased from Merck, Germany. Both materials were analytical grade and used without any further purification. Double distilled water was used in the entire experiment.

2.2 Apparatus

A magnetic stirrer with hot plate (DLab, USA) was used for the primary mixing and stirring of precursor and alkali solution. The hydrothermal reaction was performed in a Teflon-lined tube inside a stainless steel reactor (Autoclaves, China) inside a natural convection laboratory oven (HYSC, DO-81, Korea). The product was collected by a centrifugation machine (TG16-WS, Benchtop High-speed Centrifuge, Taiwan).

2.3 Synthesis of ZnONRs

First, a 50 mL of zinc acetate dihydrate [$Zn(CH_3COO)_2.2H_2O$] aqueous solution was prepared in a beaker. In another beaker, a 50 mL aqueous solution of NaOH was prepared by dissolving the required amounts of NaOH pellets into the water. Then, under continuous vigorous stirring, the 50 mL aqueous solution of NaOH was slowly dropped into the precursor solution. The molar ratio of $Zn(CH_3COO)_2.2H_2O$ and NaOH were 1:2. The mixture turned milky after 2 hours of stirring at room temperature. Then, the solution mixture was transferred to a stainless steel autoclave and heated at 170 ºC in an oven for 12 hours by the little modification of the published report (Moulahi & Sediri, 2014). Next, the autoclave was allowed to cool down at room temperature. Then, the product was collected and centrifuged at 10100 rpm and washed with double distilled water 3 times. Finally, the product is dried at 120 ºC for 3 hours and calcined at 550 ºC for 4 hours before characterization using different techniques.

2.4 Characterization of synthesized ZnONRs

Formation of ZnONRs was assumed primarily with the aid of UV–vis at room temperature using a spectrophotometer, UV-1800, Shimadzu, Japan, with the wavelength between 200 nm and 800 nm using quartz cuvettes having a path length of 10 mm. The crystal structure of the synthesized products was examined using an X-ray diffractometer (Phillips X'Pert PRO PW 3040, Netherlands) with CuKα radiation in a 2θ-θ setup. The scanned value of 2θ angle was between 10° and 90° at a scanning rate of 0.02°/0.6 s. The measured data were compared with the data from the Joint Committee for Powder Diffraction Studies (JCPDS) file for silver (BD Card No. 01-070-8072). Transmission electron microscopy (TEM, TALOS F200X, 200 KeV, Netherlands) with 200 kV acceleration voltages was used to examine the particle size and morphology of the synthesized ZnONRs. The calcined product was re-

dispersed in water and the TEM grid was prepared using the ZnONRs dispersion droplets on the TEM grid. EDX was taken to know the elements present and their percentage using an energy dispersive X-ray spectrometer section of the same instrument.

3. Results and Discussion

3.1 UV–vis spectroscopy

The growth of ZnONRs was assumed primarily through UV–vis spectroscopy. UV–vis spectroscopy technique can evaluate the structural formation of nanomaterials. A UV–vis spectrum of the product sample was taken immediately after the synthesis using a spectrophotometer with the variable wavelength ranging from 200 nm to 800 nm in quartz cuvettes having a path length of 10 mm. Figure 1 shows the UV–vis spectrum of synthesized ZnONRs. Sample for UV–vis analysis was collected just after the centrifugation and washing of the product and it was prepared by re-dispersing in the water as a solvent. The color of the sample dispersed in water was whitish. A photo of the sample is seen in the inset of Figure 1. An identical absorption peak of ZnO appeared at 376 nm indicates the presence of ZnONRs (Wu & Wu, 2007).

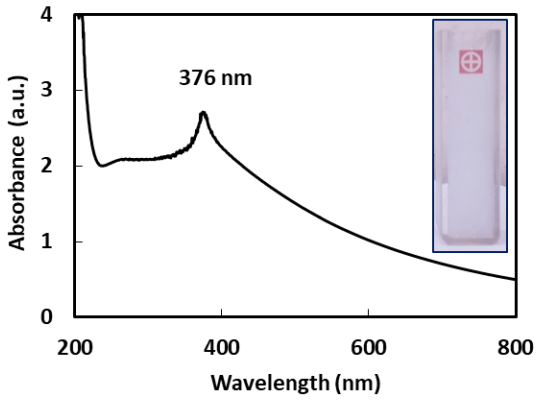

Figure 1. UV–vis spectrum of the synthesized ZnONRs dispersed in water.

3.2 Powder XRD analysis

The crystalline nature and phase structure of synthesized ZnONRs powder were confirmed by analysis of the XRD spectrum. The XRD pattern of synthesized ZnONRs is presented in Figure 2. The corresponding diffractogram in 2 theta range 10–90º with a Bragg's reflection of (100), (002), (101), (102), (110), (103), (200), (112), (201), (004) and (202) at 31.70º, 34.32º, 36.17º, 47.41º, 56.46º, 62.67º, 66.22º, 67.76º, 68.91º, 72.32º and 76.75º indicated hexagonal wurtzite phase of ZnONPs, comparing with standard card [BD Card No. 01-070-8072]. Besides, no other peaks were observed that may arise due to impurity. These findings indicate, single-phase structure of ZnONRs was synthesized (Tshabalala *et al*., 2012), (Suresh *et al*., 2018).

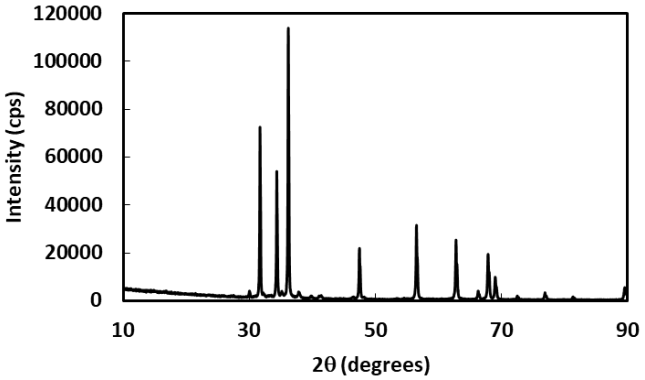

Figure 2. XRD pattern of the synthesized ZnONRs.

3.3 TEM analysis

The surface morphology of synthesized ZnONRs was characterized using TEM analysis. Figure 3 shows a typical TEM image of the synthesized ZnO which indicated that rod-shaped particles were formed. Various sizes of the rods were formed with different diameters and lengths as shown in Figure 3(a). Notably, no branching of rods is observed, which implies that the ZnO nanorods were grown from spontaneous nucleation with high crystal perfection. The aspect ratio (*a.r.=l/d*) of a ZnONR was obtained by dividing the length of the ZnONR with the diameter of a ZnONR as shown in Figure 3(b). The aspect ratio has great significance in many applications. Generally, a high aspect ratio offers better results in some application. Average length and diameter of the nanorods are measured to be 266 nm and 121 nm, respectively which is comparable to previous results (Roy & Chakraborty, 2020). In this study, the smallest diameter of a single ZnONR was obtained as 59 nm which indicates the formation of nano-scale ZnO. The higher aspect ratio of ZnONRs with smaller diameters is preferable for some applications (Liu & Zeng, 2003). The largest diameter was measured as 235 nm which may be due to aggregation. Thus, the lowest aspect ratio of the smallest image was calculated as 1 and that of the highest aspect ratio was calculated as 5. The mean aspect ratio of ZnONRs was obtained as 2.20 by measuring the diameters and lengths of ZnONRs and by calculating their average from the TEM images which provide a high surface to volume ratio.

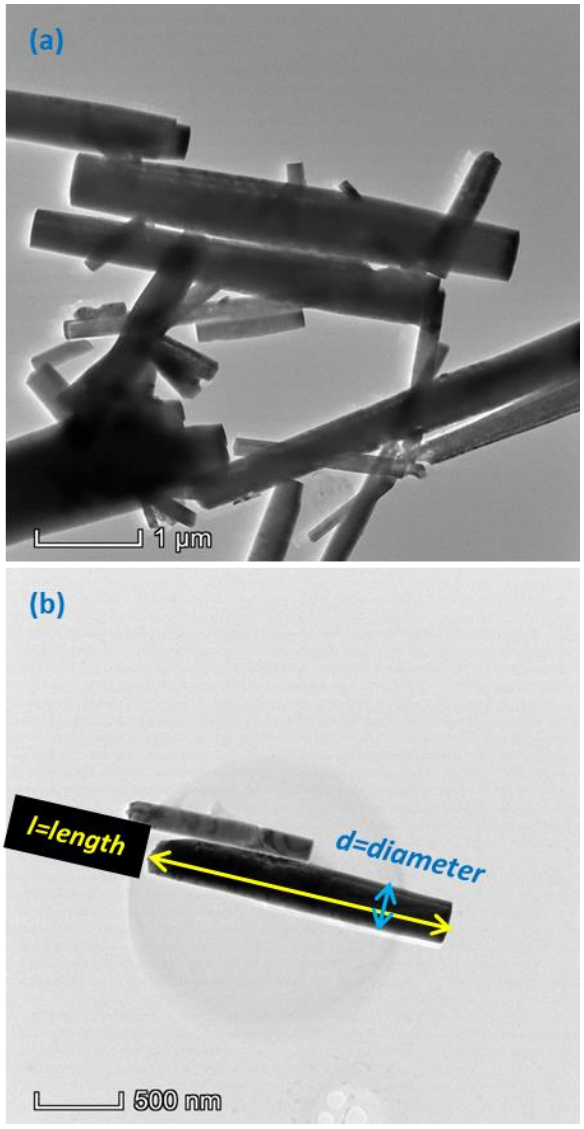

Figure 3. TEM images of the synthesized ZnONRs; (a) Nanorods with different sizes, diameters and lengths, and (b) aspect ratio calculation from diameter and length of a ZnONR.

3.4 EDX analysis

The elemental composition analysis of synthesized ZnONRs was carried out using EDX spectroscopy as shown in Figure 4. Three strong absorption peaks of Zn between 1-10 eV indicate high purity of thus synthesized NRs (Jose *et al*., 2018), (Nagajyothi *et al*., 2013), (Taylor *et al*., 2015). Another strong sharp peak accreted in the spectrogram due to oxygen, this EDX data further confirmed the synthesis of ZnONRs. Very small 2 peaks appeared for Cu is may be due to the copper grid used to take the sample on it.

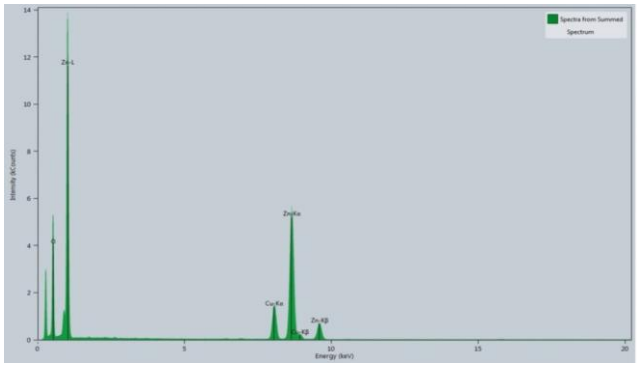

Figure 4. EDX spectrum of the synthesized ZnONRs.

The elemental percentage obtained from the EDX analysis of synthesized ZnONRsis given in Table 1.

Table 1. Elemental percentage of hydrothermally synthesized ZnONRs obtained from EDX analysis.

Element	Mass%	Atom%
Zn	67.51	45.16
O	15.87	43.39

Calculation includes the percentage for Cu from the copper grid. Roughly, the ratio of Zn:O=1:1 is similar to the published results (Liu & Zeng, 2003). The similar atom percent of Zn and O reflects the consistency of the formula of ZnO.

4. Conclusion

In the present work, ZnONRs were prepared successfully through a hydrothermal method using $[Zn(CH_3COO)_2.2H_2O]$ precursor. All the characterization and analyzed results supported the zinc oxide nanorods formation. A λmax at 376 nm of UV–vis spectrum indicated ZnONRs formation. XRD analysis confirmed the crystalline structure hexagonal wurtzite phase of ZnONRs. TEM analysis revealed the 2.20 aspect ratio of synthesized ZnONRs. Low uniformity distribution and aggregations are seen in TEM micrographs. ESD analysis indicated the high purity of the product. All the results confirmed the successful synthesis of ZnO nanorods with high surface-to-volume ratio by hydrothermal method. In the next work, we hope to focus further on the size control of ZnONRs by preventing aggregation and their possible applications.

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