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Synthesis of ZnO nanorod-like structures using pomegranate juice

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ABSTRACT

In this work, pomegranate juice was used not only as reductant, but also as capping agent for self-assembly of trifocal nanostructures to form rod-like ZnO microstructures. Pomegranate juice was applied as reductant because of the presence of anthocyanin molecules in its ingredients. Besides pomegranate juice, $(\text{NO}_3)_2 \cdot 3\text{H}_2\text{O}$ was used as zinc sources for the preparation of rod-like ZnO nanostructures. The as-synthesized products were characterized by X-ray diffraction (XRD), Energy Dispersive X-ray spectroscopy (EDS), scanning electron microscope (SEM). Finally, the efficiency of ZnO nanoparticles as a photocatalyst for the decolorization of methylene blue (MB) using visible light irradiation has been evaluated. © 2015 Trade Science Inc. - INDIA

KEYWORDS

Photocatalytic degradation;
Pomegranate juice;
Electron microscopy;
ZnO Nano structures.

INTRODUCTION

Nanostructure materials have attracted much attention in the last few years due to their unique properties that are different from the bulk materials^[1]. Zinc sulfide as an important semiconductor with wide bandgap (3.6 eV) has been widely used for the light emitting diodes^[4], flat panel displays, electroluminescent and infrared devices^[2]. Transition metal chalcogenides, as unique combinations, have attracted many attentions because of their special physical and chemical properties, and broad application in many fields. Recently, nano-scale chalcogenides are assuming great importance both in theory and in practice owing to their novel properties as a consequence of the large number of surface atoms and the three-dimensional confinement of the electrons^[3]. These unique properties lead to appearance of new

application, such as carbonylation^[4], oxygen-lead selenide interaction^[5], fabrication of diffractive optical elements^[6], and synthesis of (Z)-tamoxifen^[7]. For semiconducting ternary chalcogenides, AB_mC_n (A = Cu, Ag, Zn, Cd, etc.; B = Al, Ga, In; C = S, Se, Te) are also very attractive, due to their unique thermoelectric and photocatalytic properties^[8]. One of them is ZnO, which has different structures^[9]. ZnO a compound of mercury that exists in two forms, red zinc oxide and yellow mercuric oxide. Use as a chemical intermediate for mercury salts, organic zinc compounds, chlorine monoxide, antiseptic in pharmaceuticals, pigment and glass modifier, fungicide, preservative in cosmetics, analytical reagent, formerly used in antifouling paints and as a material for cathodes for mercury batteries^[10]. ZnO was the most unusual one in terms of its structural properties at ambient pressure, which are largely deter-

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mined by the strong tendency for linear coordination of Zn to form the O–Zn–O chain geometry^[11]. The structure of ZnO is built up of planar O–Zn–O zigzag chains lying in the *ac*-plane. The band gap of the ZnO at room temperature was measured to be 2.19 eV from the photoconductivity, and n-type electrical conductivity has been reported^[12]. In general, there are many effective methods for the preparation of transition metal chalcogenides such as microwave irradiation^[13], hydrothermal^[14], and solvothermal^[15]. Among various techniques developed for the synthesis of metal chalcogenides, thermal decomposition is a novel method to produce stable monodispersed^[16] and it is a rapidly developing research area. As compared to conventional method, it is much faster, cleaner and economical. However, an improvement in the thermal decomposition process should be made in preparing copper nanoparticles with controllable size and shape in order to extend the application areas and satisfy the needs of fundamental research. In this manuscript, the production method of ZnO nanoparticles is reported. One-dimensional (1-D) nanostructures of zinc(II) acetate were synthesized by the sublimation process of $\text{Zn}(\text{NO}_3)_2 \cdot 3\text{H}_2\text{O}$ powder; then, ZnO nanostructures were prepared by solid-state thermal decomposition of the as-produced $\text{Zn}(\text{NO}_3)_2 \cdot 3\text{H}_2\text{O}$ nanostructures. The utilized method has many advantages since it is a controllable, free solvent, template less, and economical method. The produced nanostructures were characterized by SEM, TEM, XRD, IR and EDAX.

EXPERIMENTAL

Materials and physical measurements

All the chemicals reagents used in our experiments were of analytical grade and were used as received without further purification. XRD patterns were recorded by a Rigaku D-max C III, X-ray diffractometer using Ni-filtered $\text{Cu K}\alpha$ radiation. Scanning electron microscopy (SEM) images were obtained on LEO-1455VP equipped with an energy dispersive X-ray spectroscopy. TEM images were obtained on a Philips EM208S transmission electron microscope with an accelerating voltage of 100 kV.

FT-IR spectrum was recorded on a magna Nicolet 550 spectrophotometer in KBr pellets. The energy dispersive spectrometry (EDS) analysis was studied by XL30, Philips microscope.

Synthesis of ZnO nanostructures

In a typical experiment, first, a certain amount of pomegranate juice was added dropwise into the zinc nitrate solution (2 mmol of $\text{Zn}(\text{NO}_3)_2 \cdot 3\text{H}_2\text{O}$ dissolved in 20 mL of distilled water) under magnetic stirring, and then the sodium hydroxide solution (1 mmol of NaOH dissolved in 10 mL of distilled water) was added dropwise into the above solution. The obtained mixture was stirred at room temperature for 30 min. The resultant white precipitates were filtered, washed by distilled water and absolute ethanol and dried at 60 °C in vacuum. The experiment was carried out by using 0.5, 1, 1.5, 2 mL of pomegranate juice at the same conditions sample 1-4 respectively.

RESULTS AND DISCUSSION

In recent years, there has been major interest in the amplification of coordination compounds for the synthesis of nanomaterials^[17]. Using new compounds can be highly useful since they can open new ways to prepare nanomaterials to control the shape and size distribution of nanostructures. In this work, $\text{Zn}(\text{NO}_3)_2 \cdot 3\text{H}_2\text{O}$ was applied as zinc precursor by using of pomegranate juice at the same conditions for the preparation of road-like ZnO nanostructures. XRD patterns ($10 < 2\theta < 80$) of the as-synthesized ZnO is shown in Figure 1. The XRD pattern of the as-synthesized ZnO indicated the formation of monoclinic phase. All reflection peaks of the XRD pattern for ZnO nanoparticles are indexed well to orthorhombic phase (JCPDS No. 80-0074) with calculated cell parameters $a = 3.3110 \text{ \AA}$ and $b = 5.5260 \text{ \AA}$. Based on XRD data, the crystallite diameter (D_c) of ZnO nanoparticles was calculated as 35 nm using the Scherer equation^[18]:

$$D_c = K\lambda / \beta \cos\theta \text{ Scherer equation}$$

where β is the breadth of the observed diffraction line at its half intensity maximum, K is the so-called shape factor, which usually takes a value of about

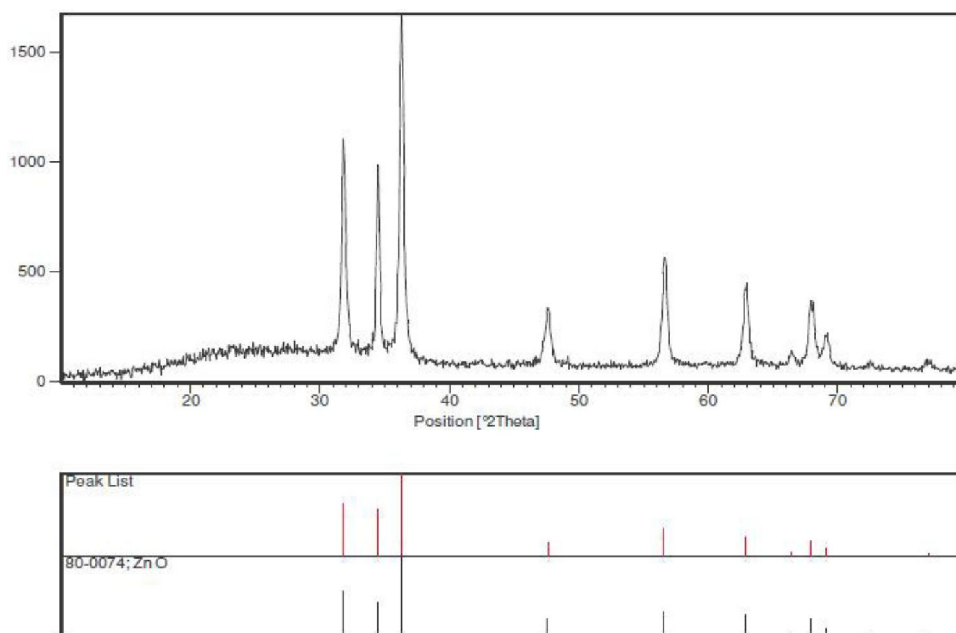


Figure 1 : XRD patterns of ZnO nanostructure (sample 4).

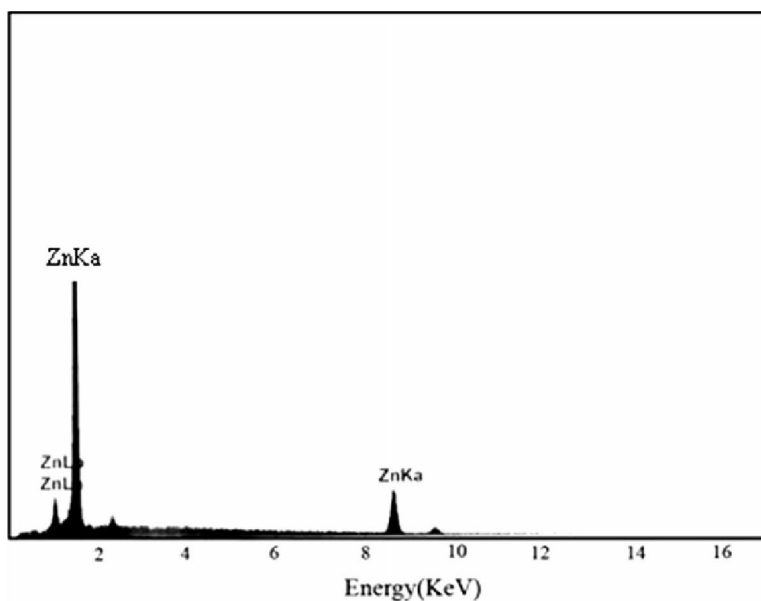


Figure 2 : EDAX pattern of ZnO (sample 4)

0.9, and λ is the wavelength of X-ray source used in XRD. A typical EDAX spectrum of ZnO nanoparticles, as shown in Figure 2, indicates the presence of Zn in the product. In addition, neither N nor C signals were detected in EDAX spectrum. Therefore, both XRD and EDAX analyses show that pure ZnO nanoparticles are successfully produced via the mentioned synthetic route. The effect of the amount of pomegranate juice on the morphology of the products was investigated. When 0.5 mL of pomegranate juice was used, particle-like shapes with ir-

regular particle sizes in the range of 45–50 nm were formed (Figure 3a), sample 1. Figure 3b, sample 2, shows SEM image of the product synthesized by 1 mL of pomegranate juice. In this stage, uniform nanoparticles with grain size of about 35 nm were obtained. Although morphology of the products prepared by 1.5 mL, sample 3, (Figure 3c) and 1 mL (Figure 3b) of pomegranate juice were the same, the presence of some rod shapes was observed in the SEM image of the product synthesized using 2.5 mL of pomegranate juice, sample 4, (Fig-

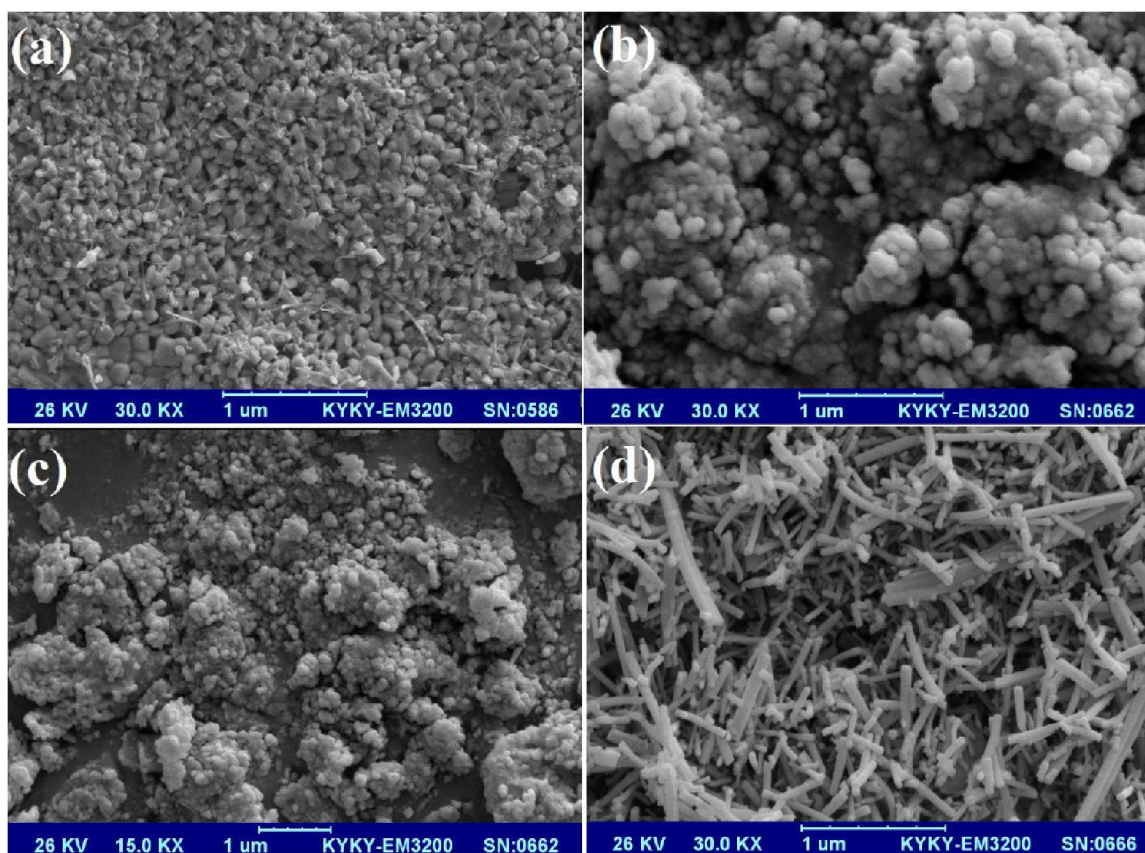


Figure 3 : SEM images of the ZnO nanostructure in (a) 0.5 ml (b) 1ml (c) 1.5 ml (d) 2 ml pomegranate juice at the same conditions

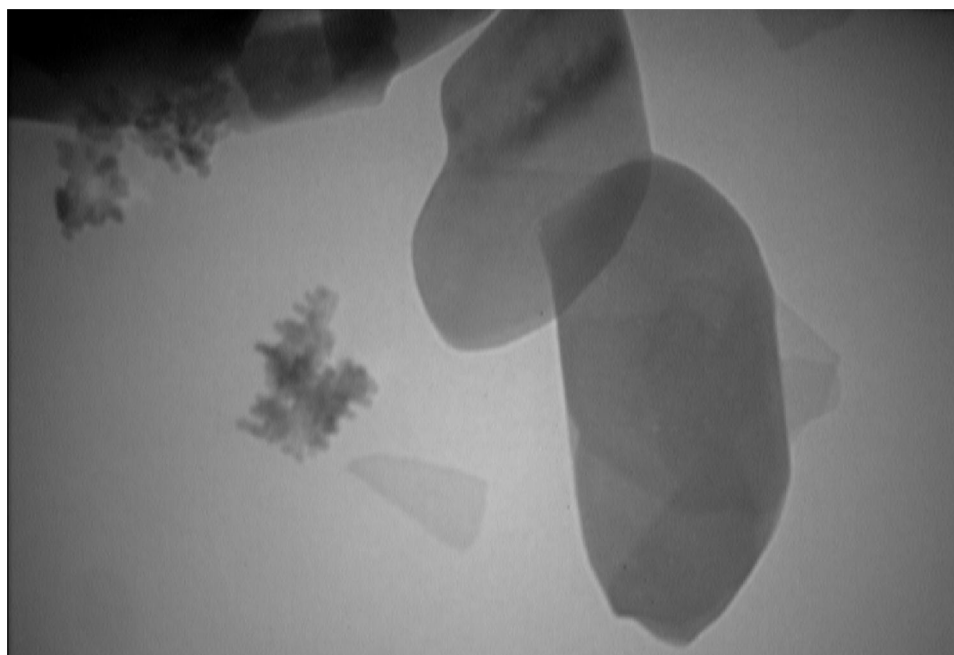


Figure 4 : TEM image of the ZnO nanoparticles synthesized from the 2 ml pomegranate juice (sample 4)

ure 3d). TEM image of ZnO nanoparticles is shown in Figure 4. The ZnO nanostructure consists of separated road-like nanostructures with particle size of

45 nm almost consistent with what observed from SEM image of ZnO nanoparticles. Figure 5 shows FT-IR spectrum of the vibration peaks correspond-

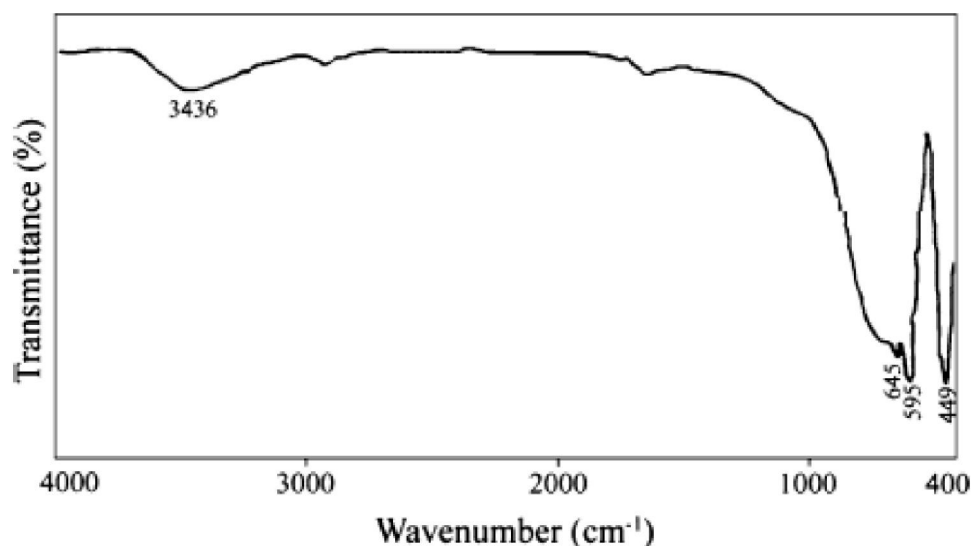


Figure 5 : FT-IR spectrum of ZnO (sample no.4)

ing to the spinel structure are identified at about 449, 595 and 645 cm^{-1} . According to Pramanik's results^[27], the spinels display stretching bands in the 500–900 cm^{-1} range, associated with the vibrations of metal–oxygen. These bands are ascribed to the Zn–O vibrations related to tetrahedral $[\text{ZnO}_4]$ groups corresponding to regular spinel structure^[19]. A weak peak centered at 3,436 cm^{-1} can be attributed to stretching vibration of the O–H band of H_2O molecules that was absorbed on the surface of the nanoparticle^[20].

CONCLUSIONS

In summary, ZnO nanostructures with different morphologies have been successfully prepared via a green method at ambient temperature. Using of pomegranate juice both as a clean reducing agent and capping agent is the novelty of this work. The XRD results showed that pure cubic phase ZnO powders were formed with the aid of this method.

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