

Simple and Low Temperature Method for Preparation of Nanocrystalline ZnO in Presence of [EMIM][EtSO₄] and Their Photocatalytic Activities

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Abstract:

Simple, low temperature and environmentally benign green route is proposed for preparation of nanocrystalline ZnO in presence of a low-cost and halide-free room-temperature ionic liquid (RTIL) by refluxing at 95 °C for 60 minutes. The X-ray diffraction (XRD) studies display that the products are well-crystallized in the form of wurtzite hexagonal. Morphology of the as-prepared ZnO was characterized by scanning electron microscopy (SEM) and the results demonstrate that the prepared nanocrystalline ZnO in presence of the RTIL is smaller than that of prepared in water. Energy dispersive X-ray spectroscopy (EDX) investigations reveal that the products are extremely pure. Diffuse reflectance spectra (DRS) of the prepared sample in the neat RTIL shows blue shift (0.33 eV) relative to the bulk ZnO that can be attributed to quantum confinement effect of nanocrystalline ZnO. Investigation of photocatalytic degradation of methylene blue (MB) on the prepared samples demonstrates that rate constant of the reaction increases with the RTIL content of the media.

Keywords: Zinc oxide; Room-temperature ionic liquid; Nanocrystalline; Photocatalysis.

1. INTRODUCTION

In recent years nanocrystalline semiconductors have attracted considerable interest due to quantum size effect they exhibit [1,2]. Nanometric semiconductors present novel properties because of large number of surface atoms and three-dimensional confinement of the electrons. Among various semiconductors, ZnO nanomaterials are the most frequently studied because of their interest in fundamental study and also their applications in solar energy conversion, luminescence, photocatalysis, electrostatic dissipative coating, transparent UV protection films and chemical sensors [3-6]. ZnO is biocompatible and can be directly used for biomedical applications without any additional coating [7]. Moreover,

searching new methodology to synthesize nano-sized ZnO is of great importance for different applications. For these reasons, various methods such as thermal decomposition, chemical vapor deposition, sol-gel, spray pyrolysis, and precipitation have been developed for the fabrication of nano-sized ZnO [8-12]. Among these synthetic routes, precipitation approach compared with other traditional methods provides a facile way for low-cost and large-scale production, which does not need expensive raw materials and complicated equipments [12]. Morphological control of nanocrystalline semiconductors is of great significance for exploring new applications of the compounds due to the interesting size and shape dependent properties [13]. However, high temperature or long reaction time

was usually involved in these methods. Also, most of the methods involved environmentally malignant chemicals and organic solvents, which are toxic and not easily degraded in the environment.

Room-temperature ionic liquids (RTILs) have been widely studied as a new kind of reaction media owing to their unique properties such as extremely low volatility, wide liquid temperature range, good thermal stability, designable structure, high ionic conductivity, air and water stability, low toxicity, nonflammability, and wide electrothermal windows, etc.[14-19]. Furthermore, they readily dissolve many organic, inorganic and organometallic compounds. RTILs have attracted increasing attention as the green, high-tech reaction media of the future [20] and they have recently considered as potential new media for nanomaterials synthesis [21-24]. One of the largest barriers to the application of RTILs in various fields arises from their high-cost relative to conventional solvents. The most commonly used RTILs have PF_6^- and BF_4^- ions [25]. RTILs with these ions are known to decompose in the presence of water and toxic and corrosive species are formed as a result [26,27]. The RTILs with alkyl sulfate anions are halogen-free and relatively hydrolysis-stable compounds and they could be an interesting alternative for industrial application due to the fact that they avoid the liberation of toxic and corrosive materials into the environment [28].

In this paper, for a first time, a simple refluxing method was applied for preparation of nanocrystalline ZnO in presence of a halide-free and low-cost RTIL, 1-ethyl-3-methylimidazolium ethyl sulfate ([EMIM][EtSO₄]) at about 95°C for 60 minutes.

2. EXPERIMENTAL

2.1. Materials

Zinc acetate ($\text{Zn}(\text{CH}_3\text{COO})_2 \cdot 2\text{H}_2\text{O}$), sodium hydroxide and ethanol were of highest purity available and employed without further purification. The ionic liquid synthesized according to the literature [29].

2.2. Instruments

The X-ray diffraction (XRD) patterns were recorded on Philips Xpert X-ray diffractometer, employing scanning rate of 1°/min in the 2θ range from 20° to 80°. Surface morphology and distribution of particles were studied *via* LEO 1430VP scanning electron microscope (SEM), using an accelerating voltage of 15 kV. The purity and elemental analysis of the products were obtained by energy dispersive analysis of X-rays (EDX) on the same LEO 1430VP instrument with the accelerating voltage of 20 kV. The samples used for SEM and EDX observations were prepared by transferring the particles, which at first were dispersed in the ethanol in glass substrate attached to the SEM stage. After allowing the evaporation of ethanol from the substrate, the particles on the stage were coated with a thin layer of gold and palladium. Diffuse reflectance spectra (DRS) were recorded by a Scinco 4100 apparatus.

2.3. Preparation of nanocrystalline ZnO

In a typical synthesis procedure, zinc acetate dihydrate (5 g) was dissolved in 50 ml of distilled water, and 50 ml of the RTIL under stirring at room temperature. Then, aqueous solution of NaOH (5 M) was slowly added dropwise into the solution under magnetic stirring. Addition of NaOH was continued until pH of the solution was reached to 13. The formed white precipitates were refluxed at approximately 95°C for 60 min. The precipitate was centrifuged to get the precipitate out and washed two times with double distilled water and ethanol to remove the unreacted reagents and then dried in an oven at 70°C. To investigate the effect of the RTIL on properties of the products, one more comparative sample was prepared, keeping the reaction parameters constant except that the product is prepared in water as solvent. Furthermore, in order to demonstrate the effect of solvent composition, the nanocrystalline ZnO was prepared in the neat RTIL.

2.4. Photocatalysis experiments

Photocatalytic activities of the prepared samples were studied by photodegradation of methylene blue (MB). A photochemical reactor provided with water

circulation arrangement to maintain the temperature at 25°C, was used in the experiments. The solutions were magnetically stirred and continuously aerated by a pump to provide oxygen and complete mixing of the reaction solution. A UV Osram lamp of 125 W with the major fraction of irradiation occurring at 365 nm as source was used. The lamp was fitted on the top of the reactor. Prior to illumination, a suspension containing 0.1 g of ZnO and 250 ml of MB (3×10^{-5} M) was continuously stirred in the dark for 30 minutes, to attain adsorption equilibrium. Samples were taken from the reactor at regular intervals and centrifuged to remove the photocatalyst before analysis by spectrophotometer at 664 nm corresponding to maximum absorption wavelength of MB. The adsorption capacity, q_e (mol/g), of the prepared nanocrystallines was calculated by a mass–balance relationship [30]. In order to prevent photocatalytic degradation of the dye, the adsorption experiments were carried out in dark.

3. RESULTS AND DISCUSSION

To investigate the effect of the RTIL on properties of the products, parallel experiments were carried out. The synthetic procedures were similar to each other, except for the solvents. The phase and purity of the samples were determined by XRD, and the typical diffraction patterns are shown in Figure 1. All the diffraction peaks are in agreement with the JCPDS file of ZnO (JCPDS 36-1451), which can be indexed as a wurtzite hexagonal phase of ZnO with the lattice constants of $a=b=3.2498$ Å, and $c=5.2066$ Å. No peaks related to possible impurities are observed. The diffraction peaks correspond to (100), (002), (101), (102), (110), (103), (200), (112), (201), (004) and (202) planes of ZnO crystal system. The average particle size, was calculated using Scherrer's equation [31]. The mean particle sizes (with assumption that the particles are spherical) obtained for nanocrystalline ZnO prepared in water, aqueous solutions of the RTIL with 1:1 composition

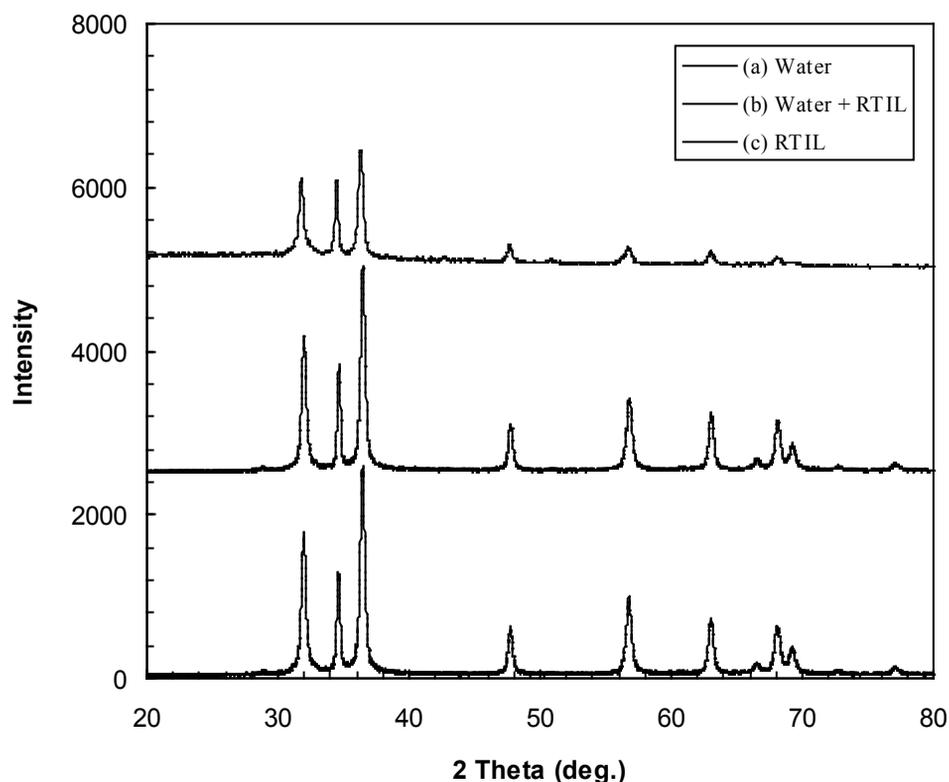


Figure 1: XRD patterns for nanocrystalline ZnO prepared in (a) water; (b) aqueous solution of the RTIL and (c) the neat RTIL

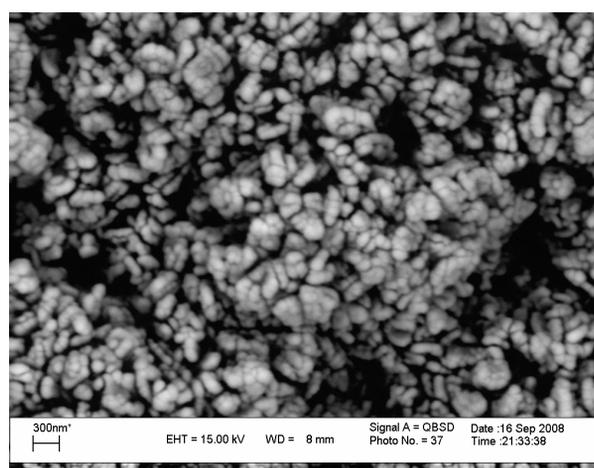
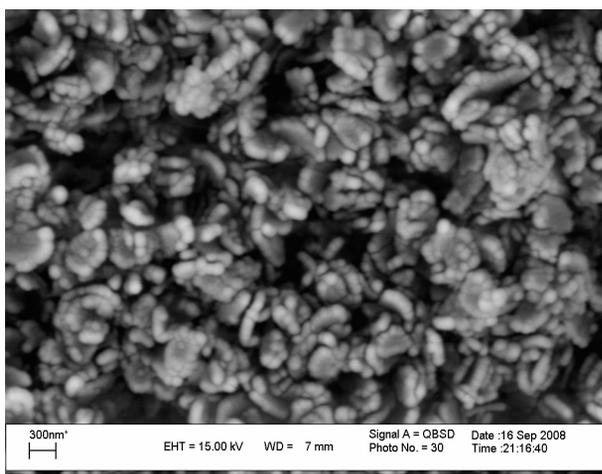
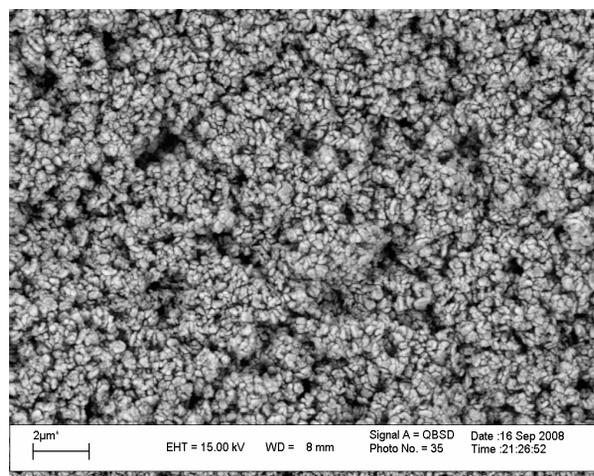
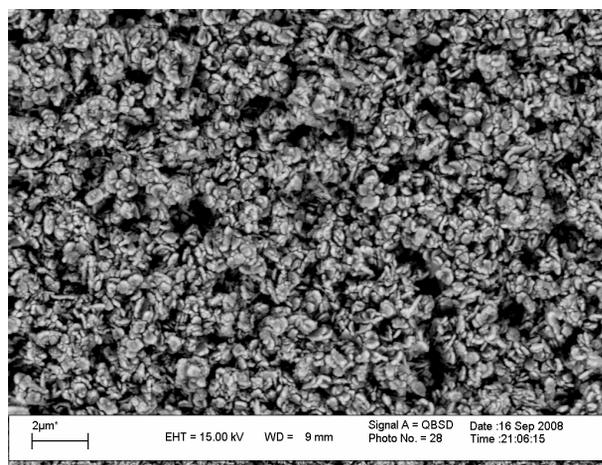


Figure 2: SEM images for nanocrystalline ZnO prepared in water at various magnifications.

Figure 3: SEM images for nanocrystalline ZnO prepared in aqueous solution of the RTIL at various magnifications.

(in volume) and the neat RTIL are 20.8, 20.2 and 16.8 nm, respectively. Then, mean particle size of the nanocrystalline ZnO decreases as the amount of the RTIL increases in the reaction media.

Morphology of the nanocrystalline ZnO prepared in various media was investigated by SEM which their records are shown in Figs. 2-4. As can be seen from Figure 2, morphology of the as-prepared ZnO nanocrystalline in water is irregular nanoplates. Also, as-prepared nanocrystalline ZnO in aqueous solutions of the RTIL is irregular nanoparticles with smaller size (Figure 3). Size of the nanocrystalline ZnO prepared in the neat RTIL is very smaller (Figure 4). Then, it is evident that the size of nanocrystalline ZnO prepared in presence of the

RTIL is smaller than the prepared products in water.

The purity and composition of the products were studied by EDX and the results were displayed in Figure 5. Other peaks in this figure correspond to gold, palladium and silicate which are due to sputter coating of glass substrate on the EDX stage.

Figure 6, exhibit DRS of as-prepared nanocrystalline ZnO prepared in (a) the neat RTIL, (b) aqueous solution of the RTIL and (c) water. As can be seen, absorption wavelength for the nanocrystalline ZnO prepared in the neat RTIL (335 nm) is lower than that of water (360 nm) and bulk ZnO (384 nm). The band gap energy for the nanocrystalline ZnO prepared in the neat RTIL (3.70 eV) is increased compared to that of bulk ZnO (3.37 eV). This can

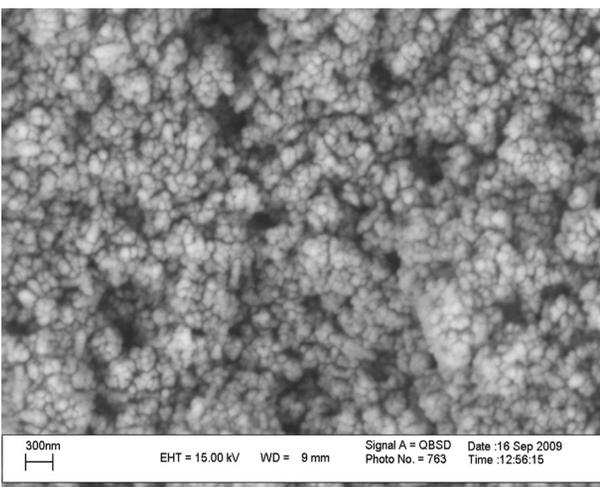
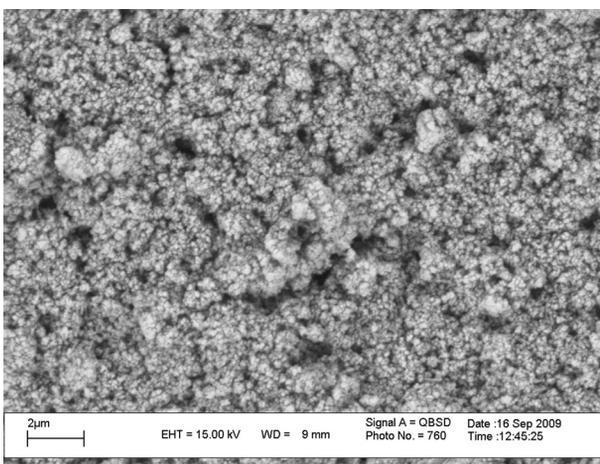


Figure 4: SEM images for nanocrystalline ZnO prepared in the neat RTIL at various magnifications.

be attributed to quantum confinement effect of the nanocrystalline ZnO [32].

Photocatalytic activities of the prepared samples were studied by photodegradation of MB. In Figure 7, photodegradation of MB on nanocrystalline ZnO prepared in various media is exhibited. It is clear that photodegradation of MB by nanocrystalline ZnO prepared in the neat RTIL is higher than the ones at other conditions. As can be seen, complete degradation of MB using nanocrystalline ZnO prepared in the neat RTIL can be occur at about 130 minutes which is far less than the corresponding time for the prepared sample in water.

Observed first-order rate constants of the photodegradation reaction can be obtained using

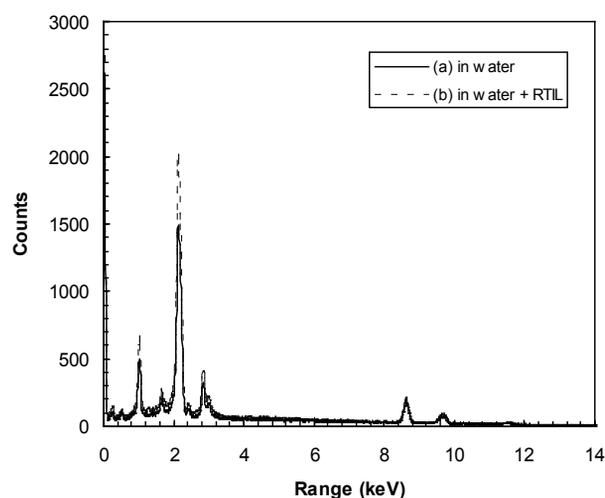


Figure 5: EDX patterns for nanocrystalline ZnO prepared in (a) water and (b) aqueous solution of the RTIL

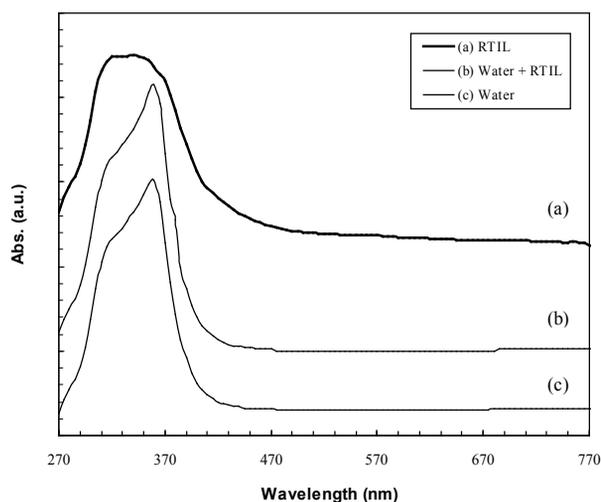


Figure 6: DRS for nanocrystalline ZnO prepared in (a) water, (b) aqueous solution of the RTIL and (c) the neat RTIL

plots of $\ln [MB]$ or $\ln A$ (logarithm of absorbance) versus irradiation time [33]. Rate constant of the reaction on the prepared samples in water, aqueous solution of the RTIL and the neat RTIL are 11.4×10^{-3} , 14.7×10^{-3} and $28.0 \times 10^{-3} \text{ min}^{-1}$, respectively. Therefore, observed first-order rate constant of the reaction on the nanocrystalline ZnO prepared in presence of the RTIL is greater than the prepared sample in water. The photocatalytic activity of semiconductors is mainly determined by crystal structure, surface area,

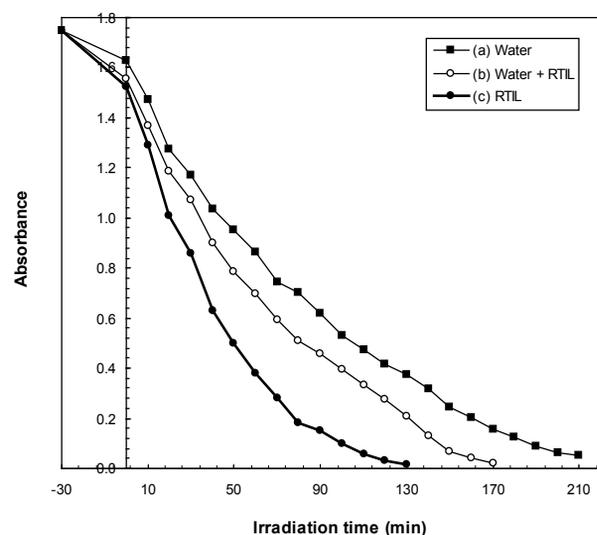


Figure 7: Photodegradation of MB on nanocrystalline ZnO prepared in (a) water, (b) aqueous solution of the RTIL and (c) the neat RTIL.

size of particles, band-gap energy and morphology [34]. The small-sized nanoparticles with high surface area are effective substrates for adsorption of pollutant molecules and the light [35]. In order to compare ability of the prepared nanoparticles for adsorption of MB molecules, the adsorption experiment was performed after 60 minutes in dark and adsorption capacity (q_e) of the prepared nanocrystallines was calculated. The values of q_e for MB adsorption on the nanocrystalline ZnO prepared in water, aqueous solution of the RTIL and the neat RTIL are 4.42×10^{-6} , 5.91×10^{-6} and 7.95×10^{-6} mol/g, respectively. It is clear that the adsorption capacity of MB molecules on the nanocrystalline ZnO prepared in the neat RTIL media is higher than that of the water. Therefore, significant improvement of photocatalytic activity of the prepared sample in presence of the RTIL should be related to the higher surface area of the nanocrystalline ZnO due to smaller size of the sample. Moreover, a limiting factor that controls the efficiency of photocatalysis is the rapid recombination of photogenerated electrons and holes in the semiconductor particles [36]. Recombination of the electron-hole pair within the semiconductor particle is drastically reduced with decreasing particle size [37]. Hence, because of

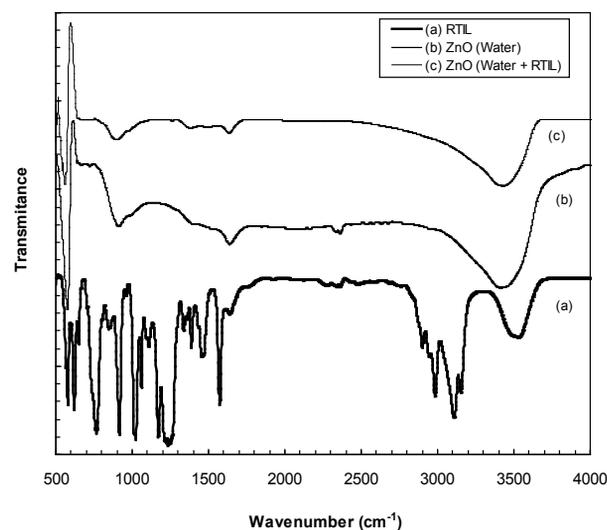


Figure 8: FT-IR spectra of (a) the RTIL and nanocrystalline ZnO prepared in (b) water and (c) aqueous solution of the RTIL.

smaller size, recombination rate of electron and hole for the nanocrystalline ZnO prepared in presence of the RTIL will be lower than the prepared sample in water. For these reasons, photocatalytic activity of the prepared sample in presence of the RTIL will be higher than the prepared sample in water.

Due to the large surface/volume ratio and the existence of dangling bonds, freshly formed nanocrystalline ZnO have a tendency to aggregate until they become stable. The RTIL, [EMIM][EtSO₄], consists of [EMIM]⁺ cations and [EtSO₄]⁻ anions. In presence of the RTIL, the oxide moieties of ZnO nuclei are highly solvated by [EMIM]⁺ ions by electrostatic and hydrogen-bonding interactions [35,38]. Then, the activities of freshly generated ZnO will be greatly inhibited by [EMIM]⁺ ions, so the growth of the ZnO nanoparticles will markedly be modified. The low interfacial tension of RTILs give rise to high nucleation rates, thus enabling the generation of small nanoparticles [38]. Thus, similar to our previous works [39,40], size of the nanocrystalline ZnO prepared in presence of the RTIL is lower than the prepared sample in water.

FT-IR spectra of nanocrystalline ZnO prepared in water and aqueous solution of the RTIL along with the spectra for the RTIL are displayed in

Figure 8. As can be seen, the FT-IR spectra for the nanocrystalline ZnO prepared in two conditions are similar. Moreover, there is no IR absorption peaks corresponding to the RTIL in nanocrystalline ZnO prepared in aqueous solution of the RTIL. Then, it can be concluded that nanocrystalline growth process is accomplished by eliminating the RTIL at the interface. Similar results have been reported in preparation of various nanomaterials [41].

4. CONCLUSIONS

A simple refluxing method was proposed for preparation of nanocrystalline ZnO in presence of a halide-free and low-cost RTIL. This environmentally benign green method needs low temperature and is template-free which remarkably shortens preparation time and avoids the complicated synthetic procedures. The as-prepared nanocrystalline ZnO in the neat RTIL show a blue shift of 50 nm that can be attributed to quantum confinement effect of nanocrystalline ZnO. The method is simple and convenient route to obtain larger quantity of nanocrystalline ZnO. Investigation of photocatalytic activity for the prepared nanocrystallines demonstrates that the activity for the prepared samples in presence of the RTIL is considerably higher than the ones prepared in water.

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