

Preparation and Characterization of ZnO Nanocrystallines in the Presence of an Ionic Liquid Using Microwave Irradiation and Photocatalytic Activity

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Fast, simple and template-free method is proposed for preparation of ZnO nanocrystallines in the presence of 1-ethyl-3-methylimidazolium ethyl sulfate, [EMIM][EtSO₄], a room-temperature ionic liquid (RTIL) under microwave irradiation. The powder X-ray diffraction (XRD) studies display that products are excellently crystallized in the form of wurtzite hexagonal structure. Energy dispersive X-ray spectroscopy (EDX) investigations reveal that the products are extremely pure. The results obtained by scanning electron microscopy (SEM) demonstrate that mean size of ZnO nanocrystallines decreases with microwave irradiation time and the RTIL content of media. Diffuse reflectance spectra (DRS) of the ZnO nanocrystallines shows blue shift relative to the bulk ZnO, which can be attributed to quantum confinement effect of ZnO nanocrystallines. A possible formation mechanism of the ZnO nanocrystallines in aqueous solution of the RTIL is presented. Photocatalytic activity of the ZnO nanocrystallines towards photodegradation of methylene blue (MB) was carried out. The results demonstrate that photocatalytic activity of the ZnO nanocrystallines increases with microwave irradiation time and the RTIL content of media.

Keywords: Zinc oxide, Room-temperature ionic liquid, Nanocrystalline, Microwave irradiation, Photocatalysis

INTRODUCTION

Nanomaterials have attracted considerable interest in the past decade because of their unique properties as well as their potential industrial applications. Semiconductor nanomaterials have attracted remarkable attention in recent years due to novel optical, electrical and mechanical properties [1-4]. Nanometer-sized particles have very different physical and chemical properties from bulk materials. When the crystallite dimension of a semiconductor particle falls below a critical radius of approximately 50 nm, the charge carriers appear to behave quantum mechanically like simple particles in a box. This confinement produces a quantization of discrete electronic states and increases the effective band gap of the

semiconductor [5,6]. ZnO is known as an important semiconductor which has been studied extensively in the past few years due to its fundamental and technological characteristics. Its various attractive properties, such as wide band gap (3.37 eV), large exciton binding energy, and excellent chemical stability, suggest a host of possible practical applications as in gas sensors [7], ceramics [8], field emission devices [9], luminescent materials [10], biomedical [11] and photocatalysis [12]. Therefore, ZnO has been considered as one of the important materials and its applications are expanding continuously. No doubt, it will be widely used in various scientific and technical fields in the future. Therefore, searching new methodology to synthesize nano-sized ZnO is of great significance for both fundamental study and practical applications. Various methods such as thermal decomposition, chemical vapor deposition, sol-gel,

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spray pyrolysis, and precipitation have been developed for the fabrication of nano-sized ZnO [13-17]. 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 received considerable attention due to their advantageous chemical and physical properties [18,19]. There is significant progress in the applications of RTILs to synthetic-organic chemistry, catalysis, separation, electrochemistry, biopolymers and molecular self-assemblies [18-21]. RTILs have recently received a great deal of attention as potential new green media for nanomaterials synthesis [22-25]. The amalgamation of RTILs with nanotechnology could lead to some major advances in material science [26]. One of the major barriers to the application of RTILs in various fields arises from their high cost relative to conventional solvents. In order to overcome this problem, also better tune and tailor the physicochemical properties of the RTIL of interest in a favorable fashion, researchers have started to focus on RTIL-based mixed green molecular solvent systems [27]. Moreover, the most commonly used RTILs have PF_6^- and BF_4^- ions [28]. RTILs with these ions are known to decompose in the presence of water and as a result, toxic and corrosive species, such as hydrofluoric and phosphoric acids are formed [29,30]. The RTILs with alkyl sulfate anions are halogen-free and relatively hydrolysis-stable compounds which could be an interesting alternative for industrial applications due to the fact that they bar the liberation of toxic and corrosive materials into the environment [31].

Microwave irradiations have been used for acceleration of organic reactions for some time, because the method is generally fast, simple, energy efficient and less time consuming [32]. Microwave irradiation has shown very rapid growth in its application to materials science due to its unique reaction effects such as rapid volumetric heating and the consequent dramatic increase in reaction rates [33,34]. RTILs are excellent microwave-absorbing agents due to their high ionic conductivity and polarizability, thus leading to a high heating rate and a significantly shortened reaction time [35]. For these reasons, microwave-assisted room-temperature ionic liquid (MARTIL) method has been applied for the preparation

of various nanomaterials [36-39]. The MARTIL method is a fast and environment friendly route to the preparation of nanostructured materials.

In continuation of our investigations into nanomaterial preparation [40-44] and RTILs [45-49], MARTIL method was applied for the preparation of ZnO nanocrystallines in the presence of an RTIL. For the above mentioned reasons, halide-free RTIL, 1-ethyl-3-methylimidazolium ethyl sulfate ([EMIM][EtSO₄]) was used in this work [50]. The selection of the RTIL was justifiable by the fact that it can be obtained at a relatively low price and its synthesis method is simple [50]. Consequently, a template-free, cost effective, and fast route is proposed to obtain larger quantity of ZnO nanocrystallines.

MATERIALS AND METHODS

Materials

Zinc acetate ($\text{Zn}(\text{CH}_3\text{COO})_2 \cdot 2\text{H}_2\text{O}$ extra pure), sodium hydroxide and ethanol were obtained from Merck, and employed without further purification. The ionic liquid was 1-ethyl-3-methylimidazolium ethylsulfate, [EMIM][EtSO₄], and synthesized according to the literature [50]. Double distilled water was used for all the experiments.

Instruments

The X-ray diffraction (XRD) pattern was recorded on Philips Xpert X-ray diffractometer with Cu K α radiation ($\lambda=0.15406$ nm), employing scanning rate of 1°/min in the 2 θ range from 10° to 70°. 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 sample used for SEM and EDX observations was prepared by transferring the particles, which at first were dispersed in the ethanol to 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 apparatus. A domestic microwave oven (2.45 GHz and 1000 W) was used for sample preparation.

Preparation of ZnO nanocrystallines

In a typical synthesis procedure, zinc acetate dihydrate (3.30 g) was dissolved in 50 ml of distilled water, and 50 ml of the RTIL. Then, aqueous solution of NaOH (5 M) was slowly added drop wise into the solution under magnetic stirring at room temperature. Addition of NaOH was continued until pH of the solution reached to 13. The solution was irradiated in air with 55% of output using a domestic microwave oven for 5 min. The formed milky color suspension was centrifuged to get the precipitate out and washed three times with double distilled water and ethanol respectively to remove the unreacted reagents and dried in an oven at 50 °C for 24 h. 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 was prepared in water as solvent. In order to demonstrate the effect of solvent composition, ZnO nanocrystallines were prepared in aqueous solutions of the RTIL with 1:4 composition (1 water + 4 RTIL, in volume). Also, in order to demonstrate the effect of microwave irradiation time in aqueous solutions of the RTIL, two comparative samples were prepared with irradiation times of 10 and 15 minutes.

Photocatalysis experiments

To examine the photocatalytic activity of the prepared samples, photodegradation of methylene blue (MB), which is a typical dye resistant to biodegradation, was investigated. A cylindrical Pyrex photochemical reactor with 400 ml capacity provided with water circulation arrangement to maintain the temperature at 25 °C, was used in the experiments. The solution was 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 was used. Prior to illumination, a suspension containing 0.1 g of the photocatalyst and 250 ml of MB (3.13×10^{-5} M) was stirred continuously in the dark for 30 min, to attain adsorption equilibrium. Samples were taken from the reactor at regular intervals and centrifuged to remove the catalyst before the analysis by the spectrophotometer at 664 nm corresponding to maximum absorption wavelength (λ_{max}) of MB.

RESULTS AND DISCUSSION

In order to investigate the effect of solvent and microwave irradiation time on the properties of the products, parallel experiments were carried out. The synthetic procedure was the same for all experiments, except for changes in the media and microwave irradiation time. The phase and purity of the samples were determined by XRD, whose typical diffraction pattern is 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 crystalline phase of ZnO with the lattice constants of $a = b = 3.2498 \text{ \AA}$, and $c = 5.2066 \text{ \AA}$. The sharp diffraction peaks manifest that the as-prepared ZnO nanocrystallines have high crystallinity. The diffraction peaks correspond to (100), (002), (101), (102), (110), (103), (200), (112), (201), (004) and (202) planes of ZnO crystal system. The results indicate that the products consist of pure phases and no characteristic peaks are observed for other impurities, such as Zn(OH)_2 .

The morphology of the ZnO nanocrystallines prepared in water and aqueous solution of the RTIL was investigated by scanning electron microscope (SEM) whose records at different magnifications are shown in Figures 2-5. It is evident that structures of the ZnO nanocrystallines produced in aqueous solution of the RTIL with 5 and 10 irradiation times are mainly nanoplates. On the contrary, the sample prepared in aqueous solution of the RTIL with irradiation time of 15 minutes changes to nanoparticles with smaller size. Also, in order to demonstrate the effect of solvent composition, ZnO nanocrystallines was prepared in aqueous solutions of the RTIL with 1:4 composition whose corresponding images are depicted in Figure 5. It is clear that the mean size of the ZnO nanocrystallines decreases with RTIL content of the media. Although the nanoparticles are agglomerating, the boundaries between single crystallites are clearly observable. Thus, the role of RTIL as a solvent is of significance in obtaining smaller nanoparticles.

Purity and composition of the products were studied by energy dispersive X-ray spectroscopy (EDX) which is displayed in Figure 6. The curve reveals the presence of Zn and O peaks in all as-prepared samples. Other peaks in this figure correspond to gold, palladium and silicate which are

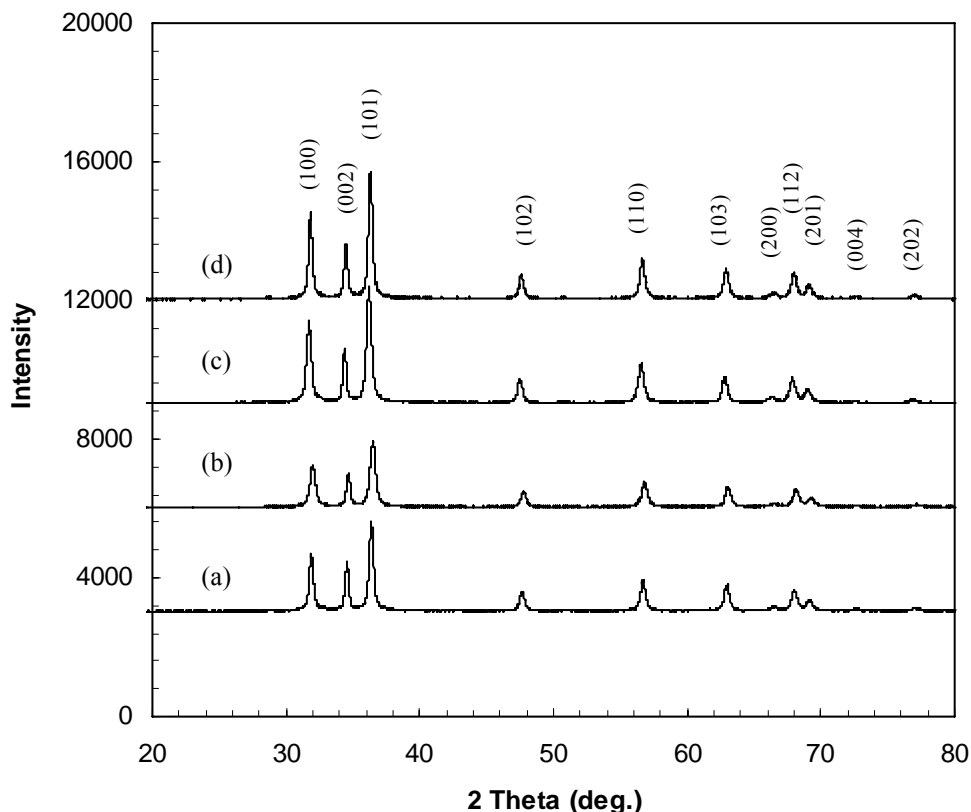


Fig. 1. The powder XRD pattern of ZnO nanocrystallines prepared in water (a), and aqueous solution of the RTIL with 1:1 composition using microwave irradiation time of 5 (b), 10 (c) and 15 minutes (d).

due to sputter coating of glass substrate on the EDX stage. It is clear that the as-prepared ZnO nanocrystallines are extremely pure.

Figure 7 exhibits diffuse reflectance spectra (DRS) of as-prepared ZnO nanocrystallines. An absorption maximum at about 350 nm (3.54 eV) was observed for the as-prepared samples. The band gap energy is increased compared with that of bulk ZnO (3.37 eV); the enlargement of band gap or blue shift can be attributed to the quantum confinement effect of the ZnO nanocrystallines.

Based on the experimental results, a possible formation mechanism of the ZnO nanocrystallines using aqueous solution of the RTIL is presented. The freshly formed ZnO nanocrystallines have a tendency to aggregate until they become stable. When aqueous solutions of the RTIL are used

as a reaction medium, the solute is solvated by ions. The RTIL, [EMIM][EtSO₄], consists of [EMIM]⁺ cations and [EtSO₄]⁻ anions. Thus, [EMIM]⁺ cations can combine with oxide moieties of ZnO nuclei through electrostatic attraction [51]. The imidazolium ring is an electron-withdrawing group and can attract the electron pair shared by hydrogen and carbon of position 2 for imidazolium ring [52], thus the hydrogen-bonding between the RTIL and oxide moieties of ZnO nuclei is strong. As soon as the ZnO nanocrystal nuclei are formed, they get coated by the RTIL, and thereby provide a control on the growth. Meanwhile, the activities of freshly generated ZnO surface are greatly inhibited by [EMIM]⁺ ions, so that the growth of the ZnO nanocrystals is markedly decreased. In aqueous solution, with low RTIL content, small ZnO particles grow and eventually form nanoplates with larger

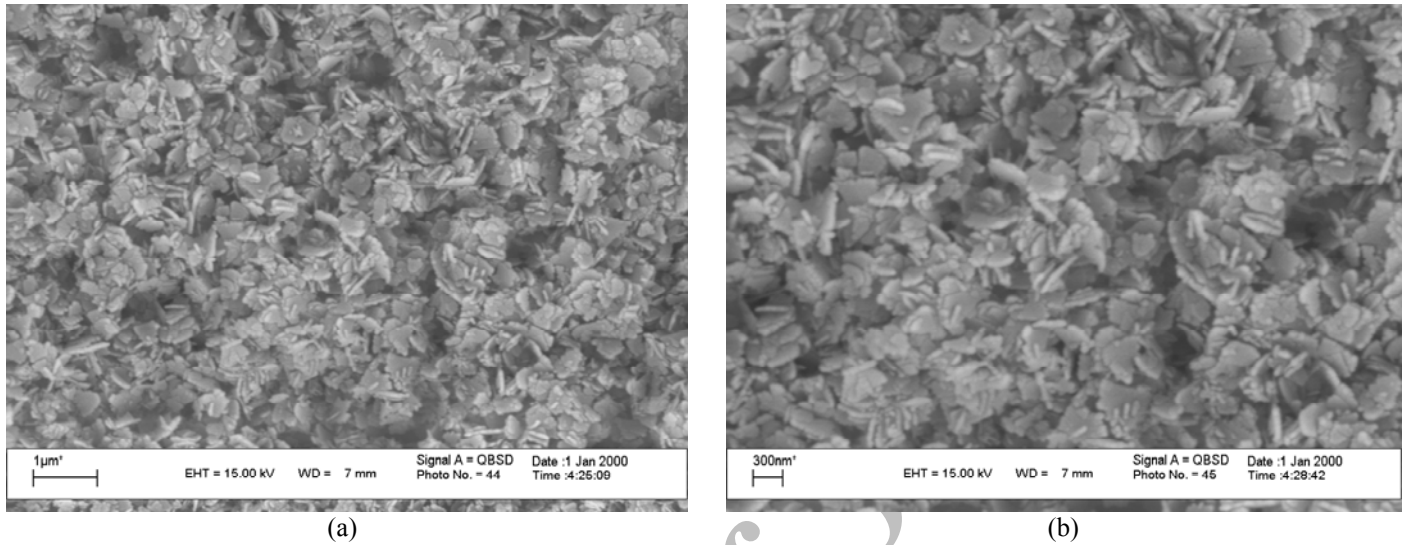


Fig. 2. The SEM image of ZnO nanocrystallines prepared in aqueous solution of the RTIL with 1:1 composition (in volume) using 5 minutes microwave irradiation at various magnifications.

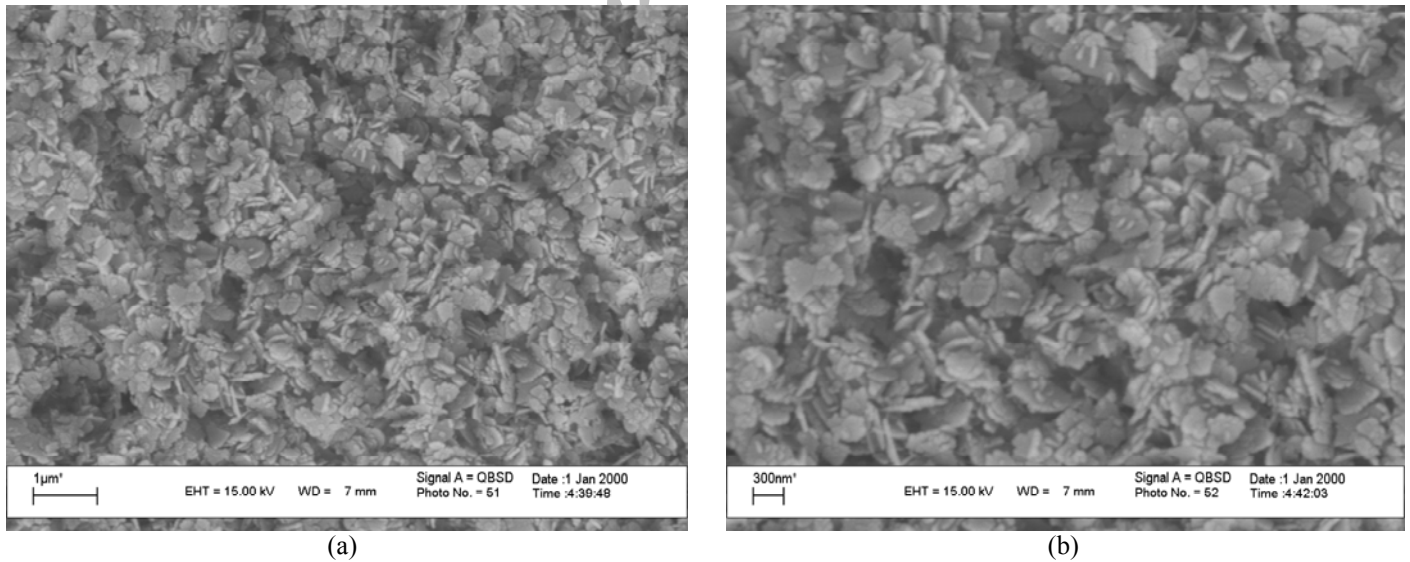


Fig. 3. The SEM image of ZnO nanocrystallines prepared in aqueous solution of the RTIL with 1:1 composition (in volume) using 10 minutes microwave irradiation at various magnifications.

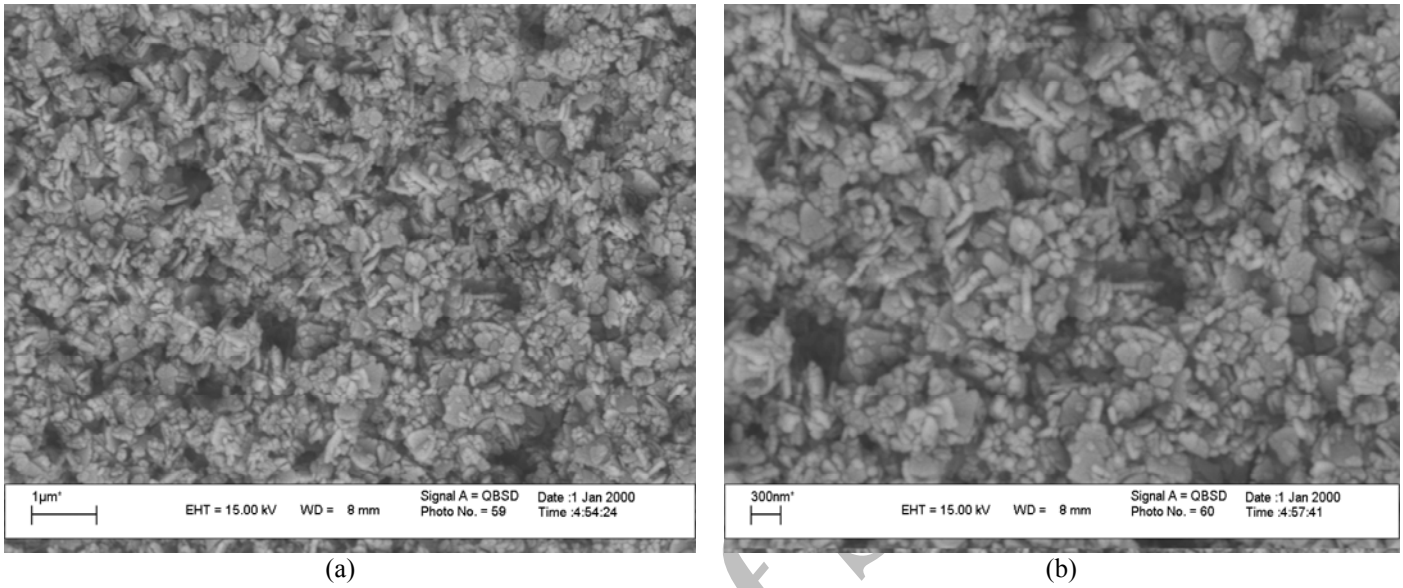


Fig. 4. The SEM image of ZnO nanocrystallines prepared in aqueous solution of the RTIL with 1:1 composition (in volume) using 15 minutes microwave irradiation at various magnifications.

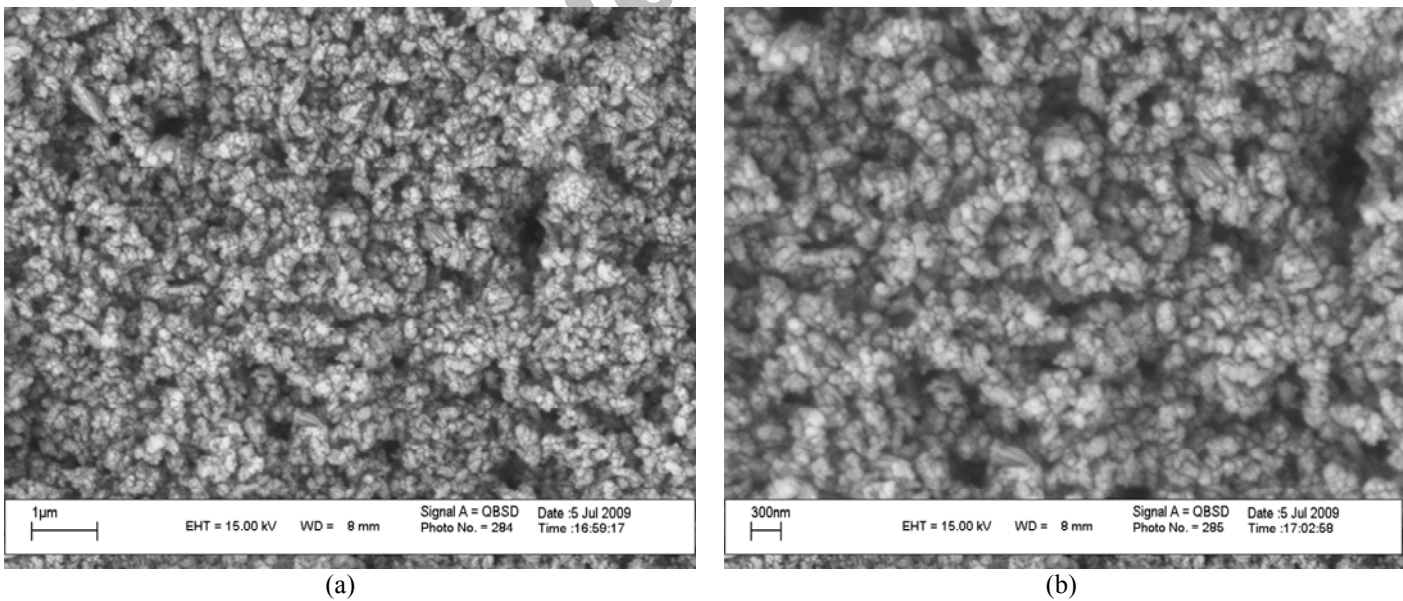


Fig. 5. The SEM image of ZnO nanocrystallines prepared in aqueous solution of the RTIL with 1:4 composition (in volume) using 10 minutes microwave irradiation at various magnifications.

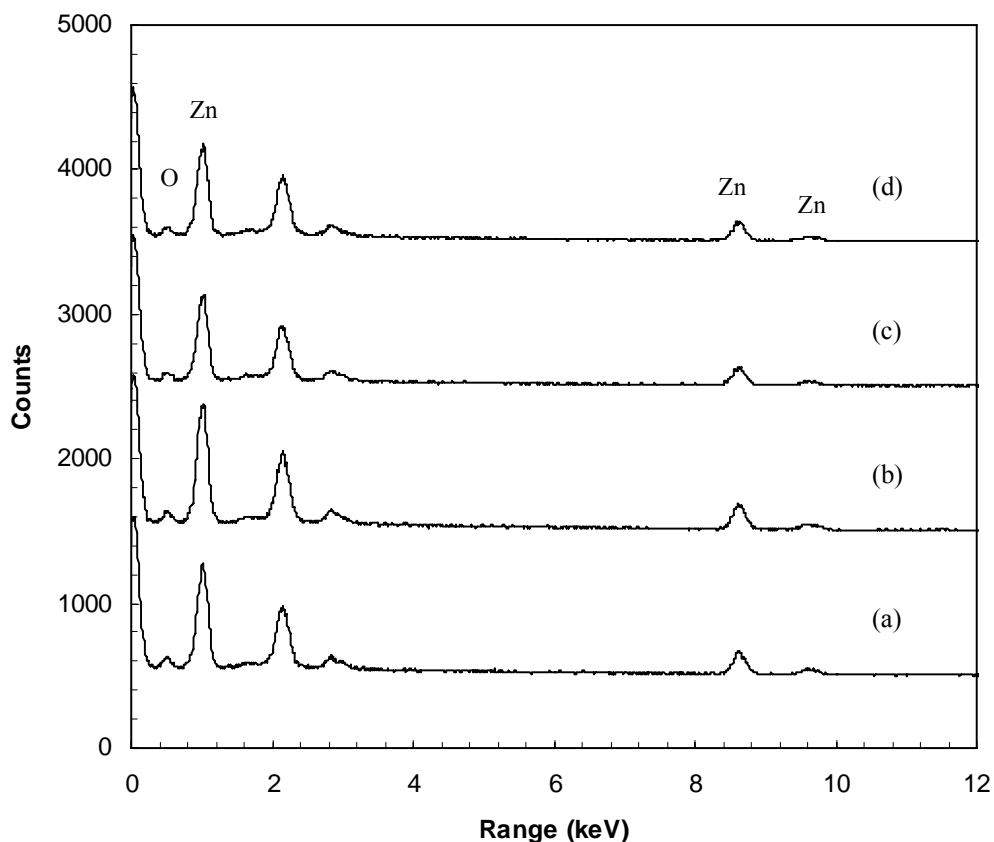


Fig. 6. The EDX pattern of ZnO nanocrystallines prepared in water (a), aqueous solution of the RTIL with 1:1 composition using microwave irradiation time of 5 (b), 10 (c) and 15 minutes (d).

size. Addition of the RTIL to the reaction media greatly decreases the size of ZnO nanocrystallines. This is due to the hydrogen-bonding interactions formed between the hydrogen atoms at position 2 of the imidazolium ring and the oxide ions of ZnO crystal cores and electrostatic interactions between them, that may act as an effective bridge to connect the produced nuclei of zinc oxide and cations of the ionic liquid, playing a crucial role in controlling the growth of the nanocrystals in aqueous solutions of the RTIL, especially in solutions with higher content of the RTIL. Also, this can be attributed to the higher nucleation rate at aqueous solution of the RTIL [53]. The presence of larger amounts of the RTIL suppresses the growth of ZnO nanocrystallines which is likely due to faster nucleation rate in the solution because, the faster the nucleation rate, the smaller the nanocrystallines size.

To examine photocatalytic activity of the prepared samples, photodegradation of methylene blue (MB) which is a typical dye resistant to biodegradation was investigated. In Figure 8, photodegradation of MB on ZnO nanocrystallines prepared in water, aqueous solution of the RTIL with 1:1 and 1:4 compositions is demonstrated. It is clear that photodegradation of MB on ZnO nanocrystallines prepared in aqueous solution of the RTIL with 1:4 composition are higher than the other prepared samples. Complete degradation of MB using ZnO nanocrystallines prepared in aqueous solution of the RTIL with 1:4 composition can occur approximately at 180 minutes which is considerably lower than the corresponding time for the ZnO nanocrystallines prepared in water.

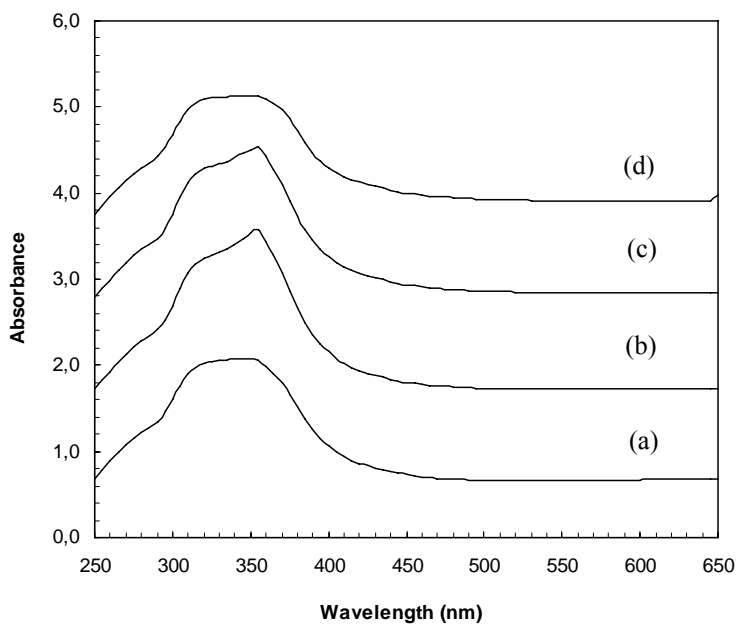


Fig. 7. The diffuse reflectance spectra (DRS) of ZnO nanocrystallines prepared in water (a), aqueous solution of the RTIL with 1:1 composition (in volume) using microwave irradiation time of 5 (b), 10 (c) and 15 minutes (d).

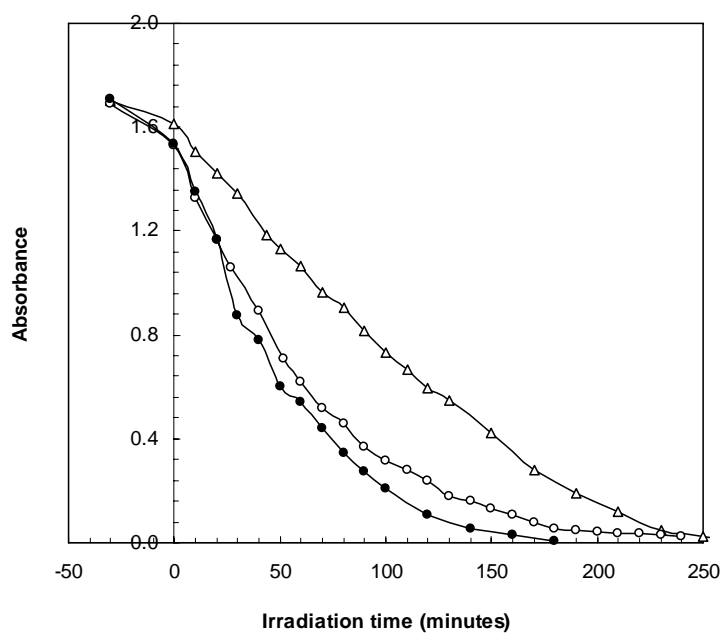


Fig. 8. Photodegradation of MB using ZnO nanocrystallines prepared in water (Δ), aqueous solution of the RTIL with 1:1 composition (in volume) (\circ) and aqueous solution of the RTIL with 1:4 composition (in volume) using 10 minutes microwave irradiation (\bullet).

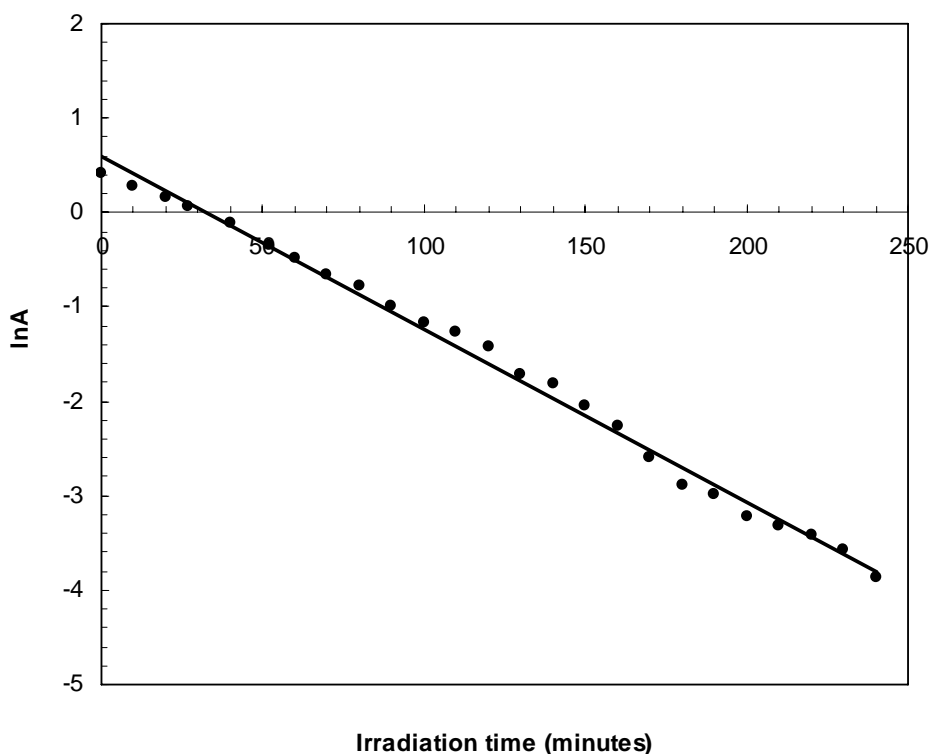


Fig. 9. Plot for logarithm of absorbance *versus* irradiation time for photodegradation of MB using ZnO nanocrystallines prepared in aqueous solution of the RTIL with 1:1 composition (in volume) using 10 minutes microwave irradiation.

In general, dependence of photocatalytic reaction rate on concentration of the organic pollutants is well-described by the following kinetic model [54]:

$$\text{rate} = -\frac{d[\text{MB}]}{dt} = \frac{kK[\text{MB}]}{1 + K[\text{MB}]} \quad (1)$$

where k is first-order rate constant of the reaction and K is adsorption constant of the pollutant on the photocatalyst. Also, $[\text{MB}]$ is concentration of MB (mol/l) at any time and t is the irradiation time. Equation (1) can be simplified to a pseudo first-order equation [54]:

$$\ln \frac{[\text{MB}]}{[\text{MB}]_0} = -k_{\text{obs}}t = k_{\text{obs}}t \quad (2)$$

in which k_{obs} is the observed first-order rate constant of the photodegradation reaction. Observed rate constant for

photocatalytic degradation of MB on the prepared ZnO nanocrystallines was calculated using plots of $\ln[\text{MB}]$ or logarithm of absorbance ($\ln A$) *versus* irradiation time (Figure 9). Observed first-order rate constant of the reaction by ZnO nanocrystallines prepared in water, aqueous solution of the RTIL with 1:1 and 1:4 compositions using 10 minutes irradiation time are 10.5×10^{-3} , 18.3×10^{-3} and $24.1 \times 10^{-3} \text{ min}^{-1}$, respectively. It is clear that the observed first-order rate constant of the reaction using ZnO nanocrystallines prepared in aqueous solution of the RTIL with 1:4 composition is approximately 2.3 times greater than the prepared sample in water.

In order to investigate the effect of microwave irradiation time on photocatalytic activity of the as-prepared ZnO nanocrystallines, photodegradation of MB using the prepared samples was investigated. In Figure 10, photodegradation of

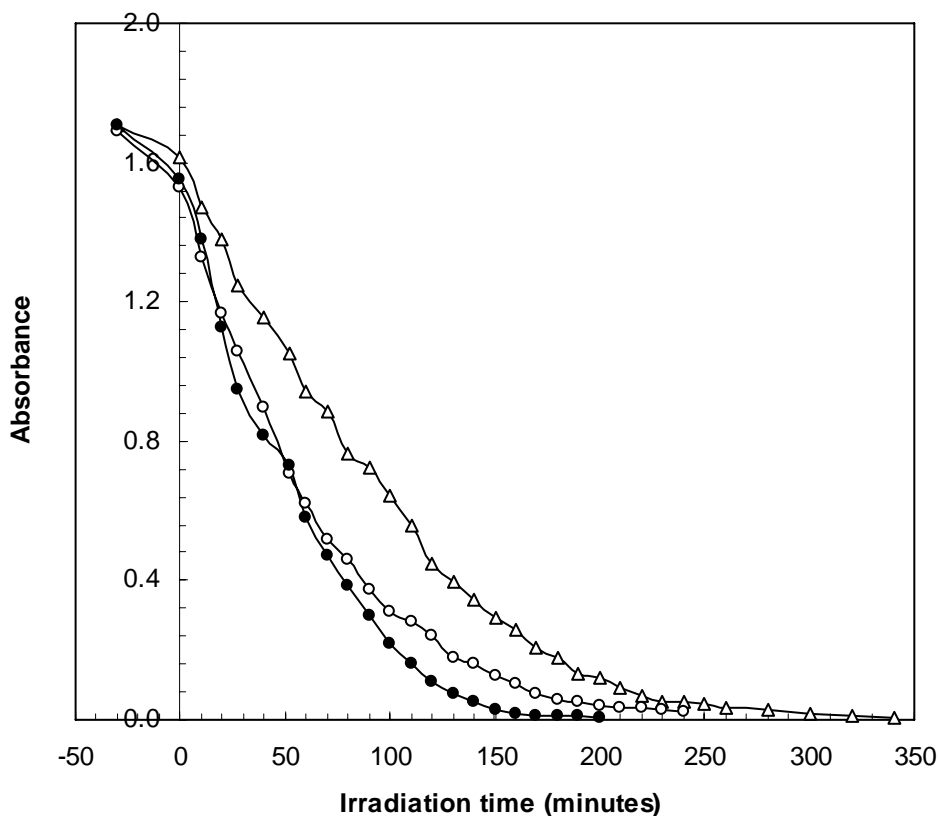


Fig. 10. Photodegradation of MB using ZnO nanocrystallines prepared in aqueous solution of the RTIL with 1:1 composition (in volume) using microwave irradiation time of 5 (Δ), 10 (\circ) and 15 minutes (\bullet).

MB on ZnO nanocrystallines prepared by microwave irradiation time of 5, 10 and 15 minutes in aqueous solution of the RTIL with 1:1 composition are demonstrated. It is clear that photodegradation of MB on ZnO nanocrystallines prepared by irradiation time of 15 minutes are higher than the other samples. Observed first-order rate constant of the reaction by microwave irradiation time of 5, 10 and 15 minutes are 11.8×10^{-3} , 18.3×10^{-3} and $21.2 \times 10^{-3} \text{ min}^{-1}$, respectively.

Generally, the catalytic activity is dependent on calcination temperature of the photocatalysts [55]. In order to study the effect of calcinations temperature on the photodegradation reaction, ZnO nanocrystallines prepared in aqueous solution of the RTIL with 1:1 composition were calcined at various temperatures for 2 h whose results are depicted in Figure 11. It

is clear that photodegradation of MB increases with calcinations temperature of the sample and then decreases. Optimum calcination temperature for the prepared ZnO nanocrystallines is 300 °C. The observed first-order rate constant of the reaction on ZnO nanocrystallines calcined at room temperature, 200, 300 and 400 °C are 21.2×10^{-3} , 26.6×10^{-3} , 35.6×10^{-3} and $32.7 \times 10^{-3} \text{ min}^{-1}$, respectively.

The photocatalytic activity of the semiconductors is mainly determined by crystal structure, surface area, size of particles, band-gap energy and morphology [56]. The small-sized nanocrystallines with high surface area are effective substrates for adsorption of pollutant molecules and the light [51]. Therefore, significant improvement of photocatalytic activity of the ZnO nanocrystallines prepared in aqueous solution of the RTIL with higher RTIL content and higher microwave

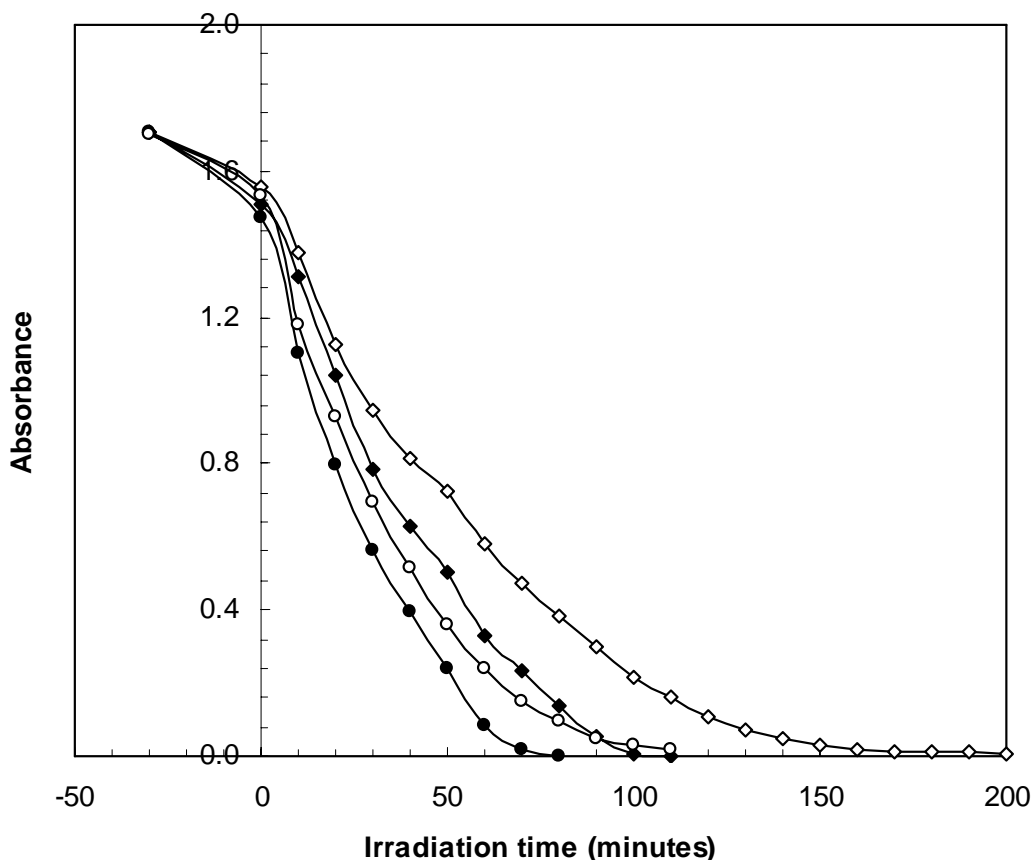


Fig. 11. Photodegradation of MB using ZnO nanocrystallines prepared in aqueous solution of the RTIL with 1:1 composition (in volume) and 15 minutes microwave irradiation without calcination (\diamond), calcination at 200 (\blacklozenge), 300 (\bullet) and 400 °C (\circ).

irradiation time should be related to the higher surface area of the as-prepared nanocrystallines due to smaller size of the prepared samples. Moreover, a limiting factor that controls the efficiency of photocatalysis is the rapid recombination of photogenerated electrons and holes in semiconductor particles [57]. Recombination of the electron-hole pair within the semiconductor particle is drastically reduced with decreasing particle size [58]. Hence, due to smaller size, recombination rate of electron and hole for the ZnO nanocrystallines prepared in the presence of the RTIL with longer microwave irradiation time and higher RTIL content is lower than the prepared sample in other conditions.

CONCLUSIONS

In summary, we have developed a simple and rapid one-step method for the controlled synthesis of ZnO nanocrystallines using microwave irradiation. In this method, aqueous solution of a low cost and halide-free RTIL was applied as solvent and morphology controller. This environmentally benign green method is fast, template-free and low cost which remarkably shortens the preparation time and avoids the complicated synthetic procedures. The as-prepared ZnO nanocrystallines show a blue shift of 34 nm that can be attributed to quantum confinement effect of ZnO

nanocrystallines. Investigation of photocatalytic activity for the prepared nanocrystallines reveals that the photocatalytic activity of the prepared samples increases with microwave irradiation time and the RTIL content of the media. Also, the effect of calcination temperature on the photocatalytic activity of the ZnO nanocrystallines was studied and the optimum value was determined to be 300 °C.

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