

## Simple and Low Temperature Preparation and Characterization of CdS Nanoparticles as a Highly Efficient Photocatalyst in Presence of a Low-Cost Ionic Liquid

V. Taghvaei<sup>a</sup>, A. Habibi-Yangjeh<sup>a,\*</sup> and M. Behboudnia<sup>b</sup>

<sup>a</sup>*Department of Chemistry, Faculty of Science, University of Mohaghegh Ardabili, P.O. Box 179, Ardabil, Iran*

<sup>b</sup>*Department of Physics, Urmia University of Technology, P.O. Box 57155-419, Urmia, Iran*

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A simple and low temperature method is proposed for preparation of CdS nanoparticles in presence of 1-ethyl-3-methylimidazolium ethyl sulfate, [EMIM] [EtSO<sub>4</sub>], a room-temperature ionic liquid (RTIL). The powder X-ray diffraction (XRD) studies display that the products are excellently crystallized in the form of cubic structure and size of the nanoparticles prepared in presence of the RTIL is smaller than that prepared in water. Energy dispersive X-ray spectroscopy (EDX) investigations reveal that the products are very pure and nearly stoichiometric. The results obtained by scanning electron microscopy (SEM) demonstrate that the CdS nanoparticles prepared in presence of the RTIL have lower tendency for aggregation relative to the prepared sample in water. Diffuse reflectance spectra (DRS) of the product prepared in the neat RTIL, shows 1.52 eV blue shift relative to bulk CdS, which can be attributed to quantum confinement effect of the CdS nanoparticles. A possible formation mechanism for CdS nanoparticles in presence of the RTIL is presented. Photocatalytic activity of the CdS nanoparticles towards photodegradation of methylene blue (MB) using UV and visible lights was performed. The results demonstrate that observed first-order rate constant for photodegradation of MB on CdS nanoparticles prepared in the neat RTIL are about 20 and 6 times greater than the prepared sample in water using visible and UV lights, respectively.

**Keywords:** Cadmium sulfide, Room-temperature ionic liquid, Nanoparticle, Photocatalysis, Semiconductor

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### INTRODUCTION

Nanotechnology has potential to create a wide range of new, exciting and innovative applications for environment and other sectors such as medicines, electronics and communication [1–4]. Optical properties of nanosized semiconductor crystallites could be changed so that they are different from their corresponding bulk materials. This is the so-called quantum confinement effect, which is observed as a blue shift in absorption spectra with decreasing of particle size [5]. Photocatalysis, an advanced oxidation technology,

employing semiconductors as photocatalysts is a promising method for the treatment of contaminated ground, surface, and wastewaters containing various organic pollutants [6–9]. This method is a clean, low temperature and non-energy intensive approach for treatment of pollutants. Among semiconductors, TiO<sub>2</sub> and ZnO are considered to be the most suitable for photocatalytic degradation of pollutants due to their chemical inertness and greater resistance to photo-corrosion [10, 11]. However, they have several limitations. Ultraviolet light is required for their photocatalytic activities [12]. Only about 3% of the solar spectrum consists of UV light and employing TiO<sub>2</sub> and ZnO for such purposes means inefficient utilization of solar energy. Instead, utilization of sunlight for such

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\*Corresponding author. E-mail: ahabibi@uma.ac.ir

purposes would be cost effective. Therefore, there is a need to look for other nanomaterials which possess good photocatalytic properties in visible range [13-15].

CdS (with  $E_g = 2.42$  eV at room temperature) has promising applications in multiple technical fields including mechanical, optoelectronic, solar cells, photodegradation of water pollutants and hydrogen generation by visible light [16-20]. Therefore, preparation of CdS nanoparticles has been a very popular research area in recent years [21-26]. Generally these reactions are complicated and require high temperature, long reaction time and use of toxic and highly sensitive compounds. A direct and simple method seems to be required.

Room-temperature ionic liquids (RTILs) have been widely studied as a new kind of reaction media owing to their unique physicochemical properties such as extremely low volatility, wide liquid temperature range, good thermal stability, air and water stability and low toxicity [27-31]. 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 [32] and they have recently received a great deal of attention as potential new media for nanomaterials preparation [33-38]. One of the largest barriers to the application of RTILs arises from their high-cost relative to conventional solvents. Also, the most commonly used RTILs have  $\text{PF}_6^-$  and  $\text{BF}_4^-$  ions [39]. RTILs with these ions are known to decompose in the presence of water and accordingly, toxic and corrosive species, such as hydrofluoric and phosphoric acids are formed [40, 41]. The RTILs with alkyl sulfate anions are halogen-free and relatively hydrolysis-stable compounds and they could be an interesting alternative for industrial applications due to the fact that they avoid the liberation of toxic and corrosive materials into the environment [42].

Recently, CdS nanoparticles have been mainly prepared in high-cost and halide containing RTILs [43-46]. In these papers, there are no extensive investigations about influence of RTILs on properties of the prepared nanoparticles. In addition, photocatalytic activity of CdS nanoparticles prepared in presence of RTILs has not been reported.

For these reasons, in continuing our investigations about preparation of nanomaterials [47-50], a simple and low temperature method is proposed for preparation of CdS nanoparticles in presence of a RTIL. Novelty of the paper is

application of a low-cost and halide-free RTIL [51]. Therefore, a low temperature, cost effective, and simple route is proposed to obtain larger quantity of CdS nanoparticles. Moreover, for a first time, effect of a RTIL on photocatalytic activity of the prepared CdS nanoparticles was investigated.

## MATERIALS AND METHODS

### Materials

Cadmium acetate ( $\text{Cd}(\text{CH}_3\text{COO})_2 \cdot 2\text{H}_2\text{O}$  extra pure), thioacetamide (TAA,  $\text{CH}_3\text{CSNH}_2$  GR for analysis) and absolute ethanol were obtained from Merck, and employed without further purification. The ionic liquid was 1-ethyl-3-methylimidazolium ethylsulfate, [EMIM] [EtSO<sub>4</sub>], and synthesized according to the literature [51]. Double distilled water was used for the experiments.

### Instruments

The X-ray diffraction (XRD) pattern was recorded on Philips Xpert X-ray diffractometer with Cu K $\alpha$  radiation ( $\lambda = 0.15406$  nm), employing scanning rate of 1°/min in the 2 $\theta$  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 sample used for SEM and EDX observations was prepared by transferring the particles, which at first was 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) recorded by a Scinco 4100 apparatus.

### Preparation of CdS nanoparticles

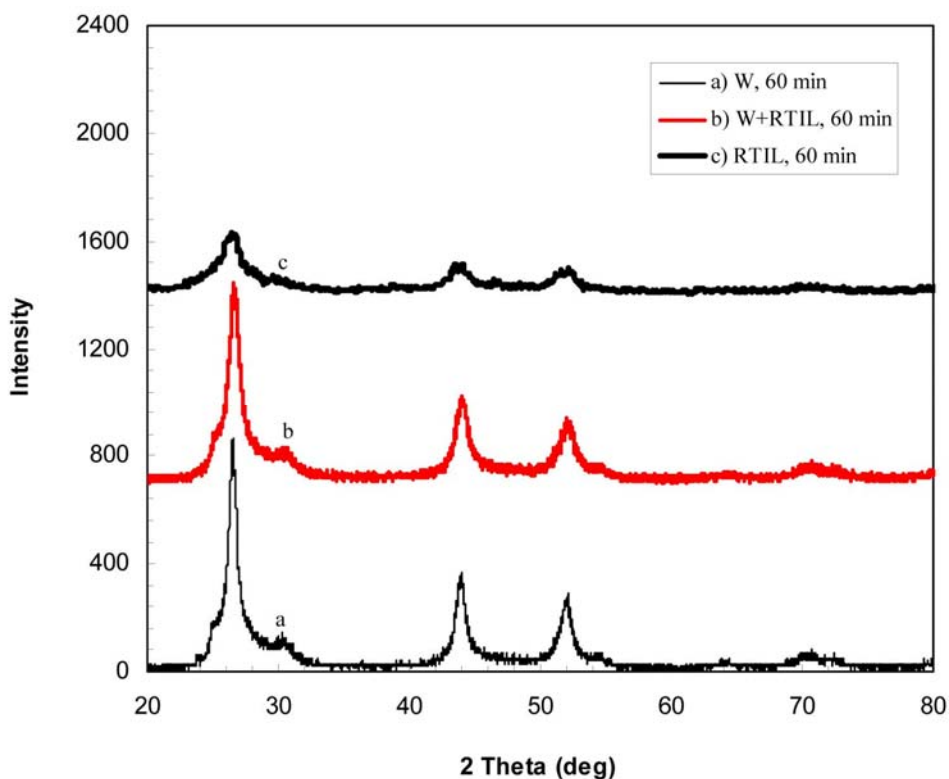
In a typical synthesis procedure, cadmium acetate dihydrate (5.06 g) was dissolved in 12.5 ml of distilled water, and 12.5 ml of the RTIL under stirring at room temperature. In addition, 1.50 g of TAA was dissolved in 12.5 ml of distilled water, and 12.5 ml of the RTIL. Then, the TAA solution was slowly added into the solution of cadmium acetate under magnetic stirring. The solution was refluxed at approximately

95 °C for 60 min. The formed yellow 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 effect of the RTIL on properties of the products, two more comparative samples were prepared, keeping the reaction parameters constant except that the products are prepared in water and RTIL as solvent. Also, in order to demonstrate effect of refluxing time on photocatalytic activity of the prepared sample in aqueous solutions of the RTIL, two comparative samples were prepared with refluxing time of 15 and 30 min, respectively.

### Photocatalysis experiments

In order to examine photocatalytic activity of the prepared nanoparticles, photodegradation of methylene blue (MB) which is a typical dye resistant to biodegradation has been

investigated. A photochemical reactor 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 and a tungsten lamp of 150 W as visible source ( $\lambda > 420$  nm) were used. The lamp was fitted on the top of the reactor. Prior to illumination, a suspension containing 0.1 g of the photocatalyst and 250 ml of MB ( $3 \times 10^{-5}$  M) was stirred continuously in the dark for 30 minute, 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 ( $\lambda_{\max}$ ) of MB. The prepared photocatalysts were stored in a desiccator to prevent moisture adsorption and to retain photocatalytic activity. The adsorption



**Fig. 1.** The powder XRD patterns for CdS nanoparticles prepared in (a) water, (b) aqueous solution of the RTIL (1:1 in volume) and (c) the neat RTIL by refluxing at 60 minutes.

capacity,  $q_e$  (mol/g), of the prepared photocatalysts was calculated by a mass-balance relationship, which represents the amount of adsorbed dye per amount of the photocatalyst:

$$q_e = \frac{(C_o - C_e)V}{W} \quad (1)$$

where  $C_o$  and  $C_e$  are concentrations of the dyes in solution (mol/dm<sup>3</sup>) at  $t = 0$  and time of equilibrium.  $V$  is volume of the solution (dm<sup>3</sup>) and  $W$  is weight of the dry adsorbent (g). In order to prevent photocatalytic degradation of the dye, the adsorption experiments were carried out in dark.

## RESULTS AND DISCUSSION

In order to investigate the effect of solvent on properties of the products, parallel experiments were carried out. The synthesis procedure was similar to each other, except for changes in the solvent. The phase and purity of the samples were determined by XRD and the typical diffraction patterns are shown in Figure 1. The diffraction peaks correspond to (111), (200), (220), (311) and (331) planes of cubic CdS crystal system (JCPDS 42-1411). No peaks attributable to possible impurities are observed. It is clear from the figure that the products have the same cubic crystal structure and the peak broadening in the patterns indicates that the CdS nanoparticles are very small in size. In addition to identification of the crystalline phases, the XRD data were used to estimate size of

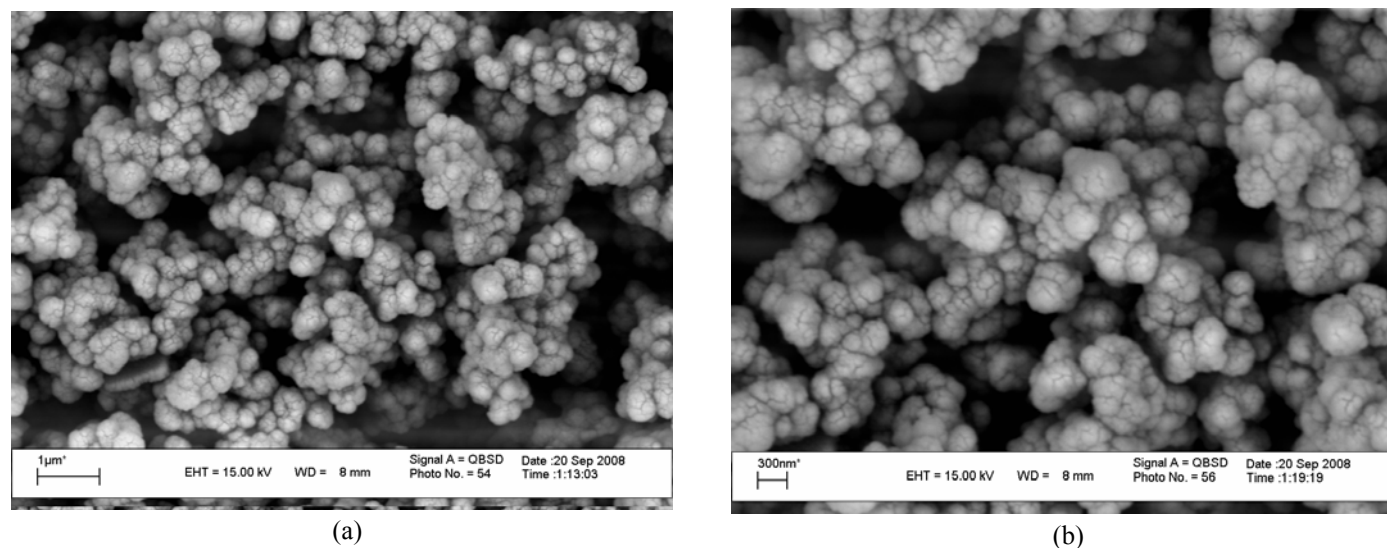
the constituent crystallites by Scherrer's equation [52]. The average particle size,  $D$ , was determined using Eq. (2):

$$D = K \lambda / (B \cos \theta) \quad (2)$$

where  $\lambda$  is the wavelength of X-ray radiation (0.15406 nm),  $K$  the Scherrer's constant ( $K = 0.9$ ),  $\theta$  the characteristic X-ray radiation ( $2\theta = 44.30^\circ$ ) and  $B$  is the full-width-at-half-maximum of the (220) plane (in radians). The mean particle sizes obtained for as-prepared CdS nanoparticles in water, aqueous solutions of the RTIL and neat RTIL by refluxing at 60 min are 9.8, 8.5 and 5.2 nm, respectively. Therefore, mean particle sizes decrease as amount of the RTIL increases in the reaction media and the RTIL effectively prevent growth of the nanoparticles.

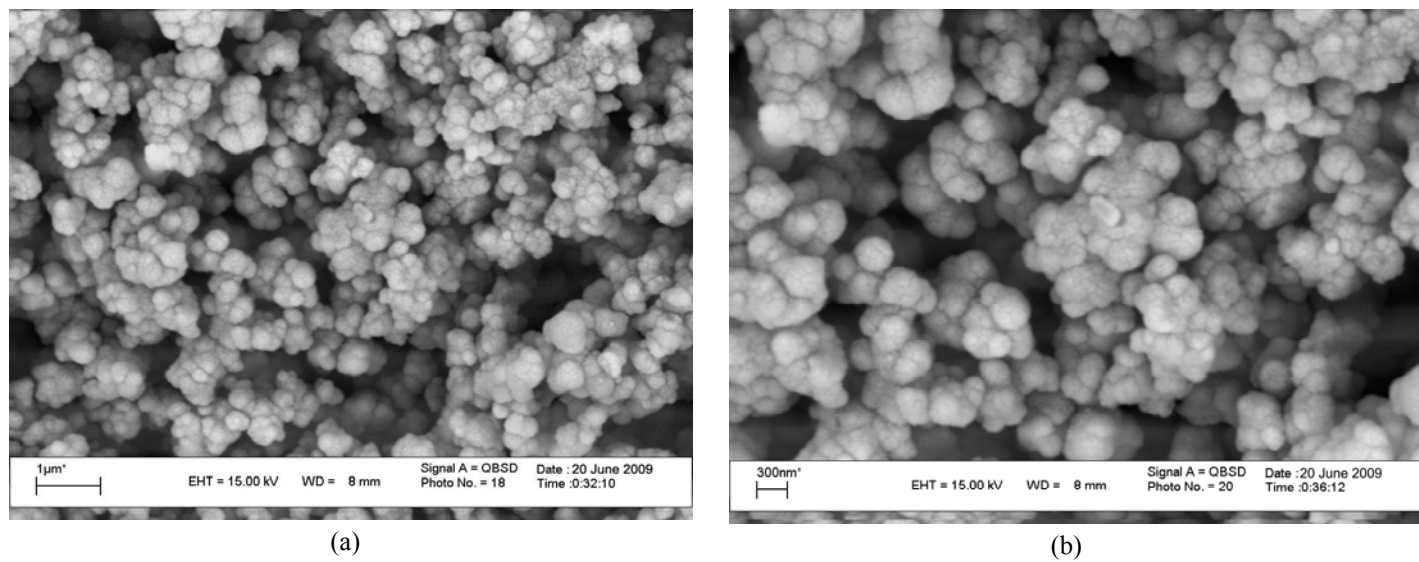
Morphology of the CdS nanoparticles was investigated by scanning electron microscope (SEM) which their records at different magnifications are shown in Figs. 2-4. It is evident that structure of the nanoparticles produced in water as solvent, is highly aggregated possessing irregular shapes and size of the particles is very high. In comparison, the samples prepared in presence of the RTIL have lower aggregation and size of aggregated nanoparticles, especially in neat RTIL, is small. Therefore, the RTIL as a solvent has important role in obtaining smaller nanoparticles.

Purity and composition of the products were studied by energy dispersive X-ray spectroscopy (EDX) and is displayed in Fig. 5. The curve reveals the presence of Cd and S peaks

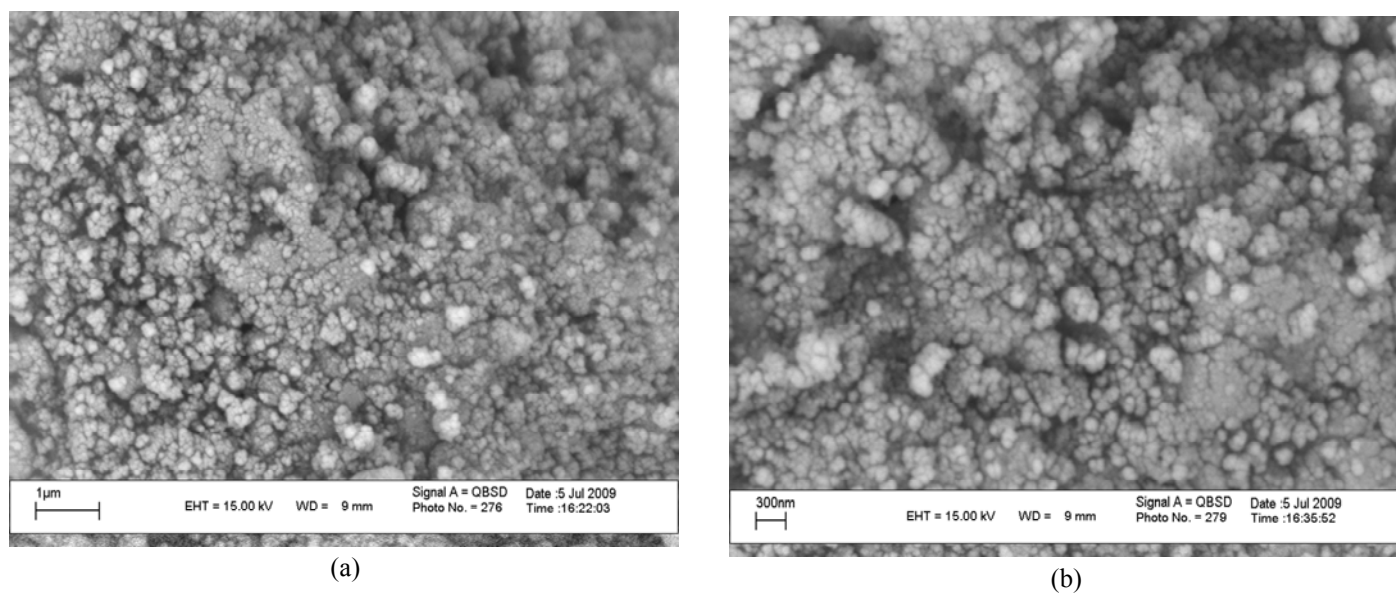


**Fig. 2.** The SEM images for CdS nanoparticles prepared in water at various magnifications by refluxing at 60 minutes.

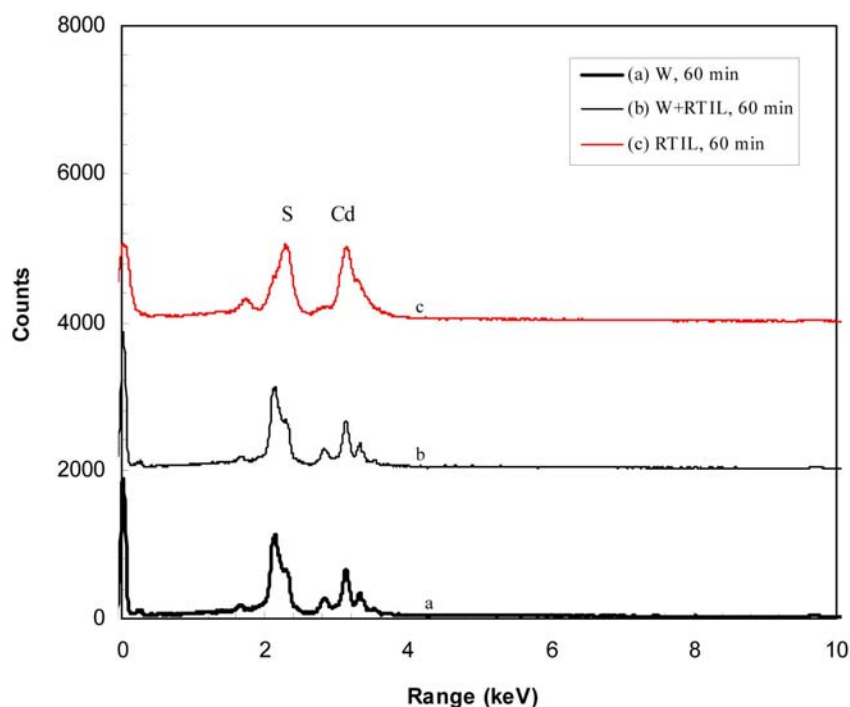
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**Fig. 3.** The SEM images for CdS nanoparticles prepared in aqueous solution of the RTIL (1:1 in volume) at various magnifications by refluxing at 60 minutes.



**Fig. 4.** The SEM images for CdS nanoparticles prepared in the neat RTIL at various magnifications by refluxing at 60 minutes.



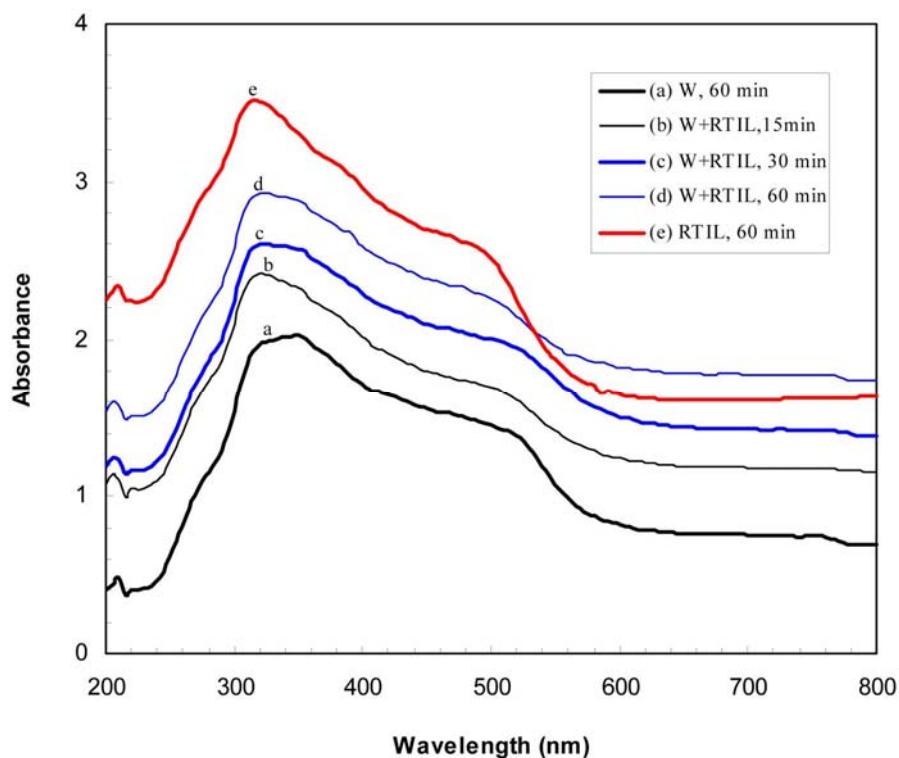
**Fig. 5.** The EDX patterns for CdS nanoparticles prepared in (a) water, (b) aqueous solution of the RTIL (1:1 in volume) and (c) the neat RTIL by refluxing at 60 minutes.

and the average atomic percentage ratio of Cd:S are 55.5:44.5, 58.6 : 41.4 and 51.7 : 48.3 for the nanoparticles prepared in water, aqueous solution of the RTIL and the neat RTIL, respectively by refluxing for 60 min. Other peaks in this figure correspond to gold, palladium and silicate which are due to sputter coating of glass substrate on the EDX stage and were not considered in elemental analysis of Cd and S. It is clear that the as-prepared CdS nanoparticles are adequately pure.

Fig. 6 exhibits diffuse reflectance spectra (DRS) of CdS nanoparticles prepared in water, aqueous solution of the RTIL with various refluxing time and neat RTIL. Absorption maxima for the CdS nanoparticles prepared in water, aqueous solutions of the RTIL and neat RTIL are 350, 325 and 315 nm. Band gap energy for the samples was calculated using wavelength of maximum absorption that is related to difference in energy of valence band and conduction band of semiconductors [53, 54]. The band gap energy for the CdS nanoparticles prepared in the neat RTIL is 3.94 eV, which is relatively increased compared to that of bulk CdS (2.42 eV).

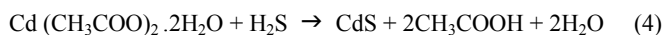
The expansion of band gap (1.52 eV) or blue shift can be attributed to the quantum confinement effect of CdS nanoparticles. It is clear that blue shifts for the nanoparticles prepared in the neat RTIL are higher than the other samples. This confirms the results obtained from XRD and SEM studies. In addition, the prepared samples have broad peaks around 400-550 nm. Hence, the samples have suitable absorption in UV and visible ranges of spectrum.

Based on the experimental results, a possible formation mechanism of the low aggregated CdS nanoparticles using the RTIL is presented. As the Gibbs free energy of the surface is usually very high due to the large surface/volume ratio and the existence of dangling bonds, freshly formed nanoparticles have a tendency to randomly aggregate until they become stable. For this reason the CdS nanoparticles prepared in water as solvent are highly aggregated. When aqueous solutions of the RTIL (specially neat RTIL) is used as a reaction medium, the solute is solvated by ions, thus, the reaction proceeds in an environment different from that water or ordinary organic



**Fig. 6.** The diffuse reflectance spectra (DRS) for CdS nanoparticles prepared in (a) water, (b), (c) and (d) aqueous solution of the RTIL (1:1 in volume) at various refluxing time and (e) the neat RTIL.

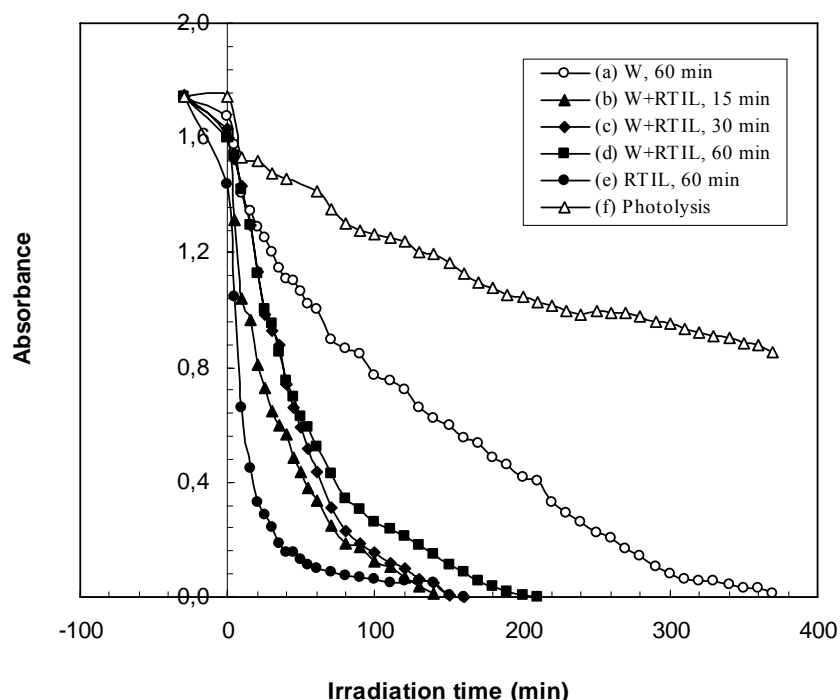
solvents are used. The possible reaction for CdS formation is as follows:



The RTIL, [EMIM][EtSO<sub>4</sub>], consists of [EMIM]<sup>+</sup> cations and [EtSO<sub>4</sub>]<sup>-</sup> anions. The imidazolium ring is an electron-withdrawing group and it can attract the electron pair shared by hydrogen and carbon of position 2 in imidazolium ring [55]; thus the hydrogen-bonding between the RTIL and sulfide moieties of CdS nuclei is strong. In addition, [EMIM]<sup>+</sup> cations can combine with sulfide moieties of CdS nuclei through electrostatic attraction [56]. Then, as soon as the CdS nanoparticle nuclei are formed, they are coated by the RTIL, thereby producing a control on the growth. Meanwhile, the activities of freshly generated CdS surface will be greatly inhibited by [EMIM]<sup>+</sup> ions, so growth of the CdS nanoparticles will markedly be modified. In absence of the RTIL, small CdS nanoparticles grow and form CdS aggregates with large size.

Moreover, it is well known that size of the products depends on nucleation rate of the products. The low interfacial tension of RTILs give rise to high nucleation rates, thus enabling the generation of small nanoparticles [57]. For this reason, the rate for nucleation of CdS nanoparticles prepared in presence of the RTIL is higher than the prepared sample in water. As a result, size of the nanoparticles prepared in presence of the RTIL is lower than the prepared sample in water. Recently, similar results have been reported in preparation of nanomaterials [55, 58].

To examine photocatalytic activity of the prepared samples, photodegradation of methylene blue (MB) which is a typical dye resistant to biodegradation has been investigated. In Fig. 7, photodegradation of methylene blue on CdS nanoparticles prepared in water, aqueous solution of the RTIL with various refluxing times and the neat RTIL along with photolysis using UV irradiation is demonstrated. It is clear that photodegradation of MB on CdS nanoparticles prepared in



**Fig. 7.** Photodegradation of MB using UV light by CdS nanoparticles prepared in (a) water and aqueous solution of the RTIL (1:1 in volume) by refluxing at (b) 15, (c) 30, (d) 60 minutes, (e) the neat RTIL along with (f) Photolysis.

presence of the RTIL are extremely higher than the prepared sample in water. Moreover, refluxing time does not have major effect on photocatalytic activity of the nanoparticles and confirm DRS results, which can be attributed to small changes in size of the nanoparticles. Complete degradation of MB using CdS nanoparticles prepared in the neat RTIL can be occur approximately at 140 minutes which is considerably lower than the corresponding time for the particles prepared in water.

Also, in order to compare the photocatalytic activity of the CdS nanoparticles using visible light, photodegradation of MB was considered and the results were illustrated in Fig. 8. It is clear that the reaction rate for photodegradation of MB on CdS nanoparticles prepared in presence of the RTIL with various refluxing time are greater than the prepared sample in water. As can be seen, complete degradation of MB on CdS nanoparticles prepared in the neat RTIL can be occur about at 350 min which is very lower than corresponding time for the other samples. Thus, photocatalytic activity for the CdS

nanoparticles prepared in presence of the RTIL using UV and visible sources are considerably higher than the prepared sample in water.

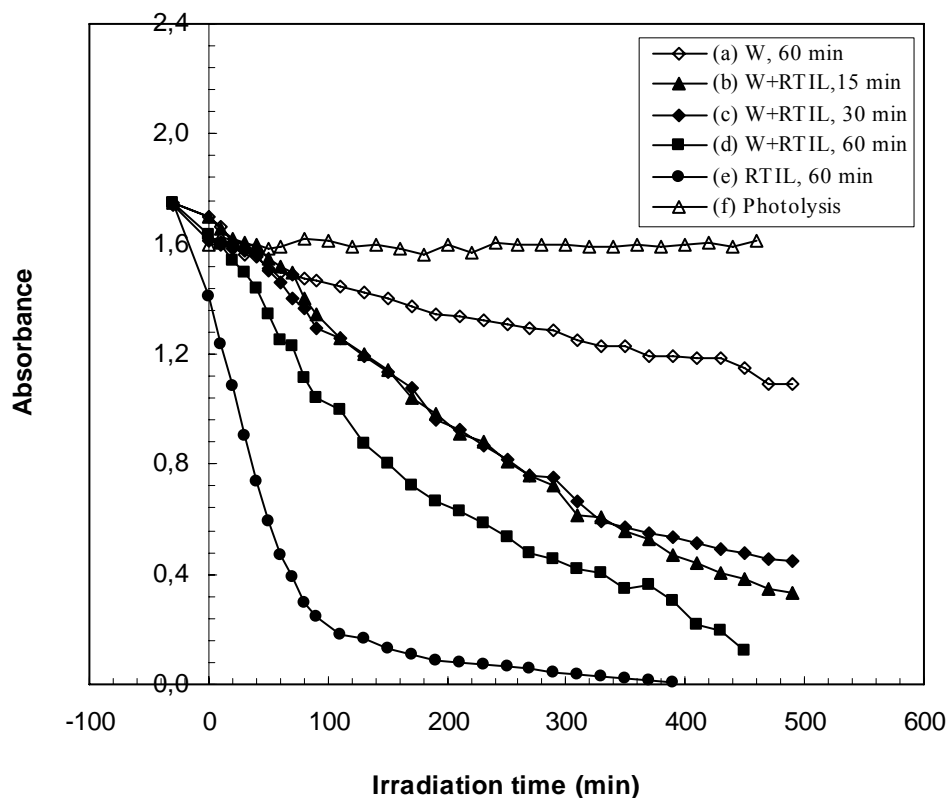
In general, dependence of photocatalytic reaction rate on concentration of the organic pollutants is well described by the following kinetic model [59]:

$$\text{rate} = -\frac{d[MB]}{dt} = \frac{kK[MB]}{1 + K[MB]} \quad (5)$$

where  $k$  is first-order rate constant of the reaction and  $K$  is adsorption constant of the pollutant on the photocatalyst. In addition,  $[MB]$  is concentration of MB (mol/l) at any time and  $t$  is the irradiation time. Equation (5) can be simplified to a pseudo first-order equation [59]:

$$\ln \frac{[MB]_0}{[MB]} = -k_{obs}t = k_{obs}t \quad (6)$$

in which  $k_{obs}$  is observed first-order rate constant of the photodegradation reaction. Observed rate constants for photocatalytic degradation of MB on the prepared CdS nanoparticles were calculated using plots of  $\ln[MB]$  versus



**Fig. 8.** Photodegradation of MB using visible light by CdS nanoparticles prepared in (a) water and aqueous solution of the RTIL (1:1 in volume) by refluxing at (b) 15, (c) 30, (d) 60 minutes, (e) the neat RTIL along with (f) Photolysis.

irradiation time and the results were tabulated in Table 1. It is clear that the observed first-order rate constant of the reaction using CdS nanoparticles prepared in the neat RTIL are about 20 and 6 times greater than the prepared sample in water using visible and UV irradiations, respectively.

Fig. 9 demonstrates the dynamic adsorption of MB on CdS nanoparticles prepared in (a) water, (b) aqueous solution of the RTIL (1:1 in volume) and (c) the neat RTIL by 60 min refluxing. The values of  $q_e$  for MB adsorption on CdS nanoparticles prepared in water, aqueous solution of the RTIL

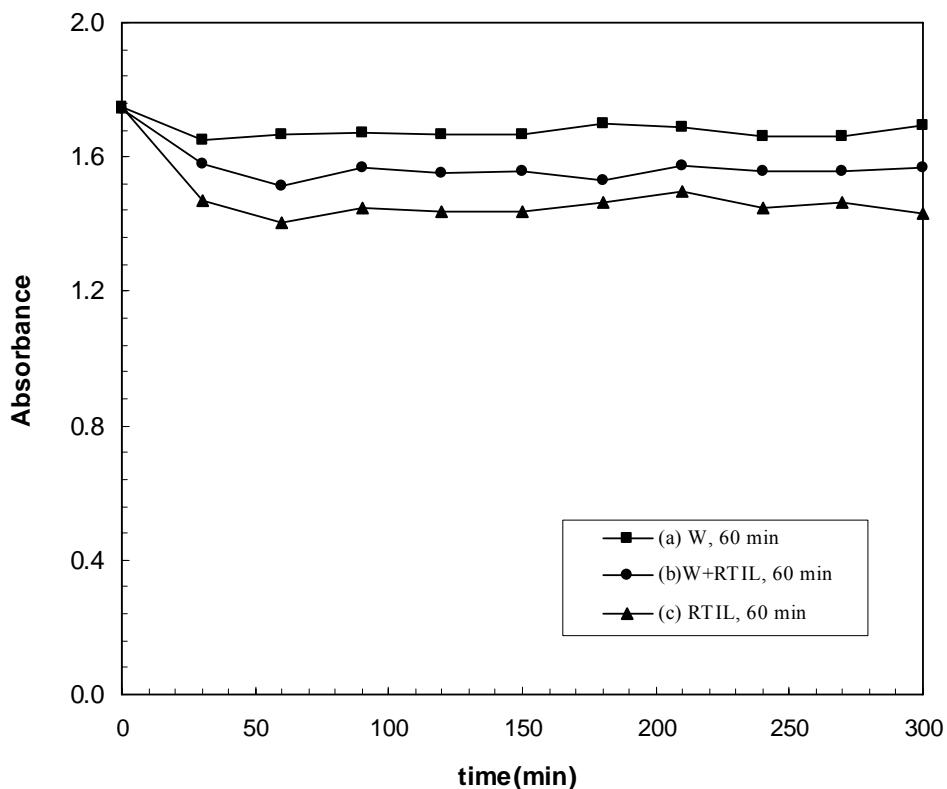
**Table 1.** Observed first-order rate constant for photocatalytic degradation of MB on CdS nanoparticles prepared in water, aqueous solutions of the RTIL and neat RTIL.

Light source	$k_{obs}/\text{min}^{-1}$				
	Water	Water + RTIL <sup>a</sup>	Water + RTIL <sup>b</sup>	Water + RTIL <sup>c</sup>	neat RTIL
Visible	$7.75 \times 10^{-4}$	$2.88 \times 10^{-3}$	$3.38 \times 10^{-3}$	$4.51 \times 10^{-3}$	$1.58 \times 10^{-2}$
UV	$6.20 \times 10^{-3}$	$2.13 \times 10^{-2}$	$2.20 \times 10^{-2}$	$1.69 \times 10^{-2}$	$3.73 \times 10^{-2}$

a) Refluxing time is 15 min.

b) Refluxing time is 30 min.

c) Refluxing time is 60 min.



**Fig. 9.** Dynamic adsorption of MB at 25 °C on CdS nanoparticles prepared by refluxing at 60 minutes in (a) water, (b) aqueous solution of the RTIL (1:1 in volume) and (c) the neat RTIL.

(1:1 in volume) and the neat RTIL are  $2.0 \times 10^{-6}$ ,  $6.58 \times 10^{-6}$  and  $1.18 \times 10^{-5}$  mol/g, respectively. It is clear that adsorption ability of MB molecules on CdS nanoparticles prepared in presence of the RTIL is higher than the prepared sample in water. Therefore, solvent applied for preparation of the nanoparticles has major influence on the adsorption capacity of the prepared samples.

The photocatalytic efficiency of the semiconductors is mainly determined by crystal structure, surface area, size of particles, band-gap energy and morphology [60]. The small-sized nanoparticles with high surface area are effective substrates for adsorption of pollutant molecules and the UV or visible lights [56]. Therefore, significant improvement of photocatalytic activity for the CdS nanoparticles prepared in presence of the RTIL should be related to the higher surface area of the nanoparticles due to lower aggregation. Moreover, a limiting factor that controls the efficiency of photocatalysis

is the rapid recombination of photogenerated electrons and holes in the nanoparticles [61]. Recombination of electron-hole pair within the semiconductor particle is drastically reduced with decreasing particle size [62]. Hence, recombination rate of electron and hole for the CdS nanoparticles prepared in presence of the RTIL will be lower than the prepared sample in water. For these reasons, photocatalytic activity of CdS nanoparticles prepared in presence of the RTIL will be considerably higher than the prepared sample in water.

## CONCLUSIONS

CdS nanoparticles were prepared in presence of 1-ethyl-3-methylimidazolium ethyl sulfate, [EMIM] [EtSO<sub>4</sub>], as a low-cost and halide-free RTIL. This environmentally benign green method is fast, simple and low temperature which remarkably

shortens preparation time and avoids the complicated synthetic procedures. The as-prepared CdS nanoparticles show a blue shift of approximately 1.52 eV which can be attributed to quantum confinement effect of the CdS nanoparticles. In this method, aqueous solution of the RTIL can act as solvent for reactants and morphology templates for the products at the same time, which enable the preparation of inorganic materials with improved properties. Investigation of photocatalytic activity for the prepared nanoparticles using UV and visible lights reveals that photocatalytic activity of the prepared samples in presence of the RTIL is considerably higher than the prepared sample in water.

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