

## **Synthesis of TiO<sub>2</sub> nanoparticles in pure 2-hydroxyethylammonium formate room temperature ionic liquid and investigation of its photocatalytic properties**

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Received November 2010; Accepted December 2010

### **ABSTRACT**

TiO<sub>2</sub> nanoparticles were synthesized by modified sol-gel method using pure room temperature ionic liquid (RTIL) 2-hydroxyethylammonium formate as a reaction medium. The structure and morphology of TiO<sub>2</sub> nanoparticles were characterized with X-ray powder diffraction (XRD), BET surface analysis and scanning electron microscopy (SEM). TiO<sub>2</sub> nanoparticles were synthesized in open and closed vessels. The TiO<sub>2</sub> nanoparticles prepared in open vessel present only anatase crystal phase after calcination at 500°C but the TiO<sub>2</sub> prepared in closed vessel presents anatase and rutile phases after calcination at 500°C. The photocatalytic efficiency decreases with increasing of ethanol and water as molecular solvent in preparation step of nanoparticles. The degradation percent can reach over 97% at the optimal catalyst concentration (2.0 g/L) in 120 minutes irradiation.

**Keywords:** TiO<sub>2</sub>; 2-hydroxyethylammonium formate; Methylene Blue; Photodegradation

### **INTRODUCTION**

In recent years great efforts have been devoted to the study of the photocatalytic degradation of organic and inorganic contaminants of water and air [1–11]. The overall efficiency of photocatalytic processes depends, first of all, on several physicochemical features of the semiconductor, such as the position of its band gap potential, the crystalline phase composition, the surface properties, and the mobility and recombination rate of the charge carriers generated during UV-light irradiation.

Among wide band-gap semiconductors, TiO<sub>2</sub> is of special interest for various purposes due to some specific properties (n-type semiconductor, chemical and mechanical stability, negligible photo-corrosion, biocompatibility combined with a comparably low-cost of preparation). This combination makes this material useful and efficient in a wide range of applications including e.g. photocatalysis [12–16], self-cleaning applications [17], solar cells [18, 19], optoelectronic devices [20] and gas sensors [21]. In all these applications, various forms of TiO<sub>2</sub> (including nanoparticles, nanorods, nanotubes and nanofibres, synthesized by various methods, for review

see e.g. [22]) are employed as they have a comparably larger surface area than flat TiO<sub>2</sub> films prepared by thermal or anodic oxidation.

In nature, TiO<sub>2</sub> can crystallize in the three polymorphs anatase, rutile and brookite. Anatase is thermodynamically less stable than rutile and exhibits a shorter wavelength absorption edge. Frequently present in nanosized TiO<sub>2</sub> particles, it is largely recognized to be the most active phase in oxidative detoxification reactions [23]. The surface enthalpies of these three natural TiO<sub>2</sub> polymorphs are distinctly different and the obtained modification highly depends on the preparation method and sample post-treatment. Anatase is the most stable modification for small particle samples with high surface areas, followed by brookite and rutile [24].

Ionic liquids (ILs) are attracting much interest in various areas of chemical synthesis [25],

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electrochemistry [26, 27], separations and biotransformations, owing to their unique physicochemical characters [28, 29]. Furthermore, they readily dissolve many organic, inorganic and organometallic compounds. One of the biggest disadvantages of application of RTILs in various fields arises from their high-cost relative to conventional solvents. Moreover, RTILs with  $\text{PF}_6^-$  and  $\text{BF}_4^-$  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 [30, 31]. But, RTILs with formate anions have very low cost and are halogen-free. They are relatively hydrolysis stable compounds and 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. 2-Hydroxyethylammonium formate has been described to have high solvating ability for some inorganic and organic materials such as  $\text{Na}_2\text{SO}_4$ ,  $\text{NH}_4\text{Cl}$ ,  $\text{KBr}$  and polyaniline. This ionic liquid has very low cost and with a melting point of  $-82^\circ\text{C}$ , it is a promising solvent for low temperature reactions [32].

Recently, there are some reports about the combination of nanomaterials with ionic liquids. Han et al. studied the effect of  $\pi$ - $\pi$  stacking of water miscible ionic liquids  $[\text{Bmim}][\text{BF}_4]$  and  $[\text{Omim}][\text{BF}_4]$  on morphology of mesoporous  $\text{TiO}_2$  prepared via sol-gel method [33]. Alammar et al. investigated the sonochemical preparation of anatase  $\text{TiO}_2$  nanoparticles in the ionic liquid 1-(3-hydroxypropyl)-3-methylimidazolium-bis(trifluoromethylsulfonyl)amide under ambient conditions [34]. Hiu et al. prepared the anatase mesostructured  $\text{TiO}_2$  nanocrystals in a mixture of 1-butyl-3-methyl-imidazolium tetrafluoroborate ( $\text{BMIM}^+\text{BF}_4^-$ ) ionic liquid and water by a low temperature hydrothermal method [35]. Zhai et al. [36] reported the preparation of rutile  $\text{TiO}_2$  in a carboxyl containing ionic liquid, 1-methylimidazolium-3-acetate chloride ( $[\text{AcMIm}]\text{Cl}$ ). Hu et al. [37] synthesized mesostructured anatase  $\text{TiO}_2$  particles and nanodisperse spheres with high surface area in 1-(2-hydroxyethyl)-3-methylimidazolium based ionic liquids. Zhai et al. [38] synthesized nanostructured  $\text{TiO}_2$  particles by sol-gel method with room temperature ionic liquid  $[\text{BMIM}][\text{PF}_6]$ . Paramasivam et al. [39] showed

that  $[\text{BMIM}][\text{BF}_4]$  can directly be used to grow well-defined layers of self-organized  $\text{TiO}_2$  nanotubes. Li et al. reported the synthesis of polycrystalline CdS hollow nanospheres with diameter of about 130 nm in high yield by an ionic liquid assisted template-free hydrothermal method [40].

In traditional sol-gel process, it is necessary to use water and acidic or basic catalyst combined with alcoholic solvent for hydrolysis and condensation steps. The approach introduced in this study is to avoid water in sol-gel process by using only pure room temperature ionic liquid (RTIL, 2-hydroxyethylammonium formate) as solvent. The prepared samples were characterized with X-ray powder diffraction (XRD), BET surface analysis and scanning electron microscopy (SEM).

## EXPERIMENTAL

Ethanol was obtained from Merck, ethanolamine and formic acid from Riedel de Haen. The chemicals were of the highest purity available and purified according to the literature [41]. The ionic liquid was prepared as described in literature [32]. 2-Aminoethanol (59.9 g, 0.1 mole) was placed in a three necked flask equipped with a reflux condenser, a dropping funnel and a thermometer. The flask was mounted in an ice bath. Under vigorous stirring with a magnetic stirrer, 38 ml (0.1 moles) formic acid was added dropwise to the flask in about 45 minutes. Stirring was continued for 24 hours at room temperature to obtain a colorless viscous clear liquid. Synthesized ionic liquid was identified via H-NMR and FT-IR spectroscopy as described elsewhere [32]. The ionic liquid was degassed for 2 hours in vacuum (0.3 mbar at  $80^\circ\text{C}$ ) before use. 2-Hydroxyethyl ammonium formate is miscible with water and small alcohols and phase separation can not be observed even for weeks [32]. Mixed solvents were prepared by carefully mixing the components by weight. Karl Fischer titrations showed no detectable presence of water in freshly synthesized IL.

In a typical synthesis of  $\text{TiO}_2$  in pure ionic liquid, 0.5 ml of titanium tetraisopropoxide (TTIP) was mixed with 25 ml of 2-hydroxyethylammonium formate. After

homogenization of the mixture, hydrolysis of TTIP occurred slowly in RTIL with H<sub>2</sub>O adsorbed from air. The mixed solution was stirred for 23h at room temperature and then divided in two vessels and aged in clean room for 5 days in closed and open vessels. For comparison, TiO<sub>2</sub> nanoparticles were synthesized in 1:1 ionic liquid and molecular solvents (ethanol and water). The procedure was similar to pure ionic liquid media. 0.5 ml of titanium tetrakisopropoxide (TTIP) was mixed with 25 ml of solvent mixture. After homogenization of the mixture, hydrolysis of TTIP occurred slowly. The mixed solution was stirred for 23h at room temperature and aged in clean room for 5 days. The obtained disperse system was diluted with dimethylformamid to decrease the viscosity of RTILs. Afterward, the product was gathered by centrifugation. The residual of RTILs in the product were removed by extracting the sample with dimethylformamid in a closed vessel at room temperature. One micro liter of solvent after extraction was injected to the gas chromatograph. The extraction process was repeated several times with the fresh solvent until the RTILs were completely removed from the sample (the ionic liquid peak was disappeared in chromatogram). The final white powders were dried in an oven at 100 °C for further characterization. The morphology of the as-prepared products was characterized and analyzed using scanning electron microscopy (SEM), BET surface analysis and X-ray diffraction (XRD) after calcinations at 500°C in air atmosphere.

Specific surface area was obtained from nitrogen adsorption-desorption isotherms at 77 K performed in an automatic Quantachrom apparatus (Model Quantasorb) with Belsorp adsorption-desorption data analysis software in the 0.05–0.995 relative pressure ranges. BET surface area was calculated from a linear part of the BET plot according to IUPAC recommendations.

XRD of the catalyst was carried out from 12° to 70° (2 $\theta$ ) using a Bruker D4 X-ray diffractometer operating at 40 kV and 30 mA with Cu K $\alpha$  radiation ( $\lambda$ = 1.542 Å ) and a Ni filter. Counts were accumulated every 0.02 (2 $\theta$ ) at a scan speed of 1° (2 $\theta$ /min) in 25 °C.

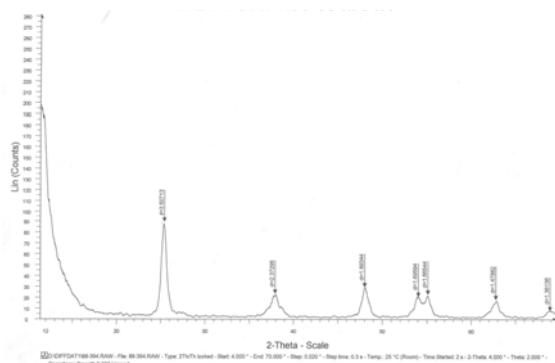
Catalytic behavior of as prepared nanoparticles was examined by Methylene blue (MB) photodegradation, which is a typical dye resistant to biodegradation, under ultraviolet light. Photocatalysis experiments were performed in a cylindrical pyrex reactor with about 250 mL capacity. The reactor provided with water circulation arrangement to maintain the temperature at 25±0.1 °C. 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 with 125W was used as UV source. The lamp was fitted on the top of the reactor. Prior to illumination, a suspension containing 2 g/L of the nanoparticle and 150 ml of MB (20 ppm) 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 photocatalyst before analysis by spectrophotometer at 664nm corresponding to maximum absorption wavelength ( $\lambda_{max}$ ) of MB.

## RESULTS AND DISCUSSION

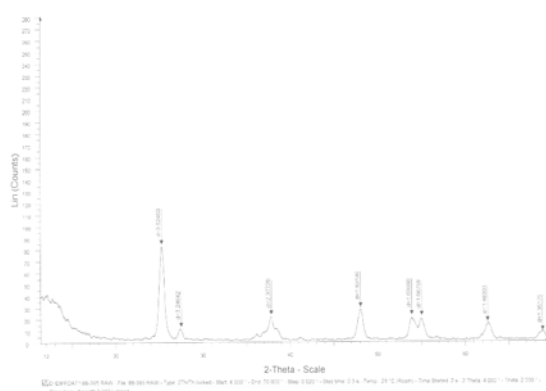
Table 1 shows the preparation conditions of various TiO<sub>2</sub> nanoparticles. One can see from Table 1 that only S3 was synthesized in closed vessel and all other samples were synthesized in open vessel. In S1, S2 and S3 we used pure ionic liquid. Karl Fischer titrations showed no detectable presence of water in freshly synthesized RTIL; thus water molecules for hydrolysis step of TTIP was presented from air. 2-hydroxyethylammonium formate is very hygroscopic ionic liquid. For comparison, in S4 we used 50:50 mixture of ionic liquid and ethanol as solvent. As previous samples, we don't use any water in this sample. Finally, in S5, we used mixture of 50:50 ionic liquid and water as solvent. In all samples we don't use any acidic or basic catalyst for sol gel processes.

The first method that we used for characterization of the samples was X-ray diffraction. The samples synthesized in room temperature don't show crystalline pattern in XRD without calcination. All samples were calcined in 500°C for 2 hours. After calcination, S2 shows only anatase phase. One can see in Fig. 1. that the XRD pattern exhibits peaks in 2 $\theta$ =25.2, 38, 48, 53.9, 54.1, 63 and 68.9 that is the standard diffraction pattern of the anatase form. But other

samples show an additional peak in  $2\theta=27.3$ . This peak is one of the rutile standard peaks. The XRD pattern of S3 was presented as an example in Fig. 2. As one can see, thermal stability of S2 in  $500^\circ\text{C}$  is higher than other samples. Anatase to rutile phase transformation was seen for  $\text{TiO}_2$  ordinarily in temperatures around  $500^\circ\text{C}$ . For Samples S1, S3, S4 and S5 we can see this phase transformation in XRD patterns but for sample S2, XRD patterns only shows anatase form. This is due to its preparation conditions. Sample prepared in pure ionic liquid in open vessel during 23 hours shows thermal stability in comparison with other synthesis conditions. In addition, XRD patterns don't show any crystalline impurity in synthesized  $\text{TiO}_2$  samples.



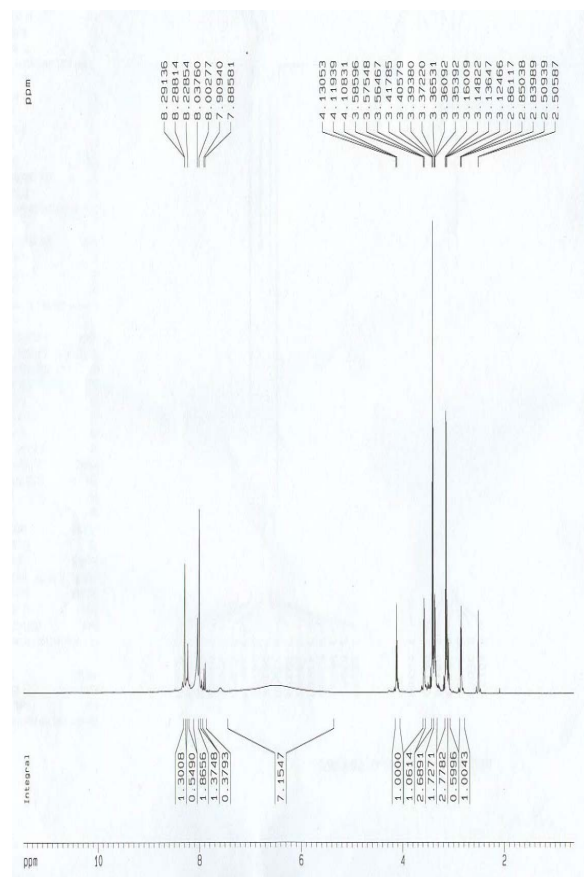
**Fig. 1.** XRD Pattern of  $\text{TiO}_2$  sample synthesized in open vessel.



**Fig. 2.** XRD pattern of  $\text{TiO}_2$  sample synthesized in closed vessel.

Fig. 3. and 4. show the H-NMR and FT-IR spectra of ionic liquid. From Fig. 3. one can see the complete synthesis of 2-hydroxyethylammonium

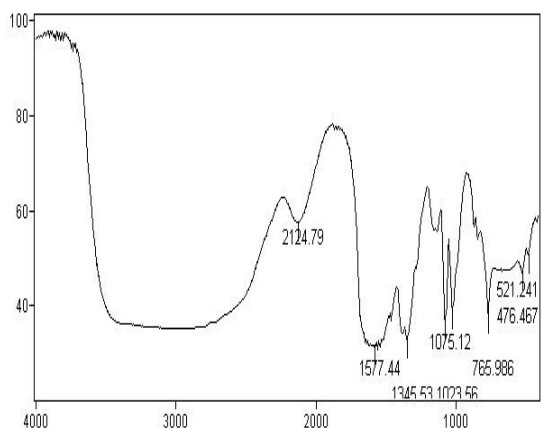
formate ionic liquid. H atoms bond to carbon atom were appeared in 2-4 ppm. Hydrogen atoms of OH and  $\text{NH}_3^+$  were seen in 8 ppm area [32]. As one can see the peak of  $\text{NH}_2$  hydrogen atoms, that show the unreacted amine with formic acid, were disappeared in H-NMR spectrum. In addition we can't see any impurity (additional peak) in H-NMR spectrum of ionic liquid.



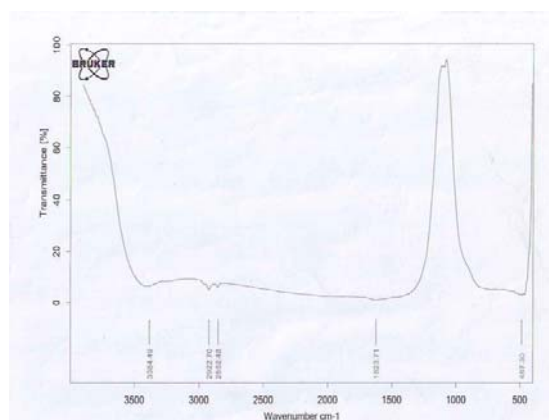
**Fig. 3.** H-NMR spectrum of 2-hydroxyethylammonium formate ionic liquid.

Important peaks of 2-hydroxyethylammonium formate in FT-IR are for OH,  $\text{NH}_3^+$  and CO groups. In fig. 4., carbonyl peak was appeared in  $1577\text{cm}^{-1}$  but other two peaks were hid under water peak and we can only see a single broad peak in  $2500\text{--}3500\text{cm}^{-1}$ . In addition, this broad peak shows the hygroscopic nature of ionic liquid.

Fig. 5. shows the FT-IR spectrum of one of synthesized  $\text{TiO}_2$  samples (S2). One can see in this spectrum only the standard peaks of  $\text{TiO}_2$  and the adsorbed water. From fig. 5. one can see that no peaks of ionic liquid exist in  $\text{TiO}_2$ , and then no impurity exist in synthesized Titania.



**Fig. 4.** FT-IR spectrum of 2-hydroxyethylammonium formate ionic liquid.

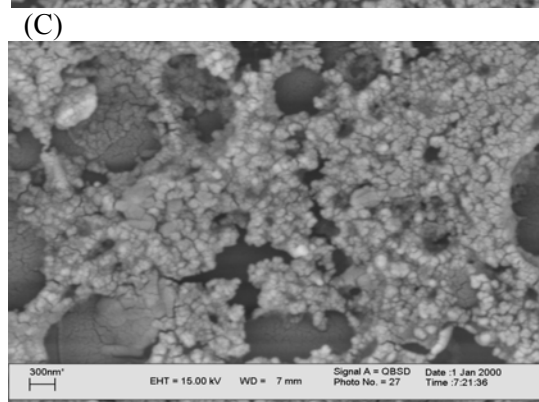
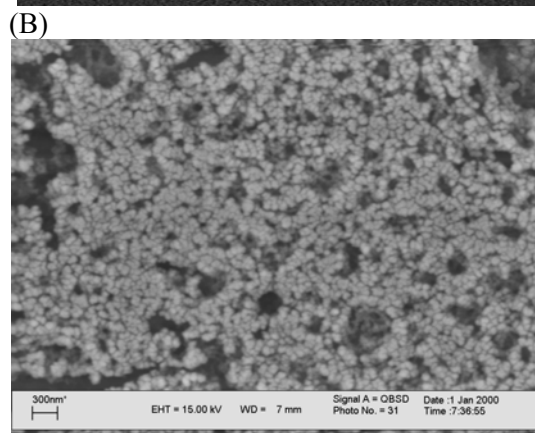
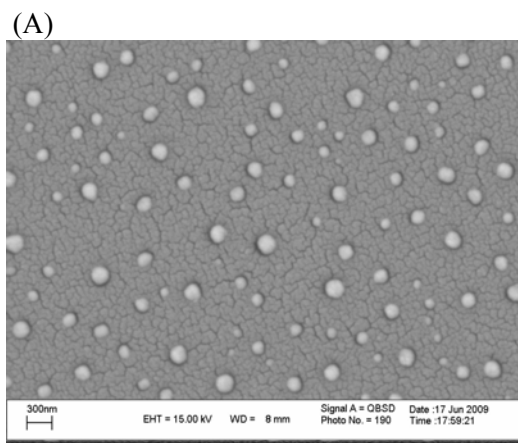


**Fig. 5.** FT-IR Spectra of TiO<sub>2</sub> sample synthesized in open vessel.

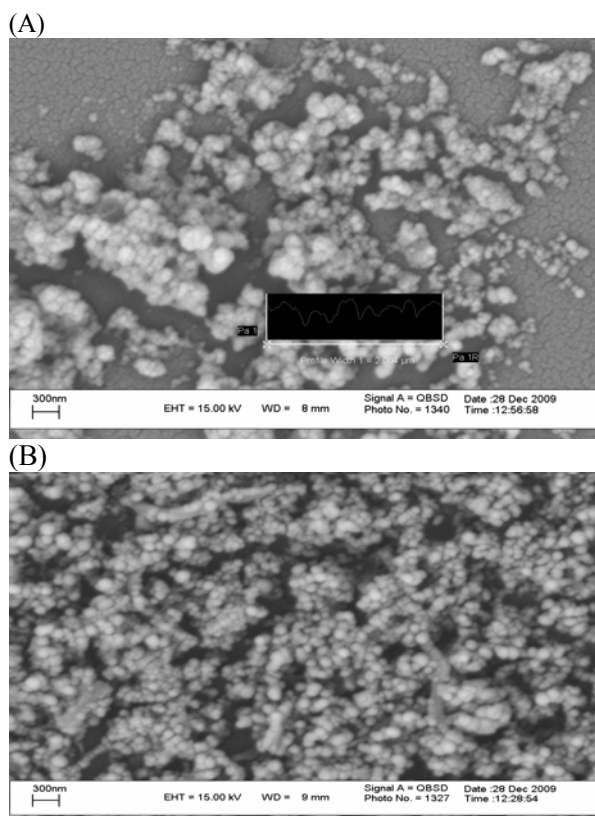
The BET analysis results of the sample were shown in Table 1. As one can see, the specific surface area of the catalyst is dependent on the preparation method. Sample S2 has greatest and sample S1 has smallest surface area. It can be due the sintering during calcination processes of the catalyst.

Fig. 6. shows the SEM images of samples synthesized in pure ionic liquid. One can see in 6A that when gellation time was 6 hours, big spheres of TiO<sub>2</sub> were formed. The size of Titania nanoparticles were between 50-375 nm. Furthermore, synthesis of TiO<sub>2</sub> from TTIP precursor was not complete and a layer of TiO<sub>2</sub> was observed in background of the image. In 6B, TiO<sub>2</sub> nanoparticles were synthesized in open vessel and gellation time was 23 hours. In this image, we see the complete conversion of precursor to Titania. The distribution of particle size is narrow and nanospheres diameter are between 30-40 nm. Fig.

6C. shows the nanoparticles synthesized in closed vessel. The gellation time of this sample was 23 hours. Like Fig. 6B., in this case the conversion of the precursor to nanoparticle is nearly complete but the shape of nanoparticles is not completely spherical and the size distribution of particles is wider than Fig. 6B. The size of particles in Fig. 6C. is between 65-150 nm.



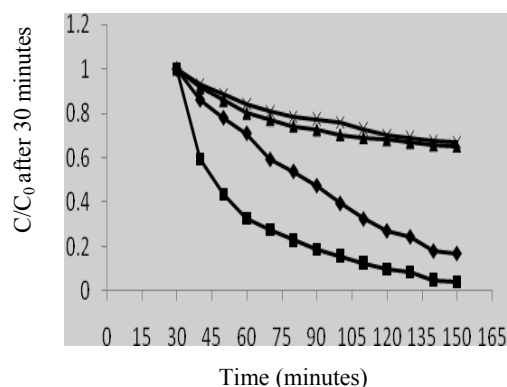
**Fig. 6.** SEM images of TiO<sub>2</sub> nanoparticles in pure ionic liquid. A) gellation time was 6 hours in open vessel. B) gellation time was 23 hours in open vessel. C) gellation time was 23 hours in closed vessel.



**Fig. 7.** SEM images of TiO<sub>2</sub> nanoparticles in pure ionic liquid. A) 12.5mL water and 12.5 mL IL, gelation time was 23 hours in open vessel. B) 12.5mL ethanol and 12.5 mL IL, gelation time was 23 hours in open vessel.

In fig. 7., one can see the SEM images of Titania nanoparticles synthesized in mixture of ionic liquid and molecular solvents. Fig. 7A. shows the effect of water as cosolvent. It is obvious that particles synthesized in water/IL mixture are not spherical and have wide size distribution. The diameter of Titania nanoparticles are between 40 and 135 nm. Titania nanoparticles synthesized in ethanol/IL mixture have good spherical shape (fig. 7B.) but as we see in water/IL mixture, they have

wide diameter distribution (between 40 and 140 nm).



**Fig. 8.** Catalytic activity of TiO<sub>2</sub> nanoparticles synthesized in various conditions. (■: pure ionic liquid, open vessel; ♦: ionic liquid water mixture; ▲: ionic liquid ethanol mixture; × pure ionic liquid, 2closed vessel).

For comparison of the catalytic activity of Titania nanoparticles, we use them for photocatalytic degradation of Methylene Blue in aquatic media. For 30 minutes, the mixtures (including 150 mL, 20ppm Methylene Blue and 2g/L catalyst) were kept in dark condition. Table 2 shows the results of the adsorption of Methylene Blue on Titania. As one can see, the catalyst S2 adsorbs the solute better than other catalysts. It can be due to its greater surface area (Table 1). After 30 minutes, the mixtures were irradiated by UV light and the photodegradation reaction was started. As one can see in Fig. 8., the activity of S3 (catalyst made in pure ionic liquid in open vessel) was higher than other catalyst. It can be due to its greater BET surface area and crystallinity of the solid sample.

**Table 1.** Synthetic conditions of various TiO<sub>2</sub> samples

Sample	Ionic Liquid/mL	Ethanol/mL	Water/mL	Gelation Time/hr	Particle Size/nm	Surface Area/m <sup>2</sup> g <sup>-1</sup>	Crystal Phase	
S1	25	0	0	6	50-375	57.3	Anatase/rutile	Open vessel
S2	25	0	0	23	30-40	192.8	anatase	Open vessel
S3	25	0	0	23	65-150	125.3	Anatase/rutile	Closed vessel
S4	12.5	12.5	0	23	41-139	132.4	Anatase/rutile	Open vessel
S5	12.5	0	12.5	23	41-135	151.7	Anatase/rutile	Open vessel

**Table 2.** Adsorption of Methylene Blue in dark condition by various catalysts in 30 minutes

Catalyst	Initial absorbance in UV-Vis	Absorbance in UV-Vis after 30 minutes	Adsorption percent
S2	1.848	1.421	23.1
S3	1.843	1.614	12.4
S4	1.747	1.501	16.6
S5	1.858	1.517	18.4

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