Synthesis of Ag doped SiO2-TiO2 aerogels with nano-sized microcrystalline anatase structure through IL control

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Abstract. In this paper, Ag doped SiO2-TiO2 aerogels with nano-sized microcrystalline anatase structure through a sol-gel way, ionic liquid(IL), 1 – butyl- 3 - methylimidazole bromide ([bmim]Br), is used as a structure control agent. The catalysts were characterized by SEM, XRD and nitrogen adsorption-desorption isotherms (BET analyses). The photocatalytic activities were investigated by degradation of active brillant blue under UV-light. It was demonstrated that IL facilitate the formation of mesoporous and anatase microcrystalline structure at around ambient condition, without calcination. Both at sol-step and gel-step, the concentration of IL aqueous solution prominently effected on the structure properties of catalysts. Surface area, crystalline grain dimension and microporous structure all played important roles in the degradation reactions. The catalyst with 1/10 Si/Ti ratio, 385.2 m2g-1surface area and 6.2nm crystalline grain size, showed excellent photocatalytic degradation rate up to 99.7%.

1. Introduction

TiO2, regarded as the most efficient environmental semiconductor photocatalyst has been widely studied over past sixty years. The principle of photocatalysis is absorption of photons with energy larger than the band gap of TiO2, electrons are excited from the valence band to the conduction band, creating electron-hole pairs. These charge carriers migrate to the surface and react with the chemicals adsorbed on the surface to decompose chemicals. The photocatalytic activity of a semiconductor is largely controlled by (i) the light absorption properties, e.g., light absorption spectrum and coefficient, (ii) reduction and oxidation rates on the surface by the electron and hole, (iii) and the electron-hole recombination rate. A large surface area with a constant surface density of adsorbents leads to faster surface photocatalytic reaction rates. In this sense, the larger the specific surface area, the higher the photocatalytic activity is. On the other hand, the surface is a defective site; therefore, the larger the surface area, the faster the recombination. The higher the crystallinity, the fewer the bulk defects, and the higher the photocatalytic activity is. Hightemperature treatment usually improves the crystallinity of TiO2 nanomaterials, which in turn can induce the aggregation of small nanoparticles and decrease the surface area. Optimal conditions are sought by taking these considerations into account and may vary from case to case[1-2].
Silica–titania is one of the important binary oxide materials and has been widely used for academic purpose and industry [3-5]. It has attracted widely interest due to their potential applications as the catalyst in various reactions from fine chemistry to photocatalytic removal of the water pollutant. The properties of silica–titania materials depend on the structure, composition, and homogeneity of the prepared material [5].

Aerogels have been receiving a considerable attention because of their unique properties, i.e., very low density, extremely high surface area, high porosity, low thermal conductivity and low dielectric permittivity [1-5]. TiO2 has been used to treat various industrial wastewater owing to its excellent photocatalysis activity. However TiO2 aerogels are restricted because of its poor network structure. SiO2-TiO2 aerogels have higher surface area, stronger network structure, higher absorbing capacity and better photocatalytic properties than TiO2 aerogels [6].

SiO2-TiO2 aerogels are of immense importance in various applications such as adsorption, sensing, and catalysis.

Nowadays, ionic liquids (IL) have been used as effective solvents or co-solvents or template to synthesize aerogels by ambient pressure drying instead of using supercritical drying because of their excellent thermal stability, highly conductivity, wide electrochemical widow, negligible vapor tension and special solubility [7-9]. Sheng Dai et al. [10] have successfully used IL as effective solvents to synthesize silica aerogels with high surface area (720 m2g-1), large pore volume (1.4 cm3g-1) and stable aerogel network structures without the need for supercritical drying processes. Kyesang Yoo et al. [11] synthesized anatase-containing nanostructured TiO2 particles with surface area of 273 m2g-1 using ionic liquid 1-butyl-3-methylimidazolium hexafluorophosphate as an effective additional solvent by the sol–gel method at low temperature. My team has successfully prepared SiO2-TiO2 aerogels with high surface area and good photocatalysis activity using IL by ambient pressure drying [12,13]. Usually, SiO2-TiO2 aerogels don’t have anatase crystal structure before calcinations. It is well known that crystal types of include anatase, brookite and rutile, among which the anatase possesses the best photocatalyst activity. Traditionally, anatase TiO2 is obtained by calcinations which can reduce surface area of aerogels. So, it is important to obtain anatase TiO2 avoiding calcinations.

In this paper, Ag doped SiO2-TiO2 aerogels were synthesized at ambient pressure by using IL, 1-butyl-3-methylimidazolium bromide ([bmim]Br) as cosolvent and aging agent. In the two step sol-gel process, tetraethyloxy silicate (TEOS) and tetrabutyl titanate (TBT) were used as precursors and glacial acetic acid and urea were used as catalysts. Acetic acid glacial as a kind of weak acid could decrease the hydrolytic rate of precursors and urea as a kind of weak base could control the rate of polycondensation reaction so that TEOS and TBT would precede hydrolysis and polycondensation simultaneously. The influence of the SiO2/TiO2 molar ratios, the IL/(SiO2+TiO2) molar ratio ratios, the different dosage of Ag on aerogels was investigated and the aerogels were characterized by nitrogen adsorption analysis, scanning electron microscopy (SEM) and X-ray diffraction (XRD). The photocatalytic properties of the aerogels were also evaluated by the degradation of reactive brilliant blue in aqueous solution under UV-light.

2. Experimental

2.1. Preparation of aerogels
Tetraethyl orthosilicate (TEOS) and butyl titanate (TBT) as precursors were obtained from Dongtai Tianjin Kemiu Chemical Reagent Co. and used as received. Acetic acid glacial and urea as catalysts were produced by Tianjin Dongzheng fine chemical reagent factory. Miconazole and butyl bromide used to synthesize [bmim]Br were bought from Guangfu Chemical Co. Ethanol and cyclohexane were both analytical reagents.

The ionic liquids, 1-butyl 3-methylimidazole bromide ([bmim]Br), were synthesized according to the method reported in the literature [14]. SiO2 sols and TiO2 sols were prepared separately. SiO2 sols were generated by mixing TEOS, absolute alcohol, deionized water, glacial acetic acid, urea and
IL ([bmim]Br) together with vigorous stirring in the molar ratio of 1:7 : 4.62 : 0.002 : 0.04 : x. TEOS and half of absolute alcohol were fully mixed as solution A and the rest of the materials were fully mixed as solution B, then solution B was added into solution A, drop by drop, while stirring and SiO2 sols were prepared. About 30 minutes later, TiO2 sols were also prepared at the same way by mixing TBT, absolute alcohol, deionized water, glacial acetic acid, urea and IL ([bmim]Br) together in the molar ratio of 1 : 18 : 3.75 : 1.8 : 0.04 : x. Then SiO2 sols and TiO2 sols were mixed together at different SiO2/TiO2 molar ratios and 0.1mol/L aqueous ethanolic silver nitrate was added into the mixed sols after stirring for 10 minutes. The final sols were sharply stirred for about 30 min and then was kept at 60℃ for gelation.

The gels obtained were aged by aqueous IL solution of different constituents at 60℃ for 4 days and then was soaked in excess cyclohexane for 1 day and in excess absolute alcohol for 4 days (change solution four times a day) in order to remove IL in gels. The wet gels were dried at 60℃ for 8 hours and at 80℃ for 8 hours at ambient pressure, and then the aerogels were obtained without calcination.

2.2. Characterization
The aerogel samples were characterized without any other treatment. Nitrogen adsorption-desorption analysis (Nova 1200e Surface Area and Pore Size Analyzer) was used to determine available surface area and pore volume. The average pore size, pore volume and surface area were obtained from BET analysis, applying the cylindrical model. X-Ray diffraction analysis (XRD) was performed using a D/max-3B analyzer (Cu-Kα, 40 kV, 30 mA) to analyze the crystal structure. The surface appearance and porous structure of the aerogels were investigated by electron microscopy (SEM) (Hitachi S-2500).

2.3. Photocatalytic reaction
The photocatalytic performance of the aerogel samples was evaluated by decolorization of organic dye of reactive brilliant blue. The 0.1g block of untreated aerogel samples were used to decolorize 200ml reactive brilliant blue solution (20mg/L). In the first 30 minutes, photocatalytic reaction was performed in the dark. Take the supernatant and measure absorbance by UV spectrophotometer to evaluate adsorption performance. Afterwards, photocatalytic reaction was performed under 145W UV-light irradiation. About 3 hours later, measure the absorbance of the supernatant to evaluate photocatalytic performance of aerogels. The detection wavelength of UV spectrophotometer was performed at 590nm. The photocatalytic degradation rate was calculated by the formula: photocatalytic degradation rate=(A0 — A)/A0*100%.

3. Results and discussion
3.1. Characterization of aerogels
The aerogel samples were prepared at different SiO2/TiO2 molar ratios of 10, 5, 1, 1/5, 1/10 (noted as 10Si-Ti, 5Si-Ti, Si-Ti, Si-5Ti, Si-10Ti) and the x=1. The Ag was doped by Ag/(SiO2 +TiO2)molar ratio of 1% and the aerogels were aged by 1mol/L aqueous IL solution. Obviously, the increase of SiO2/TiO2 molar ratios had been found to prolong the time for gel, increase transparency and reduce cracking of aerogels. The densities of aerogel samples were lower as the increase of SiO2/TiO2 molar ratios.

The porous structures of aerogels were studied by Nitrogen adsorption-desorption. It could be seen from Table 1 that Si-Ti, Si-5Ti and Si-10Ti aerogel samples had significantly higher surface areas than 10Si-Ti and 5Si-Ti aerogel samples. Furthermore, pore volumes of aerogels synthesized with more SiO2 value were lower than pore volumes of aerogels synthesized with more TiO2 value. The Nitrogen adsorption-desorption isotherms of aerogel samples were illustrated in Fig. 1 and isotherm of Si-Ti, Si-5Ti and Si-10Ti aerogels exhibited typical IV curves, which were characteristic of predominantly mesoporous materials based on the IUPAC classification [15]. It was also obvious that
isotherm patterns of 10Si-Ti and 5Si-Ti aerogels didn’t have the characteristics of any porous microstructure.

These conclusions ran somewhat counter to conventional wisdom and the cause might be that IL made a so great influence on the structural formation of network. Based on the analysis above, the possible mechanisms of IL were conjectured. In the sol-gel process, [bmim]Br played a uniformity and stabilization role to the system due to its special characteristics including formation of high polarizability, hydrogen-bonding networks, low interface tension and low interface energy. It had been known that TEOS had lower hydrolytic condensation rate than TBT. In the preparation process of 10Si-Ti and 5Si-Ti aerogels, since there was not enough TBT to form network structure, small amount of TiO2 particles were synthesized and dispersed in a homogeneous phase due to special solubility and high polarizability of IL. On account of lots of TEOS, huge SiO2 network structure was formed. TiO2 particles were locked into in the pores and SiO2 network structure and this led to the very small surface area of 10Si-Ti and 5Si-Ti aerogels. In the preparation process of Si-5Ti and Si-10Ti aerogels, there was lots of TBT in the homogeneous system so that TiO2 network structure was formed.

Simultaneously, little TEOS polymerized with TBT to form network structure but not formed particles, which prevented blocking network structure, so Si-5Ti and Si-10Ti aerogels had a high surface area. In the preparation process of Si-Ti, since the same amount of TEOS and TBT were dispersed in a homogeneous phase, SiO2-TiO2 hybrid network was formed and this made the highest surface area of Si-Ti aerogels. In consideration of lower hydrolytic condensation rate of TEOS than TBT, there was SiO2 network mostly in the outermost of aerogels so that it was very rough and uneven in surface of aerogels, matching the conclusions from SEM morphology in the sections below.

**Table 1.** BET analysis results of the aerogel samples at different SiO2/TiO2 molar ratios

| Sample   | 10Si-Ti | 5Si-Ti | Si-Ti | Si-5Ti | Si-10Ti |
|----------|---------|--------|-------|--------|---------|
| Surface Area/m²g⁻¹ | 95.6    | 93.6   | 484.9 | 396.8  | 385.2   |
| Pore Radius/nm    | 3.948   | 4.126  | 11.442| 10.322 | 5.296   |
| Pore Volume/cm³g⁻¹ | 0.025   | 0.024  | 0.776 | 0.758  | 0.549   |

**Figure 1.** Nitrogen adsorption-desorption isotherms of the aerogels made in different SiO2/TiO2 molar ratios (10Si-Ti, 5Si-Ti, Si-Ti, Si-5Ti, Si-10Ti). 1% Ag was doped in aerogels and IL was used by n(IL)/n(SiO2+TiO2) =1

The X-ray powder diffraction (XRD) patterns of aerogel samples were shown in Fig.2 and it showed that the different SiO2/TiO2 molar ratios had a significant impact on the formation of anatase phase of the TiO2. Fig.2 indicated that IL ([bmim]Br) had the capacity for good anatase crystallinity under the premise of enough TiO2 in the SiO2/TiO2 aerogels even though aerogels were prepared by ambient pressure drying at low temperature (60°C and 80°C) and without calcination. The crystalline nature became more prominent with increase in the content of TiO2 in SiO2/TiO2 aerogels. The pattern of Si-10Ti aerogel sample showed the diffraction peaks assigned to anatase structure of TiO2 and the crystalline phase was indexed in the light of available XRD data for TiO2 crystal structure. The size of crystal was roughly calculated by Scherrer Equation. Increased SiO2/TiO2 molar ratios
resulted in bigger anatase nanocrystals and average sizes ranged from 0.4 nm for 10Si-Ti to 5.2 nm for Si-10Ti.

Figure 2. X-ray powder diffraction (XRD) patterns of aerogel samples made in different SiO2/TiO2 molar ratios (10Si-Ti, 5Si-Ti, Si-Ti, Si-5Ti, Si-10Ti).

Fig.3 showed the SEM morphology of composite aerogels (10Si-Ti, Si-Ti, Si-10Ti) and pure TiO2, respectively. The results stated that aerogels except the aerogel synthetized in SiO2/TiO2 molar ratio of 10 had nano-porous microstructure. From Fig.3 (a), the 10Si-Ti aerogel was composed of dense layers and did not show any porous microstructure under SEM observation. From Fig.4 (c), it indicated clearly that Si-10Ti aerogels were densely agglomerated by nanoparticles and of porous structure. Pure TiO2 aerogels had a fundamentally similar image to Si-10Ti aerogels. In the Fig.4 (b), SEM image showed that Si-Ti aerogels had a looser network structure and larger pores. These results were consentaneous with table1 and confirmed the conjecture about the possible mechanisms of IL.

Figure 3. SEM images of the aerogels made at SiO2/TiO2 molar ratios((a)10Si-Ti,(b) Si-Ti,(c) Si-10Ti) and(d) Pure TiO2

3.2. Photo-catalytic performance of aerogels

It was showed in the Fig.4 that photocatalytic degradation rate of the aerogel samples was increased with the decrease of SiO2/TiO2 molar ratios regularly. Degradation reaction was carried out without the UV light in the dark at the first 30 minutes and reactive brilliant blue was largely adsorbed by aerogels because of its absorption capability. It was seen from Fig.4 that the degradation rates of the first 30 minutes corresponded to the surface areas of aerogel samples and the conclusion illustrated the surface area of aerogel played an important part in the photocatalytic performance. Later on, degradation reaction continued for 150 minutes under single UV irradiation and anatase TiO2 played a greater role in photocatalytic reaction. The photocatalytic degradation rate of the aerogel sample in Si-10Ti was best up to 99.77% at 170 minutes. The result shows photocatalytic performance was both
relevant to high surface area and anatase micro-crystal phase. After photocatalytic reaction, most of the aerogel samples were still blocky so that aerogels as catalyst would been more easily recycled.

![Figure 4](image)

**Figure 4.** Adsorption and photocatalytic degradation rate curves for 200 mL. 20 mg/L reactive brilliant blue solution with 0.1g blocky aerogel samples made at different SiO2/TiO2 molar ratios (10Si-Ti, 5Si-Ti, Si-Ti, Si-5Ti, Si-10Ti).

3.3. Effect of doping Ag nanoparticles

The aerogels were prepared in different ratios n(Ag)/n(SiO2+TiO2)=0, 1%, 5%, 10% (noted as 0Ag-Si-10Ti, 1Ag-Si-10Ti, 5Ag-Si-10Ti, 10Ag-Si-10Ti,) in order to investigate the effect of various Ag values to aerogels. The SiO2/TiO2 molar ratio of aerogels was fixed at 1/10 and the IL/( SiO2+TiO2) molar ratio was fixed at 1(x=1). The aerogels were aged by 1mol/L IL aqueous solution.

The XRD patterns of Ag doped SiO2-TiO2 aerogels were displayed in Fig.5. It was obviously seen that the pattern of 10Ag-Si-10Ti aerogel sample showed the diffraction peaks which the XRD patterns of other aerogel samples didn’t have and the peaks were in agreement with peak position of silver metal. The diffraction peaks were corresponded to the (110) planes of silver shifted from 39° to 31°. The cause of the disappearance of other patterns might be that there was too little Ag value to detect.

![Figure 5](image)

**Figure 5.** X-ray powder diffraction (XRD) patterns of aerogel samples with various Ag values

The values of Ag doped aerogels also made an important effect on the photocatalytic performance [16-19]. Both 0Ag-Si-10Ti and 10Ag-Si-10Ti aerogel samples (0.1g) were used to decolorize 200ml reactive brilliant blue solution (20mg/L) under UV-light. After 1 hour later, the photocatalytic degradation rate of 10Ag-Si-10Ti aerogel sample was up to 88.61% while the photocatalytic degradation rate of 0Ag-Si-10Ti aerogel sample was only 61.54%. The result showed Ag could improve photocatalytic activities.
3.4. Effect of IL on anatase crystallinity

Figure 6. (a) X-ray powder diffraction (XRD) patterns of aerogel samples prepared at different ratios n(IL)/n(SiO2+TiO2)=0, 1, 2, 3 in the first step(0IL-Si-10Ti, 1IL-Si-10Ti, 2IL-Si-10Ti, 3IL-Si-10Ti)

Figure 6. (b) X-ray powder diffraction (XRD) patterns of aerogel samples aged by variable IL aqueous solution of 0, 1mol/L, 2mol/L, 3mol/L, 4mol/L in the second step

In the process of the preparation of aerogels, there were two steps where IL ([bmm][Br]) was used as follows: the first step was the preparation of SiO2 sols and TiO2 sols and IL was used as cosolvent; the second step was aging process and the gels were aged by IL aqueous solution.

Aerogels without Ag doped were prepared using IL as cosolvent at different ratios n(IL)/n(SiO2+TiO2) =0, 1, 2, 3 (noted as 0IL-Si-10Ti, 1IL-Si-10Ti, 2IL-Si-10Ti, 3IL-Si-10Ti, respectively) in the first step. The SiO2/TiO2 molar ratio of aerogels was fixed at 1/10 and the aerogels were aged by deionized water rather than IL aqueous solution. The other series of aerogels without Ag doped were prepared without IL as cosolvent in the first step and the SiO2/TiO2 molar ratio of aerogels was also fixed at 1/10. The aerogels were aged by variable IL aqueous solution of 0, 1mol/L, 2mol/L, 3mol/L, 4mol/L (noted as Si-Ti-0, Si-Ti-1, Si-Ti-2, Si-Ti-3, Si-Ti-4, respectively).

These aerogels were analyzed by XRD and the size of crystal was roughly calculated by Scherrer Equation. The patterns in Fig.6(a) showed the aerogels using IL as cosolvent appeared microcrystalline anatase and it was obviously that [bmm][Br] played a very important role in the size of crystal. 1IL-Si-10Ti and 2IL-Si-10Ti aerogels had bigger crystal grain dimension of 6.2nm and 5.6nm, respectively, than 0IL-Si-10Ti aerogels of 2.6nm,and on the contrary, 3IL-Si-10Ti aerogels had smaller crystal grain dimension of 1.7nm. The patterns in Fig.6 (b) showed the aerogels, which aged with deionized water instead of IL aqueous solution, also appeared microcrystalline anatase. Si-10Ti-1 and Si-10Ti-2 aerogels had bigger crystal grain dimension of 6.6nm and 5.3nm than 0IL-Si-10Ti
aerogels of 2.6nm while Si–10Ti–3 and Si–10Ti–4 aerogels didn’t have TiO2 microcrystalline anatase nearly. These showed that appropriate [bmmim]Br used as cosolvent and IL aqueous solution of proper concentration used as aging agent were both beneficial to form microcrystalline anatase. Under optimal conditions of n(IL)/n(SiO2+TiO2)=1 and IL aqueous solution of 4mol/L, the best anatase crystallinity were achieved to 6.2nm and 6.6nm, respectively.

Special solubility and dispersing effect of IL to sol–gel precursors were estimated to cause the results above. Appropriate IL made sol–gel precursors distributed evenly in a homogeneous phase, which had a positive effect on formation of microcrystalline anatase with larger crystal size. Whereas, excess IL engendered too high mucosity of solution and this was disadvantageous for the diffusion and polycondensation of sol–gel precursors. In this case, it was difficult to form microcrystalline anatase of the big size, and even anatase.

4. Conclusions
Ag doped SiO2-TiO2 aerogels with nano-sized microcrystalline anatase and high surface area were successfully prepared using IL ([bmmim]Br) by ambient pressure drying at low temperatures and without calcination. It was found that the SiO2/TiO2 molar ratios influenced aerogels formation and the optimal SiO2/TiO2 molar ratio was 1/10. Aerogels in SiO2/TiO2 molar ratio of 1/10 had a surface area as high as 385.2m2g-1, big anatase crystallinity of 6.2nm and good photocatalytic degradation rate up to 99.7%. It was also found that the increase of Ag amount would effectively improve photocatalytic abilities of aerogels. Appropriate [bmmim]Br used as cosolvent and IL aqueous solution of proper concentration used as aging agent were both beneficial to form microcrystalline anatase. In the paper, the optimal conditions were n(IL)/n(SiO2+TiO2)=1 and IL aqueous solution of 1mol/L. However, mechanisms of IL was not entirely clear and needed to work on later.

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