

TiO₂ particles for the preparation of photocatalytic membranes using ionic liquid self-assembling sol-gel methods

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1. Introduction

Mesoporous titania membranes have received significant attention in recent years because of their unique characteristics such as high water flux, semiconductance, photocatalysis, and chemical resistance over other membrane materials including γ -alumina, silica and zirconia[1]. The potential applications of titania membranes include ultrafiltration processes and catalytic/photocatalytic membrane reactor systems for liquid and gas separations[2]. However, their practical applications are limited due to the reduction of porosity and surface area at the elevated temperatures.

Antonelli and Ying [3] first synthesized mesoporous TiO₂ with high surface area and narrow pore size distribution by a sol-gel method with phosphorus-containing surfactants as templates. After then, various techniques of surfactant templating have been employed on preparing mesoporous TiO₂ with high surface area. However, typical sol-gel derived materials are amorphous in nature, requiring further heat treatment to obtain crystallized materials. This calcination step usually involves rapid thermal transformation, resulting in particle agglomeration and grain growth. Therefore, it is highly desirable to synthesize crystalline TiO₂ nanostructures at ambient temperature without further heat treatment since this will save energy in the preparation steps.

The approach introduced in this study is to use water immiscible room temperature ionic liquid (WIRTIL) as a templating material instead of

amphiphilic organic molecules and as an additional solvent with alcohol solvents used in the traditional sol-gel methods. Ionic liquids (ILs) are an exceptional type of solvent consisting virtually only of ions. Ionic liquids have practically no vapor pressure and possess tunable solvent properties [4,5]. In this study, we used various ionic liquids as a template in sol-gel methods to prepare mesoporous TiO₂ materials. The low vapor pressure of the ionic liquid could assist in reducing the problem of gel shrinkage during sol ageing and gel drying, which could prevent crack formation and reduction of surface area. Hence, mesoporous TiO₂ particles with high surface area was successfully synthesized using room temperature ionic liquids. This method can be easily extended to prepare mesoporous TiO₂ films and membranes for practical applications.

2. Experimental

Titanium tetraisopropoxide (TTIP, 97%, Aldrich) was first mixed with isopropanol (iPrOH, 99%, Fisher) at a C₃H₇OH/TTIP molar ratio of 30. Among the ionic liquids shown in Table 1 [Bmim][PF₆] was used as a standard ionic liquid (IL) in this study. The IL of [Bmim][PF₆] was added into the mixed solution to a various IL/TTIP molar ratio from 0 to 5 and then stirred for 10 min. Hydrolysis and condensation were conducted at room temperature, by adding the mixed solution slowly into deionized water up to a H₂O/TTIP molar ratio of 100. In order to investigate the effect of water concentrations, the H₂O/TTIP molar ratio was varied from 25 to 150 at constant IL/TTIP molar ratio of 3. The mixed solution was stirred vigorously for 30 min. The product was recovered by filtration, washed thoroughly with deionized water and dried at 100 °C for 2 h. A light-yellowish white powder was obtained. The entrapped IL and organics were extracted by refluxing the above powder in acetonitrile (HPLC grade, Fisher) at room temperature for 12 h. The subsequent product was also recovered by filtration, washed and dried at 100 °C. The final product was a white powder.

The structural properties of TiO₂ particles were determined from the nitrogen isotherms at 77 K measured in a Micromeritics ASAP 2020 apparatus. The XRD patterns were collected with a Siemens (D500) powder X-ray Diffractometer using CuK α radiation (wavelength 1.5406 Å) to determine

the crystal structure and crystallinity of the TiO₂ particles. Transmission electron micrographs of the prepared TiO₂ particles were done using CM20 microscope (Philips) at 200 kV with LaB6 filament to visually characterize the TiO₂ nanostructure. Compositional analysis of the TiO₂ particles was conducted using an energy dispersive X-ray spectroscopy (EDX, Oxford Isis) connected to the IIR-TEM. A Fourier transform infrared spectroscopy (FTIR, Bio-Rad) was used to study the C-H stretching vibrational infrared spectra of the IL around 2900 cm⁻¹ and other residual organics.

3. Results and Discussion

The prepared TiO₂ particles were initially heat-treated at low temperature of 100 °C for 1 h. The EDX analysis clearly showed only Ti and O elements present in the final product and the C-H stretching vibrational infrared spectra of the IL around 2900 cm⁻¹ disappeared after solvent extraction, meaning that most of the IL and other organics were removed by the extraction with acetonitrile.

Powder X-ray diffraction (XRD) patterns of this sample are shown in Fig. 1. All the peaks in the pattern are assigned to anatase TiO₂ without any indication of the other crystalline products and they are relatively broad due to the nanosize of the crystals. It is worthy to note that the TiO₂ particles show anatase crystalline phase, although they were only dried at low temperature. The small-angle diffraction pattern shows one single peak, which indicates disordered mesoporous structure without long range order in the pore arrangement.

The N₂ isotherms of the sample were studied at 77K. The isotherm pattern exhibits type IV-like, which is a characteristic of mesoporous materials based on the IUPAC classification. A sharp inflection of adsorbed volume at P/P₀ = 0.45 (hysteresis loop) and a relatively steep desorption branch indicate a distribution of various sized cavities but with the same entrance diameter. This means the existence of mesoporosity with similar sized entrances in the materials, being in agreement with the small-angle diffraction peak in Fig. 1. The pore size distribution based on the desorption branch of the isotherm is relative narrow with an average pore diameter of 4.5 nm. The narrow pore

size distribution indicates good homogeneity of the pores. The BET surface area and specific pore volume of the materials are about 273 m²/g and 0.308 cm³/g, respectively. The TEM image shown in Fig. 2 exhibits a disordered wormhole-like pore structure which is consistent with the smallangle XRD result. The pore size estimated by TEM analysis is in agreement with N₂ adsorption data as well.

4. References

- [1] K.N.P. Kumar et al., J. Mater. Chem., 3, 1151 (1993).
- [2] T. Tsuru, D. Hironaka, T. Yoshioka, M. Asaeda, Sep. Puri. Tech., 25, 307 (2001).
- [3] D.M. Antonelli, J.Y. Ying, Angew. Chem. Int. Ed. Engl., 34, 2014 (1995).
- [4] P. Wasserscheid, W. Krcm, Angew. Chem. Int. Ed. Engl., 39, 3772 (2000).
- [5] T. Welton, Chem. Rev., 99, 2071 (1999).

Table 1: Room Temperature Ionic Liquids

Symbol	Full Name
[Bmim][PF ₆]	1-Buthyl-3-methylimidazolium hexafluorophosphate
[Bmim][BF ₄]	1-Buthyl-3-methylimidazolium tetrafluoroborate
[Bmim][CF ₃ SO ₃]	1-Buthyl-3-methylimidazolium trifluoromethanesulfonate
[Hmim][PF ₆]	1-Hexyl-3-methylimidazolium hexafluorophosphate

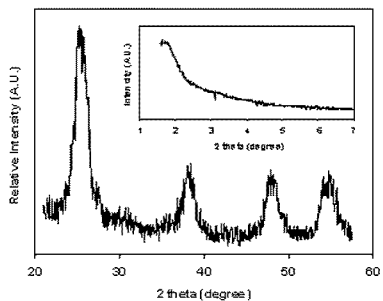


Figure 1: XRD patterns of anatase nanostructured TiO₂ particles. Insert is the small-angle diffraction pattern of sample.

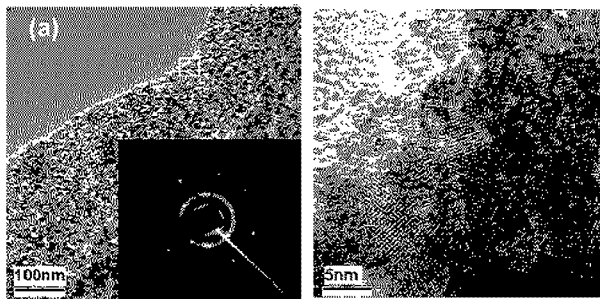


Figure 2: High resolution TEM images of the IL-templated TiO₂ particles calcined at 100°C; the inset is a selected area electron diffraction pattern recorded at an instrument camera length of 25 cm.