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# Room temperature ionic liquids as templates in the synthesis of mesoporous silica via a sol–gel method

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ABSTRACT

With various RTILs as templates, amorphous mesoporous silica gel materials were synthesized according to a proper sol–gel method. The materials display pore diameter of 3–12 nm, pore volume of 0.4–1.3 $cm^3/g$ and BET surface area of 300–800 $m^2/g$. The effect of variations of the anions and cations of ILs, the alkyl chain length on imidazolium cation and IL concentration in the reaction system on the pore structure and thermal stability of the silica gel materials was preliminarily studied. It is suggested that, the pore size of silica gel can be tuned by variations of ILs and IL content. The different kind of the anions of ILs could largely impact the properties of the obtained silica gel materials. The mesoporous silica gels with 1-alkyl-3-methylimidazolium tetrafluoroborate as templates possessed larger pore sizes of 5–12 nm and higher thermal stability than the materials obtained with other ILs as templates.



## 1. Introduction

Porous materials have become more and more important in either science or technology. They can be grouped into three classes based on their pore diameter ($d$): microporous, $d < 2.0$ nm; mesoporous, $2.0 < d < 50$ nm; macroporous, $d > 50$ nm. Among them, mesoporous materials have attracted more attention due to tailoring ability of the pore structure over a wide range, and the potential applications in catalysis, separations, nanoelectronics, sensors, and spacial host materials for substances or reactions [1]. In the synthesis of uniform mesoporous materials, various templates have been employed [2–9]. In detail, templating by individual molecules, micelles, and emulsions or latex particles can gives rise to mesopores. Since 1992, various surfactants, ionic [10–13] or neutral [13,14], as templates, have been introduced to direct the formations of mesopores in the material based on hydrothermal or sol–gel methods.

Room temperature ionic liquids (RTILs) have received considerable attentions in many areas of chemistry and industry due to their superior properties such as high thermal stability, nonflammability, and essentially zero vapor pressure [15–17]. However, their potential as templates and reaction media for nanocomposite materials is relatively less reported. As a new kind of templates, ILs can be recycled more easily, which is considered to be economical and environmental friendly. In addition, the great diversity of ILs may not only enrich the organic template family but also lead to porous materials with novel structure and properties. Meanwhile, nanoporous materials with ILs supported or templated had also potential applications in catalysis and separations [18,19]. Thus, it is valuable to carry out investigations on the synthesis and properties of ILs templated porous materials. During the past decade, 1-alkyl-3-methylimidazolium salts with $Cl^-$ and $Br^-$ anions ($C_n$MImCl and $C_n$MImBr, where $n = 2–18$) have been used as templates in mesoporous material synthesis according to hydrothermal crystallization procedure, and the results suggested that ILs performed in a similar manner to the alkyltrimethylammonium family of templates [20]. A variety of ILs, $C_n$MImCl, were used as templates to prepare monolithic, super-microporous silica with lamellar order via the nanocasting technique, displaying a very regular structure with *ca.* 1.2–1.5 nm in pore diameter [21]. So far, the majority of the reports are focused on the ILs with long alkyl side chain on the imidazolium cation and halide anions [20–25], which could direct the formation of mesophase in the synthesis system to produce well-ordered microporous and mesoporous materials. $BMImBF_4$, a short-chain IL was used as the template to produce monolithic mesoporous silica with wormhole framework via a convenient sol–gel nanocasting technique [26]. The properties of ILs can be notably changed with variations of cation and anion. Thus, the diversity of the selected ILs as the template in sol–gel synthesis can have important effect on the properties of the obtained porous materials. However, RTILs with varied composed cations and an-

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ions as templates to synthesize porous materials are less reported yet [27].

In this work, according to a proper sol–gel method, various RTILs with RMIm (R, alkyl) and Th cation and $BF_4$, $NTf_2$, $N(CN)_2$, $CF_3SO_3$ (Scheme 1) as a new kind of recyclable templates were employed in the synthesis of mesoporous silica gel materials. In addition, the effect of the variation of ILs, the IL template content on the pore structure and thermal stability of silica gel was also investigated herein.

## 2. Experimental

### 2.1. Materials and reagents

All chemicals used in the experiments were of analytical grade, and were used without further purification. Silver dicyanamide $AgN(CN)_2$ was purchased from Aldrich and used as received.

### 2.2. Synthesis of ILs

$BMImBF_4$, $HMImBF_4$, $OMImBF_4$, $BMImNTf_2$, $BMImCF_3SO_3$, $BMImN(CN)_2$ were synthesized and purified according to the literature [17]. S-butylthiophene dicyanamide $BThN(CN)_2$ was synthesized in our lab through following procedure: S-butyltetrahydrothiophene chloride was prepared with high yield from the reaction of tetrahydrothiophene and appropriate amount of chlorobutane in acetone. Silver dicyanamide $AgN(CN)_2$, (4.0 g, 11 mmol) was added to a solution of BThCl (5.2 g, 11 mmol) in water (60 ml), and the resulting suspension was stirred for 24 h. Then the filtrate was evaporated under vacuum. The obtained crude compound was dissolved in dichloromethane and the solution was dried over anhydrous magnesium sulphate. Finally, the colorless $BThN(CN)_2$ was obtained by subjecting the liquid to a higher vacuum to eliminate volatile components.

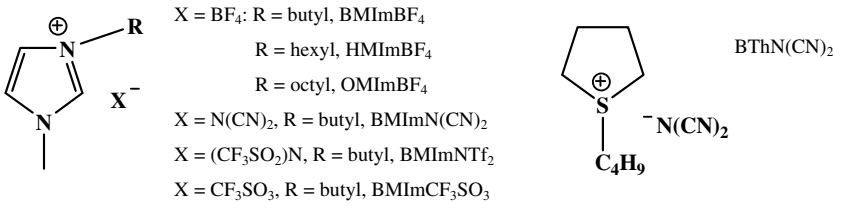
### 2.3. Preparation of IL incorporated nanocomposites (IL-sg) and silica gel materials (wsg-IL)

IL (0.05–1.0 g) was dissolved into the solution of tetraethyl orthosilicate (5.00 ml) and ethanol (2.50 ml) and was stirred for 2 h under 40 °C. Then the solution was cooled to room temperature into which 2.50 ml hydrochloride aqueous solution (mixture of 10.00 ml distilled water and 1.00 ml 37% concentrated hydrochloride acid) was added dropwise under vigorous stirring. After 5 h, the solution was exposed to a vacuum at 60 °C for 2 h for the removal of the ethanol solvent during which a transparent gel was formed. Then after the gel was aged for 12 h in air at 60 °C, the obtained materials with different IL loading in mass were subjected to a higher vacuum at 80 °C for 5 h to eliminate the volatile components. The loadings of ILs were calculated through the ratio of the mass of the ILs initially employed to the total amount of IL-sg materials finally obtained.

IL-sg was washed with mixture of ethanol and acetone (v/v, 1:1) under refluxing for 6 h and this procedure was repeated for at least thrice for the vigorous washing of IL, and then was filtrated. The solid of silica gel was dried at 80 °C under higher vacuum for 5 h, denoted as wsg-IL.

### 2.4. Characterizations and instruments

BET surface area, average pore volume, and average pore diameter of the porous silica gel materials were measured by physisorption of $N_2$ at 77 K over a Micromeritics ASAP 2010. Before




**Scheme 1.** RTILs templates involved in the synthesis of mesoporous silica gel materials.

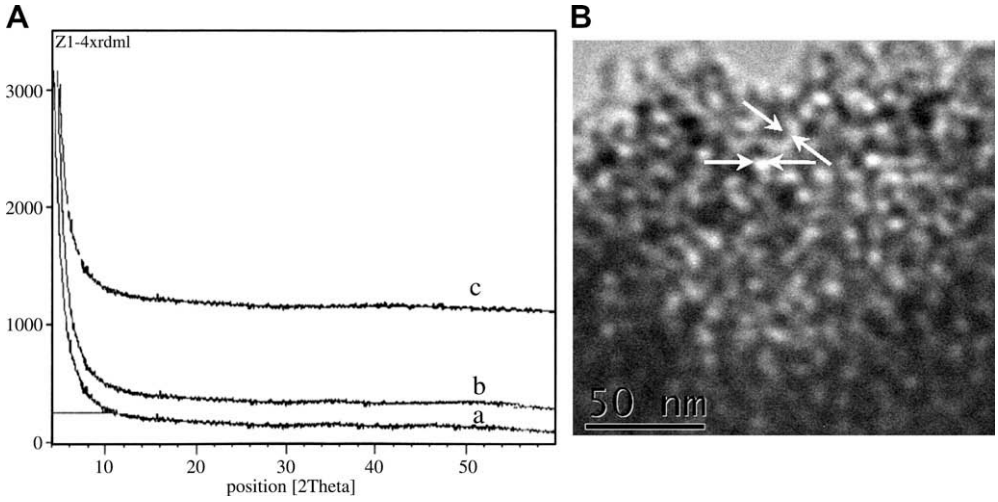



**Fig. 1.** (A) XRD patterns of wsg-$BMImBF_4$ with $BMImBF_4$ loading of: (a) 15 wt%, (b) 25 wt%, and (c) 25 wt% after being calcined at 500 °C. (B) TEM image of wsg-$BMImBF_4$ with $BMImBF_4$ loading of 15 wt%.