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## Self-Assembly of Metal Oxide Nanoparticles into Hierarchically Patterned Porous Architectures Using Ionic Liquid/Oil Emulsions

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Hierarchically patterned macroporous TiO<sub>2</sub> structures can be fabricated via the spontaneous self-assembly of TiO<sub>2</sub> nanoparticles prepared using a mixture of 1-octadecene (ODE) and an ODE-immiscible 1-alkyl-3-methylimidazolium-based ionic liquid as the reaction medium. A study of the influence of side chain lengths of ionic liquids ( $n = 4, 8,$  or  $16$ ) reveals that this parameter can be further used to fine-tune the morphologies of the products. This synthetic methodology can also be extended to the formation of patterned macroporous ZrO<sub>2</sub> and Fe<sub>3</sub>O<sub>4</sub> structures. Finally, the potential reasons for the formation of hierarchical structures are discussed and the implications to further research are proposed.

### 1. Introduction

Ionic liquids, a family of low-temperature molten salts composed of organic cations and inorganic or organic anions, typically exhibit negligible vapor pressures, large liquidus ranges, good thermal stabilities, and tunable solubilities for inorganic and organic molecules. They hold great potential for extraction technologies, organic catalysis, and materials synthesis.<sup>1–5</sup> In particular, the use of ionic liquids as solvents, additives, templates, or precursors may lead to materials with unique structures and properties (e.g., metal structures,<sup>6,7</sup> silicas,<sup>8,9</sup> metal oxides,<sup>10,11</sup> metal chalcogenides,<sup>12,13</sup> metal salts,<sup>14–16</sup> open-framework structures,<sup>17–20</sup> and ionic-liquid-modified materials).<sup>21</sup>

The self-assembly of inorganic building blocks into hierarchical structures is an interesting topic,<sup>22–25</sup> but the use of ionic liquids as media has been rarely reported. Zhou and Antonietti synthesized spherical TiO<sub>2</sub> sponges (70–100 nm) composed of TiO<sub>2</sub> nanoparticles (2–3 nm) using a mixture of TiCl<sub>4</sub>, [C<sub>4</sub>Mim][BF<sub>4</sub>], and water.<sup>11</sup> Yan and co-workers made CeO<sub>2</sub> spheres composed of nanoparticles using a mixture of Ce(NO<sub>3</sub>)<sub>3</sub>, [C<sub>16</sub>Mim][Br], and ethanol.<sup>26</sup> Ying and co-workers fabricated hierarchical CaMoO<sub>4</sub> microspheres composed of nanoparticles using a mixture of CaCl<sub>2</sub>, Na<sub>2</sub>MoO<sub>4</sub>, [C<sub>4</sub>Mim][Cl], and water.<sup>27</sup> Du et al. made SrCO<sub>3</sub> spheres composed of nanoparticles by refluxing a solution of SrCl<sub>2</sub>, NaOH, and 1,1,3,3-tetramethylguanidinium lactate in the presence of CO<sub>2</sub>.<sup>16</sup> Interestingly, Chen and Dong fabricated two-dimensionally patterned Pt nanostructures at the air–water interface via the self-assembly of ionic-liquid-stabilized Pt nanoparticles,<sup>28</sup> but the fabrication of similar macroporous patterns using ionic liquids has not been achieved in other systems.

Our group has been interested in the synthesis of inorganic materials using ionic liquids. We have reported the synthesis of SiO<sub>2</sub> aerogels,<sup>8,29</sup> mesoporous SiO<sub>2</sub>,<sup>30</sup> mesoporous organosilicas,<sup>31,32</sup> surface-modified mesoporous carbon,<sup>33</sup> ZnO flowers,<sup>34</sup>

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and porous carbons<sup>35</sup> using ionic liquids. The primary feature of the above synthesis methodologies reported by us and others is that ionic liquids are used as replacement solvents for conventional solvents. Nevertheless, few investigations have focused on the use of mixed or biphasic solvent systems involving both conventional organic and “neoteric” ionic liquid solvents.<sup>10</sup> In one interesting example, Nakashima and Kimizuka fabricated hollow TiO<sub>2</sub> microspheres at the interface between a toluene droplet and a toluene-immiscible ionic liquid with vigorous stirring.<sup>10</sup> These new mixed or biphasic solvent systems may open up new avenues in controlling the morphologies of materials.

In the present work, we report an interesting finding that TiO<sub>2</sub>, ZrO<sub>2</sub>, and Fe<sub>3</sub>O<sub>4</sub> nanoparticles can self-assemble into hierarchical architectures using a combination of a nonpolar solvent and an ionic liquid immiscible in that nonpolar solvent. The resulting morphologies of metal oxide materials obtained are analogous to the patterned Pt structures reported by Chen and Dong.<sup>28</sup> Recently, Han and co-workers developed an aminolysis route to monodisperse TiO<sub>2</sub> nanorods and nanoparticles.<sup>36</sup> In their synthesis, Ti(OiPr)<sub>4</sub> dissolved in 1-octadecene solvent was chemically modified with oleic acid (C<sub>17</sub>H<sub>33</sub>COOH) as a chelating ligand to minimize the amount of TiOR groups accessible for rapid hydrolysis. The resulting (C<sub>17</sub>H<sub>33</sub>COO)<sub>x</sub>Ti(OiPr)<sub>4-x</sub> complex underwent aminolysis with oleylamine (C<sub>18</sub>H<sub>35</sub>NH<sub>2</sub>) to generate TiO<sub>2</sub> nanoparticles and nanorods with tunable aspect ratios, but no patterned structure was observed.<sup>36</sup> On the basis of their synthesis procedure, we serendipitously found that the replacement of the 1-octadecene solvent by an emulsion composed of 1-octadecene and an ionic liquid may lead to the hierarchical self-assembly of the so-formed TiO<sub>2</sub> nanoparticles into novel macroporous architectures. Furthermore, this methodology was extended by employing several ionic liquids containing different chain lengths and by using various metal alkoxide precursors, yielding unique results.

## 2. Experimental Section

**2.1. Synthesis.** Titanium isopropoxide (99.999%), oleic acid (90%), oleylamine (70%), 1-octadecene (90%, Acros), zirconium butoxide (80 wt % solution in 1-butanol), 1,2-hexadecanediol (90%), diphenyl ether (99 + %), and iron(III) acetylacetonate (99.99 + %) were from Aldrich unless otherwise indicated above. The ionic liquids 1-butyl-3-methylimidazolium bis(trifluoromethylsulfonyl)imide ([C<sub>4</sub>Mim][Tf<sub>2</sub>N]),<sup>37</sup> 1-octyl-3-methylimidazolium bis(trifluoromethylsulfonyl)imide ([C<sub>8</sub>Mim][Tf<sub>2</sub>N]),<sup>38</sup> and 1-hexadecane-3-methylimidazolium bis(trifluoromethylsulfonyl)imide ([C<sub>16</sub>Mim][Tf<sub>2</sub>N])<sup>38</sup> were synthesized according to the literature.

To synthesize TiO<sub>2</sub>, 5.0 mL of 1-octadecene, 1.6 mL of oleic acid, and 1.0 mL of [C<sub>4</sub>Mim][Tf<sub>2</sub>N] were dried and degassed at 80 °C under N<sub>2</sub> flow in a 50 mL three-neck flask for 1 h, and 0.3 mL of titanium isopropoxide was injected via a syringe. The solution was aged at 80 °C for 20 min, heated to 260 °C, and kept at 260 °C for 5–10 min. Thereafter, 1.28 mL of oleylamine was injected under vigorous magnetic stirring (1200 rpm) to initiate aminolysis. The vigorous stirring is important to avoid phase separation between 1-octadecene (ODE) and the ODE-immiscible ionic liquid. The reaction mixture was aged at 260 °C for 1 h and then cooled down to room temperature. The resulting product contained an upper crude colloid layer and a bottom

ionic liquid layer. The crude TiO<sub>2</sub> colloids were collected for further treatment to recover nanomaterials.

The crude colloids were diluted in hexane, flocculated with acetone, and centrifuged to precipitate TiO<sub>2</sub>. The white-yellow powder was redispersed in hexane, subjected to a second dispersion–precipitation purification step using the hexane/acetone pair, and then redispersed in hexane. To prepare scanning and transmission electron microscopy (SEM/TEM) samples, the colloids redispersed in hexane were dropped onto TEM grids and allowed to dry in air at room temperature. For X-ray diffraction (XRD) measurements, the powder was further subjected to two more rounds of purification and was then dried at 80 °C overnight. TiO<sub>2</sub> was also prepared using [C<sub>8</sub>Mim][Tf<sub>2</sub>N] or [C<sub>16</sub>Mim][Tf<sub>2</sub>N], where the aminolysis reaction was carried out at 300 °C and other conditions were the same as above. The synthesis procedures of ZrO<sub>2</sub> and Fe<sub>3</sub>O<sub>4</sub> were based on the literature,<sup>36,39</sup> except that an ionic liquid was added into the reaction mixture (more details given in the Supporting Information).

**2.2. Characterization.** TEM images were recorded on a Hitachi HD2000 scanning transmission electron microscope with an EDX attachment. XRD data were collected on a PANalytical powder diffractometer using Cu Kα radiation. High-resolution (HR) TEM images were taken on an HF-2000 electron microscope. Brunauer–Emmett–Teller (BET) surface areas were measured by N<sub>2</sub> adsorption–desorption at 77 K using a Micromeritics Gemini instrument. Fourier transform infrared (FT-IR) spectroscopy was carried out in a diffuse reflectance cell (cell volume about 6 cm<sup>3</sup>) in a Nicolet Nexus 670 FT-IR spectrometer using a MCT/A detector with a spectral resolution of 4 cm<sup>-1</sup>.

## 3. Results and Discussion

Ionic liquids with C<sub>4</sub>, C<sub>8</sub>, and C<sub>16</sub> chains were used as additives to synthesize TiO<sub>2</sub>. Since these ionic liquids do not dissolve readily in 1-octadecene solvent, vigorous magnetic stirring (1200 rpm) was adopted to create metastable emulsions containing droplets. Figure 1 shows the corresponding SEM images with relatively lower (left images) and higher (right images) resolutions. The material synthesized using a combination of 1-octadecene and [C<sub>4</sub>Mim][Tf<sub>2</sub>N] has a foamlike morphology with near round macropores representative on a large scale (Figure 1A, Supporting Information Figure S1). The macropores have a distribution of sizes. A closer look indicates that there are smaller pores on the order of a few hundred nanometers embedded in the micrometer-sized TiO<sub>2</sub> cavities (Figure 1B, Supporting Information Figure S2). The existence of this feature may be because bigger cavities connect to each other, leading to the formation of smaller connecting holes.<sup>24,40,41</sup> For comparison, the material synthesized using a combination of 1-octadecene and [C<sub>8</sub>Mim][Tf<sub>2</sub>N] has a lower population of macropores, the macropores are embedded into the predominant TiO<sub>2</sub> matrix, the mean pore size is smaller (Figure 1C), and the shape of the pores is clearly more rounded (Figure 1D). Finally, when using a combination of 1-octadecene and [C<sub>16</sub>Mim][Tf<sub>2</sub>N], the resulting material has yet smaller pores and high pore density but wider size distributions and irregular shapes (Figure 1E, F). We speculate that the origin of such a chain-length effect may be related to the different physicochemical properties (e.g., solubility, viscosity, polarity) of ionic liquids with different chain lengths. One may also argue that long alkyl chains (e.g., C<sub>16</sub>) would allow the ionic liquid to dissolve more in 1-octadecene than short alkyl chains (e.g., C<sub>4</sub>) would, so that emulsions are not stabilized and then spherical pores cannot be embedded in the final product (Figures 1E, F). Regardless of the

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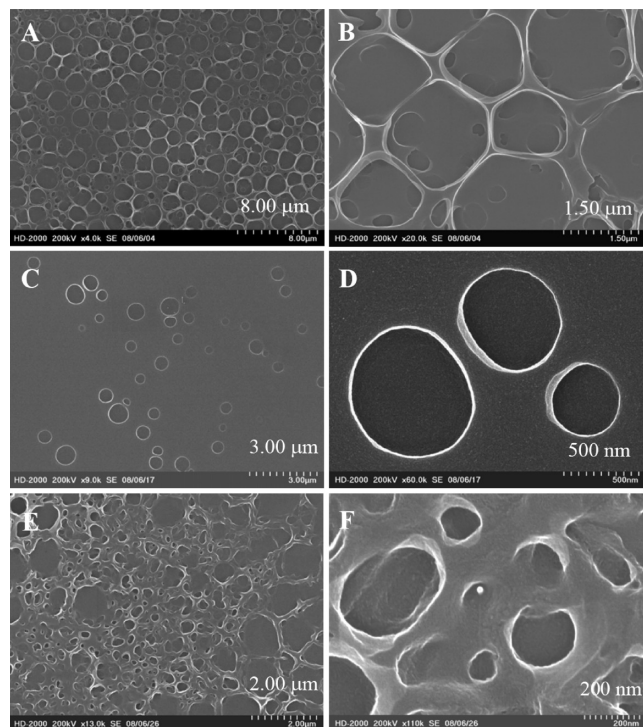
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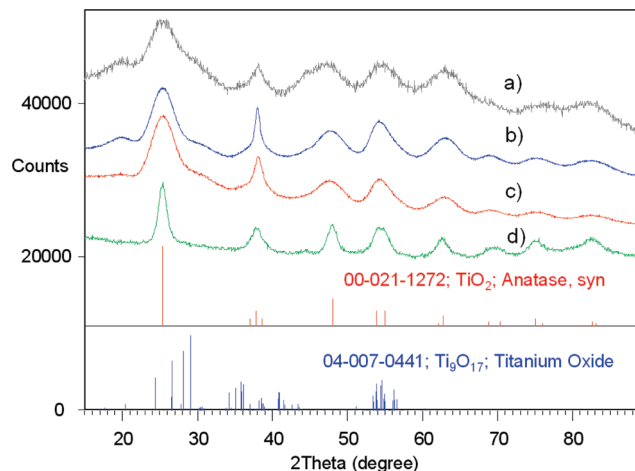


**Figure 1.** SEM images of patterned  $\text{TiO}_2$  structures formed using a combination of 1-octadecene and  $[\text{C}_4\text{Mim}][\text{Tf}_2\text{N}]$  (top images),  $[\text{C}_8\text{Mim}][\text{Tf}_2\text{N}]$  (middle images), or  $[\text{C}_{16}\text{Mim}][\text{Tf}_2\text{N}]$  (bottom images). For each sample, two representative SEM images are shown, with relatively lower resolutions (left images) or higher resolutions (right images).

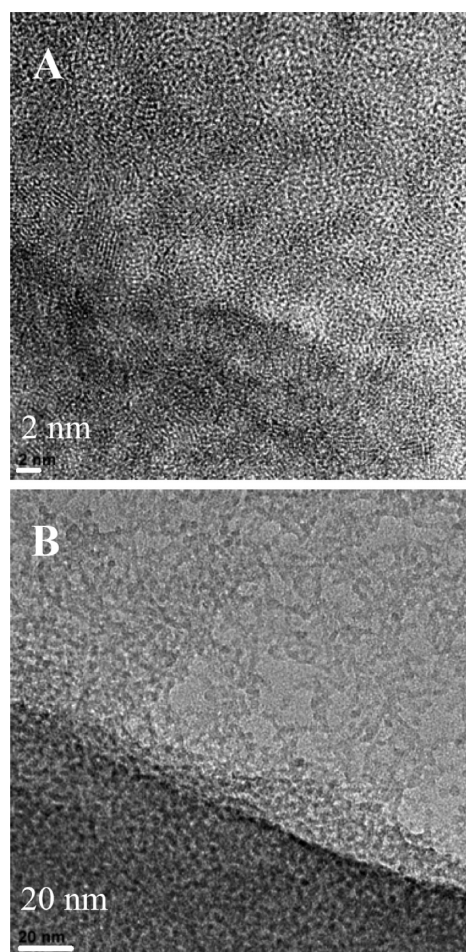
reasons, we predict that different morphologies will form under different experimental conditions (e.g., concentration of ionic liquid, stirring rate, reaction temperature) even if a single ionic liquid is used. Systematic experiments are needed in the future to better understand the exact formation mechanisms and to test our prediction.

We investigated the chemical nature of the resulting materials. As shown in Figure 2, the  $\text{TiO}_2$  samples prepared using a combination of 1-octadecene and any specific ionic liquid all have broad XRD peaks characteristic of nanoparticles. Anatase  $\text{TiO}_2$  is determined to be the predominant crystal phase, and  $\text{Ti}_3\text{O}_5$  is observed as only a very minor product. The presence of an additional amorphous phase is possible because the peaks of as-synthesized samples are much broader than those for a sample calcined at  $400^\circ\text{C}$ . Representative SEM images in Figures S3 and S4 in the Supporting Information show that the  $\text{TiO}_2$  architectures are composed of nanoparticles and nanorods. Note that a similar synthesis protocol without the addition of ionic liquids was reported to lead to the formation of similar  $\text{TiO}_2$  nanoparticles and nanorods, but no formation of patterned structures was observed.<sup>36</sup> With higher resolutions, the HRTEM images in Figure 3 and Supporting Information Figure S5 show the presence of not-so-well-developed  $\text{TiO}_2$  nanocrystals. The  $\text{TiO}_2$  lattice fringes can be seen, although not particularly clearly. The tiny  $\text{TiO}_2$  nanocrystals are possibly embedded within an amorphous  $\text{TiO}_2$  matrix.

We attempted to synthesize patterned macroporous  $\text{ZrO}_2$  and  $\text{Fe}_3\text{O}_4$  structures. Previously reported procedures were adopted,<sup>36,39</sup> with the difference being that an ionic liquid was added into the reaction mixture to create emulsions upon vigorous stirring. Figure 4 shows the SEM images with relatively lower (left images) and higher (right images) resolutions. The  $\text{ZrO}_2$  material prepared

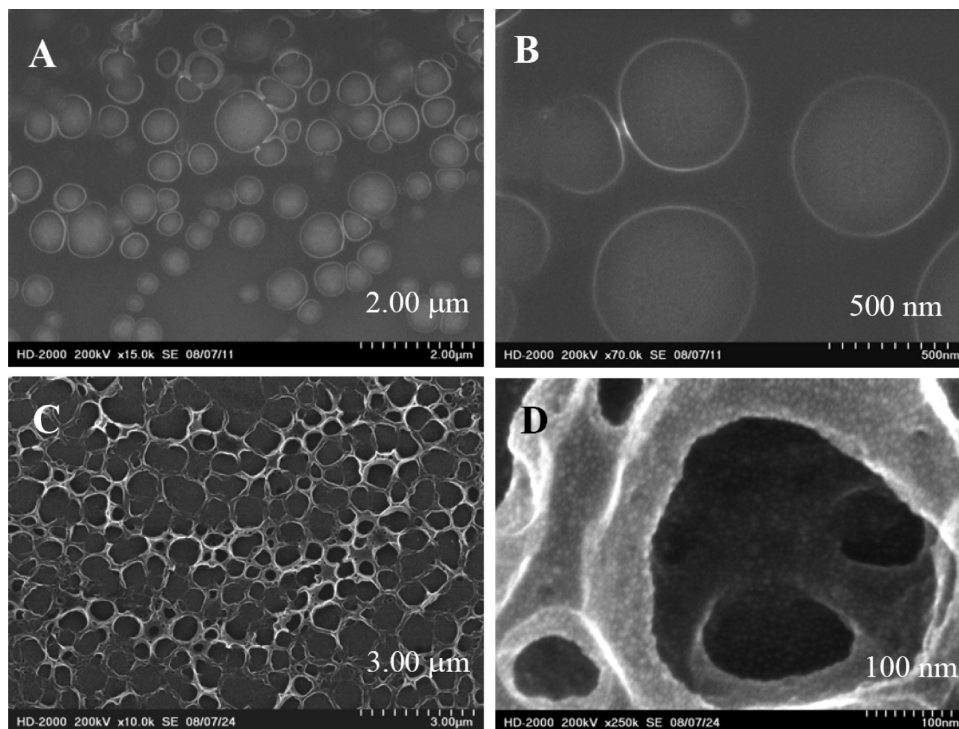


**Figure 2.** XRD patterns of as-synthesized  $\text{TiO}_2$  prepared using a combination of 1-octadecene and  $[\text{C}_4\text{Mim}][\text{Tf}_2\text{N}]$  (a),  $[\text{C}_8\text{Mim}][\text{Tf}_2\text{N}]$  (b), or  $[\text{C}_{16}\text{Mim}][\text{Tf}_2\text{N}]$  (c) as the solvent, together with XRD data of  $400^\circ\text{C}$  calcined  $\text{TiO}_2$  synthesized using a combination of 1-octadecene and  $[\text{C}_8\text{Mim}][\text{Tf}_2\text{N}]$  (d).



**Figure 3.** HRTEM images of  $\text{TiO}_2$  structures formed using a combination of 1-octadecene and  $[\text{C}_{16}\text{Mim}][\text{Tf}_2\text{N}]$ . From top to bottom, the scale bars represent 2 and 20 nm, respectively.

using a combination of 1-octadecene and  $[\text{C}_4\text{Mim}][\text{Tf}_2\text{N}]$  exhibits a membranelike morphology (Figure 4A, B), analogous to the  $\text{TiO}_2$  structure prepared using a combination of 1-octadecene and  $[\text{C}_8\text{Mim}][\text{Tf}_2\text{N}]$  (Figure 1C, D). The macropores are round and close to 600 nm, on average, but the sizes differ considerably



**Figure 4.** SEM images of  $\text{ZrO}_2$  structures formed using a combination of 1-octadecene and  $[\text{C}_4\text{Mim}][\text{Tf}_2\text{N}]$  (top images), together with SEM images of  $\text{Fe}_3\text{O}_4$  structures formed using a combination of diphenyl ether and  $[\text{C}_4\text{Mim}][\text{Tf}_2\text{N}]$  (bottom images).

(Figure 4A, B). XRD data demonstrate that the material is composed of small  $\text{ZrO}_2$  nanoparticles (Supporting Information Figure S6).  $\text{Fe}_3\text{O}_4$  prepared using an emulsion composed of diphenyl ether and  $[\text{C}_4\text{Mim}][\text{Tf}_2\text{N}]$  has a foamlike morphology (Figure 4C, D). There are smaller pores embedded in the bigger pockets, and the thick walls are composed of nanoparticles (Supporting Information Figures S7 and S8). No formation of macroporous structures was reported without using ionic liquids,<sup>36,39</sup> underscoring the key role of using ionic liquids in our case. Comparing the  $\text{TiO}_2$  (Figure 1A, B),  $\text{ZrO}_2$  (Figure 4A, B), and  $\text{Fe}_3\text{O}_4$  (Figure 4C, D) materials synthesized using a combination of a solvent (1-octadecene or diphenyl ether) and  $[\text{C}_4\text{Mim}][\text{Tf}_2\text{N}]$ , the common feature is that macropores are formed, although the morphologies are not exactly the same. The difference in morphologies is justified, considering that the compositions of the respective reaction mixtures (containing metal precursors, solvents, capping agents, additives, etc.) are not the same. Dong and Chen also found different Pt morphologies under different experimental conditions.<sup>28</sup>

Finally, we studied the fate of the prepared  $\text{TiO}_2$  and  $\text{ZrO}_2$  after calcination. The as-synthesized solid materials do not have detectable surface areas because macropores do not have sufficient surface areas measured by  $\text{N}_2$  adsorption–desorption, whereas potential mesopores between nanoparticles are capped by organic ligands. Preliminary FT-IR data indicate the presence of organic moieties on as-synthesized  $\text{TiO}_2$ . These organic moieties may play a role in stabilizing the size of nanoparticles and their morphologies. Such organic species can be removed upon calcination in air (Supporting Information Figure S9). Once the as-synthesized samples were calcined, they gave high surface areas, being  $205 \text{ m}^2/\text{g}$  for  $\text{TiO}_2$  synthesized using a combination of 1-octadecene and  $[\text{C}_{16}\text{Mim}][\text{Tf}_2\text{N}]$  and  $214 \text{ m}^2/\text{g}$  for  $\text{ZrO}_2$  synthesized using a combination of 1-octadecene and  $[\text{C}_4\text{Mim}][\text{Tf}_2\text{N}]$ . Their pore size distributions are relatively narrow, and pores are classified into the mesoporous regime (Supporting Information Figure S10). TEM data indicate that there are

numerous  $\text{TiO}_2$  nanoparticles packed together, forming irregular interparticle mesopores (Supporting Information Figure S11), whereas the patterned macroporous structures are totally lost, implying that the formed macroporous structures are metastable.

It should be emphasized that the chief attraction of this paper is not on the formation of mesoporous  $\text{TiO}_2$  (i.e., the final product after calcination; Supporting Information Figures S10 and S11), because the synthesis of mesoporous  $\text{TiO}_2$  using ionic liquids has been well documented,<sup>11,42,43</sup> not to mention the fact that the mesopores formed upon calcination are not ordered ones but derive from the random packing of  $\text{TiO}_2$  nanoparticles. Instead, we believe that the most interesting finding in this work is the self-assembly of  $\text{TiO}_2$  nanoparticles into patterned macroporous structures without calcination. Although there are numerous publications treating the morphological control of  $\text{TiO}_2$  nanostructures,<sup>44–46</sup> examples of patterned  $\text{TiO}_2$  structures reminiscent of those presented in the current work remain scarce.<sup>24</sup> Pine and co-workers fabricated ordered macroporous  $\text{TiO}_2$  and  $\text{ZrO}_2$  using oil-in-formamide emulsions stabilized by triblock copolymers.<sup>47–49</sup> Very recently, Kimura and co-workers made hierarchical  $\text{TiO}_2$  films by adding hydrophobic 1,3,5-triisopropyl benzene in an aqueous solution of a triblock copolymer.<sup>50</sup> Nevertheless, the patterns of macropores reported<sup>50</sup> are not as regularly organized as those achieved here. To the best of our knowledge,

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our current work is the first to report the formation of macroporous metal oxide structures involving the use of ionic liquids.

We think that the water-immiscible ionic liquids used in the current study may lead to the formation of unique oil-in-oil (o/o) emulsions for the synthesis of morphologically interesting metal oxides. These polar ionic liquids do not dissolve in nonpolar solvents such as 1-octadecene and diphenyl ether adopted here, as witnessed by the phase separation upon cessation of stirring. However, the relatively polar ionic liquids and the nonpolar 1-octadecene or diphenyl ether may form metastable emulsions under the vigorous stirring conditions adopted in our synthesis. Therewith, we postulate that the ionic liquid droplets may serve as templates for the formation of macroporous structures. A similar model was proposed by Imhof and Pine for the preparation of uniform macroporous ceramics and plastics by emulsion templating,<sup>48</sup> although no ionic liquid was involved in any of those studies. Kimura and co-workers also proposed a similar model for the preparation of semicrystalline TiO<sub>2</sub> films containing hierarchical mesopores and macropores.<sup>50</sup> In their model, water-miscible triblock copolymer in water templates the formation of mesopores whereas water-immiscible 1,3,5-triisopropylbenzene droplets induce the formation of macropores surrounding the droplets. An alternative explanation to our empirical observations is that ionic liquids themselves are known to direct the self-organization of nanoparticles into unique architectures,<sup>11,16,26–28</sup> and that the ionic-liquid-modified metal oxide nanoparticles may undergo self-assembly into patterned macroporous patterns. Chen and Dong also fabricated macroporous Pt patterns composed of ionic-liquid-modified Pt nanoparticles at the air–water interface.<sup>28</sup> They mentioned that the driving force for such self-assembly is the tendency for reducing interfacial energy.<sup>28</sup> The detailed mechanism on the formation of patterned structures using these novel ionic-liquid-based mixed solvent systems warrants further systematic investigation.

#### 4. Conclusions

Macroporous TiO<sub>2</sub> structures comprising semicrystalline TiO<sub>2</sub> nanoparticles were fabricated by using a combination of 1-octadecene and [C<sub>*n*</sub>Mim][Tf<sub>2</sub>N] (*n* = 4, 8, 16) as the reaction

medium under vigorous stirring. The overall morphology of the resultant TiO<sub>2</sub> is dependent upon the chain length of the ionic liquid used, presumably due to the different physicochemical properties of the ionic liquids. The methodology was also extended to the self-assembly of ZrO<sub>2</sub> and Fe<sub>3</sub>O<sub>4</sub> nanoparticles into patterned macroporous structures. The macroporous structures collapse after undergoing high-temperature calcination to remove capping organic species, and mesopores caused by the random packing of nanoparticles open up.

To the best of our knowledge, the self-assembly of metal oxide nanoparticles into patterned macroporous structures involving the use of ionic liquids has never been reported. Although the synthesis mechanism is not particularly clear at the moment, the formation of oil-in-oil (o/o) emulsions may provide a feasible explanation. Alternatively, the structure-directing role of ionic liquids in self-assembly may also be considered. Further systematic experiments may be carried out by using different ionic liquids with different cations, anions, solubilities, and viscosities, by varying the concentrations of reagents and ionic liquids involved, by changing the sizes and shapes of droplets, by tuning the stirring rate and reaction temperature, and by attempting to synthesize other metal oxides, metal chalcogenides, and metal salts using this methodology. The detailed synthesis mechanism deserves further research in the future.

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**Supporting Information Available:** Further details of the synthesis of ZrO<sub>2</sub> and Fe<sub>3</sub>O<sub>4</sub>, SEM images, HRTEM and Z-contrast TEM images, XRD patterns, FT-IR data, and N<sub>2</sub> adsorption–desorption isotherms. This material is available free of charge via the Internet at <http://pubs.acs.org>.