

水热条件下金红石纳米晶在离子液体[C₁₂mim]Cl 中的制备

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摘要: 在室温离子液体 1-十二烷基-3-甲基氯化咪唑([C₁₂mim]Cl)中,通过水热法制备了具有单晶结构的金红石纳米材料。采用 X 射线衍射、扫描电镜和透射电镜对样品进行了表征,结果显示所得样品为纯金红石相,形貌呈棒状。扫描电镜和透射电镜图样显示金红石纳米棒的直径约为 15 nm,长度在 10~100 nm 之间。高分辨透射电镜图样显示金红石纳米棒为单晶结构,并沿 *c* 轴方向生长。实验结果表明离子液体[C₁₂mim]Cl 中的 Cl⁻有利于金红石相生成,[C₁₂mim]⁺起到了模板剂的作用并提高了金红石纳米棒的结晶度。

关键词: 金红石纳米晶; 离子液体; [C₁₂mim]Cl

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Preparation of Rutile Nanocrystal in Ionic Liquid of [C₁₂mim]Cl Solution under Hydrothermal Condition

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Abstract: The rutile nanomaterials with single crystal structure were prepared in room temperature ionic liquid (IL) of 1-dedocyl-3-methylimidazole chlorid ([C₁₂mim]Cl) under hydrothermal condition. Characterizations of the products were performed by XRD, SEM, and TEM. XRD results reveal that only rutile phase is formed in the ionic liquid of [C₁₂mim]Cl. SEM and TEM micrographs show that rod-like rutile nanocrystals are generated with diameter of 15 nm and variable length from 10 to 100 nm. HRTEM micrographs illustrate that the rutile particles are real single crystal and grow along *c*-axis. It is suggested that the formation of rutile crystals is due to the presence of ionic liquid. Not only does the Cl⁻ favor the formation of rutile phase, but the [C₁₂mim]⁺ also plays a role as template and enhances the particles crystallization.

Key words: rutile nanocrystal; ionic liquids; [C₁₂mim]Cl

0 Introduction

Titanium dioxide (TiO₂) is a versatile material and has been investigated extensively due to its unique optoelectronic and photochemical properties, such as high refractive index, high dielectric constant, and excellent optical transmittance in the visible and near-IR region as well as high performance photocatalysis for

water splitting and for degradation of organics^[1-2]. TiO₂ exists in three main crystalline forms (anatase, rutile, brookite), and each crystalline structure presents different physical and chemical properties with different functionalities. In general, anatase possesses higher electrochemical performance than rutile phase, whereas rutile has higher chemical stability and refractive index. In recent years, rutile nanomaterials

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have received increasing attention because it has been demonstrated comparable performance to anatase in application to photocatalysis, dye-sensitized solar cells (DSCs) and so on^[3-6]. However, the synthesis of rutile nanomaterials usually requires time-consuming reactions at elevating temperature, even via hydrothermal processes^[7-12]. Therefore, a feasible synthesis of rutile nanomaterials with high crystallinity under mild condition is still a challenge target.

Recently, a new solvent system, room-temperature ionic liquids (ILs), has been developed and widely used as a new kind of reaction media owing to their intrinsic properties^[13]. Many inorganic nanostructures^[14-16], including titanium dioxide^[17-23], have been fabricated via various ILs-involved processes. Here we report the preparation of well crystalline rutile nanorods in presence of ionic liquid of 1-dedocyl-3-methylimidazole chlorid ([C₁₂mim]Cl) and the corresponding mechanism.

1 Experimental

A typical preparation of rutile nanocrystals was as follows: 0.5 mL of TiCl₄ and 1 g of [C₁₂mim]Cl (The [C₁₂mim]Cl was pre-synthesized and purified according to literature^[24].) were dissolved in 20 mL of HCl (0.5 mol · L⁻¹) under strong magnetic stirring till the solution became transparent. And then, the solution was transferred to a Teflon-lined stainless steel autoclave and kept at 120 °C for 12 h. The final white precipitates were filtrated and washed several times using deionized water and ethanol in turn, until pH value of the filtrate was about 7, and then was dried overnight at 80 °C. Finally, white powder was obtained (sample A). A control experiment was used to reveal the effect of [C₁₂mim]Cl. The sample obtained from the control was denoted as sample B. Sample B was also composed of white powder.

XRD patterns of the samples were recorded on a Rigaku D/max 2500 V/PC diffractometer using Cu K α radiation ($\lambda=0.154\ 056\ \text{nm}$ after K α 2 stripping, 40 kV, 100 mA), employing a scanning rate of $0.033^\circ \cdot \text{s}^{-1}$ in the 2θ range from 20° to 65° . The morphology and size of samples were characterized by scanning electron microscopy (SEM) on Rigiku 6700F (10 kV) and

transmission electron microscopy (TEM) images (JEOL-1011, 100 kV). High resolution transmission electron microscopy (HRTEM) was also used to get more structure details of rutile nanocrystals on Tecnai G2 20 S-Twin transmission electron microscope (200 kV).

2 Results and discussion

The crystal forms for as-prepared samples obtained are shown in Fig.1. A is the XRD patterns of TiO₂ particles obtained in [C₁₂mim]Cl. It is easily seen that all diffraction peaks of the sample A are in good agreement with the standard rutile pattern (PDF No. 65-0191). No other peaks at 25° or 31° are found, indicating that this sample is free from both anatase and brookite crystal phases. Moreover, the sharper diffraction peaks imply the higher crystallinity of rutile grains in sample A. On the other hand, the sample B prepared in absence of [C₁₂mim]Cl is not such a pure rutile phase. The weak peak at 25° (marked by asterisk) indicates the impurity of anatase.

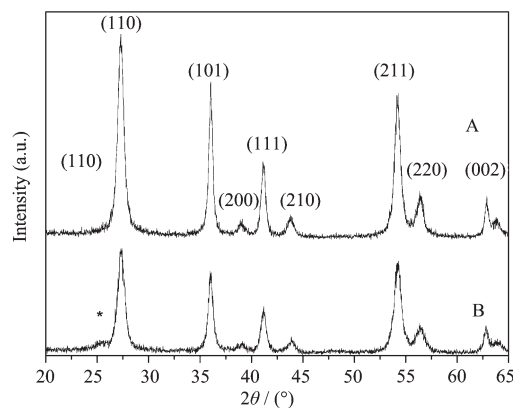


Fig.1 XRD patterns for as-prepared rutile nanoparticles within [C₁₂mim]Cl (A) and without [C₁₂mim]Cl (B) at 120 °C for 12 h

The electron microscopy images (SEM and TEM) for the as-prepared rutile nanoparticles are shown in Fig.2. a and b are SEM and TEM micrographs of as-prepared sample A in the presence of [C₁₂mim]Cl, respectively. The rod-like nanoparticles are clearly observed and the size is about 20 nm in diameter and 50 ~100 nm in length. As a comparison, the SEM micrographs of sample B are shown in c. Unlike the sample A, the sample B contains many irregular

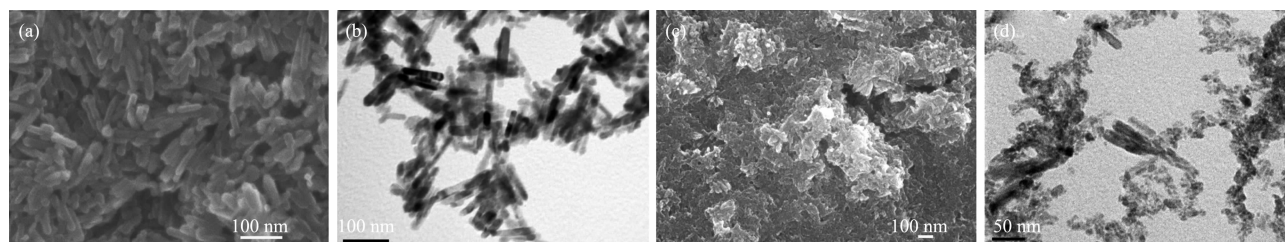


Fig.2 Electron micrographs for as-prepared rutile particles: (a) and (b) are sample A, (c) and (d) are sample B

nanoparticles. One can see that some particles present rod-like embryos, but radially aggregate together. It suggests that the [C₁₂mim]Cl favors the formation of rutile nanorods and increases the rutile nanorods crystallinity. TEM micrograph (Fig.2d) shows that few nanoparticles have rod shape, indicating low crystallinity. This is also consistent with the results obtained from XRD pattern and SEM micrographs, which suggest that [C₁₂mim]Cl enhances the crystallization of the rutile nanocrystals.

The HRTEM obtained micrographs of sample A are shown in Fig.3. The dimension of rutile nanorods is uniform in diameter, but various in lengths, indicating that the rutile particles grow up lengthwise. White arrows of A and B, respectively, point out the cubic and rod-like nanocrystals. The corresponding high magnification images are illustrated by Fig.3b and c.

Both of images reveals the rutile particles are single crystalline with interplanar spacing of about 0.327 nm (Fig.3b and c) and 0.249 nm (Fig.3c), respectively, which correspond to the (110) and (101) crystalline planes. It is possible that the rutile nanorods grow up by stacking along [101] direction lying on the (110) plane, which is the most thermodynamically stable plane of rutile. However, as demonstrated by most cases of previous works^[10,25-28], rutile nanoparticles would like to grow up along [001] direction to form nanorods or nanowhiskers. This is mainly due to the highest surface free energy of (001) surface^[29]. However, the obtained rutile nanocrystals in this system present stacking growth of Ti-O octahedrons along [101] direction. We attribute it to the effect of [C₁₂mim]⁺, which serves as the template to control the crystals growth by capping on the surface.

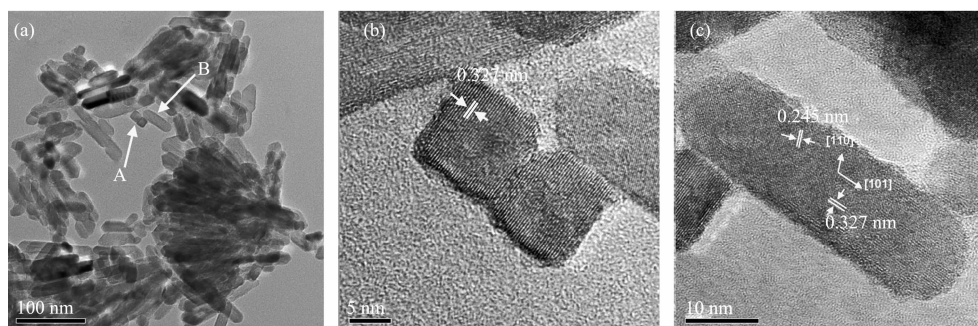


Fig.3 HRTEM micrographs for sample A, (a) low magnification image, (b) high magnification image of cubic particles pointed out by arrow A, (c) high magnification image of rod-like particles pointed out by arrow B

Based on our results, we suggest here a formation mechanism for rutile nanocrystals. Anatase is the crystal phase that forms first in all solution synthesis process^[25-27], thus the formation of anatase is inevitable at the early stage of the reaction process in diluted solution of HCl in absence of [C₁₂mim]Cl (Fig.1b). As a kind of electrolyte, [C₁₂mim]Cl will provide concentrated Cl⁻ to favor the formation of rutile nuclei

in solution^[22]. Furthermore, [C₁₂mim]⁺ can also act as template by covering on the particle surface to arrange the particle growth. In general, H atoms of imidazolium ring, which preferentially form H bonding with anions in absolute ionic liquid^[33], are readily adsorbed on (001) surface and hinder the Ti-O octahedrons stacking along [001] direction. Consequently, (101) surface is preferentially selected as growth plane. Although the

above discussion explains the formation of rutile crystals, nevertheless, further investigations are still needed to get further understanding of the formation mechanism for the present rutile nanocrystals.

3 Conclusions

In summary, rutile nanocrystals with rod shape in the presence of ionic liquid of $[\text{C}_{12}\text{mim}]\text{Cl}$ on a large scale. The XRD, SEM and TEM results show that the as-prepared rutile nanorods in IL are about 20 nm in diameter and 50 ~100 nm in length. The formation mechanism on rutile nanorods is also suggested.

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