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An Ionic Liquid-assisted Hydrothermal Synthesis of CeO_2 Nanorods

CHEN Ting, JIANG Wei-Hui, ZHANG Xiao-Jun, XIE Zhi-Xiang, LIU Jian-Min, JIANG Wan

(School of Material Science and Engineering, Jingdezhen Ceramic Institute, Jingdezhen 333001, China)

Abstract: CeO_2 nanorods were synthesized by a hydrothermal method at 160℃ from $CeCl_6{\cdot}6H_2O$ and $NH_3{\cdot}H_2O$ in the presence of an ionic liquid 1-butyl-3-methyl-imidazolium chloride ([Bmim]Cl). The phase and morphology of the resulting products were characterized by X-ray diffraction (XRD) and high-resolution transmission electron microscopy (HRTEM), respectively. The results reveal that morphology of CeO_2 prepared in the presence of the ionic liquid is nanorod while it changes to irregular nanoparticle without ionic liquid. The resulting nanorods are about 13–25 nm in diameter and 200–500 nm in length. With the increase of ionic concentration, nanorods were disappeared gradually and nanoparticles were obtained. Moreover, increasing the hydrothermal temperature to 180℃, nanospheres at size of 19–24 nm could be synthesized by aggregation of ~2 nm nanocrystals.

Key words: cerium oxide; soft template; hydrothermal treatment; ionic liquid; nanorod

Nanorods have attracted great attention due to their so-called size- and shape-dependent physical properties. The ability to control the uniformity of the size, shape, composition, crystal structure, and surface properties is essential for investigating and exploiting their unique properties[1]. In recent years, CeO_2 has received intense interest owing to its wide direct band gap (E_g=3.15 eV), high dielectric constant (ε=24.5), excellent chemical and thermal stability[2]. Therefore, it has widespread applications in catalysts[3], fuel cells[4], oxygen permeation membranes[5], optical films[6], gas sensors[7], and other fields. Controllable synthesis of CeO_2 nanostructure with different morphologies and sizes has been reported by many researchers in the recent years, such as nanoparticles[2], nanotubes[8], nanorods[2], and nanowires[3]. However, it is hard to form 1D nanocrystals due to its isotropic structure while truncated octahedral shaped CeO_2 particles have been obtained[9]. Li, *et al*[2] reported that CeO_2 nanorods were prepared by CTAB assisted method at room temperature. Hydrothermal synthetic route was reported as another facile and efficient way to obtain CeO_2 nanorods[10-12]. The raw materials and the surfactants were the critical conditions for the formation of CeO_2 nanorods[11-12]. However, different surfactants have different effects on the growth kinetics of CeO_2 nanorods[11], and the detailed mechanisms are still unknown.

Ionic liquid (IL) is a widely used solvent and template to synthesis inorganic materials due to its low volatility, wide liquid temperature range, good thermal stability, good dissolving ability, designable structures, high ionic conductivity, and wide electrochemical window, and so on[13-17]. Especially, it is considered to be a “green” solvent compared with other environmentally malignant chemicals and organic solvents, thus, increasing worldwide interest in inorganic synthesis. Some inorganic materials, such as sheaf-like CuO[13], narcis-like ZnO[14], ZnO nanorods[15], SnS and LaF_3 nanoparticles[16-17], have been prepared in ILs. For CeO_2 nanostructure, Li, *et al*[18] reported CeO_2 monodisperse spheres with diameter of 100–150 nm, which were aggregated of 3.5 nm nanocrystals in the presence of IL ([C_{16}Mim]Br) as a template and solvent. Brezesinski, *et al*[19] fabricated the mesoporous CeO_2 thin film by using [C_{16}Mim]Cl as a template. In this study, the CeO_2 nanorods were synthesized *via* IL combined hydrothermal method. The morphology of the resulting products was investigated and the possible explanation for the formation structure was also presented.

1 Experimental

In a typical process, 5 mmol $CeCl_3{\cdot}6H_2O$ and ionic liq-

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Biography: CHEN Ting (1984–), female, candidate of PhD. E-mail: chenting12@gmail.com

Corresponding author: JIANG Wei-Hui (1965–), professor. E-mail: jwhjiang@163.com

uid [Bmim]Cl were dissolved in 10 mL deionized water under vigorous stirring, and then 15 mL diluted $NH_3 \cdot H_2O$ (25wt%) was added dropwise until the solution change from transparent to purple. The addition amount of [Bmim]Cl was 5, 10 and 25 mmol, respectively. Then, the mixture was transferred to a Teflon-lined autoclave and maintained at 160℃ for 24 h, and cooled to room temperature. Finally, the yellow precipitate was separated by centrifugation, washed with deionized water and absolute ethanol several times and dried. The structure and morphology of the resulting product were characterized by using XRD (Rigaku TTRIII), SEM (JSM-6700F, JEOL), HRTEM (JEM-2010, JEOL), FTIR (Nicolet 5700) and XPS (PHI Quantera SXM).

2 Results and discussion

The crystallinity and phase characteristics of products were analyzed by using XRD patterns of the samples, as shown in Fig. 1. All the diffraction peaks are in agreement with the JCPDS file (JCPDS 81-0792, a=b=c=0.54184 nm), which can be indexed as a cubic fluorite phase of cerium with space group Fm3m (225). No peaks attributable to other phase, such as $Ce(OH)_4$ or other components, are observed in the patterns, indicating that IL combined hydrothermal method is an effective approach to synthesize pure CeO_2. The mean crystallite size of the synthesized CeO_2 sample in the presence of IL has an average grain size of 12 nm which is calculated based on the Scherrer's equation. Furthermore, for the prepared CeO_2 sample in absence of IL, the increase in crystallinity is observed.

Figure 2 presents the FT-IR spectra of the as-prepared CeO_2 and IL. The peaks at 1570 and 1168 cm^{-1} assigned to imidazolium $V_{(C–N)}$ stretching and $V_{(C–H)}$ stretching of [Bmim]Cl[13]. The peaks at 2958, 2931 and 2850 cm^{-1} assigned to alkyl $V_{(C–H)}$ stretching, while around 1458 cm^{-1} assigned to alkyl $V_{(C–H)}$ bending[13]. For the broad band centered around 3400 cm^{-1} is attributed to –OH stretching of adsorbed water on the surface of the as-prepared CeO_2. In addition to the bands in the 850–1600 and 2800–3000 cm^{-1} regions due to the Ce–O stretching frequency below 450 cm^{-1}, which confirms the formation of CeO_2[2]. No peaks attributable to IL is observed for the as-prepared CeO_2, indicating that the IL is weakly adsorbed on the surfaces of CeO_2 nanorods and has been removed entirely after washing. Figure 2(b) shows the EDS spectrum of the CeO_2 nanorods. It confirms that the sample only contains Ce and O elements, and no peaks from other elements can be observed. XPS measurement of the nanorods is shown in Fig. 2(c). The binding energies in the XPS spectra presented are calibrated using the C1s signal (285 eV). The wide energy scan also reveals that the CeO_2 consists of Ce and O elements and the IL molecules can be completely removed.

The electron microscopy images of the as-prepared nanorods are shown in Fig. 3. It is obviously that nanorods is facilely synthesized by hydrothermal procedure with IL assisted, and the size of the nanorods is 13–25 nm in diameter and 200–500 nm in length, which is longer than the reported CeO_2 nanorods[2,13]. According to the HRTEM image in Fig. 3 (c), it shows that the interplanar spacing isabout 0.31 nm, close to the {111} lattice spacing of CeO_2. The selected area electron diffraction (SAED) pattern in

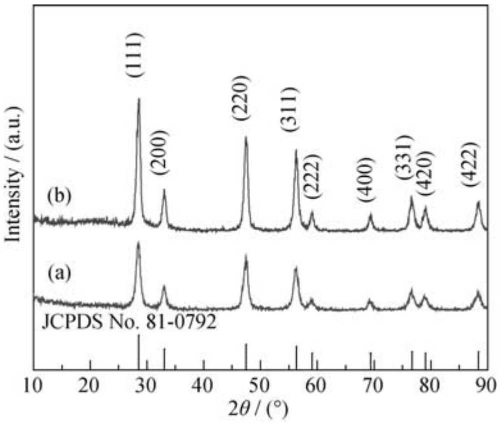

Fig. 1 XRD patterns of the as-synthesized CeO_2 in ionic liquid [Bmim]Cl (a), and in absence of [Bmim]Cl (b)

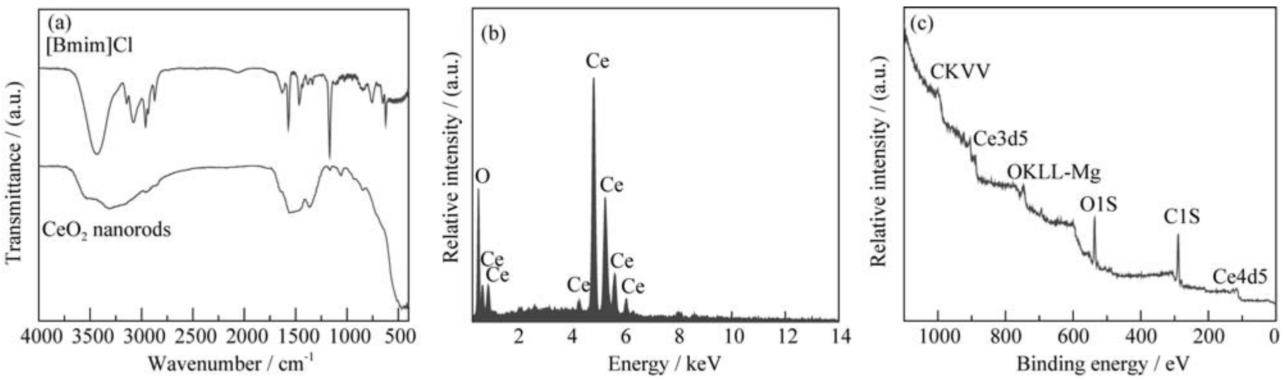

Fig. 2 FT-IR (a), EDS (b) and XPS (c) spectra of the as-synthesized CeO_2 nanorods

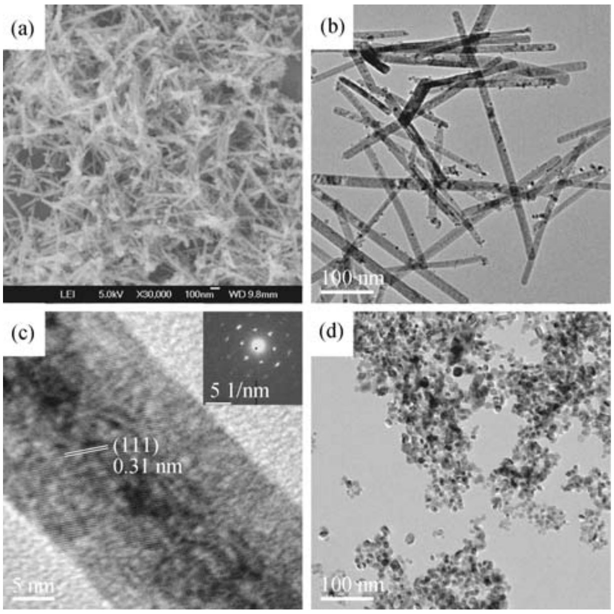

Fig. 3 Typical SEM (a), TEM (b), HRTEM (c) images of the as-synthesized CeO_2 in IL at 160℃ with molar ratio n_{IL}/n_{Ce}=1, and TEM image in absence of IL (d)
The inset in (c) shows the SAED pattern

inset confirms that the nanorods have a monocrystalline structure. Indeed, no regular nanostructure can be found in the absence of IL during the hydrothermal process, as shown in Fig. 3(d).

When the addition amount of IL was increasing gradually (n_{IL}/n_{Ce}=2, 5), CeO_2 nanorods changed to nanoparticles, as shown in Fig. 4(a) and 4(b). Meanwhile, hydrothermal temperature plays another important role in the preparation of CeO_2 nanorods. Increasing temperature to 180℃, all of the nanorods disappear, while nanosphere with the diameter of 19–24 nm is observed as the aggrega tion of the primary ~2 nm nanocrystals (Fig. 4(c)). In order to study the formation mechanism, the mixed solution before hydrothermal treatment was also examined. The thin and delicate nanofilms were fabricated by organics and a bit of CeO_2 nanocrystals (Fig. 4(d)).

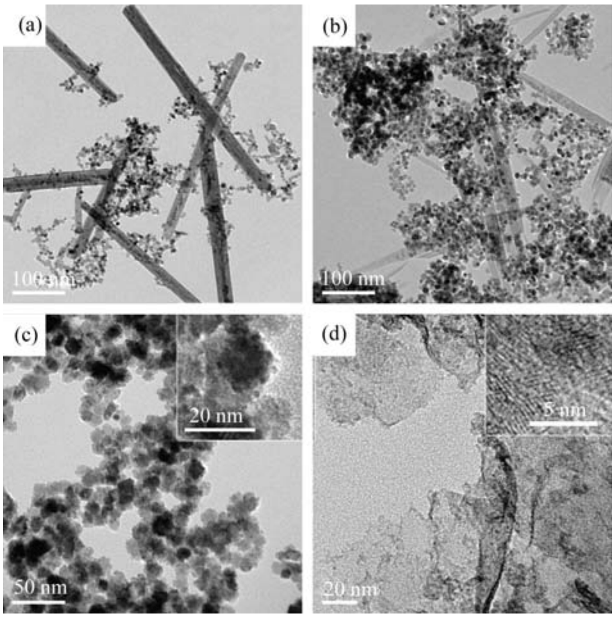

Fig. 4 TEM images of as-synthesized CeO_2 with the molar ratio n_{IL}/n_{Ce}=2 at 160℃ (a), n_{IL}/n_{Ce}=5 at 160℃ (b), n_{IL}/n_{Ce}=2 at 180℃ (c), and the mixed solution before hydrothermal treatment (d)

Summing up the above results, the most plausible formation mechanism of CeO_2 nanostructure is shown in Fig. 5. At the beginning of the experiment, hydrolysis $CeCl_3 \cdot 6H_2O$ gives rise to the formation of CeO_2 nuclei. The ionic pairs of the IL which has large cation $[Bmim]^+$ and anion Cl^- are adsorbed around it and act as self assembly template[15]. Therefore, the long chain of IL hinders the increasing rate of particles, and preorganized solvent structure encourages the CeO_2 to undergo self organization for the formation rod-like structure[15,20]. Without the aid of IL, the resulting CeO_2 is irregular. Moreover, it is well known that ILs have lower surface tension than normal solvent, such as 40 mN/m and 72 mN/m for [Bmim]Cl and water, respectively[21]. Therefore, when the IL is excessive (n_{IL}/n_{Ce}=2 or 5), the nucleation rate of CeO_2 becomes quicker. In addition, the excessive IL increases the viscosity of the solution and slows down the mass transfer[11], resulting the nanoparticles formation. Increasing the hydrothermal temperature, the primary ~2 nm nanocrystals were synthesized with the assistance of IL, which played a critical role in controlling the size distribution of the nanocrystals. Subsequently, these primary nanocrystals spontaneously aggregated to form the nanospheres with diameter of 19–24 nm due to the demands of energy minimization, and the IL molecules absorbed on the surface of nanocrystals were eventually removed[22]. Therefore, the addition of IL not only affects the rate of nucleation during the oxide crystallization, but also influences the growth which is essential to predict the size and the shape of the nanomaterials.

3 Conclusion

CeO_2 nanorods were prepared by a hydrothermal method assisted by an ionic liquid [Bmim]Cl. High level of crystallinity and no contamination of $Ce(OH)_4$ or other components were proved from the XRD, FT-IR, EDS and XPS analysis of the as-synthesis CeO_2. TEM results revealed that without the aid of [Bmim]Cl, CeO_2 nanocrystals with no regular morphology were obtained. The IL served as a template and solvent for the formation of CeO_2 nanostructure. It benefits the formation of oriented nucleation, leading to the construction of anisotropic growth of the

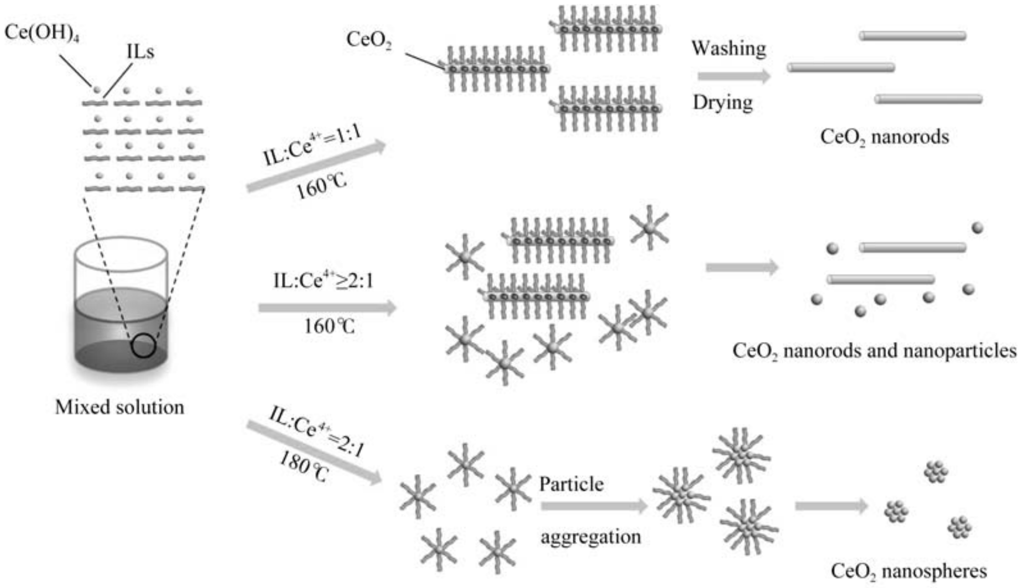

Fig. 5 Schematic illustration of the formation mechanism of CeO_2 with various morphologies *via* IL combined hydrothermal method

nanorods. Increasing the IL addition amount, the nanorods were changed to nanoparticles. Moreover, higher hydrothermal temperature leads to the generation of nanospheres with diameter of 19–24 nm, which are aggregated of ~2 nm nanocrystals.

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离子液体辅助水热合成 CeO_2 纳米棒

陈 婷, 江伟辉, 张筱君, 谢志翔, 刘健敏, 江 莞

(景德镇陶瓷学院 材料学院, 景德镇 333001)

摘 要: 以 $CeCl_6·6H_2O$ 和 $NH_3·6H_2O$ 为原料, 使用离子液体 1-丁基-3 甲基咪唑氯盐([Bmim]Cl)辅助水热法在 160℃下合成了 CeO_2 纳米棒。采用 X 射线衍射(XRD)和高分辨透射电子显微镜(HRTEM)对样品的结构和形貌进行了表征。实验结果表明: 使用离子液体辅助水热法制备的产物为 CeO_2 纳米棒, 而没有离子液体时产物则为外形无规则的纳米颗粒。所制备的纳米棒直径为 13~25 nm, 长度为 200~500 nm。增大离子液体的用量将得到纳米颗粒。此外, 升高水热温度至 180℃所得样品为直径 19~24 nm 的纳米球, 该纳米球由 2 nm 的纳米晶团聚而成。

关 键 词: 氧化铈; 软模板; 水热; 离子液体; 纳米棒

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