

Synthesis of CeO₂ nanosheets with a room temperature ionic liquid assisted method

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Abstract: CeO₂ nanosheets were directly synthesized by a precipitation process with the aid of 1-butyl-3-methyl-imidazolium ionic liquids at room temperature. The anion species and the concentration of the room temperature ionic liquids (RTILs) have a great influence on the morphology of the resulting products. The as-prepared CeO₂ is irregular and agglomerated seriously in the absence of RTILs, while it changes from nanocube to nanosheet with increasing the RTIL concentration or decreasing the polarity and hydrophilicity in the orders [Bmim]Cl > [Bmim]Br > [Bmim]BF₄ > [Bmim]PF₆. The CeO₂ nanocubes have relatively uniform grain size distribution with size of 4.5–6.4 nm, and the nanosheets are assembled by a great deal of nanocrystalline whose length and width extend to hundreds of nanometers. The as-synthesized CeO₂ exhibits an excellent removal capacity for the organic pollutant Congo red dye, indicating its potential use in practical wastewater treatment.

Keywords: ceria; nanocrystalline; ionic liquid; room temperature; catalysis

1 Introduction

Cerium oxide (CeO₂), as a wide band gap semiconductor oxide ($E_g = 3.15$ eV), has attracted a great deal of attention due to its widespread applications in catalysts, fuel cells, optical films, polishing materials, gas sensors, etc. [1,2]. Recently, controlled synthesis of nano-sized CeO₂ with desirable morphology and structure has become one of the essential topics in material and chemistry science, owing to its unique physical and chemical properties when its size is reduced to nanometer scale. Therefore,

nano-sized CeO₂ with different shapes, such as nanoparticles [1], nanotubes [3], nanopolyhedrons [4], nanorods [2], and nanowires [5], etc., was reported in recent years. However, chemical synthesis of nano-sized CeO₂ with environmental friendly and economical efficient pathways, which is suitable for large-scale production, still remains a tremendous challenge.

Room temperature ionic liquids (RTILs) are well-known “green” solvents used widely in organic synthesis because of their low vapor pressure, wide liquid range, high ionic conductivity, high thermal stability, and extreme solvency [6–8]. Especially, RTIL assisted route can avoid the thermal treatment at high temperature, which means it is a low-cost, simple, and environmentally friendly way. There are various

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reports about the synthesis of inorganic nanomaterials in RTILs, such as zeolites [6], Pb_2Co [7], CuO [8], ZnO [9], TiO_2 [10], etc. For CeO_2 , Li *et al.* [11] developed a thermal treatment at 300°C to prepare monodisperse spherical CeO_2 of ca. 100–150 nm by using 1-hexadecyl-3-methylimidazolium bromide ($\text{C}_{16}\text{MimBr}$) as both template and solvent. In this paper, a new strategy was proposed to prepare CeO_2 nanosheets in RTILs at room temperature, which possesses extraordinary advantages, including single-step, scalable, and environmentally friendly. The effects of the RTIL species and the concentration on the morphology were investigated systematically. The potential explanation for the formation structure was also presented here.

2 Experimental

Nano-sized CeO_2 was obtained by using precipitation method with RTILs assisted. In this study, RTILs were 1-butyl-3-methyl-imidazolium ionic liquids, i.e., $[\text{Bmim}]\text{Cl}$, $[\text{Bmim}]\text{Br}$, $[\text{Bmim}]\text{BF}_4$, and $[\text{Bmim}]\text{PF}_6$. Briefly, a RTIL was dissolved with 10 mL deionized water and 22.5 mL $\text{NH}_3\cdot\text{H}_2\text{O}$ under stirring. Subsequently, a solution of $\text{CeCl}_3\cdot 6\text{H}_2\text{O}$ was added with mole ratios $n([\text{Bmim}]^+)/n(\text{Ce}^{3+})=0:1, 4:1, 8:1,$ and $12:1$. The mixture was stirred vigorously for 2 h, followed by being aged for 48 h, centrifugal washing, and air-dry. The structure and morphology of the resulting products were characterized by using X-ray diffraction (XRD, Rigaku TTRIII), transmission electron microscopy (TEM, JEM-2010, JEOL), Fourier transform infrared spectroscopy (FT-IR, Nicolet 5700), differential thermal analysis and thermogravimetric analysis (DTA–TG, PHI 5000C ESCA), and X-ray photoelectron spectroscopy (XPS, PHI Quantera SXM). The degradation of Congo red dye was carried out in an aqueous solution at room temperature using CeO_2 nanosheets as catalyst [1]. Briefly, the proper amounts (10 and 15 mg) of CeO_2 nanosheets were added to 50 mL of Congo red dye solution with different concentrations (50 and $80\text{ mg}\cdot\text{L}^{-1}$) under stirring vigorously. Subsequently, 4 mL of the dispersion was extracted and then centrifuged for 10 min to discard any sediment at different intervals. The concentration of the centrifuged solution was monitored through a wavelength scan on a UV-2401PC spectrophotometer.

3 Results and discussion

Figure 1(a) shows DTA–TG curves of the precipitates prepared by the RTIL assisted method. TG curve of the precipitates shows an overall weight loss of approximately 9% up to 400°C , while DTA curve presents only an endothermic peak at 150°C due to the evaporation of absorbed water, suggesting not any chemical reaction taken place at high temperature. The FT-IR spectra of $[\text{Bmim}]\text{Cl}$ and the prepared CeO_2 are shown in Fig. 1(b). The bands at 3143.6, 3078.5, and 1169.2 cm^{-1} are attributed to the stretching vibration of C–H in imidazole ring, while 1632.2, 1571.6, and 1465.9 cm^{-1} are related to the skeleton stretching vibration of the imidazole ring [8,9]. The bands at 2960.4, 2935.5, and 2870.8 cm^{-1} are related to the alkyl C–H stretching vibration [8,9]. The FT-IR spectrum of the prepared CeO_2 displays significant differences that the absorption bands at about 1510.2, 1356.6, and 1046.7 cm^{-1} are similar to the standard spectrum of CeO_2 Sadler (SDBS 40343) [1], indicating that the RTIL molecules can be completely removed by centrifugal washing. Figures 1(c) and 1(d) show the XRD patterns of the synthesized CeO_2 , which evidence that all the products are single phase cubic fluorite structure CeO_2 (JCPDS No. 81-0792) having space group $Fm\bar{3}m$ (225), without any detectable impurity phases. The peak intensity of the samples in the presence of RTILs is weaker than that of the blank one, and reduces in the orders: $[\text{Bmim}]\text{Cl} > [\text{Bmim}]\text{Br} > [\text{Bmim}]\text{BF}_4 > [\text{Bmim}]\text{PF}_6$, demonstrating that the RTIL species have obviously impact on the degree of crystallinity and the particle size. Moreover, the intensity decreases with increasing the RTIL amount, indicating the RTILs enhance the homogeneous distribution and reduce the particle size simultaneously.

Figure 2 presents the shape dependence of CeO_2 on the RTIL species. The particles are well-defined as nanocubes with the size range of 4.5–6.4 nm in the presence of $[\text{Bmim}]\text{Cl}$ (Figs. 2(a) and 2(b)). The similar morphology was reported in the hydrothermal process at 265 and 180°C by using oleylamine and polyvinyl pyrrolidone as surfactants [12,13], indicating that RTIL assisted method is a low-cost and efficient approach to synthesize CeO_2 nanocubes. The samples obtained in other three RTILs show nanosheet morphology (Figs. 2(c)–2(f)), and the area inverses to

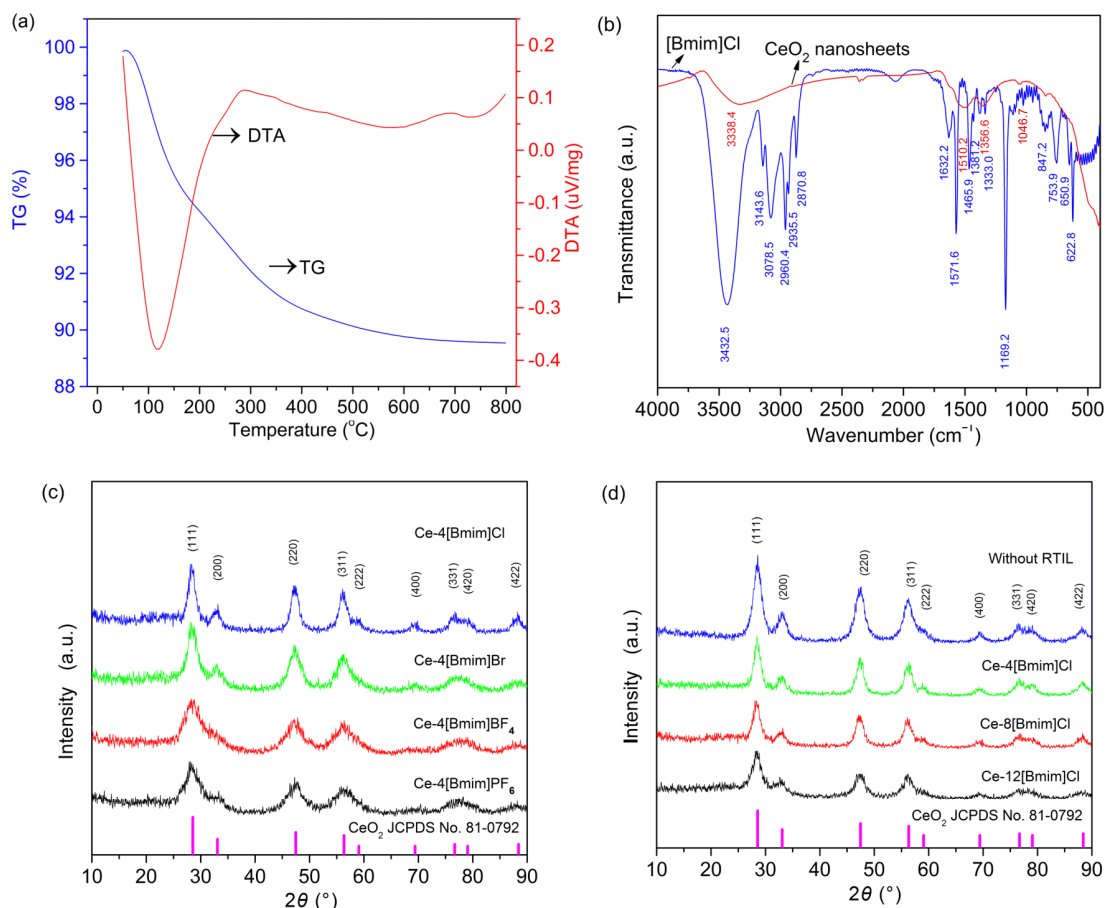


Fig. 1 (a) DTA–TG curves, (b) FT-IR spectra, and XRD patterns of the as-synthesized CeO₂ in the presence of (c) different RTIL species and (d) different amounts.

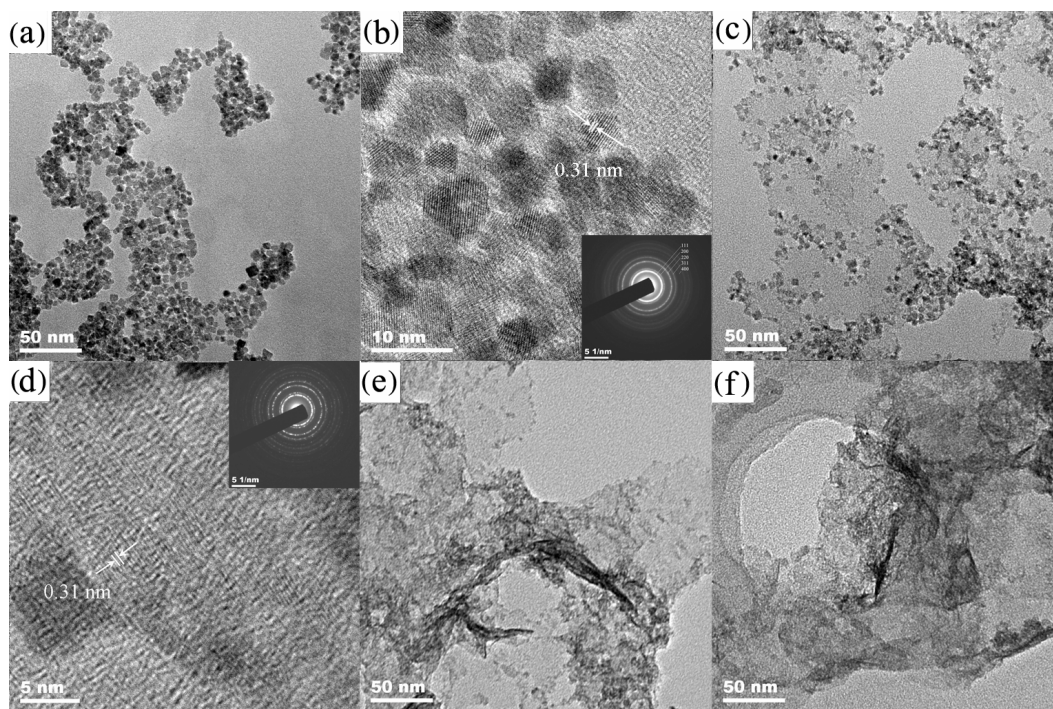


Fig. 2 TEM images of the as-synthesized CeO₂ in the presence of different types of RTILs with mole ratio $n[\text{Bmim}^+]/n(\text{Ce}^{3+}) = 4:1$: (a) and (b) [Bmim]Cl, (c) and (d) [Bmim]Br, (e) [Bmim]BF₄, and (f) [Bmim]PF₆.

the polarity and hydrophilicity ($[\text{Bmim}]\text{Cl}] > [\text{Bmim}]\text{Br}] > [\text{Bmim}]\text{BF}_4] > [\text{Bmim}]\text{PF}_6]$ [14]. The high polarity and hydrophilicity correspond to the easy nucleation, followed by template to nanocube shape. On the contrary, lower polarity and hydrophilicity cause the weaker nuclei [14], which are generated and self-assembled to minimize the surface energy, and then transformed into CeO_2 nanosheets.

Figure 3 shows the TEM images of the samples obtained at different RTIL amounts. It clearly shows that the ceria particles obtained in the absence of RTILs are irregular and greatly agglomerated, while the samples develop to nanosheets and the degree of agglomeration decreases in the rise of the RTIL

amount. With increasing the RTIL amount, the viscosity of the solution is increased and the mass transfer slows down, resulting in the tiny primary building block formation and then oriented aggregation to nanosheets [15]. Summing up the above results, the most plausible formation mechanism of nano-sized CeO_2 via RTIL assisted method is shown in Fig. 4. The RTIL species and concentration not only affect the nucleation during the ceria crystallization, but also influence its growth and agglomeration processes. Large anion and high concentration of the RTILs are beneficial to the CeO_2 nanosheet formation.

Figure 5(a) illustrates the Ce 3d XPS spectra of CeO_2 nanosheets ($n([\text{Bmim}]\text{Cl}]/n(\text{Ce}^{3+}) = 12:1$). The

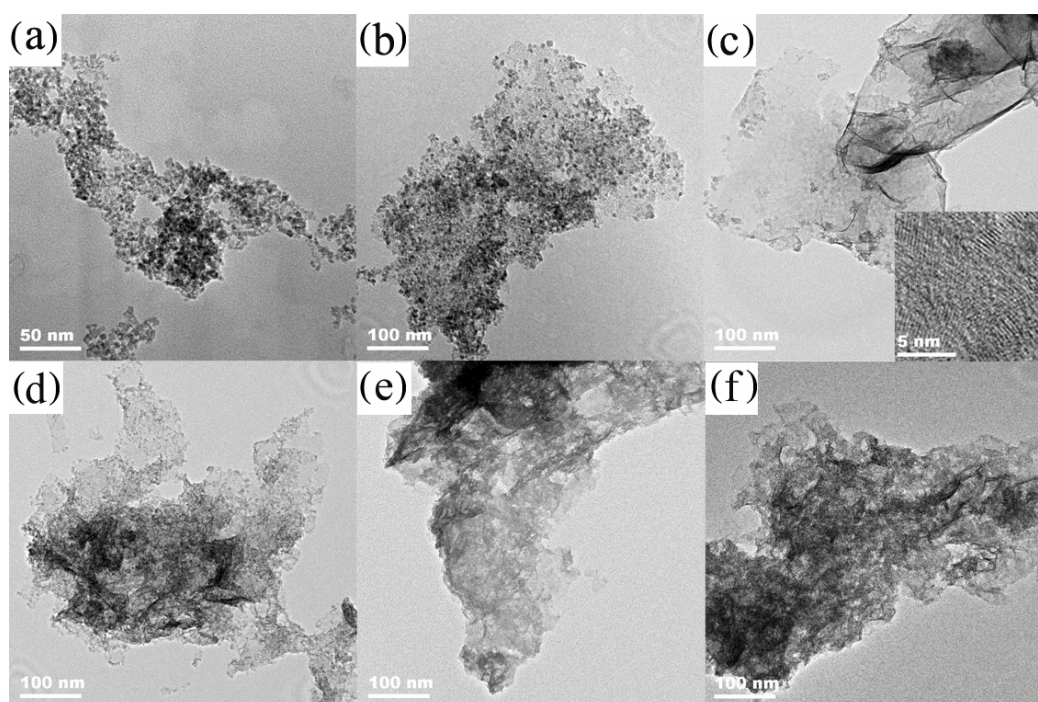


Fig. 3 TEM images of the prepared CeO_2 nanostructure with different mole ratios $n([\text{Bmim}]\text{Cl}]/n(\text{Ce}^{3+}) =$ (a) 0:1, (b) 8:1, (c) 12:1, and (d) $n([\text{Bmim}]\text{Br}]/n(\text{Ce}^{3+}) = 8:1$, (e) $n([\text{Bmim}]\text{BF}_4]/n(\text{Ce}^{3+}) = 8:1$, (f) $n([\text{Bmim}]\text{PF}_6]/n(\text{Ce}^{3+}) = 8:1$.

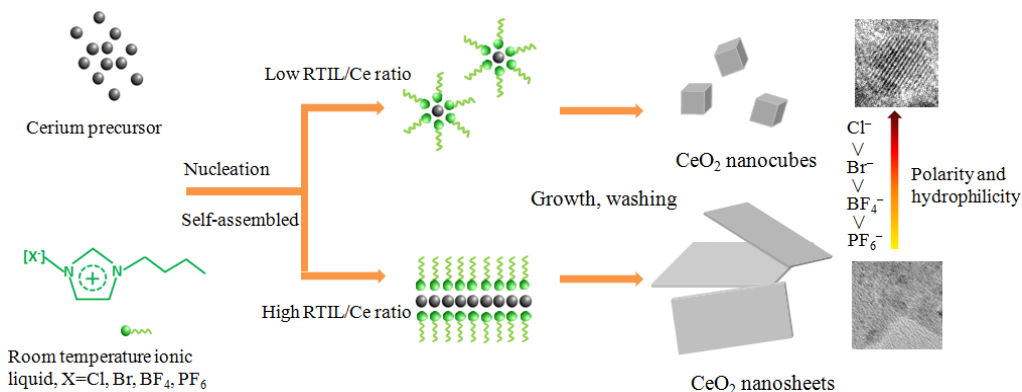


Fig. 4 Schematic diagram of the proposed mechanism for the formation of the nano-sized CeO_2 via RTIL assisted method.

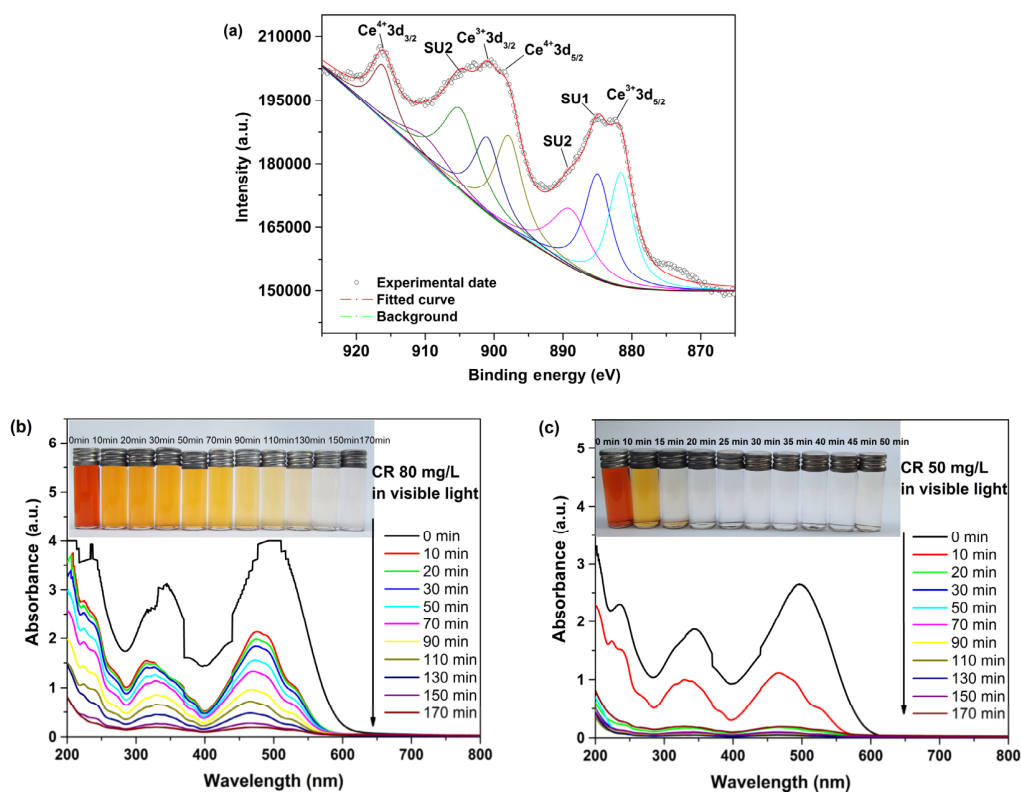


Fig. 5 (a) XPS spectra of the CeO₂ nanosheets and UV–Vis absorption spectra of CR solutions (50 mL) degraded by different amounts of CeO₂ nanosheets: (b) 300 mg·L⁻¹ and (c) 200 mg·L⁻¹.

peaks corresponding to Ce⁴⁺3d_{3/2} and Ce⁴⁺3d_{5/2} are located at binding energies of 916.6 and 898.6 eV, respectively [1,2]. Likewise, the peaks of Ce³⁺3d_{3/2} and Ce³⁺3d_{5/2} are shown at binding energies of 901.6 and 882.4 eV, respectively. The shake-up satellite peaks are observed at 907.6, 885.2, and 889 eV of Ce³⁺3d_{3/2} and Ce³⁺3d_{5/2}. The experiment result confirms that both tetravalent Ce⁴⁺ and trivalent Ce³⁺ coexist in the CeO₂ nanosheets, which is a result of oxygen vacancy [1,2]. The application of the CeO₂ nanosheets for the degradation of organic pollutant Congo red (CR) dye is illustrated in Figs. 5(b) and 5(c). It is obvious that the main absorption peaks of Congo red, i.e., 343 and 493 nm, have basically disappeared after a few minutes, indicating that the CeO₂ nanosheets have high catalytic activity due to the large surface area and presence of oxygen vacancies [1].

4 Conclusions

Pure fluorite type CeO₂ was achieved with the aid of ionic liquids at room temperature. The morphology was greatly influenced by RTIL species and concentration. The sample in the absence of RTILs

showed irregular morphology and great aggregation, while it changed from nanocubes to CeO₂ nanosheets when increased the RTIL amounts or decreased the polarity and hydrophilicity in the orders [Bmim]Cl > [Bmim]Br > [Bmim]BF₄ > [Bmim]PF₆. The CeO₂ nanosheets showed a great degradation performance of Congo red dye, making it a promising candidate for wastewater treatment.

Acknowledgements

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