## Ultrasonic-assisted Solution-Phase Synthesis and Property Studies of Hierarchical Layer-by-Layer Mesoporous CeO<sub>2</sub>

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Hierarchical layer-by-layer quadrangle CeO<sub>2</sub> was prepared through ultrasonic-assisted solution-phase synthesis strategy using cerium oxalate as the precursor. The as-prepared mesoporous CeO<sub>2</sub> displayed a surface area of 98.7 m<sup>2</sup> g<sup>-1</sup> and pore diameters of 2.0–10.0 nm. The high-resolution TEM image revealed that the layer structures of the CeO<sub>2</sub> were made of numerous nanocrystal particles with the crystallite size of about 13–15 nm. High energy and cavitation of ultrasonic wave assists cerium oxalate precursor in building the layer-by-layer quadrangle staking. UV–vis absorption spectrum showed that the direct allowed transition bandgap energy for the as-prepared CeO<sub>2</sub> was 2.91 eV. Moreover, the CeO<sub>2</sub> exhibited good photocatalytic property for degrading Rhodamine B solution under UV radiation.

Keywords: Mesoporous material, Nanostructure, CeO<sub>2</sub>, Optical properties, Catalytic properties

#### Introduction

Recently, ultrasonics sonochemical method has been proved to be a useful approach to obtain micronanostructual materials.<sup>1–5</sup> The cavitation phenomena derived from ultrasound can induce chemical changes, which lead to many unique properties in the irradiated solution and particles suspended in the same.<sup>6</sup> However, CeO<sub>2</sub> has been widely applied in catalysis,<sup>7</sup> oxygen sensors,<sup>8</sup> solid fuel cells<sup>9,10</sup>, UV adsorbents,<sup>11</sup> and so on. Among numerous CeO<sub>2</sub>, mesoporous CeO<sub>2</sub> has attracted much attention due to their porous structure and high surface area which can provide more active sites.<sup>12</sup> Many methods have been used to synthesize the mesoporous CeO2, including sol-gel chelating method,<sup>12</sup> electrospinning method,<sup>13</sup> microwave-assisted sol-gel method,14 solvothermal and hvdrothermal methods,<sup>15,16</sup> biotemplates method,<sup>17</sup> and so on. In this work, we report an ultrasonic-assisted solutionphase synthetic method to prepare mesoporous CeO<sub>2</sub> with layer-by-layer quadrangle structure. In addition, its optical and catalytic activities were investigated.

#### Experimental

All the chemicals and reagents were of analytical grade and used as received without further purification. First, preparation of cerium oxalate precursor by using ultrasonic reactor with working frequency being fixed at 400 Hz and electric power being controlled at 200 W (KQ5200B; Kunshan Shu Mei Ultrasonic Instrument Co., Ltd., China). In a water–glycerol complex solvent (5.0 mL water and 10 mL glycerol), 1.0 mL Ce(NO<sub>3</sub>)<sub>3</sub> (0.15 mM) aqueous solution was

added. After ultrasonic oscillation for 2 min, 1.0 mL cetyltrimethyl ammonium bromide (CTAB) aqueous solution  $(0.05 \text{ g mL}^{-1})$  and 1.0 mL oxalic acid aqueous solution (0.35 mM) were added dropwise into the mixture successively and white precipitates formed immediately. The above mixture was ultrasonic oscillated for another 5 min, centrifuged, washed with water, and dried at 70 °C for 12 h. Afterward, the above precursor was calcined in air at 400 °C for 4 h to obtain yellow CeO<sub>2</sub>. Structural analysis of the powder samples was performed by X-ray diffraction (XRD) using (ARL XTRA diffractometer, ARL, Switzerland) using Cu-K $\alpha$  radiation with 2 $\theta$  from 5 to 80°. The TG measurement was operated on an (STA449F3 apparatus, NETZSCH-Gerätebau GmbH, German) with 10 °C min<sup>-1</sup> heating rate. The Brunauer-Emmett-Teller (BET) analysis was conducted with (3Flex instrument, Mike company, USA) at -196 °C and the pore-size distributions were calculated by the Barrett-Joyner-Halenda (BJH) method. The microstructure investigations were carried out on Quanta FEG450 field-emission scanning electron microscopy (SEM, FEI company, USA) and JEOL JEM-2010F transmission electron microscope (TEM). Optical absorption spectra were obtained from (Shimadzu, Shimadzu Corporation, Japan) UV-2600 UV-vis spectrophotometer. Photocatalytic activity was evaluated through Rhodamine B (RhB) decomposition under UV irradiation. Typically, CeO<sub>2</sub> (0.2 g) was dispersed in 250 mL RhB aqueous solution (10 mg  $L^{-1}$ ). The reaction cell was bubbled with air. After the dispersion was stirred for 60 min in the dark to ensure adsorption-desorption equilibrium, it was exposed to UV irradiation. At 20-min interval, 5 mL dispersions were taken out and centrifuged for measuring the absorbance.

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Figure 1. XRD pattern of the as-made cerium oxalate precursor.

#### **Results and Discussion**

Figure 1 shows the diffraction peak index of the cerium oxalate precursor, which can be readily indexed to the known bulk monoclinic phase cerium oxalate decahydrate coordination polymer  $[Ce_2(C_2O_4)_3 \cdot 10H_2O]_{\infty}$ .<sup>18</sup>

Figure 2 displays the thermal decomposition results of the precursor, which reveals two weight-loss processes. The one below 250 °C is corresponding to the dehydration of precursor and another one from 250 to 350 °C is ascribed to decomposition of cerium oxalate with the residue being CeO<sub>2</sub>. The TG experiment suggests that heating cerium oxalate precursor above 350 °C can obtain CeO<sub>2</sub> and the CeO<sub>2</sub> obtained may contain voids. In order to ensure decomposition of cerium oxalate precursor, 400 °C was selected as decomposition temperature in the later experiments.

Figures 3 and 4 exhibit structural analyses of the sample decomposed from the precursor at 400 °C in air, which confirms above inferences. All the diffraction peaks can be indexed to the face-centered cubic phase CeO<sub>2</sub> (JCPDF



Figure 2. TG curve of the as-made cerium oxalate precursor.



Figure 3. XRD patterns of the as-prepared CeO<sub>2</sub>.

34-0394). Figure 4 presents the N<sub>2</sub> adsorption–desorption isotherms of as-prepared CeO<sub>2</sub>. The obvious hysteresis loop ranging from 0.4 to 1.0 at relative pressure suggests the existence of a mesostructure in the CeO<sub>2</sub> particles. The isotherms display a type-H<sub>4</sub> isotherm and correspond to aggregates of narrow slit-like pores.<sup>19</sup> The BET surface area of the synthesized CeO<sub>2</sub> was 98.7 m<sup>2</sup> g<sup>-1</sup>, which was higher than that of commercial CeO<sub>2</sub> (16.3 m<sup>2</sup> g<sup>-1</sup>) and smaller than that of layer-stacking spindle-like CeO<sub>2</sub>.<sup>12</sup> Based on BJH method<sup>20</sup> and by using adsorption branch of the isotherm, pore diameters of the as-prepared CeO<sub>2</sub> were calculated to be 2.0–10.0 nm (inset Figure4). These pores should be resulted from releasing gaseous H<sub>2</sub>O and CO<sub>x</sub> during dehydration and decomposition of cerium oxalate precursor.

Figure 5(a) and (b) displays SEM and TEM images of the as-prepared cerium oxalate precursor. Figure 5(a) shows that the precursors are monodisperse and the morphologies of the precursor are hierarchical layer-by-layer quadrangle with length of side being about from 2 to 4.5  $\mu$ m, and Figure 5(b) further confirms the above microstructures.



**Figure 4.**  $N_2$  adsorption–desorption isotherms and pore distribution (inset) of the as-made CeO<sub>2</sub>.

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Figure 5. (a, b) SEM and TEM images of cerium oxalate precursor; (c) SEM, (d) TEM, (e) HRTEM images, and (f) SAED pattern of nanoparticles of the as-made  $CeO_2$ .

SEM image of the as-prepared CeO<sub>2</sub> (Figure 5(c)) displays that the CeO<sub>2</sub> particles inherit layer-by-layer quadrangle morphologies from the precursors with particle sizes being about  $1.5-3.5\mu$ m, which are smaller than those of the precursors.

For the as-prepared CeO<sub>2</sub> particles, TEM and highresolution TEM (HRTEM) images are exhibited in Figure 5 (d) and (e), respectively, and the selected area electron diffraction (SAED) pattern is presented in Figure 5(f). As shown in Figure 5(d), the magnified part of a layer-like quadrangle reveals that the layer structures are made of numerous nanocrystal particles with a crystallite size of about 13–15 nm. The visible lattice fringes with a spacing of 0.3136 nm in Figure 5(e) clearly correspond to the spacing of the (1 1 1) planes of CeO<sub>2</sub>. In Figure 5(f), electron diffraction pattern shows bright rings, which are indexed to the different planes of the cubic CeO<sub>2</sub> and in line with the XRD data.

Based on the above experiments, in order to obtain layer-by-layer quadrangle mesoporous  $CeO_2$ , it is important to obtain the uniform layer-by-layer quadrangle cerium oxalate precursor, since the as-prepared  $CeO_2$  inherits its morphology from the cerium oxalate precursor. During the experimental processes, it is found that the ultrasonic wave could affect the morphology of the final products. In order to investigate the detailed forming processes of cerium oxalate precursor hierarchical architectures, time-dependent experiments were performed (this "time" means the mixing time of all reactants), whereby the other reaction parameters were kept unchanged. Figure 6 shows the effect of ultrasonic irradiation time on the morphology and size of the precursor.

Figure 6(a) displayed the SEM image of cerium oxalate precursor prepared without the assistance of ultrasonic wave and only with general stir for 5 min after oxalic acid aqueous solution were mixed with Ce(NO<sub>3</sub>)<sub>3</sub> aqueous solution. One could find that the precursor was composed of abundant rectangular solids with nonuniformity sizes and a small amount of layer-by-layer quadrangle aggregation with length of side being about from 2 to 4.5  $\mu$ m (Figure 6(a)). When ultrasonic wave condition was employed and after the reactants were ultrasonic oscillated for 1 to 3 min

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Figure 6. SEM images of the cerium oxalate precursor prepared from the system under different ultrasonic time: (a) 0 min (only with 5 min general stirring), (b) 1 min, (c) 3 min, (d) 4 min, (e) 5 min, and (f) 6 min.

(Figure 6(b) and (c)), quadrangle aggregations and lamellar structures in the cerium oxalate precursors were found. With an extension of the ultrasonic time to 4 min (Figure 6 (d)), for the precursors, only a few of lamellar structures left and a large amount of layer-by-layer quadrangle appeared. When the ultrasonic oscillation time reached 5 min, the lamellar precursors disappeared and all of precursors became monodispersed layer-by-layer quadrangle architectures (Figure 6(e)). Further increasing ultrasonic oscillation time to 6 min, the morphologies of the precursors returned back to the mixture of lamellar and layer-by-layer quadrangle structures (Figure 6(f)). Optimum ultrasonic oscillation time for synthesis of fine and uniform layer-by-layer quadrangle precursor is 5 min.

Based on the above time-dependent analysis, the ultrasonic wave plays important roles to help forming layer-bylayer quadrangle cerium oxalate precursor. This phenomenon is maybe mainly ascribed to the high-energy and cavitation phenomena of ultrasonic wave.<sup>1,21–23</sup> By comparing Figure 6(a) and (e), it can be deduced that accumulation of the precursor to layer-by-layer quadrangle structure needs a certain amount of energy. Although the general stirring can provide some energy, which lead to the aggregation of the precursors, the total amount of energy is not enough, so only a small number of layer-by-layer quadrangle structures formed in Figure 6(a). While the ultrasonic oscillation can generate higher energy than that of general stir, which leads the precursor particles not only to growing larger but also taking place regular layer-by-layer stacking (Figure 6(e)). In addition, seen from Figure 6(b)–(f), with the prolonging of ultrasonic time, for the precursor particles, high-energy ultrasonic first help lamellar nuclei gradually become wider and longer. At the same time, the grown lamellar precursor heap together to reach a relative stable layer-by-layer quadrangle structure (Figure 6(e)). Then, this relative stable layer-bylayer quadrangle configuration collapses and disappears. Obviously, the collapses is also caused by high-energy and cavitation of ultrasonic wave.

Figures 7 and 8 show the UV–vis absorption spectra and Tauc plot for the as-prepared cerium oxalate precursor and CeO<sub>2</sub>, respectively. In Figure 7, the as-prepared CeO<sub>2</sub> exhibits adsorption band from 200 to 360 nm, which is broader than that of the precursor. From the Tauc plot, one can find that the direct allowed transition bandgap energy of CeO<sub>2</sub> is 2.91 eV (Figure 8), which is smaller than that of the well-known semiconductor CeO<sub>2</sub> (3.37 eV)<sup>24</sup> and



**Figure 7.** UV–vis absorption spectra of the as-prepared cerium oxalate precursor and CeO<sub>2</sub>.

larger than that of corresponding precursor. Also, this bandgap value is smaller than those of the nano CeO<sub>2</sub> with average diameters being 1  $\mu$ m (3.03 eV) and 5–10 nm (3.44 eV).<sup>11</sup> This phenomenon is in according with the previous reports that bandgap decreases with the increasing sizes of CeO<sub>2</sub>.<sup>25,26</sup>

For the layer-like quadrangle CeO<sub>2</sub>, Figures 9 and 10 show the photocatalytic degrading RhB results. Degradation rate is defined as: degradation (%) =  $(1 - C_i/C_0) \times 100\%$ , where  $C_0$  and  $C_i$  are RhB concentration at the initial adsorption equilibrium and at different illumination intervals, respectively.

As seen from Figure 9, in the presence of CeO<sub>2</sub>, UV irradiation of the RhB aqueous solution leads to absorbance decrease. A linear relationship between  $\ln(C_0/C_i)$  and reaction time (*t*) is shown in Figure 10, revealing that the degradation reaction follows pseudo-first-order kinetics and the corresponding kinetic equation is:  $\ln C_0/C_i = kt$  with



Figure 8. Tauc plots for the as-made cerium oxalate precursor and  $CeO_2$ .



Figure 9. The concentration of RhB with time.

*k* (min<sup>-1</sup>) being degradation rate constant. Here, the *k* is determined as 0.0647 min<sup>-1</sup>. Comparing to the mesoporous subuliform CeO<sub>2</sub> with *k* being 0.0125 min<sup>-1</sup>, BET surface area being 92.4 m<sup>2</sup> g<sup>-1</sup> and direct allowed transition bandgap energy being 3.0 eV,<sup>11</sup> this layer-like quadrangle CeO<sub>2</sub> has bigger BET surface area, smaller bandgap energy and better photocatalytic activity. This situation supports the results reported earlier.<sup>27,28</sup>

#### Conclusion

An ultrasonic-assisted solution-phase synthetic method was applied to fabricate hierarchical layer-by-layer mesoporous  $CeO_2$ . The layer-like quadrangle  $CeO_2$  are assembled numerous nanocrystal particles. Time-dependent experiments indicate that ultrasonic wave can help to preparation layer-by-layer cerium oxalate precursor. For the as-prepared  $CeO_2$ , its higher surface area and smaller bandgap energy lead to its better photocatalytic activity for degrading RhB.



**Figure 10.** A linear relationship between  $\ln(C_0/C_i)$  and reaction time.

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