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# An eco-friendly route for template-free synthesis of high specific surface area mesoporous CeO<sub>2</sub> powders and their adsorption for acid orange 7†

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An eco-friendly route was developed for the synthesis of mesoporous CeO<sub>2</sub> powders without any additional template. The original cerium precursors were separated from Ce<sup>3+</sup> aqueous solution by (NH<sub>4</sub>)<sub>2</sub>CO<sub>3</sub> or Na<sub>2</sub>CO<sub>3</sub> via a chemical precipitation method, then H<sub>2</sub>O<sub>2</sub> was introduced to induce the phase transformation from original cerium precursors to CeO<sub>2</sub> precursors with initial porous structures, finally the crystallinities of CeO<sub>2</sub> precursors were improved by a hydrothermal treatment, meanwhile the mesoporous structures of final CeO<sub>2</sub> powders were formed. The BET surface areas of mesoporous CeO<sub>2</sub> powders synthesized using (NH<sub>4</sub>)<sub>2</sub>CO<sub>3</sub> and Na<sub>2</sub>CO<sub>3</sub> as precipitants were 106.1 and 76.9 m<sup>2</sup> g<sup>-1</sup>, respectively. Moreover, a mesoporous CeO<sub>2</sub> sample with BET surface area of 100.0 m<sup>2</sup> g<sup>-1</sup> was also synthesized using commercial Ce<sub>2</sub>(CO<sub>3</sub>)<sub>3</sub>·xH<sub>2</sub>O as an existing cerium precursor under the same conditions as control, which could shorten experimental processes and reduce costs. The oxidation-induced phase transformation from original cerium precursors to CeO<sub>2</sub> precursors with initial porous structures was the precondition for further forming of mesoporous structures of final CeO<sub>2</sub> powders during the hydrothermal process. These mesoporous CeO<sub>2</sub> powders showed the rapid and effective adsorption for acid orange 7 dye from simulated wastewater without pH pre-adjustment at room temperature. Furthermore, the adsorption capacities of these mesoporous CeO<sub>2</sub> powders for removal of acid orange 7 dye were determined according to the Langmuir linear fits.

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## Introduction

Acid orange 7 (AO7) dye is one of the most common synthetic dyes in various industries ranging from dyeing to printing.<sup>1–3</sup> AO7 is considered toxic and could cause harmful health effects to human and aquatic organisms, such as skin diseases and carcinogenesis.<sup>4,5</sup> Moreover, it is difficult to biologically degrade AO7 in wastewaters because of its recalcitrant azo bond with an aromatic structure.<sup>6</sup> Therefore, it is essential to treat the industrial wastewaters containing AO7.<sup>7–9</sup> To date, many approaches have been conducted to control organic pollutants, such as biodegradation,<sup>10–12</sup> photooxidation,<sup>13,14</sup> chemical oxidation,<sup>15–17</sup> electrochemistry,<sup>18,19</sup> ultrasonic destruction<sup>20,21</sup> and adsorption.<sup>22–24</sup> Among these techniques, adsorption using adsorbents is considered to be one of the most convenient and

cost-efficient methods.<sup>25</sup> Huang *et al.* prepared a nitrilotriacetic acid anhydride modified ligno-cellulosic bio-adsorbent for removal of Cd<sup>2+</sup> and Pb<sup>2+</sup>, the maximum sorption capacities for Cd<sup>2+</sup> and Pb<sup>2+</sup> could reach 143.4 and 303.5 mg g<sup>-1</sup> at 298.0 K, respectively.<sup>26</sup> Lu *et al.* reported the removal of acenaphthene by biochar and raw biomass, and investigated the effects of coexisting metal ions and organic compounds on their sorption performances.<sup>27</sup> Moreover, Wu *et al.* reviewed the role of biochar on composting of organic wastes and remediation of contaminated soils.<sup>28</sup> The mesoporous ceria (CeO<sub>2</sub>) can serve as a promising candidate for removal of AO7 because of its high specific surface area and well-defined pore topology.

Generally, mesoporous CeO<sub>2</sub> powders are prepared by template methods with either surfactants as soft templates<sup>29,30</sup> or other porous material as hard templates.<sup>31,32</sup> However, the template methods require either additional procedures or high energy consumption in order to eliminate the hard or soft sacrificial templates, such as dissolution or heat treatment.<sup>33–35</sup> Moreover, the crystallinity of mesoporous CeO<sub>2</sub> even needs to be improved again by calcination, which easily causes the collapse of pore structures and thus reduces the specific surface area of CeO<sub>2</sub>.<sup>36</sup> To date, there are limited reports for template-free synthesis of CeO<sub>2</sub> powders with mesoporous structures. For example, Wei *et al.* fabricated mesoporous CeO<sub>2</sub> nanoflowers with a BET surface area (*S*<sub>BET</sub>) of 95.7 m<sup>2</sup> g<sup>-1</sup>, however,

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polyvinylpyrrolidone (PVP) was introduced as a structure-directing agent to synthesize  $\text{Ce}(\text{HCOO})_3$  precursor in alcoholic solution, in which formic acid and ammonia solution were also added. Then, hydrogen peroxide was introduced as an oxidant to induce the phase transformation from  $\text{Ce}(\text{HCOO})_3$  to  $\text{CeO}_2$  with inherited morphology. Finally, mesoporous  $\text{CeO}_2$  nanoflowers were obtained by following solvothermal treatment at  $150^\circ\text{C}$  for 6 h and drying at  $70^\circ\text{C}$  for 10 h.<sup>37</sup> In another study, Xie *et al.* reported a template-free hydrothermal synthesis of flower-like  $\text{CeO}_2$  powders, and its  $S_{\text{BET}}$  was  $38.8\text{ m}^2\text{ g}^{-1}$ . The potassium chlorate and dimethyl formamide were employed, and the interaction effect of them played an important role in the formation of flower-like  $\text{CeO}_2$ .<sup>38</sup> Moreover, He *et al.* synthesized mesoporous  $\text{CeO}_2$  colloidal spheres by the assembly of  $\text{CeO}_2$  nanoparticles and nanocubes, respectively. The  $S_{\text{BET}}$  of mesoporous  $\text{CeO}_2$  colloidal spheres assembled by nanoparticles and nanocubes were  $114.3$  and  $122.5\text{ m}^2\text{ g}^{-1}$ , respectively. The whole process could be divided into three steps: the  $\text{CeO}_2$  nanoparticles and nanocubes were first synthesized by a hydrothermal method and CO-assisted hydrothermal approach, respectively. Then, the  $\text{CeO}_2$  nanocrystals self-assembled into colloidal spheres *via* an emulsion-based bottom-up self-assembling method. Finally, the colloidal spheres were obtained after following drying at  $70^\circ\text{C}$  and calcination at  $350^\circ\text{C}$  for 4 h.<sup>39</sup> From the above, one sample, mild, low-cost and environment-friendly route for template-free synthesis of mesoporous  $\text{CeO}_2$  powders is desirable.

In the previous work, we presented a combined bottom-up and top-down route for template-free synthesis of mesostructured  $\text{CeO}_2$  particles using  $\text{Ce}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$  (cerium source),  $\text{NH}_4\text{HCO}_3$  (precipitant),  $\text{H}_2\text{O}_2$  (oxidant) and  $\text{H}_2\text{O}$  (solvent) as starting reagents, and its specific surface area was  $166.5\text{ m}^2\text{ g}^{-1}$ .<sup>40</sup> In this work,  $(\text{NH}_4)_2\text{CO}_3$  or  $\text{Na}_2\text{CO}_3$  was employed in place of  $\text{NH}_4\text{HCO}_3$  as a precipitant for separation of cerium precursors from  $\text{Ce}^{3+}$  aqueous solution. As an expansive research, commercial  $\text{Ce}_2(\text{CO}_3)_3 \cdot x\text{H}_2\text{O}$  powders were used as an existing precursor for synthesis of mesoporous  $\text{CeO}_2$  powders. The roles of  $\text{H}_2\text{O}_2$  were discussed, and the effects of calcination on the grain sizes and  $S_{\text{BET}}$  of mesoporous  $\text{CeO}_2$  powders were investigated. Additionally, the absorption characteristics of these mesoporous  $\text{CeO}_2$  powders for AO7 dye were investigated.

Furthermore, it is worth noting that the mesoporous  $\text{CeO}_2$  powders were synthesized in this work just using  $(\text{NH}_4)_2\text{CO}_3$ ,  $\text{Na}_2\text{CO}_3$ ,  $\text{H}_2\text{O}_2$  and  $\text{H}_2\text{O}$  without any additional reagent and post-treatment.  $(\text{NH}_4)_2\text{CO}_3$ ,  $\text{Na}_2\text{CO}_3$  and  $\text{H}_2\text{O}_2$  are accessible, cheap and safe chemistry reagents, which not only can save the cost, but also reduce the pollution degree to environment. Moreover, the route, using commercial  $\text{Ce}_2(\text{CO}_3)_3 \cdot x\text{H}_2\text{O}$  as an existing precursor for synthesis of mesoporous  $\text{CeO}_2$  powders, can shorten experimental processes and reduce costs.

## Experimental

### Materials

Cerium nitrate hexahydrate ( $\text{Ce}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$ , 99.95%), ammonium carbonate ( $(\text{NH}_4)_2\text{CO}_3$ , 99.999%), sodium carbonate ( $\text{Na}_2\text{CO}_3$ , 99.5%), hydrogen peroxide ( $\text{H}_2\text{O}_2$ , 30 wt%) and

commercial cerium carbonate hydrate ( $\text{Ce}_2(\text{CO}_3)_3 \cdot x\text{H}_2\text{O}$ , 99.9%) were supplied by Aladdin Co. Ltd. Acid orange 7 (AO7, >97.0%) was obtained from Tokyo Chemical Industry Co. Ltd.

### Synthesis of mesoporous $\text{CeO}_2$ powders

As shown in Fig. 1, firstly, the original cerium precursors were separated from  $\text{Ce}^{3+}$  aqueous solution by  $(\text{NH}_4)_2\text{CO}_3$  or  $\text{Na}_2\text{CO}_3$  *via* a chemical precipitation method. Typically, 4 mmol  $\text{Ce}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$  was dissolved into 28 mL distilled water to form a clear  $\text{Ce}^{3+}$  solution, and 16 mmol precipitant ( $(\text{NH}_4)_2\text{CO}_3$  or  $\text{Na}_2\text{CO}_3$ ) was added to the above solution under continuous stirring, immediately forming a white precipitate (labelled as Precursor 1 and Precursor 2, respectively). Meanwhile, as an extension experiment, commercial  $\text{Ce}_2(\text{CO}_3)_3 \cdot x\text{H}_2\text{O}$  powders were used as an existing precursor. The commercial  $\text{Ce}_2(\text{CO}_3)_3 \cdot x\text{H}_2\text{O}$  powders were dispersed in 28 mL distilled water, and the subsequent experimental steps were similar to that of the suspension of Precursor 1 and Precursor 2.

Then,  $\text{H}_2\text{O}_2$  was introduced to induce the phase transformation from original cerium precursors to  $\text{CeO}_2$  precursors. Typically, 7 mL  $\text{H}_2\text{O}_2$  was added to the above suspension containing Precursor 1, Precursor 2 and commercial  $\text{Ce}_2(\text{CO}_3)_3 \cdot x\text{H}_2\text{O}$ , then stirring for 30 min and aging for 3 h. The as-prepared orange precipitates using  $(\text{NH}_4)_2\text{CO}_3$ ,  $\text{Na}_2\text{CO}_3$  as precipitants and using commercial  $\text{Ce}_2(\text{CO}_3)_3 \cdot x\text{H}_2\text{O}$  as an existing precursor were labelled as Precursor 1-1, Precursor 2-1 and Precursor 3-1, respectively. Note that all operations were performed at room temperature.

The last step was the synthesis of mesoporous  $\text{CeO}_2$  powders by a hydrothermal treatment. Typically, the above  $\text{CeO}_2$  precursors in the total mother liquor were transferred into a 50 mL Teflon-lined stainless steel autoclave. After reacting at  $200^\circ\text{C}$  for 24 h, the autoclave was cooled down. Then the resulting precipitates were washed with distilled water and ethanol, and dried at  $60^\circ\text{C}$  for 24 h. These hydrothermally produced  $\text{CeO}_2$  powders were labelled as Sample 1, Sample 2 and Sample 3, respectively.

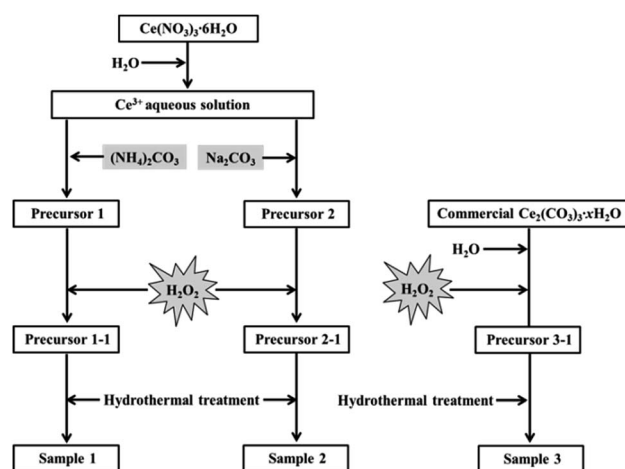


Fig. 1 Synthesis of mesoporous  $\text{CeO}_2$  using  $(\text{NH}_4)_2\text{CO}_3$ ,  $\text{Na}_2\text{CO}_3$  as precipitants, and using commercial  $\text{Ce}_2(\text{CO}_3)_3 \cdot x\text{H}_2\text{O}$  as an existing precursor in the presence of  $\text{H}_2\text{O}_2$ .



For comparison, the samples were synthesized under the same conditions as control, however, in the absence of  $\text{H}_2\text{O}_2$ . Moreover, in order to investigate the effects of calcination on the grain sizes and  $S_{\text{BET}}$  of mesoporous  $\text{CeO}_2$ , these samples (Sample 1, Sample 2 and Sample 3) were treated by following calcination at  $500^\circ\text{C}$  for 2 h, and their  $S_{\text{BET}}$  were also determined.

### Characterization

The crystallographic phases of precursors and samples were characterized by X-ray diffraction (XRD, D/Max 2200PC). The microstructures of precursors and samples were evaluated by transmission electron microscopy (TEM, JEM-2100F). The specific surface areas, pore volumes and pore size distributions of mesoporous  $\text{CeO}_2$  powders were obtained from nitrogen adsorption-desorption measurements (QuadraSorb SI).

### Adsorption studies

About 10.3 g of AO7 powders (>97.0%) were dissolved in distilled water, and diluted to 100 mL with distilled water, the as-obtained concentration of AO7 solution was  $10\text{ g L}^{-1}$ . The different concentrations of AO7 solution ( $20\text{--}120\text{ mg L}^{-1}$ ) were obtained by pipetting varied volume of the above  $10\text{ g L}^{-1}$  AO7 solution into 100 mL volumetric flask and bringing to volume by distilled water. Subsequently, 0.2 g  $\text{CeO}_2$  sample was dispersed into 100 mL of AO7 solution at varying initial concentrations (adsorbent dosage:  $2.0\text{ g L}^{-1}$ ) without pH pre-adjustments. The mixture was stirred at a constant speed (200 rpm) and temperature ( $298.0\text{ K}$ ). Then, 4 mL suspension was withdrawn at regular intervals and centrifuged. The absorbance of supernatant was measured using an UV-2600 spectrophotometer.

The Beer-Lambert law is linear relationship between the absorbance and concentration of absorbing species.<sup>41</sup> So, the concentration of AO7 dye can be converted from its absorbance based on Beer-Lambert law. The adsorption efficiency ( $\eta$ , %) and adsorption amount ( $q$ ,  $\text{mg g}^{-1}$ ) for AO7 dye were calculated using eqn (1) and (2), respectively.<sup>42</sup>

$$\eta_t = \frac{C_0 - C_t}{C_0} \times 100\% \quad (1)$$

$$q = \frac{(C_0 - C_e)V}{m} \quad (2)$$

where  $C_0$  ( $\text{mg L}^{-1}$ ) is the initial concentration of AO7 dye,  $C_t$  ( $\text{mg L}^{-1}$ ) is the concentration of AO7 dye at a given time  $t$  ( $t = 0\text{--}60\text{ min}$ ),  $C_e$  ( $\text{mg L}^{-1}$ ) is the concentration of AO7 dye at equilibrium,  $m$  (g) is the mass of  $\text{CeO}_2$  powders, and  $V$  (L) is the volume of AO7 solution.

Langmuir model as shown in eqn (3) was used to examine the adsorption characteristics of the as-obtained mesoporous  $\text{CeO}_2$  powders.<sup>43</sup> And the saturated adsorption amount ( $q_m$ ,  $\text{mg g}^{-1}$ ) was obtained based on Langmuir linear fitting of adsorption isotherm curve.

$$q = \frac{K_L q_m C_e}{1 + K_L C_e} \quad (3)$$

where  $K_L$  ( $\text{L mg}^{-1}$ ) is Langmuir constant. The eqn (3) can be rearranged to a linear form as shown in eqn (4). As observed, the plot of  $C_e/q$  against  $C_e$  can give a straight line with the slope of  $1/q_m$  and intercept of  $1/(K_L q_m)$ , and the values of  $q_m$  and  $K_L$  can be evaluated according to the slope and intercept.

$$\frac{C_e}{q} = \frac{1}{q_m} C_e + \frac{1}{K_L q_m} \quad (4)$$

## Results and discussion

### Phase characterizations of precursors

The crystallographic phases of precursors after adding the precipitant and  $\text{H}_2\text{O}_2$  were determined by XRD. Fig. 2a and b show the XRD patterns of Precursor 1 and Precursor 2 obtained by adding  $(\text{NH}_4)_2\text{CO}_3$  and  $\text{Na}_2\text{CO}_3$  to  $\text{Ce}^{3+}$  aqueous solution, respectively. As an verification and comparison, the XRD analysis of commercial  $\text{Ce}_2(\text{CO}_3)_3 \cdot x\text{H}_2\text{O}$  powders also were performed, and its XRD pattern was showed in Fig. 2c. As observed in Fig. 2a, the phase structure of Precursor 1 synthesized following adding  $(\text{NH}_4)_2\text{CO}_3$  to  $\text{Ce}^{3+}$  aqueous solution was  $\text{o-Ce}(\text{CO}_3)\text{OH}$  (JCPDS no. 41-0013; density =  $4.545\text{ g cm}^{-3}$ ). The XRD pattern of Precursor 2 in Fig. 2b was similar to that of commercial  $\text{Ce}_2(\text{CO}_3)_3 \cdot x\text{H}_2\text{O}$  in Fig. 2c, indicating its major phase of  $\text{Ce}_2(\text{CO}_3)_3 \cdot 8\text{H}_2\text{O}$  (JCPDS no. 38-0377; density =  $2.790\text{ g cm}^{-3}$ ). Moreover, the phase of precursor synthesized following adding  $\text{NH}_4\text{HCO}_3$  to  $\text{Ce}^{3+}$  aqueous solution in our previous report<sup>40</sup> was similar to that of Precursor 2 in Fig. 2b and commercial  $\text{Ce}_2(\text{CO}_3)_3 \cdot x\text{H}_2\text{O}$  in Fig. 2c. However, the difference in phase structure of original cerium precursors will subtly affect the  $S_{\text{BET}}$  of final  $\text{CeO}_2$  samples. Interestingly, the Precursor 1 synthesized following adding  $(\text{NH}_4)_2\text{CO}_3$  to  $\text{Ce}^{3+}$  aqueous solution depended on the amount of  $(\text{NH}_4)_2\text{CO}_3$ . When the amount of  $(\text{NH}_4)_2\text{CO}_3$  was less than 8 mmol, the major phase of as-obtained precursor was  $\text{Ce}_2(\text{CO}_3)_3 \cdot 8\text{H}_2\text{O}$ . And the major phase structure was  $\text{o-Ce}(\text{CO}_3)\text{OH}$  when the amount of  $(\text{NH}_4)_2\text{CO}_3$  was more than 10 mmol (see Fig. S1†).

Fig. 3a–c show the XRD patterns of precursors obtained following addition of  $\text{H}_2\text{O}_2$  (Precursor 1-1, Precursor 2-1 and Precursor 3-1, respectively). As observed in Fig. 3a–c, the peaks

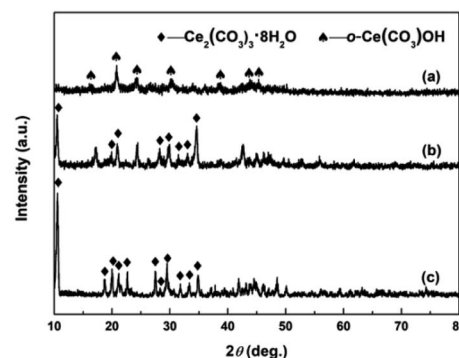


Fig. 2 XRD patterns of (a) Precursor 1, (b) Precursor 2 and (c) commercial  $\text{Ce}_2(\text{CO}_3)_3 \cdot x\text{H}_2\text{O}$ .



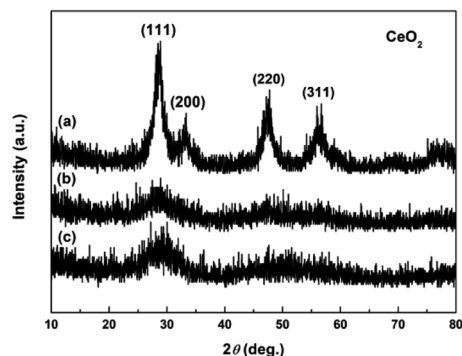


Fig. 3 XRD patterns of (a) Precursor 1-1, (b) Precursor 2-1 and (c) Precursor 3-1.

related to  $\text{Ce}_2(\text{CO}_3)_3 \cdot 8\text{H}_2\text{O}$  and  $\text{o-Ce}(\text{CO}_3)\text{OH}$  were no longer present. The XRD pattern of Precursor 1-1 in Fig. 3a displayed several relatively well-resolved peaks that could be indexed to the (111), (200), (220) and (311) planes of face-centred cubic  $\text{CeO}_2$  (JCPDS no. 34-0394; density =  $7.215 \text{ g cm}^{-3}$ ). The XRD pattern of Precursor 2-1 in Fig. 3b and Precursor 3-1 in Fig. 3c all showed three broad featureless peaks centred at  $2\theta = 29, 47$  and  $56^\circ$ , and the broad featureless peaks centred at  $2\theta = 29^\circ$  was more easily observed than others. Compared with the XRD pattern in Fig. 3a, the broad featureless peaks centred at  $2\theta = 29^\circ$  in Fig. 3b and c could be indexed to the (111) plane of  $\text{CeO}_2$  phase, but with relatively low crystallinities. Combining with the XRD analyses in Fig. 2, we can derive a conclusion that  $\text{H}_2\text{O}_2$  can induce the phase transformations from original cerium precursor ( $\text{Ce}_2(\text{CO}_3)_3 \cdot x\text{H}_2\text{O}$  or  $\text{o-Ce}(\text{CO}_3)\text{OH}$ ) to  $\text{CeO}_2$  precursor because of its oxidation.

### Physical characterizations of the hydrothermally produced $\text{CeO}_2$ powders

Fig. 4a–c show the XRD patterns of the hydrothermally produced  $\text{CeO}_2$  samples (Sample 1, Sample 2 and Sample 3, respectively). As observed, all the hydrothermally produced samples displayed several well-resolved peaks that indexed to the (111), (200), (220), (311), (222), (400) and (331) planes of face-centred cubic  $\text{CeO}_2$  (JCPDS no. 34-0394), and no additional phases were observed.

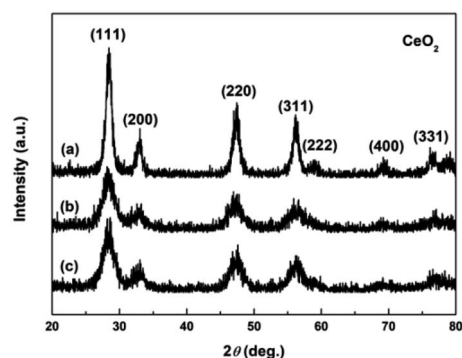


Fig. 4 XRD patterns of (a) Sample 1, (b) Sample 2 and (c) Sample 3.

Moreover, the crystallinities of the hydrothermally produced  $\text{CeO}_2$  in Fig. 4 were improved compared with that of the  $\text{CeO}_2$  precursors in Fig. 3, which may be attributed to the rearrangement of  $\text{CeO}_2$  grains with good crystallinities under certain temperatures and pressures during the hydrothermal process.<sup>40</sup> Combining with the results of XRD analyses in Fig. 3, we can draw a conclusion that the crystallinities of  $\text{CeO}_2$  precursors could be improved and the pure  $\text{CeO}_2$  samples can be obtained through a hydrothermal treatment.

To understand the microstructures of the hydrothermally produced  $\text{CeO}_2$  samples, TEM analyses were performed. Fig. 5a, c and e show the TEM images of the hydrothermally produced  $\text{CeO}_2$  (Sample 1, Sample 2 and Sample 3, respectively). As observed in Fig. 5a, c and e, the porous structure of  $\text{CeO}_2$  particles and the presence of pores around  $\text{CeO}_2$  grains can be observed. In addition, the grain size of Sample 1 was obviously greater than that of Sample 2 and Sample 3. The corresponding high-magnification TEM images of Sample 1, Sample 2 and Sample 3 were showed in Fig. 5b, d and f, respectively. The porous structures of these  $\text{CeO}_2$  particles could be further evidenced, and these  $\text{CeO}_2$  particles consisted of aggregated grains. Moreover, these pores resulted from these aggregated grains, and the calculated grain sizes were about 7.7, 4.3 and 4.8 nm for Sample 1, Sample 2 and Sample 3, respectively. The existence of pore structure resulted from these  $\text{CeO}_2$  particles possessing bigger specific surface area, consequently, more active sites can be provided for the adsorption of pollutants, which are beneficial to improving their capture capability.<sup>44</sup> The grain size of  $\text{CeO}_2$  will have an impact on the pore diameter and pore volume of  $\text{CeO}_2$  powders, and then affected their  $S_{\text{BET}}$ . Further analysis of  $S_{\text{BET}}$  was conducted by nitrogen adsorption-desorption experiments as discussed later.

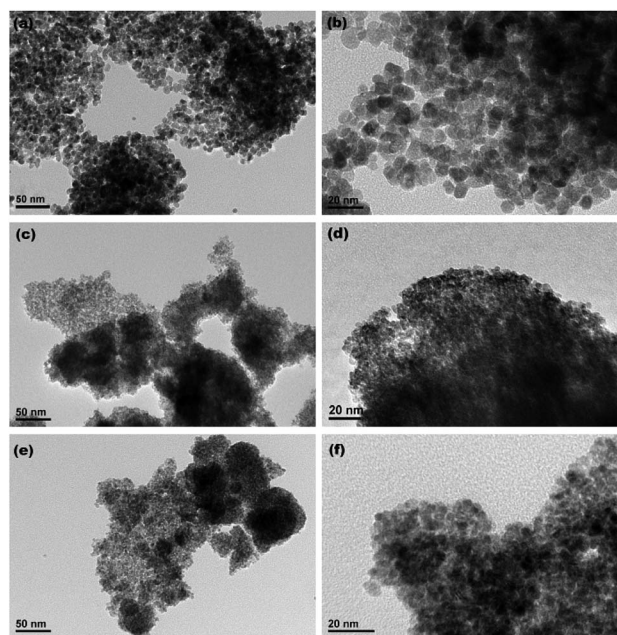


Fig. 5 TEM images of (a) Sample 1, (c) Sample 2 and (e) Sample 3 ((b), (d) and (f) show the corresponding high-magnification TEM images, respectively).



To further clarify the porous structures of the final hydrothermally produced CeO<sub>2</sub> samples (Sample 1, Sample 2 and Sample 3, respectively), nitrogen adsorption–desorption experiments were conducted to determine their  $S_{\text{BET}}$ , average pore sizes and pore volumes. Fig. 6a–c show the nitrogen adsorption–desorption isotherms of Sample 1, Sample 2 and Sample 3, respectively. From Fig. 6a–c, the recorded adsorption–desorption isotherms exhibited the hysteresis loops ranging from 0.4 to 1.0, suggesting their mesoporous structures.<sup>45</sup> Furthermore, the profiles of the nitrogen adsorption–desorption isotherms were similar to that of the mesoporous CeO<sub>2</sub> reported in previous literature.<sup>29</sup> The insets in Fig. 6a–c show the corresponding Barrett–Joyner–Halenda (BJH) pore size distribution curves. As observed the inset in Fig. 6a and b, BJH calculations for the pore size distributions presented a single distribution centred at about 7.8 and 3.4 nm for Sample 1 and Sample 2, respectively. By contrast, the BJH pore size distribution curves of Sample 3 presented two distributions centred at about 3.8 and 5.5 nm as observed the inset in Fig. 6c.

The specific surface areas were determined using Brunauer–Emmett–Teller (BET) method, the average pore sizes and pore volumes were determined by BJH analysis, and these calculated textural parameters were compiled in Table 1. From Table 1, the  $S_{\text{BET}}$  of 106.1 and 76.9 m<sup>2</sup> g<sup>−1</sup> were obtained for Sample 1, Sample 2 and Sample 3, respectively, which had a lower  $S_{\text{BET}}$  than one using NH<sub>4</sub>HCO<sub>3</sub> as a precipitant (166.5 m<sup>2</sup> g<sup>−1</sup>) in our previous report.<sup>40</sup> The average pore size and pore volume were 7.8 nm and 0.19 cm<sup>3</sup> g<sup>−1</sup> for Sample 1, while 3.4 nm and 0.05 cm<sup>3</sup> g<sup>−1</sup> for Sample 2. Moreover, the mesoporous CeO<sub>2</sub> powders synthesized using commercial Ce<sub>2</sub>(CO<sub>3</sub>)<sub>3</sub>·xH<sub>2</sub>O as an existing precursor (Sample 3) showed a  $S_{\text{BET}}$  of 100.0 m<sup>2</sup> g<sup>−1</sup>, the average pore size and pore volume were 3.8 nm and 0.10 cm<sup>3</sup> g<sup>−1</sup>.

In summary, the presented route for template-free synthesis of mesoporous CeO<sub>2</sub> powders with different  $S_{\text{BET}}$  was feasible, in which (NH<sub>4</sub>)<sub>2</sub>CO<sub>3</sub> or Na<sub>2</sub>CO<sub>3</sub> as a precipitant was used to separate original cerium precursors (Ce<sub>2</sub>(CO<sub>3</sub>)<sub>3</sub>·8H<sub>2</sub>O or o-Ce(CO<sub>3</sub>)OH) from Ce<sup>3+</sup> aqueous solution, H<sub>2</sub>O<sub>2</sub> as an oxidant

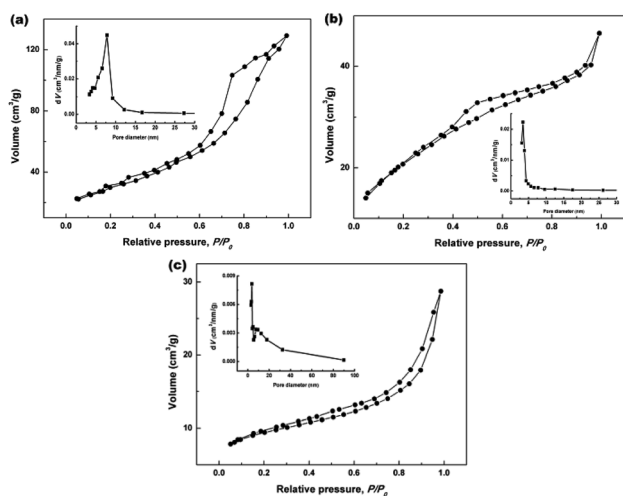
**Table 1** Texture parameters of the hydrothermally produced CeO<sub>2</sub>: Sample 1 and Sample 2 synthesized using (NH<sub>4</sub>)<sub>2</sub>CO<sub>3</sub>, Na<sub>2</sub>CO<sub>3</sub> as precipitants, and Sample 3 synthesized using commercial Ce<sub>2</sub>(CO<sub>3</sub>)<sub>3</sub>·xH<sub>2</sub>O as an existing precursor in the presence of H<sub>2</sub>O<sub>2</sub>

|                                                    | Precipitant                                     |                                 | Existing cerium precursor                                          |
|----------------------------------------------------|-------------------------------------------------|---------------------------------|--------------------------------------------------------------------|
|                                                    | (NH <sub>4</sub> ) <sub>2</sub> CO <sub>3</sub> | Na <sub>2</sub> CO <sub>3</sub> | Ce <sub>2</sub> (CO <sub>3</sub> ) <sub>3</sub> ·xH <sub>2</sub> O |
| Sample                                             | Sample 1                                        | Sample 2                        | Sample 3                                                           |
| $S_{\text{BET}}$ (m <sup>2</sup> g <sup>−1</sup> ) | 106.1                                           | 76.9                            | 100.0                                                              |
| Pore diameter (nm)                                 | 7.8                                             | 3.4                             | 3.8                                                                |
| Pore volume (cm <sup>3</sup> g <sup>−1</sup> )     | 0.19                                            | 0.05                            | 0.10                                                               |

was introduced to induce the phase transformation from these original cerium precursors to CeO<sub>2</sub> precursors, finally the mesoporous CeO<sub>2</sub> were obtained by following hydrothermal treatment at 200 °C for 24 h. It is worth noting that (NH<sub>4</sub>)<sub>2</sub>CO<sub>3</sub>, Na<sub>2</sub>CO<sub>3</sub> and H<sub>2</sub>O<sub>2</sub> are common, cheap, accessible and safe chemistry reagents, which not only can save the cost, but also can reduce the pollution degree to environment. Moreover, the route, using commercial Ce<sub>2</sub>(CO<sub>3</sub>)<sub>3</sub>·xH<sub>2</sub>O as an existing precursor for synthesis of mesoporous CeO<sub>2</sub>, can shorten experimental processes and reduce costs, and the  $S_{\text{BET}}$  of the as-obtained mesoporous CeO<sub>2</sub> powders was 100.0 m<sup>2</sup> g<sup>−1</sup>. Inspired by the template-free synthesis of mesoporous CeO<sub>2</sub> powders using commercial Ce<sub>2</sub>(CO<sub>3</sub>)<sub>3</sub>·xH<sub>2</sub>O as an existing precursor, the commercial Ce(CO<sub>3</sub>)OH should be a feasible precursor for synthesis of mesoporous CeO<sub>2</sub> powders. However, it is with great regret that the existing Ce(CO<sub>3</sub>)OH precursor cannot be obtained through purchase, so the experiment with commercial Ce(CO<sub>3</sub>)OH as an existing precursor cannot be performed. Next, the effects of H<sub>2</sub>O<sub>2</sub> on the phase structures and microstructures of samples will be investigated.

### Role of H<sub>2</sub>O<sub>2</sub>

To clarify the effects of H<sub>2</sub>O<sub>2</sub> on the phase structures of samples, the XRD analyses of samples synthesized in the absence of H<sub>2</sub>O<sub>2</sub> was performed. Fig. 7 shows the XRD patterns of the hydrothermally produced samples synthesized under the same conditions as control, however, in the absence of H<sub>2</sub>O<sub>2</sub>. From Fig. 7a and c, the hydrothermally produced Sample 1 and Sample 3 obtained in the absence of H<sub>2</sub>O<sub>2</sub> showed similar XRD patterns, and both consisted of h-Ce(CO<sub>3</sub>)OH (JCPDS no. 32-0189) and CeO<sub>2</sub> (JCPDS no. 34-0394). From Fig. 7b, the hydrothermally produced Sample 2 obtained in the absence of H<sub>2</sub>O<sub>2</sub> consisted of Ce(CO<sub>3</sub>)<sub>2</sub> (JCPDS no. 22-0542), h-Ce(CO<sub>3</sub>)OH and CeO<sub>2</sub>. The results of XRD analyses in Fig. 7 indicates that the pure CeO<sub>2</sub> cannot be synthesized in the absence of H<sub>2</sub>O<sub>2</sub>, which can be attributed to the missing link of the oxidation-induced phase transformation from original cerium precursors to CeO<sub>2</sub> precursors (see Fig. 3). In other words, the phase transformations from original cerium precursor (Ce<sub>2</sub>(CO<sub>3</sub>)<sub>3</sub>·8H<sub>2</sub>O or o-Ce(CO<sub>3</sub>)OH) to pure CeO<sub>2</sub> cannot be achieved by depending upon the following hydrothermal treatment only. Combining



**Fig. 6** Nitrogen adsorption–desorption isotherms of (a) Sample 1, (b) Sample 2 and (c) Sample 3 (the insets in (a–c) show the corresponding BJH pore size distribution curves).



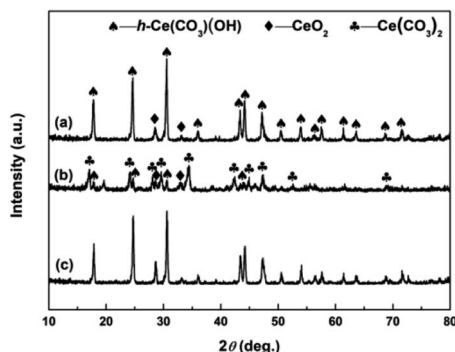


Fig. 7 XRD patterns of (a) Sample 1, (b) Sample 2 and (c) Sample 3 synthesized in the absence of  $\text{H}_2\text{O}_2$ .

the XRD results in Fig. 2–4, it further indicates that the link of addition of  $\text{H}_2\text{O}_2$  acts as a relay station for  $\text{CeO}_2$  precursors from original cerium precursors that are then forwarded to the link of hydrothermal treatment for the formation of final  $\text{CeO}_2$  products.

To understand the effects of  $\text{H}_2\text{O}_2$  on the microstructures of precursors obtained in the absence and presence of  $\text{H}_2\text{O}_2$ , TEM analyses were performed. Fig. 8a, c and e show the TEM images of Precursor 1-1, Precursor 2-1 and Precursor 3-1 synthesized in the absence of  $\text{H}_2\text{O}_2$ , respectively. As observed, all precursors synthesized in the absence of  $\text{H}_2\text{O}_2$  were dense. In contrast, the TEM images of precursors synthesized in the presence of  $\text{H}_2\text{O}_2$  in Fig. 8b, d and f revealed the porous structures. The area with lower contrast showed more and clearer pores compared to one with higher contrast, and the similar phenomenon could be observed in Fig. 5a, c and e. The formation of pore structures could be explained by the oxidation-induced phase

transformation from original cerium precursor ( $\text{Ce}_2(\text{CO}_3)_3 \cdot 8\text{H}_2\text{O}$  or  $\text{o-Ce}(\text{CO}_3)\text{OH}$ ) to  $\text{CeO}_2$  precursor that accompanied by the evolution of porous structure. It indicates that  $\text{H}_2\text{O}_2$  plays a key role in the formation of initial pore structures of  $\text{CeO}_2$  precursors, which provides the precondition for the further growth of pores during the hydrothermal process (see Fig. 5).

From the above, it can be found that  $\text{H}_2\text{O}_2$  plays an indispensable role in the development of pure  $\text{CeO}_2$ , which induces the phase transformation from original cerium precursors to  $\text{CeO}_2$  precursors with initial pore structures in the aqueous solution. Interestingly, the initial pore structures are the prerequisite for formation of final mesoporous  $\text{CeO}_2$  products during the hydrothermal process. From a chemical perspective, the formation mechanism of the original cerium precursors with dense structures and the  $\text{CeO}_2$  precursors with pore structures are summarized as eqn (5)–(8). In eqn (5) and (6), the original precipitate ( $\text{Ce}_2(\text{CO}_3)_3 \cdot 8\text{H}_2\text{O}$  or  $\text{Ce}_2(\text{CO}_3)_3\text{OH}$ ) is obtained upon the addition of  $(\text{NH}_4)_2\text{CO}_3$  or  $\text{Na}_2\text{CO}_3$  to  $\text{Ce}^{3+}$  aqueous solution, respectively (see Fig. 2). After adding  $\text{H}_2\text{O}_2$ , the original precipitates are oxidized, and  $\text{CeO}_2$  precursors with low crystallinities are formed (see eqn (7) and (8)), which supported by the XRD analyses in Fig. 3. At the same time, the by-products of  $\text{H}_2\text{O}$  and  $\text{CO}_2$  are produced. So, the phase transformation from original cerium precursors to  $\text{CeO}_2$  precursors could be due to the oxidation of  $\text{H}_2\text{O}_2$ , while the initial pores on  $\text{CeO}_2$  precursors (see Fig. 8b, d and f) could be attributed to the density difference between the original cerium precursors and  $\text{CeO}_2$  precursors and the loss of by-products ( $\text{H}_2\text{O}$  and  $\text{CO}_2$ ). Above all, the formation of pore structures could be essentially ascribed to the oxidation-induced phase transformation from original cerium precursors to  $\text{CeO}_2$  precursors that accompanied by the evolution of porous structures. After addition of  $\text{H}_2\text{O}_2$ , cerium precursors are oxidized into  $\text{CeO}_2$  and simultaneously with the formation of by-products  $\text{H}_2\text{O}$  and  $\text{CO}_2$  as shown in eqn (7) and (8). The difference in density between cerium precursors ( $\text{Ce}_2(\text{CO}_3)_3 \cdot 8\text{H}_2\text{O}$  ( $2.790 \text{ g cm}^{-3}$ ) and  $\text{o-Ce}(\text{CO}_3)\text{OH}$  ( $4.545 \text{ g cm}^{-3}$ )) and  $\text{CeO}_2$  ( $7.215 \text{ g cm}^{-3}$ ) is the main cause for the formation of pore structures of  $\text{CeO}_2$ , while the by-product  $\text{CO}_2$  bubbles play a stirring role, which are beneficial to the process of oxidation reaction and the homogeneity of  $\text{CeO}_2$  particles. Moreover, the crystallinities of  $\text{CeO}_2$  precursors could be improved and the pores grow further by following hydrothermal treatment, which supported by the XRD analyses in Fig. 4 and TEM analyses in Fig. 5.

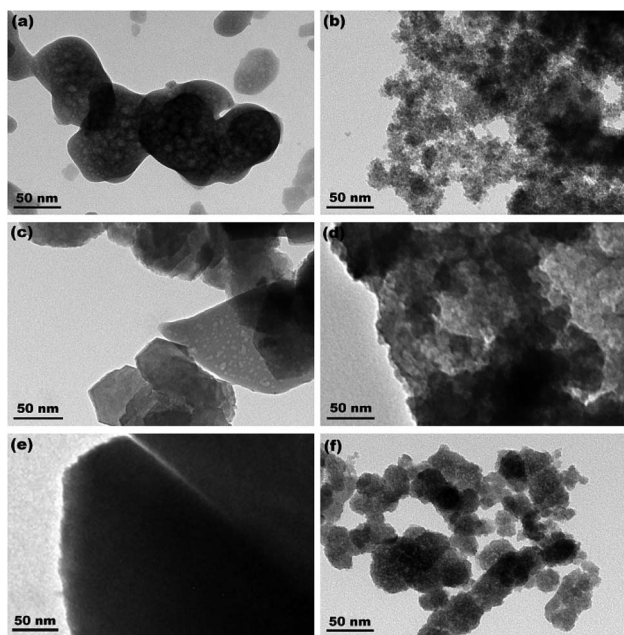
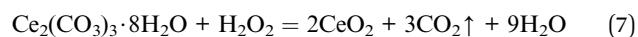
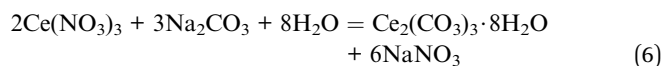
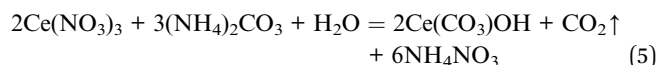


Fig. 8 TEM images of Precursor 1-1, Precursor 2-1 and Precursor 3-1 synthesized in the absence (a, c and e) and presence (b, d and f) of  $\text{H}_2\text{O}_2$ .



The  $S_{\text{BET}}$  of final mesoporous  $\text{CeO}_2$  powders not only relates to the difference in density between cerium precursors and



CeO<sub>2</sub>, but also to the particle size of original cerium precursors. The phase transformation from original cerium precursors to CeO<sub>2</sub> precursors under the stimulation of H<sub>2</sub>O<sub>2</sub> could be considered to be a diffusion process of H<sub>2</sub>O<sub>2</sub>. The surface of cerium precursors is first oxidized to CeO<sub>2</sub>, these original CeO<sub>2</sub> grains have the tendency to aggregate with time to decrease their energy, and the hole between the grains are consider as the initial porous structures, which was the precondition for further forming of mesoporous structures of final CeO<sub>2</sub> powders during the hydrothermal process. However, the content of H<sub>2</sub>O<sub>2</sub> decreases as the reaction progress, and the framework of cerium precursor is filled by the aqueous solution or by-product CO<sub>2</sub> bubbles, which could influence the diffusion of H<sub>2</sub>O<sub>2</sub> from the surface to the inside of the cerium precursor framework, and then will result in the lesser porosity (see the darker areas in Fig. 8b, d, f and 5a, c, e). Moreover, the small particle sizes of cerium precursor are favorable to the diffusion of H<sub>2</sub>O<sub>2</sub> from its surface to internal framework. The greater the difference in density, and the smaller its particle size, the more its  $S_{\text{BET}}$ . So, the  $S_{\text{BET}}$  of final CeO<sub>2</sub> products is the outcome of both the difference in density between cerium precursors and CeO<sub>2</sub> and the diffusion of H<sub>2</sub>O<sub>2</sub> from surface to internal framework of cerium precursors. This can be used to explain why Sample 1, Sample 2, Sample 3 in this work and the CeO<sub>2</sub> sample in our previous report (ref. 40) possess different  $S_{\text{BET}}$ , even if some CeO<sub>2</sub> powders are synthesized with same phase of precursor.

### Effect of calcination on $S_{\text{BET}}$ of mesoporous CeO<sub>2</sub>

In order to investigate the effect of calcination on the grain sizes and  $S_{\text{BET}}$  of samples, the hydrothermally produced mesoporous CeO<sub>2</sub> powders were furthermore treated by following calcination at 500 °C for 2 h, and the grain sizes were estimated using Scherrer's formula. Fig. 9a shows the effect of calcination on the grain sizes of mesoporous CeO<sub>2</sub> (Sample 1, Sample 2 and Sample 3, respectively). As observed, the mean grain sizes were 9.0, 4.9 and 5.7 nm for Sample 1, Sample 2 and Sample 3, respectively. After calcination, the mean grain sizes of samples increased by 14.4, 125.5 and 78.9%, which implied that the high temperature could cause the grains to grow. In addition, the hydrothermally produced CeO<sub>2</sub> using Na<sub>2</sub>CO<sub>3</sub> as a precipitant (Sample 2) treated by calcination showed the biggest change in grain size, which could ascribed to the minimum grain size in

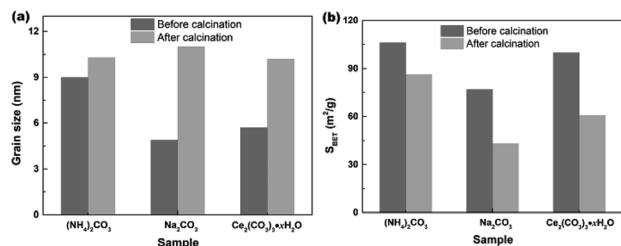


Fig. 9 Effects of calcination on the (a) grain sizes and (b)  $S_{\text{BET}}$  of the hydrothermally produced mesoporous CeO<sub>2</sub> powders: Sample 1, Sample 2 and Sample 3 in the presence of H<sub>2</sub>O<sub>2</sub> (calcination condition: 500 °C; 2 h; in air).

all hydrothermally produced CeO<sub>2</sub> samples. Fig. 9b shows the effect of calcination on the  $S_{\text{BET}}$  of mesoporous CeO<sub>2</sub> (Sample 1, Sample 2 and Sample 3, respectively). As observed, the  $S_{\text{BET}}$  of samples decreased by 18.7, 43.8 and 39.4% after calcination for Sample 1, Sample 2 and Sample 3, respectively. Moreover, the hydrothermally produced CeO<sub>2</sub> powders using NH<sub>4</sub>HCO<sub>3</sub> as a precipitant in our previous report (ref. 40) were also treated by calcination, the mean grain size increased from 5.4 to 10.9 nm with a gain of 101.8%, and the  $S_{\text{BET}}$  decreased from 166.5 to 105.9 m<sup>2</sup> g<sup>-1</sup> with a gain of 36.4%. The reduction of  $S_{\text{BET}}$  could be explained by the growing of grains or the collapse of pores during the calcination process. Obviously, the subsequent post-calcination treatment could lead to the growth of CeO<sub>2</sub> grains, which in turn reduced the  $S_{\text{BET}}$  of mesoporous CeO<sub>2</sub> powders.

### Adsorption properties

AO7 dye was selected as a model target to evaluate the adsorption abilities of mesoporous CeO<sub>2</sub> powders. Fig. 10a–c depicts the time-dependence of adsorption profiles of AO7 dye on mesoporous CeO<sub>2</sub> powders synthesized in the presence of H<sub>2</sub>O<sub>2</sub> (Sample 1, Sample 2 and Sample 3, respectively). As observed, the adsorption efficiencies of AO7 dye achieved within 60 min were 94.2, 83.4 and 89.3% for Sample 1, Sample 2 and Sample 3, respectively. Furthermore, the adsorption of AO7 dye was rapid at the early stages, and the adsorption process was mostly completed within 40 min of reaction. The rapid adsorption of these mesoporous CeO<sub>2</sub> powders for AO7 dye could be ascribed to their high  $S_{\text{BET}}$  and pore structures. The high  $S_{\text{BET}}$  could provide numerous adsorption sites for AO7 molecules, while the pore structures were conducive to the transportation of AO7 molecules to CeO<sub>2</sub> framework and increasing the effective contact areas between CeO<sub>2</sub> and AO7 molecule. Interestingly, CeO<sub>2</sub> also can serve as an alternative photocatalyst for degradation of dye.<sup>46</sup> The high  $S_{\text{BET}}$  of mesoporous CeO<sub>2</sub> powders contribute to providing more active adsorption and photocatalytic reaction sites, which favor the augmentation of photocatalytic performance.<sup>47</sup> So, the proposed mesoporous CeO<sub>2</sub> powders in this work have potential to photodegrade high density dye and dye intermediate from industrial effluents. The

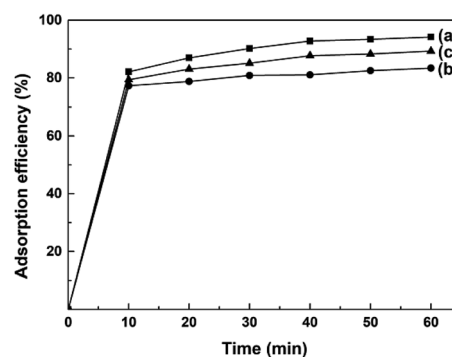


Fig. 10 Time-dependence of adsorption profiles of AO7 dye on mesoporous CeO<sub>2</sub>: (a) Sample 1, (b) Sample 2 and (c) Sample 3 synthesized in the presence of H<sub>2</sub>O<sub>2</sub> ( $T = 25$  °C; [AO7] = 40 mg L; [CeO<sub>2</sub>] = 2.0 g L;  $V = 100$  mL; in the dark; no pH pre-adjustments).



Table 2 Recent literatures on CeO<sub>2</sub> development for the adsorption of AO7 dye

| Authors                             | Operating conditions                                                                                                                                      | Adsorption efficiencies (%) | $S_{\text{BET}}$ (m <sup>2</sup> g <sup>-1</sup> ) |
|-------------------------------------|-----------------------------------------------------------------------------------------------------------------------------------------------------------|-----------------------------|----------------------------------------------------|
| Cai <sup>48</sup> <i>et al.</i>     | [CeO <sub>2</sub> ] = 0.5 g L <sup>-1</sup> ; [AO7] = 35 mg L <sup>-1</sup> ; V = 50 mL; T = —; in the dark; no pH pre-adjustments; t = 2 h               | ~23                         | 67                                                 |
| Hu <sup>49</sup> <i>et al.</i>      | [CeO <sub>2</sub> ] = 1.0 g L <sup>-1</sup> ; [AO7] = 35 mg L <sup>-1</sup> ; V = 60 mL; at room temperature; in the dark; no pH pre-adjustments; t = 1 h | ~40                         | 63                                                 |
| Arul <sup>50,51</sup> <i>et al.</i> | [CeO <sub>2</sub> ] = ~0.67 g L <sup>-1</sup> ; [AO7] = ~105 mg L <sup>-1</sup> ; V = 15 mL; T = —; in the dark; no pH pre-adjustments; t = 10 h          | Almost zero                 | 52                                                 |
| Wang <sup>52</sup> <i>et al.</i>    | [CeO <sub>2</sub> ] = 0.5 g L <sup>-1</sup> ; [AO7] = 35 mg L <sup>-1</sup> ; V = 50 mL; T = —; in the dark; pH = 6.35; t = 1 h                           | 44–56                       | 40–46                                              |
| Ge <sup>53</sup> <i>et al.</i>      | [CeO <sub>2</sub> ] = 0.5 g L <sup>-1</sup> ; [AO7] = 35 mg L <sup>-1</sup> ; V = 50 mL; T = —; in the dark; pH = 4.0; t = ~27 h                          | ~50                         | 57.5                                               |
| Yao <sup>54</sup> <i>et al.</i>     | [CeO <sub>2</sub> ] = 8.0 g L <sup>-1</sup> ; [AO7] = 60 mg L <sup>-1</sup> ; V = 25 mL; T = 25 °C; in the dark; pH = —; t = 1 h                          | ~13.3                       | 54.58                                              |
| Wen <sup>55</sup> <i>et al.</i>     | [CeO <sub>2</sub> ] = 0.5 g L <sup>-1</sup> ; [AO7] = 40 mg L <sup>-1</sup> ; V = 20 mL; T = —; in the dark; pH = 5.0; t = 1 h                            | ~20                         | <67.8                                              |
| Zang <sup>56</sup> <i>et al.</i>    | [CeO <sub>2</sub> ] = 0.5 g L <sup>-1</sup> ; [AO7] = 40 mg L <sup>-1</sup> ; V = 50 mL; T = 313 K; in the dark; no pH pre-adjustments; t = 1 h           | 12.5–37.5                   | —                                                  |

concentrations of dyes are reduced rapidly though the rapid and remarkable adsorption of mesoporous CeO<sub>2</sub> powders. The reduced concentrations of dyes are benefit to increase the transmission of exciting lights, and thus enhance the intensity of the exciting lights reached the surface of CeO<sub>2</sub>, which could improve the photocatalytic activity of CeO<sub>2</sub>.

Table 2 shows the adsorption efficiencies from the recent literatures on CeO<sub>2</sub> development for the adsorption of AO7 dye.<sup>48–56</sup> By comparing the adsorption efficiencies of CeO<sub>2</sub> in

these reported literatures, we can find the mesoporous CeO<sub>2</sub> in this work showed stronger adsorption ability and achieved the absorption equilibrium more quickly, which ascribed to the higher  $S_{\text{BET}}$  of mesoporous CeO<sub>2</sub> in this work. The adsorption mode of AO7 on CeO<sub>2</sub> could be described as a Lewis acid–base reaction between the electron-rich groups (sulfonate group, SO<sup>3-</sup>) of AO7 and empty 4f orbital of cerium ion on the surface of CeO<sub>2</sub>, which eventually formed an inner-sphere complex.<sup>48,57</sup> Moreover, CeO<sub>2</sub> could serve as an excellent adsorbent for the adsorption of other azo dyes, such as methyl orange,<sup>58</sup> congo red,<sup>59</sup> alizarin red S and eriochrome black-T,<sup>60</sup> and the adsorption of the azo dyes onto CeO<sub>2</sub> was solely associated with the oxygen atoms of SO<sup>3-</sup> group.<sup>57</sup>

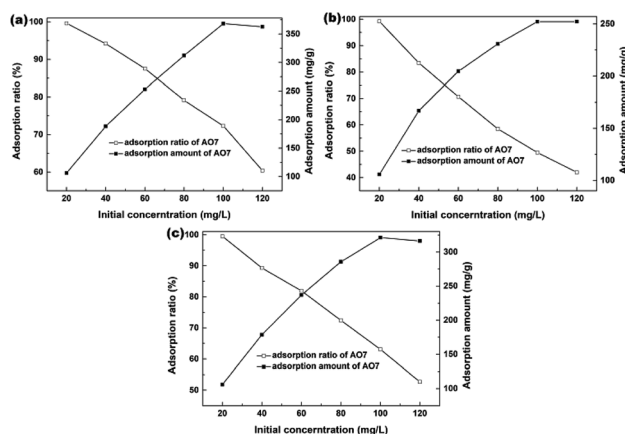


Fig. 11 Effects of AO7 initial concentration on the AO7 adsorption efficiency and adsorption amount measured in the dark and presence of mesoporous CeO<sub>2</sub>: (a) Sample 1, (b) Sample 2 and (c) Sample 3 synthesized in the presence of H<sub>2</sub>O<sub>2</sub>.

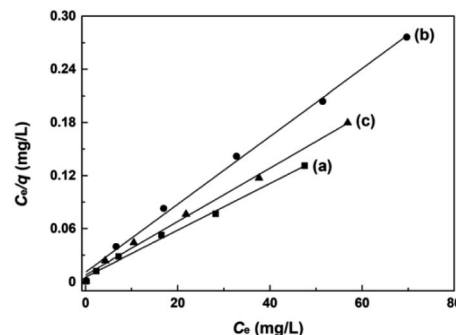


Fig. 12 Langmuir linear fits of AO7 dye adsorbed onto mesoporous CeO<sub>2</sub>: (a) Sample 1, (b) Sample 2 and (c) Sample 3 synthesized in the presence of H<sub>2</sub>O<sub>2</sub>.



**Table 3** Relevant parameters of Langmuir fitting for mesoporous CeO<sub>2</sub>: Sample 1 and Sample 2 synthesized using (NH<sub>4</sub>)<sub>2</sub>CO<sub>3</sub>, Na<sub>2</sub>CO<sub>3</sub> as precipitants, and Sample 3 synthesized using commercial Ce<sub>2</sub>(CO<sub>3</sub>)<sub>3</sub>·xH<sub>2</sub>O as an existing precursor in the presence of H<sub>2</sub>O<sub>2</sub>

|                    |                                                                               |          | Langmuir isotherm model     |                             |        |
|--------------------|-------------------------------------------------------------------------------|----------|-----------------------------|-----------------------------|--------|
| Sample             |                                                                               |          | $q_m$ (mg g <sup>-1</sup> ) | $K_L$ (L mg <sup>-1</sup> ) | $R^2$  |
| Precipitant        | (NH <sub>4</sub> ) <sub>2</sub> CO <sub>3</sub>                               | Sample 1 | 378.8                       | 0.4740                      | 0.9929 |
|                    | Na <sub>2</sub> CO <sub>3</sub>                                               | Sample 2 | 261.1                       | 0.3460                      | 0.9951 |
| Existing precursor | Commercial Ce <sub>2</sub> (CO <sub>3</sub> ) <sub>3</sub> ·xH <sub>2</sub> O | Sample 3 | 332.2                       | 0.3830                      | 0.9937 |

The effects of AO7 initial concentration on the AO7 adsorption amount and adsorption efficiency are shown in Fig. 11. For all samples, the adsorption amount increased with increasing AO7 initial concentrations until [AO7] = 100 mg L<sup>-1</sup>. In contrast, the removal efficiency decreased with increasing AO7 initial concentrations. More specifically, the removal efficiencies could reach 99.6, 99.2 and 99.5% at [AO7] = 20 mg L<sup>-1</sup> for Sample 1, Sample 2 and Sample 3 synthesized in the presence of H<sub>2</sub>O<sub>2</sub>, respectively.

The adsorption experiments of AO7 dye at varying initial concentrations onto mesoporous CeO<sub>2</sub> powders were performed, and the saturated adsorption amount of AO7 dye was obtained according to Langmuir linear fits. Fig. 12a–c shows the Langmuir linear fits of experimental data of adsorption of AO7 dye onto mesoporous CeO<sub>2</sub> powders, and the resulting isotherm constants and correlation coefficients are presented in Table 3. From Table 3, we can see that the saturated adsorption amounts ( $q_m$ ) are 378.8, 261.1 and 332.2 mg g<sup>-1</sup>, and Langmuir adsorption constants ( $K_L$ ) are 0.4740, 0.3460 and 0.3830 for Sample 1, Sample 2 and Sample 3, respectively. In addition, all associated correlation coefficients ( $R^2$ ) are greater than 0.9920, confirming that Langmuir isotherm model is a good fit for modelling the adsorption of AO7 dye onto mesoporous CeO<sub>2</sub> surface. The results indicate that the proposed route for template-free synthesis of mesoporous CeO<sub>2</sub> powders is one marker of success to effectively and rapidly remove AO7 dye.

effective removal of AO7 dye. Moreover, the saturated adsorption amounts could reach up to 378.8, 261.1 and 332.2 mg g<sup>-1</sup> without pH pre-adjustments for these mesoporous CeO<sub>2</sub> powders using (NH<sub>4</sub>)<sub>2</sub>CO<sub>3</sub>, Na<sub>2</sub>CO<sub>3</sub> as precipitants and using commercial Ce<sub>2</sub>(CO<sub>3</sub>)<sub>3</sub>·xH<sub>2</sub>O as an existing precursor, respectively. Prompted by the high BET surface area, low cost, environmental friendliness and omissible calcination process, these mesoporous CeO<sub>2</sub> powders synthesized with the routes in this work could be a promising candidate for practical application. In subsequent study, the optimization of experimental parameters will be explored, such as the additive amount of H<sub>2</sub>O<sub>2</sub>, hydrothermal treatment temperature and time, and so on.

## Conflicts of interest

There are no conflicts to declare.

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## Conclusions

The accessible, cheap and safe chemistry reagents (NH<sub>4</sub>)<sub>2</sub>CO<sub>3</sub>, Na<sub>2</sub>CO<sub>3</sub> and H<sub>2</sub>O<sub>2</sub> were employed for template-free synthesis of mesoporous CeO<sub>2</sub> powders with high BET surface areas. (NH<sub>4</sub>)<sub>2</sub>CO<sub>3</sub> or Na<sub>2</sub>CO<sub>3</sub> as a precipitant was used to separate original cerium precursors from Ce<sup>3+</sup> aqueous solution, while H<sub>2</sub>O<sub>2</sub> served as an oxidant to induce the phase transformation from original cerium precursors to CeO<sub>2</sub> precursors with initial porous structures, which was the precondition for the formation of final CeO<sub>2</sub> phase and mesoporous structures during the following hydrothermal process at 200 °C for 24 h. The BET surface areas of mesoporous CeO<sub>2</sub> powders synthesized using (NH<sub>4</sub>)<sub>2</sub>CO<sub>3</sub> and Na<sub>2</sub>CO<sub>3</sub> as precipitants were 106.1 and 76.9 m<sup>2</sup> g<sup>-1</sup>. Moreover, another route, using commercial Ce<sub>2</sub>(CO<sub>3</sub>)<sub>3</sub>·xH<sub>2</sub>O as existing precursor for synthesis of mesoporous CeO<sub>2</sub> powders with a BET surface area of 100.0 m<sup>2</sup> g<sup>-1</sup>, can shorten experimental processes and reduce costs. These mesoporous CeO<sub>2</sub> powders could be used as a suitable sorbent for rapid and



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