In-situ growth of CeO$_2$/Ce(OH)CO$_3$ composites with enhanced photocatalytic activity by the incomplete conversion of CeO$_2$ to Ce(OH)CO$_3$

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Research Article

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Abstract
In this paper, a novel strategy was used to grow CeO$_2$/Ce(OH)CO$_3$ composite in situ by the incomplete conversion of CeO$_2$ to Ce(OH)CO$_3$ using ethylene glycol (EG) as CO$_3^{2-}$ source and solvent. And the content of Ce(OH)CO$_3$ in CeO$_2$/Ce(OH)CO$_3$ composite can be controlled by changing the solvent composition. The CeO$_2$/Ce(OH)CO$_3$ composite prepared at 200°C for 24 h with a H$_2$O/EG volume ratio of 10:20 exhibited greatly enhanced visible-light activity for methylene blue (MB) degradation compared to the bare CeO$_2$. This work would provide a novel method to fabricate basic rare earth carbonates and their composites.

1. Introduction
Because of its strong redox ability, excellent UV absorption capacity, low cost, and chemical stability, cerium dioxide (CeO$_2$) is widely used in automotive three-way catalysts, UV absorbers, and photocatalysts [1–5]. However, the rapid photogenerated electron-hole recombination efficiency and the severe agglomeration of CeO$_2$ greatly limit its catalytic efficiency [6]. A lot of strategies have been used to overcome the above-mentioned issues. Among these strategies, coupling of semiconductors has been proven to be a practical and effective method to improve catalytic performance [7–10]. For instance, Wen et al. developed Ag$_2$O/CeO$_2$ composites which displayed higher rate constant than pure Ag$_2$O and CeO$_2$ for the photodegradation of enrofloxacine under visible light irradiation [11]. Wang et al. synthesized hollow BiOCl@CeO$_2$ microspheres via a precipitation-hydrothermal process, which exhibited enhanced visible-light activities towards tetracycline [12].

Cerium hydroxide carbonate (Ce(OH)CO$_3$) has attracted great attention due to its optical properties related to its different phase structures and morphologies [13]. Although Ce(OH)CO$_3$ is often used as a precursor for the preparation of CeO$_2$, it also has potential in photocatalytic applications. For example, Tong et al. reported a g-C$_3$N$_4$/CeCO$_3$OH/CeO$_2$ ternary nanocomposite, which showed a rate of hydrogen production that was over 8 times larger than that of g-C$_3$N$_4$/CeO$_2$ [14]. Therefore, the coupling of CeO$_2$ and Ce(OH)CO$_3$ is a feasible method to improve the photocatalytic activity of CeO$_2$.

Herein, we used a facile hydrothermal method to carry out the incomplete conversion of CeO$_2$ to Ce(OH)CO$_3$ for the in-situ growth of CeO$_2$/Ce(OH)CO$_3$ composites. In the hydrothermal reaction, the content of Ce(OH)CO$_3$ in CeO$_2$/Ce(OH)CO$_3$ can be tuned by changing the volume ratio of H$_2$O to EG. The CeO$_2$/Ce(OH)CO$_3$ composites exhibited enhanced photocatalytic performance of MB degradation compared with pristine CeO$_2$.

2. Results And Discussion
The crystal structure of CeO$_2$ and as-prepared samples were analyzed by X-ray diffraction as shown in Fig. 1a. All samples exhibited the well-defined diffraction peaks at 28.7°, 33.3°, 47.7°, and 56.6°, which
corresponded to the (111), (200), (220), and (311) planes of CeO$_2$ (JCPDS no. 34-0394) [15, 16]. Interestingly, the samples, prepared under the condition that the volume ratios of H$_2$O to EG were 25:5, 20:10, 15:15, and 10:20, showed several new peaks at 17.7°, 24.6°, 30.5°, 35.9°, 43.3° and 44.0°, which were assigned to the (002), (300), (032), (004), (330), and (304) planes of Ce(OH)CO$_3$ (JCPDS no. 52–0352) [17], indicating the formation of CeO$_2$/Ce(OH)CO$_3$ composite. Besides, the intensity of these peaks increased with the increasing of EG proportion in the solvent, indicating the increasing of Ce(OH)CO$_3$ content in the CeO$_2$/Ce(OH)CO$_3$ composite. The Ce(OH)CO$_3$ content in the CeO$_2$/Ce(OH)CO$_3$ composite reached the maximum value at H$_2$O/EG ratio of 10:20. Thus, the content of Ce(OH)CO$_3$ in CeO$_2$/Ce(OH)CO$_3$ composite could be controlled by adjusting the solvent composition. In the range of the volume ratio of H$_2$O to EG from 25:5 to 10:20, the smaller the volume ratio of H$_2$O to EG, the larger the content of Ce(OH)CO$_3$ in CeO$_2$/Ce(OH)CO$_3$ composite.

The FT-IR spectra of as-prepared samples were shown in Fig. 1b. The stretching vibration of Ce-O bonds caused a wide band in the range of 500–700 cm$^{-1}$ [18], and the absorption peak at 3460 cm$^{-1}$ was the stretching vibration of the hydroxyl group [19]. For the CeO$_2$/Ce(OH)CO$_3$ composites prepared under the condition that the volume ratios of H$_2$O to EG were 25:5, 20:10, 15:15, and 10:20, the broad peaks between 1417 and 1496 cm$^{-1}$ were ascribed to the stretching vibration of the CO$_3^{2-}$ groups [20]. The sharp absorption peaks at 694 cm$^{-1}$, 725 cm$^{-1}$ and 850 cm$^{-1}$ were caused by the bending vibration of the CO$_3^{2-}$ groups [21]. The XRD and FT-IR results indicated that the samples obtained when the volume ratios of H$_2$O to EG of 30:0, 5:25, and 0:30 were CeO$_2$ while at the other ratios were CeO$_2$/Ce(OH)CO$_3$ composites.

Figure 2 showed the SEM images of CeO$_2$ and as-prepared samples under different H$_2$O/EG volume ratios. CeO$_2$ displayed apparent 2D layered structure. When the volume ratios of H$_2$O to EG were 30:0 and 25:5, the 2D layered structure was destroyed and a few small particles appeared, which was attributed to the forced hydrolysis of CeO$_2$. As the amount of EG in the solvent increased, the destroyed layered structure gradually recovered and thickened, and the CeO$_2$/Ce(OH)CO$_3$ composite showed a pie-like structure with stacked pieces when the volume ratio of H$_2$O and EG was 10:20, then the morphology of the sample was consistent with the CeO$_2$ nanosheets.

Figure 3 are the XRD patterns of the samples prepared at volume ratio of H$_2$O to EG for 10:20 with different temperatures. It was clear that the samples just showed the characteristic diffraction peaks of CeO$_2$, and Ce(OH)CO$_3$ cannot be synthesized when the reaction temperature was lower than 200°C. When the reaction temperature was 200°C, the characteristic diffraction peaks of CeO$_2$ and Ce(OH)CO$_3$ were obvious, indicating the formation of CeO$_2$/Ce(OH)CO$_3$ composite. The corresponding SEM image was shown in Fig. 4. When the reaction temperature was lower than 200°C, the morphology of the sample had not been destroyed and it was still a 2D layered structure. The sample obtained at 200°C exhibited a pie-
like structure with stacked pieces. Based on the above results, it can be deduced that CeO$_2$ undergoes forced hydrolysis under the conditions of high reaction temperature, and the forced hydrolysis of CeO$_2$ is a precondition for the formation of CeO$_2$/Ce(OH)CO$_3$ composite in this reaction.

In our synthesis set-up, the reaction process of the formation of Ce(OH)CO$_3$ can be proposed. It is actually a dissolution-recrystallization process. For CeO$_2$, it was forced to hydrolyze at high temperature and released Ce$^{4+}$ which was reduced to Ce$^{3+}$ by EG. Trivalent Ce$^{3+}$ was easily changed into Ce(OH)$^{2+}$ groups. As for EG, it was gradually oxidized to oxalic acid [22], then released carbon dioxide. Then carbon dioxide reacted with water to produce CO$_3^{2-}$. Finally, Ce(OH)$^{2+}$ combined with CO$_3^{2-}$ to yield Ce(OH)CO$_3$. The reaction can be expressed as follows:

$$\text{CeO}_2 + \text{H}_2\text{O} \rightarrow \text{Ce(OH)}_4 \quad (1)$$

$$\text{Ce(OH)}_4 \leftrightharpoons \text{Ce}^{4+} + 4\text{OH}^- \quad (2)$$

$$\text{Ce}^{4+} \rightarrow \text{Ce}^{3+} \quad (3)$$

$$\text{Ce}^{3+} + \text{OH}^- \rightarrow \text{CeOH}^{2+} \quad (4)$$

$$(\text{CH}_2\text{OH})_2 \rightarrow \text{CHOCH}_2\text{OH} \rightarrow \text{CHOCOOH} \rightarrow (\text{COOH})_2 \rightarrow \text{CO}_2 \quad (5)$$

$$\text{CO}_2 + \text{H}_2\text{O} \rightarrow \text{CO}_3^{2-} + 2\text{H}^+ \quad (6)$$

$$\text{CeOH}^{2+} + \text{CO}_3^{2-} \rightarrow \text{Ce(OH)CO}_3 \quad (7)$$

Thus the forced hydrolysis of CeO$_2$ (Reaction 1) and the release of Ce$^{4+}$ (Reaction 2) were crucial for the formation of Ce(OH)CO$_3$ which was the reason why the sample prepared under low reaction temperature or with low water content in the solvent cannot produce Ce(OH)CO$_3$. Besides, Ce(OH)$_4$ cannot be completely ionized to release Ce$^{4+}$ (Reaction 2). Therefore, the conversion of CeO$_2$ to Ce(OH)CO$_3$ cannot be fully carried out, resulting the formation of CeO$_2$/Ce(OH)CO$_3$ composite. Due to the similar chemical properties, this method of synthesizing CeO$_2$/Ce(OH)CO$_3$ composite can be extended to rare earth elements with variable valences.

Figure 5 showed the UV-vis diffuse reflectance spectra of the samples obtained at 200°C for 24 h with various volume ratios of H$_2$O to EG. The absorbance intensity of CeO$_2$ nanosheets was weak. And there was no response in the visible region for CeO$_2$ nanosheets. After hydrothermal treatment, the obtained samples all showed a weak response in the visible region at the range of 450–800 nm. Besides, the UV-vis spectra of the obtained CeO$_2$/Ce(OH)CO$_3$ composites were red shifted with respect to the pure CeO$_2$ nanosheets. The above results indicated that CeO$_2$/Ce(OH)CO$_3$ composites had better visible-light response which was favorable to photocatalytic activities.
The visible-light catalytic activities of the as-prepared samples were evaluated by the degradation of MB after irradiation for 2 hours as shown in Fig. 6. Obviously, 76.87% of MB was degraded over CeO$_2$ photocatalyst. After hydrothermal treatment, the obtained samples all showed enhanced MB removal activity, among which the CeO$_2$/Ce(OH)CO$_3$ composites prepared at H$_2$O/EG ratios of 25:5, 20:10, 15:15, and 10:20 exhibited better effect. The photodegradation efficiencies of the CeO$_2$/Ce(OH)CO$_3$ composites increased with the Ce(OH)CO$_3$ content, and the highest photodegradation activity (98.84%) is observed for the CeO$_2$/Ce(OH)CO$_3$ composite prepared at a H$_2$O/EG ratio of 10:20.

### 3. Conclusions

In conclusion, the CeO$_2$/Ce(OH)CO$_3$ composites were successfully synthesized by a facial hydrothermal method. The content of Ce(OH)CO$_3$ in CeO$_2$/Ce(OH)CO$_3$ composite can be controlled only by tuning the solvent composition. All the CeO$_2$/Ce(OH)CO$_3$ composites exhibited enhanced photocatalytic activities compared with pristine CeO$_2$. The CeO$_2$/Ce(OH)CO$_3$ composite prepared at 200°C for 24 h with a H$_2$O/EG ratio of 10:20 showed the best photocatalytic performance with 98.84% MB decontamination under 2 hours visible light irradiation.

### 4. Experimental

#### Preparation of CeO$_2$ nanosheets

10 of mmol Ce(NO$_3$)$_3$·6H$_2$O was added into 10 mL of deionized water to form a clear solution. 30 of mmol NH$_4$HCO$_3$ was dissolved into 30 mL of deionized water. Then the two solutions were mixed together. After stirring for 1 h and aging for 12 h, the precipitate was collected, washed several times with distilled water and absolute ethanol, and then filtered by suction. Finally, the white precipitate was calcined at 500°C for 2 h.

#### Preparation of CeO$_2$/Ce(OH)CO$_3$ composite

50 mg CeO$_2$ nanosheets were dispersed in 30 mL of deionized water and EG mixtures (volume ratio 10:20). After stirring for 30 min, the above mixture was transferred into a 40 mL Teflon-lined autoclave and maintained at 200°C for 24 h. After being cooled to room temperature naturally, the resulting grey precipitates were collected and washed several times with distilled water and absolute ethanol and dried at 60°C.

In order to explore the synthesis mechanism, two sets of control samples were prepared just by adjusting the volume ratio of H$_2$O to EG in the reaction solvent and the reaction temperature, respectively. The volume ratios of H$_2$O to EG are 30:0, 25:5, 20:10, 15:15, 5:25, and 0:30. And the reaction temperatures are 140, 160 and 180°C.

A series of characterizations were performed on these samples. The morphology and microstructure were observed using Scanning electron microscope (SEM, Hitachi, Japan, S-3400N). The X-ray diffraction (XRD) patterns were obtained by a Rigaku X-ray Diffractometer (XRD, Japan, Ultima IV) with Cu-K$_\alpha$. 
radiation ($\lambda = 1.54056$ Å). Fourier transform infrared spectroscopy (FTIR) were recorded with Fourier transform infrared (FT-IR) spectrometer (Thermo Scientific, USA, Nicolet6700).

The photocatalytic activity was estimated by the degradation of methylene blue (MB). 10 mg of photocatalyst was dispersed in 50 mL of MB solution (10 mg/L). A 300 W Xe lamp equipped with a cutoff filter (< 420 nm) was used as the light source, and kept the distance between the light source and the solution at 10 cm. Prior to irradiation, each solution was stirred for 30 min at dark to reach the adsorption equilibrium. About 4 mL solution was taken out and centrifuged after regular interval of 30 min. The concentration of MB was determined by an UV–visible spectrophotometer (UV-vis, Hitachi, Japan, Hitachi-U3301).

**Declarations**

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**Conflict of interest** The authors declare that they have no conflict of interest.

**Data availability statement**

The data that support the findings of this study are available from the corresponding author upon reasonable request.

**References**


Figures

Figure 1

XRD (a) and FT-IR (b) spectra of ceria nanosheets and the samples obtained at 200 °C for 24 h with different volume ratios of H$_2$O to EG.
Figure 2

SEM images of (a) ceria nanosheets and the samples obtained at 200 °C for 24 h with various volume ratios of H₂O to EG: (b) 30:0, (c) 25:5, (d) 20:10, (e) 15:15, (f) 10:20, (g) 5:25 and (h) 0:30. The scale bars in (a–h) are all 5 μm.
Figure 3

XRD pattern of the samples prepared at volume ratios of H$_2$O to EG for 10:20 with different temperature.

Figure 4

SEM images of the samples prepared at volume ratios of H$_2$O to EG for 10:20 with different temperatures: (a) 140 °C, (b) 160 °C, (c) 180 °C and (d) 200 °C. The scale bars in (a–d) are all 5 μm.
Figure 5

UV-vis diffuse reflectance spectra of the samples obtained at 200 °C for 24 h with various volume ratios of H$_2$O to EG.
Figure 6

Photocatalytic degradation of methylene blue by CeO$_2$ and the samples obtained at 200 °C for 24 h with various volume ratios of H$_2$O to EG.

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