Research Article

Synthesis and Oxygen Storage Capability of CeO₂ Powders for Enhanced Photocatalytic Degradation of Acid Orange 7

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Acid Orange 7 (AO7) is one of the most common azo dyes; however, its strong azo bond makes them difficult to biologically degrade. We sought to degrade AO7 dye using CeO₂ as a promising alternative photocatalyst. CeO₂ powders were synthesized with alternative monoethanolamine (MEA), diethanolamine (DEA), and triethanolamine (TEA) as a precipitant by solvothermal process combined calcination in air. Compared to the oxygen storage capability of Blank-CeO₂ (0.186 mmol O₂/g), that of MEA-CeO₂ synthesized in the presence of MEA as a precipitant increased by 21.0%, while that of DEA-CeO₂ and TEA-CeO₂ synthesized in the presence of DEA and TEA as precipitants were decreased. Importantly, such MEA-CeO₂ exhibited the highest photocatalytic activity than Blank-, DEA-, and TEA-CeO₂ in degradation of AO7 under simulated sunlight illumination, and the removal rate of AO7 by MEA-CeO₂ could reach 98.3% within 100 min.

1. Introduction

Azo dyes, containing plural azo and aryl groups, are the most widely synthetic dyes, used for dyeing and printing of various fibers [1–3], as well as coloring of paints, plastics and rubber, etc. [4–6]. Under special conditions, azo dyes can decompose and produce more than twenty kinds of carcinogenic aromatic amines, which could change the DNA structure of the human body to cause lesions and induce cancer by activation [7–12]. Therefore, the azo wastewater must be treated harmlessly before discharge [13–15]. So far, numerous approaches have been engaged to remove azo dyes, such as electrocatalysis by destroying color groups [16, 17], biodegradation by mineralizing colorless organic intermediates [18, 19], and chemical oxidation by photocatalytic catalyst [20–22]. Among these techniques, photocatalytic degradation is a promising process of choice [23–26]. Titanium dioxide (TiO₂) is considered to be the most popular photocatalyst due to its environmental friendliness and biological inertness [27–29].

Ceria (CeO₂) is a typical rare earth oxide and can serve as catalyst [30], catalyst carrier [31], UV absorbent [32], fuel cell electrolyte [33], automobile exhaust absorbent [34], electronic ceramics [35], etc. These applications of CeO₂ benefit generally from its excellent redox property of Ce³⁺  Ce⁴⁺ and high oxygen storage capacity (OSC). It is accepted that the OSC of CeO₂ is well associated with the presence of oxygen vacancies, as well as their photocatalytic activity [36–38]. However, the researches into the photocatalytic degradation of azo dyes on CeO₂ are just beginning. For example, Aboutaleb and El-Salamony [39] prepared pure CeO₂ and Fe-doped CeO₂ nanocomposites by the precipitation and modified Sol-Gel auto combustion methods and investigated their photocatalytic activity in Congo Red azo dye under the visible light irradiation. For 1 g/L catalyst loading with 25 mg/L Congo Red solution, the degradation rates were 87, 82, and 48% for Fe-CeO₂(p), pure CeO₂, and Fe-CeO₂ (sg) after visible irradiation for 180 min, respectively. Krishnan et al. [40] prepared Sn-doped 1:2 CeO₂-Fe₂O₃ nanocomposite with different Sn contents by
the thermal decomposition method for efficient degradation of Methylene Blue (MB) and Methyl Orange (MO) dyes under visible light. The as-synthesized nanocomposite with 5%-Sn achieved nearly complete degradation for 10-50 mg/L MO solution, and the maximum degradation efficiency obtained for MB solution was 93.54-94.65% for 10-30 mg/L MB solution. Mirzaazadeh and Lashanizadegan [41] prepared CdO/CeO₂/RGO composite by a hydrothermal process for the sonocatalytic degradation of Rhodamine B (Rho B) and MO under ultrasonic irradiation. The highest degradation efficiencies of Rho B and MO were 97% and 85% within 150 min, when the initial concentration of dyes was 1.2 g/L with 20 mg/L catalyst. Despite these progresses in the synthesis of pure CeO₂ and CeO₂-based photocatalyst, it is still challenging to further improve their photocatalytic activity.

Herein, a series of CeO₂ powders were synthesized solvothermally at 120°C followed by calcination at 500°C in air using Ce(NO₃)₃·6H₂O as a cerium source and using alternative monoethanolamine (MEA), diethanolamine (DEA), and triethanolamine (TEA) as a precipitant. The relative OSC of the as-synthesized CeO₂ was quantified by O₂ temperature-programmed desorption (O₂-TPD) measurements, and the photocatalytic activity for Acid Orange 7 (AO7) was determined.

2. Experimental

2.1. Starting Materials. Ce(NO₃)₃·6H₂O (99.95%) and triethanolamine (TEA, >99.0%) were supplied by Aladdin Co. Ltd. Monoethanolamine (MEA, 99.0%) was supplied by Shanghai Xianding Biological Science and Technology Co. Ltd. Diethanolamine (DEA, 99.0%) was supplied by Shanghai Maclin Biochemical Technology Co. Ltd. Acid Orange 7 (AO7, >97.0%) was supplied by Tokyo Chemical Industry Co. Ltd., and ethanol (≥99.7%) was supplied by Chengdu Kelong Chemical Co. Ltd. All reagents were commercially obtained and used as received without further purification.

2.2. Sample Preparation. A solvothermal procedure was employed to synthesize CeO₂ precursors. Briefly, 6.0 mmol Ce(NO₃)₃·6H₂O and an appropriate precipitant (MEA, DEA, or TEA) were dissolved into 20 mL ethanol, the value of nitrogen to cerium ratio (N:Ce (mol.)) was 0.3, and then, ethanol was added to make a final volume of 25 mL. The as-formed solution was decanted into a 50 mL Teflon-lined autoclave and maintained for 24 h at 120°C. Subsequently, the resulting precipitates were washed with distilled water and ethanol and dried at 60°C for 24 h. Finally, the as-formed powders were calcined in air at 500°C for 2 h. These final CeO₂ products were labeled as MEA-CeO₂, DEA-CeO₂, and TEA-CeO₂ synthesized with TEA, MEA, and DEA as a precipitant, respectively.

For comparison, the CeO₂ sample was synthesized following the same procedure as control, however, in the absence of precipitants (MEA, DEA, and TEA), labeled as Blank-CeO₂.

2.3. Characterization. The phases of the precursors and the final products were examined by X-ray diffraction (XRD, DX-2700). The morphologies of the final products CeO₂ were examined using a field-emission Scanning Electron Microscope (SEM, Hitachi S-4800). The Brunauer-Emmett-Teller (BET) specific surface areas (S_BET) of the final products CeO₂ were obtained from nitrogen adsorption measurements (Quantachrome, Quadrasorb SI). Raman spectra were measured using a Horiba Jobin Yvon LabRam Aramis Raman spectrometer with a He-Cd laser of 325 nm.

2.4. O₂-TPD and H₂-TPR Measurements. The OSCs of the final products CeO₂ were estimated by O₂ temperature-programmed desorption (O₂-TPD) measurements, which were carried out in a plug-flow microreactor system (TP5000) with a thermal conductivity detector (TCD), and the amount of O₂ desorption during the process was measured by the TCD. The as-synthesized CeO₂ powders (~100 mg) were activated with air stream for 30 min at 400°C, changed into Helium (He) and cooled, changed into air stream for 30 min at 120°C, then purged with He stream to remove the excess O₂, and finally was conducted surface oxygen desorption at the flow of He (10 mL/min), while the temperature was raised to ~930°C (10°C/min).

H₂ temperature-programmed reduction (H₂-TPR) measurements were still carried out in the same TP5000 system, and the amount of H₂ uptake during the reduction was measured by the TCD. The as-synthesized CeO₂ powders (~50 mg) were activated with 5% O₂/He stream for 1 h at 500°C, cooled to room temperature in 5% O₂/He stream, and changed into He stream to remove the excess O₂. Finally, the H₂-TPR experiments were performed in a 5% H₂/He stream (30 mL/min) with a heating rate of 10°C/min.

2.5. Evaluation of Photocatalytic Activity. The photocatalytic activities of the as-synthesized CeO₂ powders as catalysts were evaluated by degradation of AO7 dye using an offline photocatalytic reactor attached to a 300 W pulsed Xenon lamp. Briefly, 200 mg of the as-synthesized CeO₂ powders was dispersed into 200 mL of 20 mg/L AO7 solution. Before illumination, the mixture was stirred for 60 min in dark to establish adsorption-desorption equilibrium between CeO₂ and AO7 molecules. Subsequently, the mixture was exposed to the simulated sunlight illumination originating from a 300 W pulsed Xenon lamp. The absorbance of the supernatant was measured at the maximum absorption wavelength (485 nm) for AO7 dye using a Hitachi U-3900 spectrophotometer, and the removal rate (η, %) was estimated as follows:

$$
\eta(\%) = \frac{A_0 - A_t}{A_0} \times 100,
$$

where \(A_0\) is the absorbance value of the initial AO7 solution (20 mg/L) and \(A_t\) is the absorbance value of the AO7 solution at a given time \(t\).
3. Results and Discussions

XRD analysis was employed to identify the phase composition and crystallographic structure of the precursors and the final products. Figure 1(a) shows XRD patterns of the precursors synthesized using the solvothermal process at 120°C for 24 h with alternative MEA, DEA, or TEA as a precipitant. As observed, all broad peaks had a good match with the standard CeO$_2$ pattern (JCPDS NO. 34-0394), and no additional phases for impurities such as cerium carbonate (e.g., Ce$_2$(CO$_3$)$_3$ or Ce$_2$(CO$_3$)OH) were detected, which indicated that CeO$_2$ could be successfully obtained by the solvothermal process. Moreover, compared with the JCPDS card of 34-0394, all the identified peaks were assigned to the face-centered cubic fluorite structure of CeO$_2$ and found no observable differences in the relative intensity of the peaks, which suggested that there was no preferential orientation or preferential crystal growth. After followed by calcination in air at 500°C for 2 h, all the identified peaks in Figure 1(b) were still assigned to the cubic CeO$_2$ (JCPDS No. 34-0394), no impurity phases were detected, and the intensities of the corresponding diffraction peaks were comparable. Compared to the relative intensities of the diffraction peaks in Figure 1(a), these of CeO$_2$ in Figure 1(b) were improved obviously, indicating that the crystallinity of CeO$_2$ synthesized by the solvothermal process was improved during calcination.

After O$_2$ chemisorption at 400°C with air stream on CeO$_2$, O$_2$-TPD experiments were performed in He stream, and the O$_2$-TPD spectra of Blank-, MEA-, DEA-, and TEA-CeO$_2$ powders are showed in Figures 2(a)–2(d), respectively. As observed, all broad peaks had a good match with the standard CeO$_2$ pattern (JCPDS NO. 34-0394), and no additional phases for impurities such as cerium carbonate (e.g., Ce$_2$(CO$_3$)$_3$ or Ce$_2$(CO$_3$)OH) were detected, which indicated that CeO$_2$ could be successfully obtained by the solvothermal process. Moreover, compared with the JCPDS card of 34-0394, all the identified peaks were assigned to the face-centered cubic fluorite structure of CeO$_2$ and found no observable differences in the relative intensity of the peaks, which suggested that there was no preferential orientation or preferential crystal growth. After followed by calcination in air at 500°C for 2 h, all the identified peaks in Figure 1(b) were still assigned to the cubic CeO$_2$ (JCPDS No. 34-0394), no impurity phases were detected, and the intensities of the corresponding diffraction peaks were comparable. Compared to the relative intensities of the diffraction peaks in Figure 1(a), these of CeO$_2$ in Figure 1(b) were improved obviously, indicating that the crystallinity of CeO$_2$ synthesized by the solvothermal process was improved during calcination.

After O$_2$ chemisorption at 400°C with air stream on CeO$_2$, O$_2$-TPD experiments were performed in He stream, and the O$_2$-TPD spectra of Blank-, MEA-, DEA-, and TEA-CeO$_2$ powders are showed in Figures 2(a)–2(d), respectively. As observed, it could be clearly observed that the oxygen desorption was rapid at the early stages of the process (120-170°C), reached a state of stable deoxidation, and maintained until ~600°C. The oxygen desorption peaks at 120-600°C could be attributed to the desorption of the adsorption oxygen in surface/subsurface lattice oxygen. Moreover, the amounts of oxygen desorption began to decrease gradually above ~600°C, which may be attributed to the adsorption oxygen in bulk lattice oxygen. Further analysis of the reason was conducted by H$_2$-TPR analysis as discussed later.

To understand the decrease in amounts of oxygen desorption after 600°C in Figure 2(b), H$_2$-TPR analyses were performed. Figures 3(a) and 3(b) show the profiles of Blank-CeO$_2$ and MEA-CeO$_2$ powders synthesized by solvothermal
process combined calcination in air, respectively. As observed in Figures 3(a) and 3(b), it can be clearly found that there were two obvious peaks of hydrogen reduction appearing at ~510 and ~790°C, implying the existence of two kinds of oxygen species at various coordination environments. According to Reference [42], the low temperature peaks (light yellow area, 120-600°C) could be assigned to the reduction of surface Ce$^{4+}$ cation, while the high temperature peaks (light green area, 600-930°C) could be assigned to the reduction of bulk Ce$^{4+}$ cation. In other words, there were two kinds of oxygen species on these CeO$_2$ and adsorption oxygen in surface and bulk lattice oxygen. Therefore, the decrease in amounts of oxygen desorption after 600°C in Figure 2(b) could be explained by the following. The adsorption oxygen in CeO$_2$ surface and subsurface was gradual while the lattice oxygen in CeO$_2$ bulk cannot be transferred to the CeO$_2$ surface in time. Finally, all lattice oxygen in CeO$_2$ bulk was transmitted to the CeO$_2$ surface and desorbed out; the O$_2$-TPD profiles would overlap with the baseline as well as H$_2$-TPR profiles. It was worth noting that the peak intensities of MEA-CeO$_2$ in Figure 3(b), whether the low temperature peaks (light yellow area) or high temperature peaks (light green area), were much higher than that of Blank-CeO$_2$. It indicated that the reaction of H$_2$ with MEA-CeO$_2$ was more violent during the entire temperature range of 120-930°C.

The relative OSC could be quantified using the amount of O$_2$ desorption per gram of CeO$_2$ by measuring the corresponding peak area of O$_2$-TPD profile, and the values of quantified OSC are showed in Figure 4. As observed, it was found that the OSC decreased following the order: MEA-CeO$_2$ (0.225 mmol/g) > Blank-CeO$_2$ (0.186 mmol/g) > DEA-CeO$_2$ (0.162 mmol/g) > TEA-CeO$_2$ (0.138 mmol/g). Compared to the OSC of Blank-CeO$_2$, that of MEA-CeO$_2$ synthesized in the presence of MEA as precipitant increased by 21.0%, while that of DEA-CeO$_2$ and TEA-CeO$_2$ synthesized in the presence of DEA and TEA as precipitants were decreased. Differences in OSC may be attributed to differences in particle size, morphology, and specific surface area of final products CeO$_2$; further analysis was conducted by SEM analysis and nitrogen adsorption measurements as discussed later.

Raman scattering is a widely used technique for structural analysis of CeO$_2$ due to its sensitivity to significant structural changes, such as the formation of oxygen vacancies [43]. Figure 5 shows the Raman spectra of the Blank-, MEA-, DEA-, and TEA-CeO$_2$ powders. The Raman spectra of each sample showed two peaks at about 450 and 580 cm$^{-1}$. The peak at about 450 cm$^{-1}$ was attributed to the F$_{2g}$ vibration mode of the O atoms around each Ce$^{4+}$ cation, while the band at 580 cm$^{-1}$ was known to be associated with the oxygen vacancies and had been widely observed in CeO$_2$. 

![Figure 5: Raman spectra with 325 nm laser excitation for Blank-, MEA-, DEA-, and TEA-CeO$_2$ powders.](image-url)
Furthermore, the relative oxygen vacancy concentration could be determined from the Raman spectra by the ratio of the Raman band intensity at ~580 cm\(^{-1}\) to that at ~450 cm\(^{-1}\) \((I_{580}/I_{450})\) [45]. The oxygen vacancy concentrations of Blank-, MEA-, DEA-, and TEA-CeO\(_2\) powders, which were the corresponding values of \(I_{580}/I_{450}\), were estimated as 0.39, 0.47, 0.34, and 0.29, respectively. The order of relative concentrations of oxygen vacancy \((\text{MEA-CeO}_2 > \text{Blank-CeO}_2 > \text{DEA-CeO}_2 > \text{TEA-CeO}_2)\) is the same as that of OSC in Figure 4. This result indicates that the MEA promoted the oxygen vacancies of CeO\(_2\), and the higher value might be beneficial for their OSC.

Figures 6(a)–6(d) show the SEM images of Blank-, MEA-, DEA-, and TEA-CeO\(_2\) particles synthesized by solvothermal process combined calcination in air. Figures 6(a)–6(d) show the SEM images of Blank-, MEA-, DEA-, and TEA-CeO\(_2\) particles synthesized by solvothermal process combined calcination in air, respectively. As observed in Figure 6(a), the Blank-CeO\(_2\) sample displayed near spherical aggregate particles with two diameters of ~150 nm and ~50 nm. After adding precipitant (MEA, DEA, and TEA) in the solvothermal process, the as-synthesized final products CeO\(_2\) still displayed two sizes of aggregate particles, but the smaller particles got smaller (see Figures 6(b)–6(d)). Moreover, these size values of Blank-, MEA-, DEA-, and TEA-CeO\(_2\) particles were demonstrated by statistical analysis; the size distribution histograms are showed in Figures 7(a)–7(d). Furthermore, the specific surface areas of Blank-, MEA-, DEA-, and TEA-CeO\(_2\) powders were determined using the Brunauer-Emmett-Teller method, and \(S_{\text{BET}}\) decreased following the order: MEA-CeO\(_2\) \((58.4 \text{ m}^2/\text{g})\) > Blank-CeO\(_2\) \((42.6 \text{ m}^2/\text{g})\) > DEA-CeO\(_2\) \((35.8 \text{ m}^2/\text{g})\) > TEA-CeO\(_2\) \((32.1 \text{ m}^2/\text{g})\). The ordering of \(S_{\text{BET}}\) was consistent with that of OSC, indicating that \(S_{\text{BET}}\) of CeO\(_2\) powders was the major factors in their OSC.

The adsorption capacities of final CeO\(_2\) products in the dark and the photocatalytic activities upon simulated sunlight were investigated by the removal of AO7 dye. From Figure 8, it could be observed that the removal rates of AO7 within 60 min reached 12.3, 26.6, 6.4, and 4.4% for Blank-, MEA-, DEA-, and TEA-CeO\(_2\) powders in the dark, respectively. In fact, the adsorption reactions in the dark were mostly completed within 40 min, and no significant changes were observed from 40 to 60 min, indicating that
the adsorption-desorption equilibriums between AO7 molecules and CeO$_2$ were established within the first 40 min of adsorption reactions. After illumination upon simulated sunlight for 220 min, the removal rate of AO7 was 99.8% for MEA-CeO$_2$, which was much higher than 89.5% for Blank-CeO$_2$, while only 68.4 and 46.7% for DEA- and TEA-

![Size distribution histograms](image)

**Figure 7:** Size distribution histograms of (a) Blank-, (b) MEA-, (c) DEA-, and (d) TEA-CeO$_2$ particles.

![AO7 adsorption and degradation](image)

**Figure 8:** AO7 adsorption in the dark and AO7 degradation upon illumination with a 300 W Xenon lamp in the presence of Blank-, MEA-, DEA-, and TEA-CeO$_2$ powders synthesized by solvothermal process combined calcination in air ($[\text{CeO}_2] = 1.0 \text{ g/L}$; $[\text{AO7}] = 20 \text{ mg/L}$; $V = 200 \text{ mL}$; room temperature; without pH preadjustment).

![Cycling runs](image)

**Figure 9:** Cycling runs of photocatalytic degradation of AO7 dye with MEA-CeO$_2$ particles under a 300 W Xenon lamp.
CeO₂, respectively. It was worth noting that the photocatalytic reaction on MEA-CeO₂ was completed within 100 min, the removal rate was 98.3%, no significant changes were observed from 100 to 220 min, and the removal rate of MEA-CeO₂ increased by 44.9% compared to that of Blank-CeO₂ within 100 min. It indicated that the as-synthesized MEA-CeO₂ was more suitable as a promising alternative photocatalyst for the removal of AO7 dye. In addition, the photostability of the as-synthesized MEA-CeO₂ was also evaluated through recycling experiments for photodegradation of AO7 upon illumination with a 300 W Xenon lamp. As shown in Figure 9, after four photodegradation cycles, MEA-CeO₂ showed no significant change in the photocatalytic activity within 5 h, indicating that the MEA-CeO₂ serving as photocatalyst were stable during photocatalysis.

4. Conclusions

CeO₂ powders with enhanced OSC and enhanced photocatalytic activity were synthesized by a solvothermal method at 120°C for 24 h followed by calcination at 500°C for 2 h, in which MEA served as an alternative precipitant with N : Ce (mol.) = 0.3. The OSC decrease following the order was MEA-CeO₂ (0.225 mmol/g) > Blank-CeO₂ (0.186 mmol/g) > DEA-CeO₂ (0.162 mmol/g) > TEA-CeO₂ (0.138 mmol/g). Compared to Blank-CeO₂, the OSC of MEA-CeO₂ synthesized in the presence of MEA as a precipitant increased by 21.0%. Moreover, the removal rate of AO7 was 99.8% for MEA-CeO₂, which was much higher than 89.5% for Blank-CeO₂, while only 68.4 and 46.7% for DEA- and TEA-CeO₂, respectively. The photocatalytic reaction on MEA-CeO₂ was mostly completed within 100 min, the removal rate was 98.3%, and the removal rate of MEA-CeO₂ increased by 44.9% compared to that of Blank-CeO₂ within 100 min. Moreover, the MEA-CeO₂ serving as photocatalyst were stable during the four recycling experiments for photodegradation of AO7 with a 300 W Xenon lamp, indicating that the as-synthesized MEA-CeO₂ was more suitable as a promising alternative photocatalyst for the removal of AO7 dye.

Data Availability

All data, models, and code generated or used during the study appear in the submitted article.

Conflicts of Interest

The authors declare no conflicts of interest.

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