Preparation, characterization of a ceria loaded carbon nanotubes nanocomposites photocatalyst and degradation of azo dye Acid Orange 7

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Keywords: Carbon nanotubes, ceria, nanocomposites photocatalyst, preparation, acid orange 7.

Abstract: A ceria loaded carbon nanotubes (CeO$_2$/CNTs) nanocomposites photocatalyst was prepared by chemical precipitation, and the preparation conditions were optimized using an orthogonal experiment method. HR-TEM, XRD, UV-Vis/DRS, TGA and XPS were used to characterize the photocatalyst. Nitrogen adsorption-desorption was employed to determine the BET specific surface area. The results indicated that the photocatalyst has no obvious impurities. CeO$_2$ was dispersed on the carbon nanotubes with a good loading effect and high loading efficiency without agglomeration. The catalyst exhibits a strong ability to absorb light in the ultraviolet region and some ability to absorb light in the visible light region. The CeO$_2$/CNTs nanocomposites photocatalyst was used to degrade azo dye Acid Orange 7 (40 mg/L). The optical decolorization rate was 66.58% after xenon lamp irradiation for 4 h, which is better than that of commercial CeO$_2$ (43.13%). The results suggested that CeO$_2$ loading on CNTs not only enhanced the optical decolorization rate but also accelerated the separation of CeO$_2$/CNTs and water.

Introduction

Ceria (CeO$_2$) is one of the rare earth oxides that has widely been used in the water gas shift reaction (Rodriguez et al. 2007, Vindigni et al. 2011), automotive three-way catalytic converters (Matsumoto 2004), green phosphors (Long et al. 2006), oxygen storage material (Campbell et al. 2005, Esch et al. 2005), solid fuel cells (Park et al. 2000) and antioxidants in biological model systems (Karakoti et al. 2010, Singh et al. 2011) due to its unique cubic fluorite structure (Trovarelli 2002), oxygen storage capacity (Walton 2011) and high activity.

The photocatalytic oxidation performance of ceria is the focus of research due to its relatively numerous oxygen vacancies and low redox potential (Zhang et al. 2010). Zhai et al. (Zhai et al. 2007) employed homemade CeO$_2$ nanocrystals as a catalyst for the degradation of 10 mg/L of acid black dye in water in sunlight, and the decolorization rate was 97%. Ji et al. (Ji et al. 2009) and Feng et al. (Feng et al. 2013) used CeO$_2$ as a photocatalyst to degrade acid orange II, and its photocatalytic ability was better than that of commercial TiO$_2$ (P25). Because ceria exhibits excellent photocatalytic performance, it is used as a support for loading other catalysts or as the main photocatalyst when it is loaded on other materials. The ability to load nanosized ceria particles on catalyst supports that have a high specific surface area and stability is required (Guerrero-Ruiz 1994, Soria et al. 1996, Trovarelli et al. 1995).

Because carbon nanotubes have a large specific surface area and specific catalytic property as well as due to the advances in nanotube-walls functionalized research, much interest has been focused on CNTs for use in catalytic chemistry since their discovery in 1991 (Iijima 1991). CNTs exhibit high thermal and chemical stability due to their cylindrical layered, hollow tube nanostructures, which allows them to act as catalysts to prepare loaded nanometals and metal oxide particles (Peng et al. 2005, Planeix et al. 1994). Researchers from the Chemistry Institute of Chinese Academy of Sciences used CNTs as a support for loading rare earth oxide to prepare CNTs-Eu$_2$O$_3$ one-dimensional composite catalysts in 2004 (Fu et al. 2004). Kang et al. (Kang et al. 2005) loaded platinum on CNTs to enhance the structural stability and electronic property of the CNTs. In addition, Rao et al. (Rao et al. 2012) prepared a CeO$_2$/CNTs composite catalyst to dehydrogenate and oxidize ethylbenzene to styrene in a carbon dioxide atmosphere. Peng et al. (Peng et al. 2005) utilized CeO$_2$ loaded with CNTs to remove arsenate in water.

However, for the degradation of dye wastewater, researchers only used either CeO$_2$ as a photocatalyst (Chen et al. 2011, Pouretedal et al. 2010) or CNTs as an adsorbent after pretreatment (Gao et al. 2013, Mishra et al. 2010). The use of CeO$_2$/CNTs nanocomposites materials as photocatalysts for the degradation of azo dyes has not been reported. CeO$_2$ nanoparticles and CNTs are both suspended in water, which makes their separation from water difficult. The decolorization efficiency of azo dye wastewater using CeO$_2$ nanoparticles or CNTs is limited. In this paper, we loaded CeO$_2$ on CNTs to prepare a nanocomposites catalyst that is...
easily separated from water and exhibits good decolorization performance to provide a new photocatalyst for the degradation of azo dyes.

**Materials and methods**

Various reagents employed [commercial CeO$_2$, CeCl$_3$·7 H$_2$O, NaOH, polyethylene glycol (PEG 600), ethanol and a concentrated HNO$_3$ aqueous solution] were purchased from Sinopharm Chemical Reagent Co., Ltd. in 99.99% purity or greater. Multi-walled carbon nanotubes with an average tube diameter of 80 nm and an average tube length of 20 μm were purchased from Nanjing Xianfeng Co., Ltd. Deionized water was used to prepare the solvent and wash sample in this research.

**Preparation of nanocomposites photocatalyst**

Pretreatment of carbon nanotubes: 1 g of raw CNTs was weighed into a three-necked flask (250 mL capacity), and 100 mL of a concentrated HNO$_3$ aqueous solution with a volume fraction of 65%–68% was added to the three-necked flask to treat the raw CNTs prior to purification. Then, the mixture was refluxed for 3 h at 125°C. Next, the mixture was successively washed with ethanol at first, then washed with deionized water until pH of 7 was obtained, and afterwards it was cooled to room temperature. Finally, the mixture was placed into a blast oven to dry for 24 h at 60°C and then ground prior to storage.

Preparation of nanocomposites photocatalyst: A known quantity of pretreated carbon nanotubes was mixed with a known quantity of deionized water and then ultrasonically dispersed for 10 min. After adequately stirring for 1 h, a known quantity of CeCl$_3$·7 H$_2$O with a mass ratio of Ce to C of 2:3, 1:1, 4:3 or 3:2 and PEG 600 with a ratio of polyethylene glycol mass to the total mass of carbon nanotubes and CeCl$_3$·7 H$_2$O of 1% was added. A NaOH aqueous solution (6 g/L) was slowly added dropwise until the pH reached 11.0, 11.5, 12.0 or 12.5, followed by continuous stirring for 1 h, 2 h, 3 h or 4 h, respectively, at room temperature. Then, the mixture was filtered and washed until neutral and dry, which yielded a loose black powder.

Finally, the black powder was dried and placed in a pipe furnace prior to being heated at a heating rate of 5°C/min over a temperature range of 100~700°C. Therefore, further analysis is required.

**Results and discussion**

**Results and analysis of the orthogonal test**

The stirring reaction time, cerium carbon ratio, pH, calcination temperature and holding time were investigated in this study, and the optical decolorization rate of Acid Orange 7 as evaluation index based on single factor experiments (data not shown) and designed orthogonal test program of five factors and four levels were used to determine the optimum parameters for the preparation of the CeO$_2$/CNTs nanocomposites photocatalyst. The results and analysis of the orthogonal test for the preparation of CeO$_2$/CNTs nanocomposites photocatalyst are reported in Tables 1 and 2.

As shown in Table 1, the test results indicated that the highest rate of optical decolorization was observed for No. 11 (62.14%). However, No. 11 may not be the optimal choice. Therefore, further analysis is required.

Level difference analysis was used to investigate the level changes of the various factors that impact the tested items.
When the level difference (R) is larger, there is a greater impact on the factors that vary within a target range for testing indicator values, and the correct factor is the one with the primary influence. The results in Table 2 indicate that the level difference of the calcination temperature is the largest (21.777), which indicated that it has the largest influence on the preparation. Similarly, the level difference for the pH is the smallest (3.947), which indicated that the pH has the smallest effect on the preparation. Therefore, the order of effect of each factor on the photodecolorization rate from largest to smallest is as follows: calcination temperature > holding time > stirring reaction time > cerium carbon ratio > pH.

We determined the theoretical optimal solution (Group A) based on the largest mean value of each factor (i.e., stirring reaction time of 4 h, cerium carbon ratio of 4:3, pH of 11.5, calcination temperature of 410°C and holding time of 5 min).

The choice of the optimal scheme requires a comprehensive analysis and verification test. The preceding analysis indicated that the optimum parameters for the preparation of the CeO2/CNTs nanocomposites photocatalyst include either “No. 11” or Group A. However, the best choice will need to be determined through further testing.

This verification experiment was repeated twice for each of the two schemes mentioned above, and the results indicated that the optical decolorization rates of No. 11 were 62.15% and 61.26%. In addition, the optical decolorization rates for Group A were 66.58% and 68.13%. Obviously, the optical decolorization rates of Group A are still higher than those of No. 11. Therefore, the optimized conditions for the preparation of the CeO2/CNTs nanocomposites photocatalyst are as follows: stirring reaction time of 4 h, cerium carbon ratio of 4:3, pH of 11.5, calcination temperature of 410°C and holding time of 5 min. These conditions are used to prepare the photocatalysts employed in the rest of the experiments.

Characterization of the nanocomposites photocatalyst

TEM/HRTEM

Fig. 1 shows the TEM and HR-TEM images of raw CNTs and the CeO2/CNTs nanocomposites photocatalyst. As shown in Fig. 1a (and inset), the tube-body of the CNTs is clean and well distributed after pretreatment. The TEM images of the CeO2/CNTs nanocomposites photocatalyst are shown in Fig. 1b (and inset), which indicates that the diameter of the CNTs were

| No. | A   | B   | C   | D   | E   | Photodecolorization rate (%) |
|-----|-----|-----|-----|-----|-----|--------------------------------|
| 1   | 1   | 2:3 | 11.0| 400 | 5   | 51.73                          |
| 2   | 1   | 1:1 | 11.5| 410 | 10  | 52.32                          |
| 3   | 1   | 4:3 | 12.0| 420 | 15  | 23.67                          |
| 4   | 1   | 3:2 | 12.5| 430 | 20  | 22.41                          |
| 5   | 2   | 2:3 | 11.5| 420 | 20  | 24.82                          |
| 6   | 2   | 1:1 | 11.0| 430 | 15  | 24.36                          |
| 7   | 2   | 4:3 | 12.5| 400 | 10  | 54.13                          |
| 8   | 2   | 3:2 | 12.0| 410 | 5   | 57.10                          |
| 9   | 3   | 2:3 | 12.0| 430 | 10  | 39.96                          |
| 10  | 3   | 1:1 | 12.5| 420 | 5   | 41.82                          |
| 11  | 3   | 4:3 | 11.0| 410 | 20  | 62.14                          |
| 12  | 3   | 3:2 | 11.5| 400 | 15  | 53.26                          |
| 13  | 4   | 2:3 | 12.5| 410 | 15  | 48.85                          |
| 14  | 4   | 1:1 | 12.0| 400 | 20  | 54.94                          |
| 15  | 4   | 4:3 | 11.5| 430 | 5   | 52.60                          |
| 16  | 4   | 3:2 | 11.0| 420 | 10  | 42.99                          |

A: stirring reaction time (h); B: cerium carbon ratio; C: pH; D: calcination temperature (°); E: holding time (min).

| Levels | A   | B   | C   | D   | E   |
|--------|-----|-----|-----|-----|-----|
| k1     | 37.532 | 41.340 | 45.305 | 53.515 | 50.813 |
| k2     | 40.102 | 43.360 | 45.750 | 55.102 | 47.350 |
| k3     | 49.295 | 48.135 | 43.918 | 33.325 | 37.535 |
| k4     | 49.845 | 43.940 | 41.803 | 34.832 | 41.078 |
| R      | 12.313 | 6.795 | 3.947 | 21.777 | 13.278 |

A: stirring reaction time (h); B: cerium carbon ratio; C: pH; D: calcination temperature (°); E: holding time (min).
significantly thicker after loading. In addition, the CeO$_2$ particles are uniformly loaded without agglomeration, which indicates that the product has a high loading efficiency. As shown in the HRTEM images of the CeO$_2$/CNTs nanocomposites photocatalyst in Fig. 1c, the CeO$_2$ particles are loaded on the CNTs. In addition, the diameter of the CeO$_2$ particle is 6 nm~10 nm with a single size distribution, which corresponds to the nanoparticle. The results in Fig. 1c (inset) indicate that the SAED pattern consists of a ring pattern. This typical polycrystalline ring pattern corresponds to the face-centered cubic polycrystalline structure of CeO$_2$ (Zhang et al. 2007). Fig. 1d shows a single CeO$_2$ nanoparticle, and the CeO$_2$ lattice fringes are clearly visible. The observed lattice spacing (i.e., 0.31 nm and 0.27 nm) are in good agreement with the calculated ones for the (111) and (200) crystal planes of the cubic fluorite phase of CeO$_2$ (Sathish et al. 2011).

**XRD**

Fig. 2 shows the XRD pattern of the CeO$_2$/CNTs nanocomposites photocatalyst. As shown in Fig. 2, the main peaks corresponded to the graphene structure of CNTs (002) and the face-centered cubic structure of CeO$_2$, [(111), (200), (220), (311), (222), (400), (331) and (420)], and no impurity peaks were observed. Therefore, no new substances were generated during the preparation. In addition, all of the main peaks of CeO$_2$ were consistent with the standard cubic fluorite structure of CeO$_2$ (PDF 34-0394), indicating that the prepared CeO$_2$ particles have a polycrystalline face-centered cubic structure and exist as CeO$_2$ (Chen et al. 2012), which is in agreement with the analysis of the SAED spectra. The CeO$_2$ particle size calculated using the Scherrer equation (Chen et al. 2011) for the strongest peak (111) was 8.53 nm, which was in good agreement with the results of the particle diameter (6~10 nm) obtained from the analysis of the TEM images.

**TGA**

Fig. 3 shows the TG curves of the raw CNTs and the nanocomposites photocatalyst precursor CNTs-Ce (OH)$_3$. The TG curve of the CNTs (grey line) indicated that the CNTs exhibited good heat resistance during calcination, and almost no loss of quality was observed when the temperature was lower than 500°C. When the temperature was higher than 550°C, the weight of the CNTs rapidly decreased, which indicated that the CNTs were being rapidly oxidized. When the temperature reached approximately 580°C, the CNTs completely disappeared. The TG curve of the nanocomposites photocatalyst precursor CNTs-Ce (OH)$_3$ (black line) indicated a weight loss with three steps. The first step occurs at 100~360°C due to the weight loss of precursor dehydration with a mass reduction rate of 3.55%. In the second step from 360°C to 520°C, the precursor weight decreased significantly as the temperature increased, which may be due to dehydrogenation
of the precursor Ce(OH)$_3$ to form CeO$_2$, and the CNTs were oxidized by the generated CeO$_2$ with a weight loss rate of 43.45%. When the temperature reached and exceeded 520°C, the sample weight did not vary, which indicated that Ce(OH)$_3$ had been oxidized to CeO$_2$ and the CNTs had been completely decomposed to water and carbon dioxide.

It should be noted that the heat resistance of the CNTs will be reduced greatly due to the existence of Ce(OH)$_3$ and the generation of CeO$_2$ in the calcination process, which could reduce the oxidation temperature of CNTs to 360°C. The results of previous single factor impact tests obtained by our group (data not shown) confirmed that CNTs in the precursor would be completely decomposed with a calcination temperature of 430°C and a holding time of 20 min. Therefore, the calcination temperature and holding time of the precursor should not be too high and too long (Zhang et al. 2007). However, the precursor Ce(OH)$_3$ cannot be entirely prevented from converting to CeO$_2$. In addition, the generated CeO$_2$ cannot form good crystals when the temperature is too low. Therefore, the calcination temperature should be higher than 400°C (Zhai et al. 2007), which is contradictory for preparing the nanocomposites photocatalyst. Further investigation is required to determine a balance.

At a calcination temperature of 410°C, the weight loss rate of the precursors was 8.39%. After subtracting the water loss rate of 3.55%, the CNT loss rate was less than 5%, which is acceptable during the preparation process. In addition, the calcination temperature of 410°C is reasonable and feasible based on the above analysis of TEM and XRD.

The xenon lamp simulating solar light to test its photocatalytic property is feasible.

The BET test results of the nanocomposites photocatalyst revealed that the specific surface area of CeO$_2$/CNTs was 67.82 m$^2$/g, which is nearly 70% higher than the specific surface area of raw CNTs (i.e., 40.00 m$^2$/g) and higher than that of 23.53% reported in the literature (Peng et al. 2005). Therefore, an increase in the specific surface area was achieved, resulting in an increased adsorption capacity of the nanocomposites photocatalyst.

UV-Vis/DRS and specific surface area measurements

Fig. 4 shows the UV-Vis diffuse reflectance spectra of the CeO$_2$/CNTs nanocomposites photocatalyst. As shown in Fig. 4, the prepared nanocomposites photocatalyst exhibited a strong ability to absorb light in the ultraviolet region. In addition, the band gap of the product was observed at approximately 450 nm after making the outside tangent line of the DRS curve. According to the formula $E_g = 1240/\lambda$, the corresponding band gap is 2.76 eV, which is slightly lower than that of 2.81 eV, 2.95 eV and 3.03 eV reported in the literature (Chen et al. 2012, Feng et al. 2013, Zhao et al. 2013) and theoretically results in better efficiency of light utilization. The nanocomposites photocatalyst also exhibited some capacity to absorb light in the visible light region, which implies that the utilization of the xenon lamp simulating solar light to test its photocatalytic property is feasible.

The BET test results of the nanocomposites photocatalyst revealed that the specific surface area of CeO$_2$/CNTs was 67.82 m$^2$/g, which is nearly 70% higher than the specific surface area of raw CNTs (i.e., 40.00 m$^2$/g) and higher than that of 23.53% reported in the literature (Peng et al. 2005). Therefore, an increase in the specific surface area was achieved, resulting in an increased adsorption capacity of the nanocomposites photocatalyst.

XPS

Fig. 5 shows the X-ray photoelectron spectra of the CeO$_2$/CNTs nanocomposites photocatalyst. The wide spectrum (Fig. 5a) of CeO$_2$/CNTs only shows the main peaks of the three elements (Ce, O and C) without any other elements, indicating that the sample was not contaminated by other elements during preparation and possesses high purity. Based on the XRD analysis, no incompletely reacted precursors were observed in the product. Fig. 5b shows the XPS Ce 3d spectrum of CeO$_2$/CNTs. As shown in Fig. 5b, the peaks at 882, 898, 900.5, 907.3 and 916.5 eV can be attributed to Ce (IV), and the peaks at 882 and 898 eV correspond to the Ce (IV) 3d$^4$4f$^1$ and 3d$^4$4f$^2$ final state, respectively. The spin-orbit splitting appears at 900.5, 907.3 and 916.5 eV, which corresponds to 3 $\pi$ peaks of Ce (3d)$_{\pi}$, indicating that the Ce species in the nanocomposites photocatalyst has a IV valence and exists as CeO$_2$ (Mei et al. 2010, Park et al. 1996, Zhang et al. 2010). In addition, the O 1s spectrum of the prepared CeO$_2$/CNTs is shown in Fig. 5c. As shown in Fig. 5c, the O 1s peak is primarily composed of two peaks centered at 529.1 and 531.4 eV, which are due to the lattice oxygen of CeO$_2$ (Rao et al. 2012) and the hydroxyl oxygen on the surface of CNTs or adsorbed oxygen from CeO$_2$ (Lakshminarayanan et al. 2004). In addition, the core level peak, which was located at 529.1 eV, indicated the existence of O$^\cdot$ (Zhang et al. 2007). In addition, the compound has formed a complete CeO$_2$ lattice structure, which is consistent with the XRD and TEM analysis mentioned above. Therefore, the binding energies of Ce 3d and O 1s detected by XPS are consistent with those of standard CeO$_2$.

Photocatalytic Performance Testing

The curves for the variation in the Acid Orange 7 concentration during dark adsorption and photocatalytic degradation in the presence of CeO$_2$/CNTs, commercial CeO$_2$ and raw CNTs are...
shown in Fig. 6a. As shown in Fig. 6a, the rates of Acid Orange 7 adsorption on the three materials in the dark are fast, and the adsorption-desorption equilibrium was achieved in the first 30 minutes. The adsorption efficiency of Acid Orange 7 on the CeO₂ particles without a hole-like or tubular structure was significantly lower than that on CNTs and CeO₂/CNTs. In addition, the total decolorization rate of Acid Orange 7 by the CeO₂/CNTs nanocomposites photocatalyst was as high as 80.58%, and the optical decolorization rate was 66.58% after xenon lamp irradiation for 4 h, which is better than that of commercial CeO₂ (i.e., 43.13%). This result may be due to the adsorption capacity of commercial CeO₂ being lower than that of CeO₂/CNTs, which resulted in the Acid Orange 7 molecules being more weakly adsorbed on the surface of commercial CeO₂ and affecting its subsequent optical decolorization performance (Chen et al. 2012, Ayanda et al. 2015).

**Settling Performance Testing**

Fig. 6b shows the sedimentation curves of CeO₂/CNTs, commercial CeO₂, and raw CNTs in water. Based on the integral algorithm (Tang et al. 2006), the total removal rate of the CeO₂/CNTs suspended particles at a settling velocity of 1.5 cm/min is 59.83%, which is higher than that of CNTs (16.60%) and commercial CeO₂ (44.40%), indicating that the CeO₂/CNTs prepared in this research exhibits good settling performance accelerating its separation from water.
Conclusions

CeO₂ can be loaded on CNTs uniformly to prepare a CeO₂/CNTs nanocomposites photocatalyst. The optimized conditions are as follows: stirring reaction time, 4 h; cerium:carbon ratio, 4:3; pH, 11.5; calcination temperature, 410°C; and holding time, 5 min. The prepared nanocomposites photocatalyst has no significant impurities, and the size of the CeO₂ loaded on the CNTs is 6–10 nm. In addition, CeO₂ was dispersed on the carbon nanotubes with a good loading effect and a high loading efficiency. The specific surface area of CeO₂/CNTs is 67.82 m²/g, which is nearly 70% higher than that of raw CeO₂/CNTs and water. Therefore, the prepared CeO₂/CNTs exhibit a strong absorption ability to absorb light in the ultraviolet region and exhibits some capacity to absorb light in the visible light region. The optical decolorization rate of CeO₂/CNTs to degrade azo dye Acid Orange 7 (40 mg/L) was as high as 66.58% after xenon lamp irradiation for 4 h, which is better than that of commercial CeO₂ (43.13%) with an improved settling performance. This result indicates that CeO₂ loaded on CNTs can enhance the optical decolorization rate and accelerate the separation of CeO₂/CNTs and water. Therefore, the prepared CeO₂/CNTs nanocomposites photocatalytic material exhibits potential for application in the photocatalytic treatment of azo dyes in water.

Acknowledgments

This work was financially supported by Jiangsu General College Graduate Students Research and Innovation Program, China (CXZZ13_0723).

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