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Regular Article

Yeast-template synthesized Fe-doped cerium oxide hollow microspheres for visible photodegradation of acid orange 7

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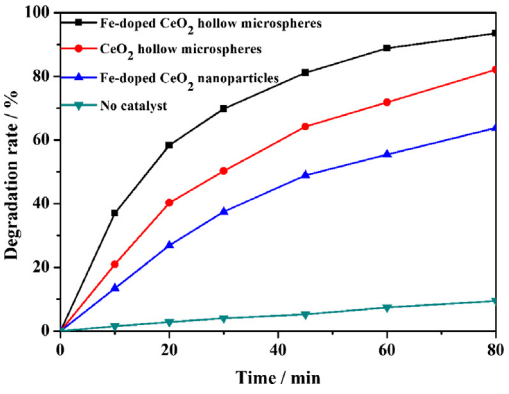
GRAPHICAL ABSTRACT

Fe-doped cerium oxide hollow microspheres obtained using yeast as a bio-template have demonstrated higher photocatalytic activity in degrading acid orange 7 under visible irradiation.



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ABSTRACT

Fe-doped cerium oxide (CeO_2) hollow microspheres were successfully synthesized by a simple co-precipitation route using yeast as a bio-template and nitrate as the oxide precursor. The products were characterized by scanning electron microscopy, X-ray diffraction, X-ray photoelectron spectroscopy, N_2 adsorption–desorption isotherms and UV–Vis diffuse reflectance spectroscopy. It was found that the products had a well-defined ellipsoidal morphology and the size of the hollow microspheres was about 1.5–2.5 μm. The formation mechanism of Fe-doped CeO_2 hollow microspheres was proposed and discussed as well. The photocatalytic test results showed that the Fe-doped CeO_2 hollow microspheres exhibited a higher photocatalytic activity in the degradation of acid orange 7 (AO7) aqueous solutions containing H_2O_2 under visible irradiation compared with CeO_2 hollow microspheres and Fe-doped CeO_2 nanoparticles, which was attributed to their more oxygen vacancies, higher specific surface area

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and lower band gap. The degradation rate of the Fe-doped CeO_2 hollow microspheres was found to be 93% after 80 min and the degradation reaction followed pseudo-first-order kinetics.

1. Introduction

Doped cerium oxides have been intensively studied over the past years because of their high thermal stability, oxygen storage capacity and catalytic activity. The properties of doped cerium oxides are closely related to their defect chemistry [1,2], which is mainly determined by the size, charge and concentration of the dopant cations. Doped cerium oxides have been reported for many applications such as photocatalysis [3,4], fuel cell [5,6], CO preferential oxidation [7,8], water gas shift reaction [9,10], partial oxidation of methane [11,12], and many others. Zr, Fe, Cu, Zn and Eu have been widely used as elements to dope ceria [13–17]. Among these, Fe can greatly increase the oxygen interchange capacity compared with other metal elements, because of the synergistic fenton and other reactions between the redox couple of the cerium (Ce^{4+}/Ce^{3+}) and iron (Fe^{3+}/Fe^{2+}) cations. Therefore, Fe-doped ceria system has received intense research interests in recent years.

Dyes are one of the major pollutants for water pollution [18–21], efficient dyes elimination is thus of great significance. Previous works demonstrated that Fe-doped ceria is an active photocatalyst for dyes degradation. For example, Pradhan et al. [22] synthesized iron-cerium mixed oxides by co-precipitation method and evaluated the solar light driven photocatalytic activity towards methylene blue, Congo red and phenol degradation. The results showed that 50% Fe-doping cerium oxides gave the highest degradation rate for all the tested dyes. Wandong et al. [14] prepared Fe-doped ceria materials of different doping amounts by hydrothermal method and demonstrated that the low doping amount of Fe^{3+} could effectively improve the concentration of Ce^{3+} and enhanced the degradation ability of AO7. Channei et al. [23] synthesized Fe-doped CeO_2 film by homogeneous precipitation and impregnation methods and evidenced that the optimal photocatalytic degradation of methyl orange under visible irradiation was achieved by 1.50 mol% Fe-doped CeO_2 film.

Fe-doped ceria materials have been synthesized by various techniques, including hydrothermal processes [3,24,25], co-precipitation [26–28], template method [29–31] and sol gel technique [32,33]. Among these, the template method has obvious advantages, such as easy control of morphology and facile synthesis conditions. However, the template synthesis of Fe-doped ceria materials has been rarely reported in previous studies. The yeast-templating method provides an economic, green, and convenient strategy compared with the traditional template-directed method. The cell wall of yeast primarily consists of glucan and mannan, which are rich in reactive functional groups, such as acid amides, hydroxyls and carbonyls [34–36], enabling the stabilization of the produced nanoparticles [37–40]. Currently, ZrO_2, Fe_2O_3, CeO_2, Co_3O_4 and SnO_2 [41–45] have been successfully synthesized using yeast templates, but Fe-doped CeO_2 hollow microspheres as photocatalyst prepared by yeast-templating method have not been reported.

In this work, Fe-doped CeO_2 hollow microspheres with high specific surface area and good thermal stability were prepared by a simple co-precipitation route using yeast as a bio-template. The photocatalytic performance was tested by measuring the decompositions of the AO7 aqueous solutions containing H_2O_2 under visible irradiation. Compared with CeO_2 hollow microspheres and Fe-doped CeO_2 nanoparticles, the Fe-doped CeO_2 hollow microspheres exhibit a higher photocatalytic degradation rate in degrading dye stuff under visible irradiation. The enhancement mechanism was proposed as well.

2. Experimental

2.1. Materials

Yeast powders were provided by Angel yeast Co. Ltd. $Ce(NO_3)_3{\cdot}6H_2O$, $Fe(NO_3)_3{\cdot}9H_2O$, NaOH, C_2H_6O and H_2O_2 (30%) were obtained from Kermel reagent Co. Ltd. (Tianjin China). AO7 was purchased from Shanghai Chemical Reagent Co. Ltd. (Shanghai, China). All the reagents were of analytical grade and used without any further purification. Distilled water was used throughout the experiments.

2.2. Synthesis of Fe-doped CeO_2 hollow microspheres

In a typical process, 1.0 g yeast powders were washed with absolute ethanol and distilled water for three times. The washed yeast was dispersed into 20 mL distilled water and was mechanically stirred thoroughly at ambient temperature. 20 mL mixed salt solution (1.0 g $Ce(NO_3)_3{\cdot}6H_2O$ and 0.01 g $Fe(NO_3)_3{\cdot}9H_2O$) was added to the above solution under stirring and kept stirring for one hour. Then, a solution (0.2 g NaOH in 10 mL distilled water) was added dropwise to the mixture under further stirring for 1 h. The mixture was aged at ambient temperature for 12 h. The precipitate was collected by centrifugation, and washed twice with distilled water and once with ethanol. Then, the precipitate was dried at 80 °C for 6 h. Finally, the Fe-doped CeO_2 hollow microspheres were obtained by calcining from room temperature to 600 °C with a heating rate of 1 °C min^{-1} and maintaining at 600 °C for 2 h. Similarly, CeO_2 hollow microspheres, and Fe-doped CeO_2 nanoparticles without templates were prepared by the same method for the comparison of photocatalytic performance.

2.3. Characterization

The morphologies and elemental analysis of the prepared products were examined by a scanning electron microscopy (SEM, SU-70, Hitachi, Japan) fitted with an energy dispersive spectrometer (EDS) at an acceleration voltage of 30 kV. The crystal structures of the samples were analyzed by X-ray diffraction (XRD, ultima IV, Rigaku, Japan) with Cu Kα radiation (λ = 0.15418 nm) at a scanning rate of 8°/min in 2θ range from 20° to 80°. X-ray photoelectron spectroscopy (XPS) measurements were determined with an X-ray spectrometer Kα (Thermo Scientific, USA). The specific surface area of the samples was measured using a surface area analyzer (BET, Tristar II 3020, Micromeritics, America) at liquid nitrogen temperature (77 K) after the products were vacuum treated at 120 °C for 5 h. The UV–Vis diffuse reflectance spectra of the products were recorded on a UV–2550 UV–Vis spectrophotometer (UV–Vis DRS, UH4150, Hitachi, Japan).

2.4. Photocatalytic activity test

The photocatalytic activity was evaluated by measuring the decomposition of the AO7 aqueous solutions containing H_2O_2 under visible irradiation. In a typical visible irradiation degradation experiment, 20 mg catalyst powders were dispersed in 50 mL AO7