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Facile Synthesis of Ag/CeO_2 Mesoporous Composites with Enhanced Visible Light Photocatalytic Properties†

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Ag/CeO_2 mesoporous composite was synthesized *via* a green and facile photodeposition method where the mesoporous CeO_2 was first calcined at 400 ºC under air atmosphere and irradiated under visible light in the presence of aqueous solution of silver nitrate. The as-obtained Ag/CeO_2 mesoporous composite is composed of silver nanoparticles attached on mesoporous CeO_2 network. For photodegradation of methylene blue under visible light irradiation, the Ag/CeO_2 mesoporous composite exhibited higher photocatalytic efficiency than pure mesoporous CeO_2.

Keywords: Ag/CeO_2, Mesoporous composite, Photodeposition, Photocatalysis, Methylene blue.

INTRODUCTION

Recently, it has become more and more popular to degrade organic dye in waste water using semiconductor under visible light. Ceria is one of the most reactive rare earth metal oxides, which has been widely researched in electrolytes for solid oxide fuel cells, oxygen storage capacitors, catalysts due to its unique crystal structure and redox behaviour between Ce^{3+} and Ce^{4+} and CeO_2 or CeO_2-based materials have also been found to be very important in environmental protection[1]. In order to promote the specific surface area for better catalytic and redox performances, mesoporous CeO_2 or its mesoporous composites are alternative choices[2,3].

Nanoparticles of metals such as copper, silver and gold show strong photoabsorption of visible light due to surface plasmon resonance[4]. As is well-known, surface plasmons exist on the surface of noble metals by a collective oscillation of free electrons. In particular, silver nanoparticles show efficient plasmon resonance in the visible region and have electronic effect under visible light. This synergistic effect is expected to play a positive role in enhancing the photocatalytic activity[5]. In this paper, Ag/CeO_2 mesoporous composite photocatalyst was synthesized *via* a facile photodeposition method and its photocatalytic activity was studied by photocatalytic degradation of methylene blue.

EXPERIMENTAL

All chemicals were analytical grade purchased from Shanghai Sinopharm Chemical Reagent Co., Ltd. and used as received without further purification. In a typical synthesis, 1 g $EO_{106}PO_{70}EO_{106}$ block copolymer (Pluronic F-127) was dissolved in 15 mL anhydrous ethanol under magnetic stirring, then 2.1706 g cerous nitrate (5 mmol) was added and stirred for another 1 h. The resulting sol solution was gelled in an beaker at 50 ºC in air for 12 h, after that, the gel was kept at 100 ºC for another 6 h and then calcined at 400 ºC for 4 h (with the calefactive rate of 1 ºC/min) to remove Pluronic F-127, which obtained the mesoporous CeO_2.

Ag/CeO_2 mesoporous composite was performed by a photodeposition method. In a typical synthesis, 0.25 g mesoporous CeO_2 dispersed in 10 mL deionized water under magnetic stirring in a beaker, then 1 g aqueous solution of silver nitrate (3.936 mg/g) was added (*i.e.*, the amount of Ag is 1wt %) and stirred for 0.5 h in a darkroom and then photoirradiated at $\lambda > 420$ nm by a 300 W Xe lamp (CEL-HXF300/CEL-HXUV300, China). The resultant powder was centrifuged and washed repeatedly with distilled water and anhydrous ethanol, then dried at 50 ºC overnight in an oven.

The products were characterized by X-ray diffraction (XRD, Shimadzu XRD-6000, CuK_α radiation), field-emission

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scanning electron microscopy (FE-SEM, FEI Quantum 400F microscope operated at 20 kV) associated with the Energy-dispersive X-ray (EDX) spectrum. The photocatalytic properties of the samples were evaluated by photodegradation of methylene blue in water under visible light irradiation from a 300W Xe light equipped with a 420 nm cutoff filter (CEL-HXF300/CEL-HXUV300, China). In every experiment, 50 mg of photocatalyst was suspended in 100 mL of a 5.0×10^{-5} M aqueous solution of methylene blue. Before the irradiation, the suspension was stirred in the dark for 0.5 h to achieve an adsorption-desorption equilibrium between the photocatalyst and methylene blue molecules. After that, the solution was exposed to the visible light irradiation under magnetic stirring. At given time intervals, 3 mL solution was sampled for analysis of the methylene blue concentration. The photocatalytic degradation process was monitored using a UV-visible spectrophotometer (Shimadzu UV2600) to record the characteristic absorption at 665 nm.

RESULTS AND DISCUSSION

Fig. 1a,b show the XRD pattern of the as-obtained CeO_2 and Ag/CeO_2 samples, respectively. It can be seen that the CeO_2 is cubic crystal system which can be refered to the JCPDS card No. 81-0792 and the as-obtained CeO_2 is with high crystallinity and purity. In the Ag/CeO_2 mesoporous composite (Fig. 1b), the Ag is cubic crystal system which can be refered to the JCPDS card No.87-0717. But the diffraction peaks are not obvious because the small amount of Ag in the composite. In addition, the EDX spectrum (Fig. 2d) shows the existence of Ag and Ce species.

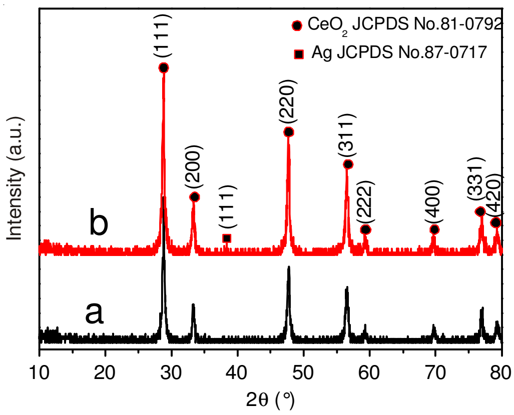

Fig. 1. XRD pattern of (a) mesoporous CeO_2 and (b) Ag/CeO_2 mesoporous composite

Fig. 2 shows the SEM image and EDX of CeO_2 and Ag/CeO_2 mesoporous compsite. Fig. 2a shows the SEM image of mesoporous CeO_2. It is observed that the sample exhibits foamlike morphology and three-dimensional (3D) macrocellular network structure, the ultralarge cell diameter is 4 μm and most of the cell diameter are less than 500 nm. Fig. 2b and c are the SEM images of Ag/CeO_2 mesoporous compsite. The foamlike structure of CeO_2 still exists after the photodeposition method. The white dots on the network are Ag nanoparticles (Fig. 2b) which come from the photodeposition of silver nitrate. From the magnified image (Fig. 2c), the average silver nanoparticles (the particles in red circles) is 140 nm.

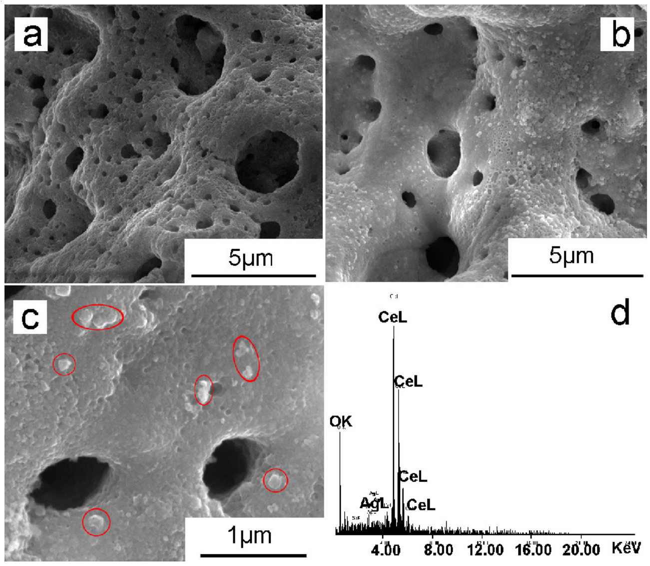

Fig. 2. (a) SEM images of mesoporous CeO_2, (b and c) SEM images with low and high magnification of Ag/CeO_2 mesoporous composite, (d) EDX spectrum of Ag/CeO_2 mesoporous composite

In order to evaluate the photocatalytic activity of the as-obtained samples, the photodegradation of methylene blue was investigated under visible light irradiation from a 300 W Xe lamp. Fig. 3 shows the UV-visible absorption spectra of aqueous solution of methylene blue exposure to the light irradiation for various durations in the presence of CeO_2 and Ag/CeO_2 as photocatalyst, respectively. The characteristic absorption of methylene blue at 665 nm decreased rapidly with extension of the exposure time. When the mesoporous CeO_2 was used as photocatalyst, as shown in Fig. 3(a), the characteristic absorption of methylene blue at 665 nm decreased rapidly with extension of the exposure time and decreased of 70 % after irradiation of 2 h. In the presence of Ag/CeO_2 mesoporous composite, as shown in Fig. 3(b), the photodegradation effiency is 82 % after irradiation of 2 h, higher than that of pure mesoporous CeO_2, which can be attributed to the presence of silver nanoparticles in the composite. Fig. 4 shows the photodegradation effiency (C_t/C_0 %) of the samples, where C_0 and C_t are the initial concentration and the reaction concentration of methylene blue, respectively. The time "-0.5 h" means the pretreatment in a darkroom. A blank test (aqueous solution of methylene blue without any catalyst) under irradiation exhibited little decrease in the concentration of methylene blue. The results indicate that the Ag/CeO_2 mesoporous composite exerts an enhanced photocatalytic performance in the photodegradation of methylene blue under visible light irradiation.

Conclusion

Ag/CeO_2 mesoporous composite was prepared by a green and facile photodeposition method. The as-obtained Ag/CeO_2 mesoporous composite is composed of Ag nanoparticles attached on mesoporous CeO_2 network. For the photodegradation of methylene blue under visible light irradiation, the Ag/CeO_2 mesoporous composite shows a higher photocatalytic activity than the pure mesoporous CeO_2 photocatalyst.

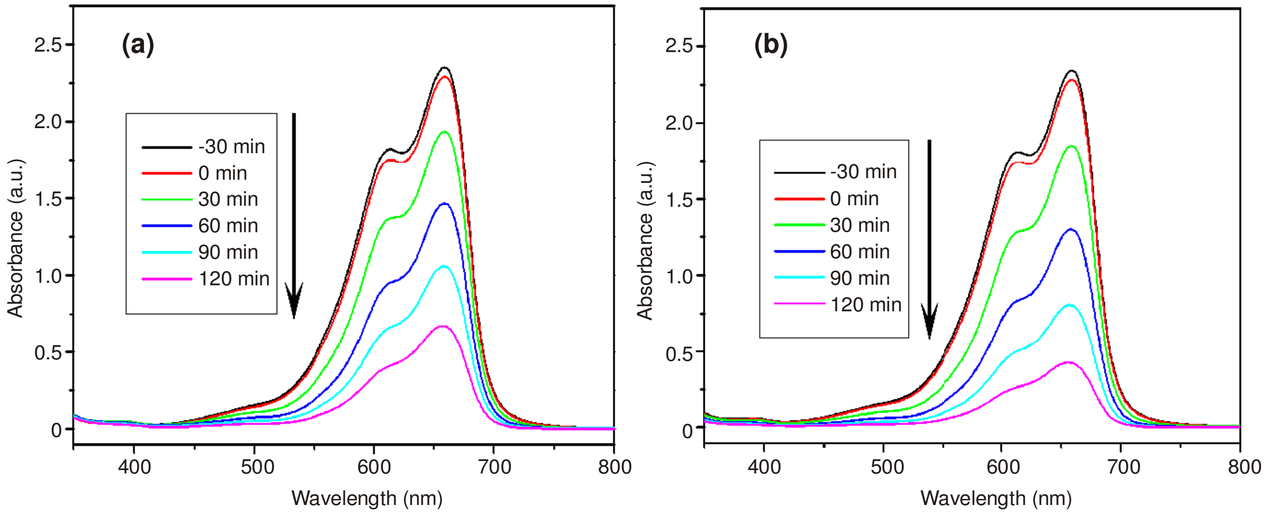

Fig. 3. Evolution of the absorption spectrum of methylene blue solution (5×10^{-5} mol/L, 100mL) in the presence of (a) mesoporous CeO_2 and (b) Ag/CeO_2 mesoporous composite under visible light irradiation

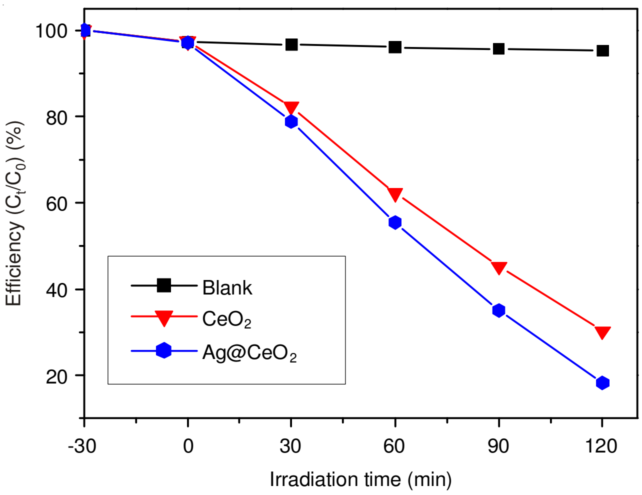

Fig. 4. Photodegradation effiency of methylene blue under visible light irradiation over different conditions

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