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Short communication

Photocatalytic activities of Ce or Co doped nanocrystalline TiO_2–SiO_2 composite films

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Abstract

Ce or Co doped nanocrystalline TiO_2–SiO_2 composite films were prepared by the sol–gel method. The high-resolution field emission scanning electron microscopy (FE-SEM) results indicated the films to be composed of round-like nano-particles or aggregates 4–10 nm in size. Compared with transition metal Co doped TiO_2–SiO_2 film, the surface of lanthanide metal Ce doped TiO_2–SiO_2 film was more uniform and smooth with smaller particles and larger specific surface area. The photocatalytic activities of the films were evaluated by degradation of an organic dye in solution. Ce doped TiO_2–SiO_2 film exhibited excellent photocatalytic activity compared to Co doped TiO_2–SiO_2 film. It is believed that the surface microstructure of the modified film and the special electronic structure of dopant Ce are responsible for improving the photocatalytic activity.

Keywords: Ce or Co doping; TiO_2–SiO_2 film; Photocatalytic activity

1. Introduction

The heterogeneous photocatalytic oxidation process has gained wide attention due to its effectiveness in degrading organic pollutants and utilizing solar light [1]. Among various oxide semiconductor photocatalysts, TiO_2 has proven to be the most widely used photocatalyst because of its strong oxidizing power, photo-stability, non-toxicity, and chemical and biological inertness, as well as its low cost. However, the practical application of TiO_2 has been limited by two problems. One is its wide band gap (3.2 eV). The other is that the photogenerated electrons and holes are extremely unstable and easily recombinative. In order to enhance the photocatalytic activity of TiO_2, many methods have been carried out, including various preparations, different carriers, ions doping, surface modifications, composite semiconductors, etc. [2–5].

Metal ions doping is a simple and effective method. Certain transition metals doping can enhance the visible light response, but metal-doped TiO_2 has a poor thermal stability. It has been found that TiO_2 composite with SiO_2 can enhance its thermal stability [6]. However, the visible light response of TiO_2–SiO_2 is weak. Interest to modify TiO_2 with a small amount of lanthanide metals arose due to their distinctive chemical, physical and electronic features recently [7].

In this article, Ce or Co doped TiO_2–SiO_2 films were synthesized by the sol–gel method. The photocatalytic activity was evaluated by photodegradation of organic dyes in solution. The mechanism of photoactivity enhancement for the modified film has been discussed.

2. Experimental

The sol of TiO_2 was prepared by the sol–gel method, as previously reported [8–10]. The preparation of SiO_2 colloid was carried out as follows: 1 mL tetraethylorthosilicate (TEOS) was added to 30 mL ethanol absolute at room temperature; then, 0.5 mL ammonium hydroxide was

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added to the above solution and the whole process was put under magnetic stirring.

TiO_2–SiO_2 composite colloid was prepared by mixing above two sols at 2/1 (TiO_2/SiO_2 volume ratio) under strong stirring. After 24 h aging, the composite colloid TiO_2–SiO_2 could be obtained. TiO_2–SiO_2 composite sol-films were coated on the surface of glass substrate (25 mm × 25 mm × 1 mm) by a controllable dip-coating device in the atmosphere. Then, a certain concentration of cobaltous nitrate hexahydrate ($Co(NO_3)_2 \cdot 6H_2O$) aqueous solution or cerium nitrate hexahydrate ($Ce(NO_3)_3 \cdot 6H_2O$) aqueous solution was doped into the surface layer of TiO_2–SiO_2 composite gel-film. In our experiment, the film did not immerse into the salt solutions, and the Ce^{3+} or Co^{2+} ions were doped into the surface layer via coating of a thin Ce^{3+} or Co^{2+}-doped TiO_2 sol onto as-dried TiO_2–SiO_2 composite film. Finally, the ions doped gel-films on glass substrate were calcined in air at 450 °C for 1 h.

Surface morphology of the TiO_2 composite film was detected using high-resolution field emission scanning electron microscopy (FE-SEM;SUPRA 55). The Brunauer–Emmett–Teller (BET) surface area of the sample was analyzed by a N_2 adsorption/desorption apparatus (ASAP 2020). Diffuse reflectance UV–vis absorption spectra of the film were recorded on a UV-vis spectrophotometer (TU-1901) with an integrating sphere accessory (IS 19-1) using a blank glass plate as a reference.

The photocatalytic activity was evaluated by the degradation of acid naphthol red (ANR) in aqueous solution. Ce or Co ions doped and undoped TiO_2–SiO_2 films were settled in 5 mL ANR solution with a concentration of 1.0×10^{-4} mol dm^{-3}. The UV–vis spectrometer was adopted to assess the photodegradation activity of the film photocatalysts. The measurements were repeated for each catalytic system, and the experimental error was found to be within the acceptable limit (±5%). Their photocatalytic degradation percentage can be calculated by the formula: $\eta=((A_0-A)/A_0)\times 100\%$, in which A_0 is the absorbency of the organic dye solution before illumination while A after it.

3. Results and discussion

3.1. Catalyst characterization

Surface morphologies of pure TiO_2, Co doped TiO_2–SiO_2, and Ce doped TiO_2–SiO_2 films calcined at 450 °C in air for 1.0 h are shown in Fig. 1. It is clear that the films are composed of round-like nanoparticles or aggregates 4–10 nm in size. Different from pure TiO_2 film, the surface of Ce or Co doped TiO_2–SiO_2 film is relatively uniform and smooth without cracks. Compared with Co doped TiO_2–SiO_2 film, Ce doped TiO_2–SiO_2 film is composed of smaller nanoparticles or aggregates. A good dispersion or reduced aggregation among particles may increase the active site–reactant contact area, and enhance photocatalytic degradation of organic dyes. EDS element analyses indicate that the atomic ratio of Ti/O/Si/Ce, and Ti/O/Si/Co in the modified TiO_2 films is 1/1.44/0.43/0.07, and 1/1.43/0.45/0.06, respectively.

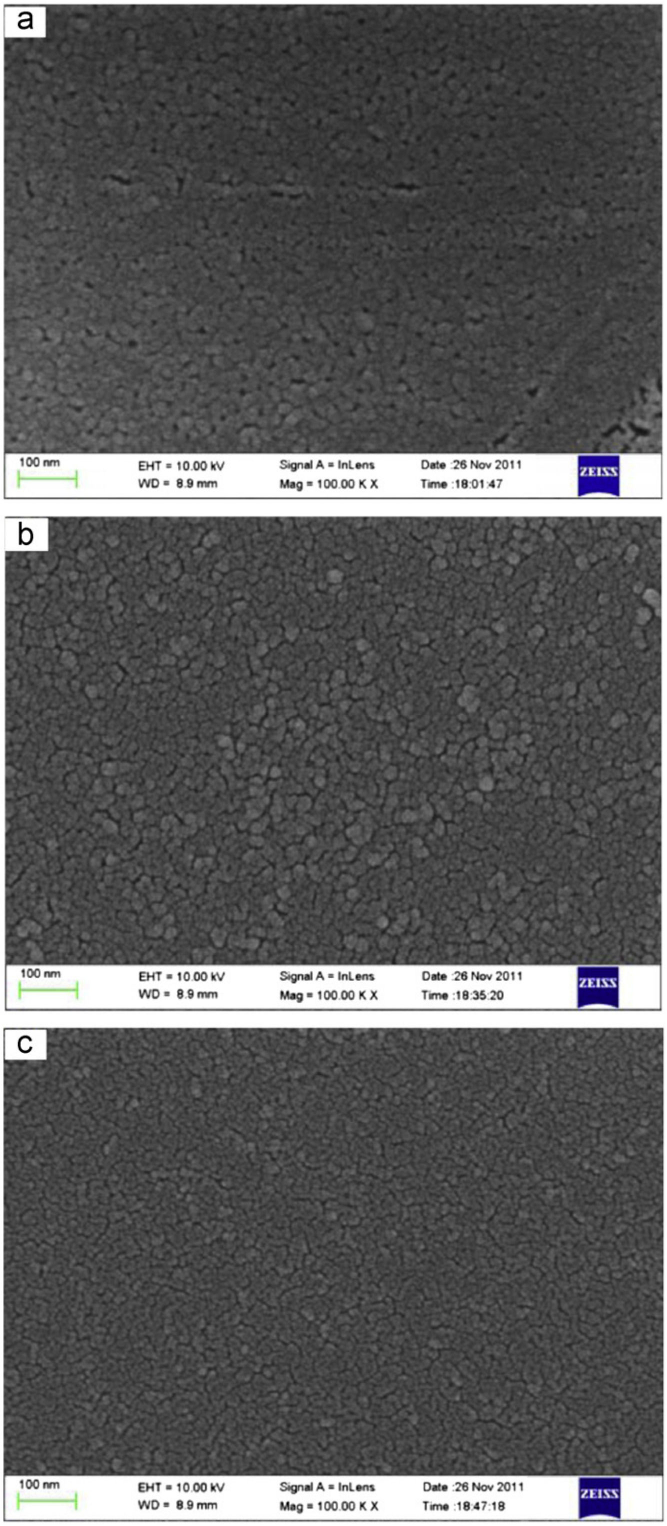

Fig. 1. FE-SEM images of (a) pure TiO_2 film, (b) Co doped TiO_2–SiO_2 film and (c) Ce doped TiO_2–SiO_2 film.

N_2 adsorption/desorption isotherms of pure TiO_2, Co doped TiO_2–SiO_2 and Ce doped TiO_2–SiO_2 powders

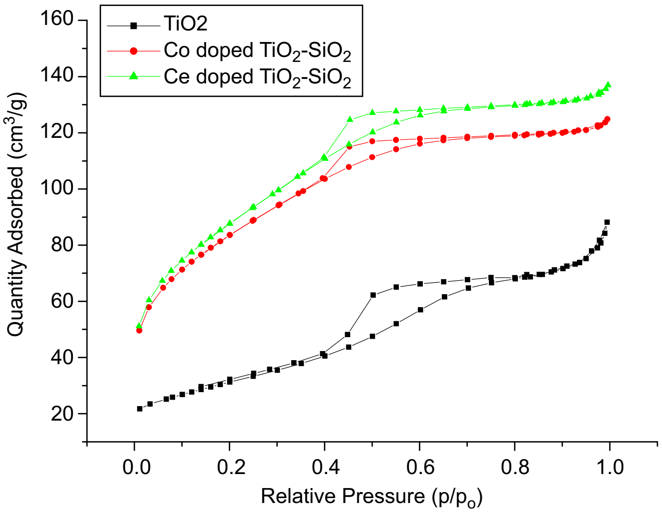

Fig. 2. N_2 adsorption/desorption isotherms of pure TiO_2, Co doped TiO_2–SiO_2 and Ce doped TiO_2–SiO_2 sample.

calcined at 450 °C in the air for 1 h are shown in Fig. 2. From Fig. 2, Ce doped TiO_2–SiO_2 sample has the highest adsorption quantities among the three samples at the same relative pressure. In our experiment, specific surface area of Ce doped TiO_2–SiO_2 sample is 306.1 $m^2\ g^{-1}$, while that of Co doped TiO_2–SiO_2 is 297.5 $m^2\ g^{-1}$, and pure TiO_2 is 68.4 $m^2\ g^{-1}$. The pore volumes are 0.21, 0.17 and 0.11 $cm^3\ g^{-1}$ for Ce doped TiO_2–SiO_2, Co doped TiO_2–SiO_2 and pure TiO_2 samples, respectively. The small pores and the large specific surface area are favorable to the photocatalytic degradation.

3.2. Photocatalytic activity measurements

Fig. 3 shows UV–vis absorption spectra (a) and degradation percentage (b) of ANR solutions using pure TiO_2 film, TiO_2–SiO_2 film, Co doped TiO_2–SiO_2 film, and Ce doped TiO_2–SiO_2 film under UV-lamp irradiation with wavelength of 365 nm for 45 min. The average intensity of UV irradiance was 6.5 mW cm^{-2} by measuring with a UV irradiance meter (Model UV-A). From Fig. 4(b), the degradation percentage of aqueous ANR using Ce doped TiO_2–SiO_2 film is 60.72%, while that of Co doped TiO_2–SiO_2 is 50.49%, TiO_2–SiO_2 film is 36.41%, and TiO_2 film is 14.21%. Therefore, we can draw the conclusion that Ce doped TiO_2–SiO_2 film has the best photocatalytic activity.

Fig. 4 shows UV–vis diffuse reflection spectra of pure TiO_2, Co doped TiO_2–SiO_2 and Ce doped TiO_2–SiO_2 films. Compared with pure TiO_2, Co doped TiO_2–SiO_2 film or Ce doped TiO_2–SiO_2 film has an obvious redshift especially when Ce is doped. As a result, more photogenerated carriers can join in the degradation reaction, which may lead to enhanced photocatalytic activity of the Ce doped TiO_2–SiO_2 film under both UV light and visible light irradiations.

Based on the above analyses, Ce doped TiO_2–SiO_2 film shows higher photocatalytic activity compared with Co doped TiO_2–SiO_2 film. This not only depends on the microstructure of the film such as surface morphology, grain size and distribution, surface area, etc. but also relates to the special electronic structure of dopant Ce ($4f^1 5d^1 4s^2$). The *f*-orbitals of lanthanide metals and the functional groups of various Lewis bases can form complexes, thus providing an absorbability of pollutants on TiO_2 surface [11]. On the other hand, the redox coupling of Ce^{4+}/Ce^{3+} or Ce^{3+}/Ce^{2+} is able to form the labile oxygen vacancies with relatively high mobility of bulk oxygen species, so Ce ions are able to effectively trap conductive band electrons, leading to a high photocatatltic activity. Moreover, Si^{4+} with higher electronegativity may replace the Ti^{3+} in TiO_2–SiO_2 composite system, leading to the formation of Si–O–Ti bonds [12]. With Si–O–Ti bonds formed, more surface defects may appear. These defects can not only capture the photogenerated electrons or holes but also increase the reaction activity of hydroxyls, both of which increase the photocatalytic activity of TiO_2.

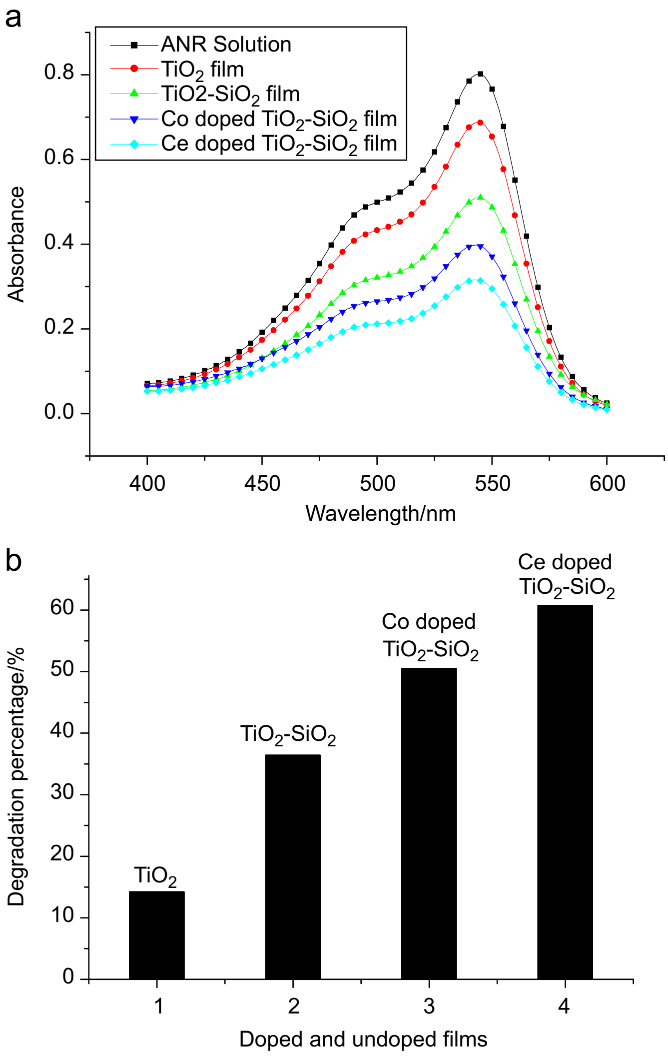

Fig. 3. UV–vis absorption spectra (a) and degradation percentage (b) of ANR solutions using pure TiO_2 film, TiO_2–SiO_2 film, Co doped TiO_2–SiO_2 film, and Ce doped TiO_2–SiO_2 film on glass substrates after irradiation for 45 min.

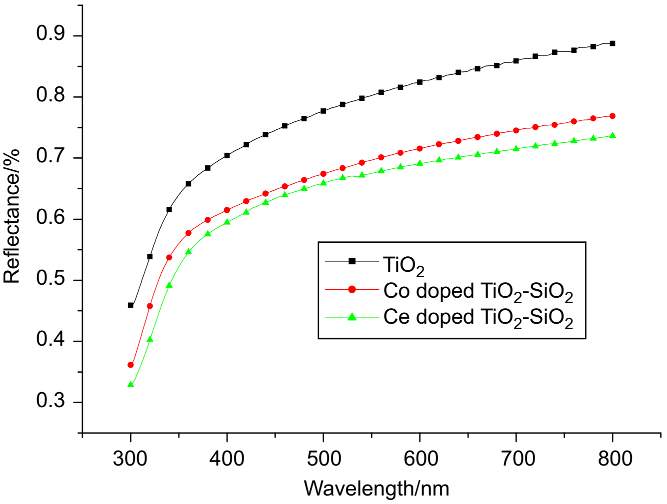

Fig. 4. Diffuse reflection UV–vis spectra of pure TiO_2, Co doped TiO_2–SiO_2 and Ce doped TiO_2–SiO_2 films.

4. Conclusions

Ce or Co doped nanocrystalline TiO_2–SiO_2 composite films were prepared by the sol–gel method. It was found that lanthanide metal Ce doped TiO_2–SiO_2 film had a higher photocatalytic activity compared with transition metal Co doped TiO_2–SiO_2 film. Moreover, small addition of lanthanide metals could reduce the number of pores produced at the film/substrate interface, enhancing the adherence of the films to the substrates, and therefore being favorable to the photocatalytic activity of the TiO_2 film after a long time exposure to air. Modification of TiO_2 with lanthanide metals might be a promising research area.

Acknowledgments

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