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A Bicomponent TiO_2/SnO_2 Particulate Film for Photocatalysis

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Plasma-enhanced chemical vapor deposition (PECVD) was used in the preparation of a series of bicomponent TiO_2/SnO_2 particulate films. The photocatalytic activities of the films are evaluated by photodegradation of phenol in solution. When both the TiO_2 and SnO_2 components of the bicomponent TiO_2/SnO_2 catalysts are accessible to reactants at the catalyst surface, photocatalytic degradation efficiencies are improved as compared to those obtained with TiO_2 films. When this condition prevails, the two components are believed to act in a cooperative manner by increasing the degree of charge carrier separation sufficient to reduce recombination, while simultaneously allowing sufficient time for photoelectrons and photoholes on the catalyst surface to form reaction intermediates (for example, the superoxide radical ion, $O_2^{\cdot -}$, formed by reaction of O_2 with photoelectrons, and the phenol radical, formed by reaction of phenol with photoholes or $OH^{\cdot}$ radicals) which cooperatively participate in later stages of the degradation process.

Introduction

TiO_2 particulate films have been widely employed in the photocatalytic decontamination treatment of polluted water and air purification.[1−5] To improve the activity of the TiO_2 catalyst,[6] it is important to decrease the recombination of photogenerated charge carriers. Coupling TiO_2 with other semiconductor materials may provide a beneficial solution for this problem.[7−9] As reported by Kamat et al.,[10,11] a high photodegradation rate of organic dyes has been achieved using particulate film prepared from a mixture of TiO_2 and SnO_2 colloidal suspensions. In their work, an electrochemical bias was applied during the electrochemically assisted photocatalytic degradation in order to promote the separation of photogenerated carriers.

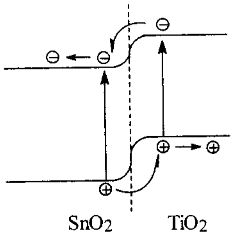

Figure 1. Schematic diagram of the charge-transfer process in the double-layered TiO_2/SnO_2 heterostructured film.

Levy et al.[7] investigated the photogenerated carrier transfer process in a double-layered TiO_2/SnO_2 heterostructured film prepared from a colloidal suspensions of TiO_2 deposited on a transparent layer of F-doped SnO_2 on glass. According to their diagram (Figure 1), photogenerated electrons in the TiO_2/SnO_2 system accumulate on the SnO_2 and holes accumulate on the TiO_2 due to the heterojunction formed at the TiO_2/SnO_2 interface. Thus, in principle, when TiO_2/SnO_2 double-layered films are used as a photocatalyst, recombination of photogenerated carriers can be suppressed without the assistance of an external electric field. However, if this kind of double-layered TiO_2/SnO_2 film is used as a photocatalyst, an open question is the fate of the photogenerated electrons accumulated in the SnO_2 layer, which may be unavailable for participating in the photocatalytic reaction, depending on the extent of coverage by the TiO_2 layer.[2]

We demonstrate here the preparation of a double-layered TiO_2/SnO_2 film with both of the two components exposed to the surface by the plasma-enhanced chemical vapor deposition (PECVD) technique. The special film structure will allow both photogenerated electrons and holes to contribute to the photocatalytic reactions.

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Table 1. Preparation Condition and Phenol Photodegradation Results of the Films

film	mass of film (mg)	deposn time (min)	degradation ratio[a] C/C_0	rate const K (min^{-1})	half-time $T_{1/2}$ (min)	specific photocatal activity[b] (mol/(g·h))
TiO_2/SnO_2	0.53/3.05	10/20	0.40	8.0×10^{-3}	87	1.6×10^{-3}
TiO_2/SnO_2	3.06/3.08	20/20	0.75	2.2×10^{-2}	31	5.2×10^{-4}
TiO_2/SnO_2	5.20/3.01	30/20	0.40	1.3×10^{-2}	54	1.6×10^{-4}
TiO_2	2.93	20	0.24	3.3×10^{-3}	210	1.5×10^{-4}
SnO_2	3.07	20	0.04	5.7×10^{-4}	1240	
blank	0	0	0.04	5.6×10^{-4}	1245	

[a] Average degradation ratio of phenol after 1 h of photocatalytic reaction. [b] Phenol degradation amount per unit mass catalyst after 1 h of photocatalytic reaction.

Experimental Section

Materials. $SnCl_4$, $TiCl_4$, and phenol were purchased from Beijing Chemical Co. All the chemicals were analytical grade and were used as received. Deionized water (18 MΩ·cm) was used in all the experiments.

Film Deposition. PECVD is an appropriate technique to prepare thin films. By getting energy from a high-frequency electric field, it can lower the reaction temperature greatly compared with the conventional chemical vapor deposition (CVD) method.[12,13] In a typical experiment, a TiO_2/SnO_2 bicomponent film was deposited on a glass slide (7.5×2.5 cm^2), except in the case of the surface photovoltaic spectrum, SPS, measurements, in which indium−tin oxide (ITO) glass was used as substrate. When a vacuum tightness of 8×10^{-2} mmHg and power output of 320 W in a homemade PECVD reactor were achieved, the O_2 and $SnCl_4$ gases were subsequently loaded into the reactor chamber which was held at a constant temperature of 110 °C. The deposition time for all SnO_2 films was 20 min. Under the same conditions, TiO_2 films were deposited on the surface of glass slides or SnO_2 films with O_2 and $TiCl_4$ as precursors. By control of the deposition time, TiO_2/SnO_2 bicomponent films of different mass ratios could be prepared (see Table 1). Following calcination at 450 °C for 30 min, the films were stored in a desiccator. One-component SnO_2 or TiO_2 film was prepared by using the similar approach.

Photocatalytic Reaction. The photodegradation of phenol was carried out in a 70 mL Pyrex glass vessel with magnetic stirring. Illumination with >290 nm was employed by using a 400 W high-pressure mercury lamp. The blank glass slide or coated slide was immersed in the solution and fixed in the vessel perpendicular to the light beam. The distance between the film and the light source was 10 cm. The phenol solution (50 ppm, 40 mL) was continuously bubbled by O_2 gas at a flow rate of 5 mL/min with a constant system temperature of 25 ± 2 °C. The residual concentration of phenol was measured through the standard colorimetric method, using 4-aminoantipyrine as the chromogenic reagent after every 1 h.

Techniques. X-ray diffraction patterns were obtained by using a Rigaku D/max γA X-ray diffractometer. Atomic force microscope (AFM) observations were carried out on a Park Scientific Instrument Autoprobe CP. The noncontact mode was used in all AFM measurements, which were carried out in air. UV−visible measurements were taken on a Shimadzu UV-365 spectrometer. X-ray photoelectron spectroscopy (XPS) experiments were carried out on a PHI 5000 instrument with an Al Kα anode. SPS measurements were carried out with a solid-junction photovoltaic cell of indium tin oxide (ITO)/sample/ITO using a light source−monochromator−lock-in-detection technique. Monochromatic light was obtained by passing light from a 500 W xenon lamp through a double-prism monochromator (Hilger and Watts, D300). A lock-in amplifier (Brookdeal, 9503-SC), synchronized with a light chopper, was employed to amplify the photovoltage signal.[14] All experiments were carried out at room temperature.

Results and Discussion

X-ray diffraction measurements show that the SnO_2 and TiO_2 layers prepared exhibit the rutile and anatase structures, respectively. Since these materials have a serious lattice mismatch, it is possible for TiO_2 to grow in an island mode on the SnO_2 layer and for both components to be exposed to the surface due to the strain effect, similar to that occurred in the Stranski−Krastanov mode growth of self-organized III−V semiconductor quantum dot structures constructed by the MBE and MOCVD methods.[15] This assumption is supported by the XPS results. The peak area ratios of Sn $3d_{5/2}$ to Ti $2p_{3/2}$ only decreased from 1:1.7 to 1:2.3 when the deposition time of TiO_2 layer increased from 10 to 30 min.[16] Figure 2 shows the AFM images of the TiO_2/SnO_2 films prepared under different TiO_2 deposition times. Although it could not be identified which particle corresponds to SnO_2, and which one corresponds to TiO_2 at the present stage, it can be concluded from these AFM observations that the TiO_2 layer grows in an island mode on the SnO_2 surface as expected. No continuous film could be observed even for a deposition time as long as 30 min.

Photodegradation results show ln C_0/C values for phenol as a function of photodegradation time, t, for the experiments catalyzed by using a TiO_2 one-component film and TiO_2/SnO_2 bicomponent films as photocatalysts, respectively. The linear correlation between ln C_0/C and t suggest a first-order reaction for all the samples. When only 0.53 mg of TiO_2 is deposited on the SnO_2 surface, the film shows higher photocatalytic activity than the one-component TiO_2 film that contains 2.93 mg of TiO_2 (see Table 1). This suggests the SnO_2 layer plays a very important role in the photocatalytic reaction. When 3.06 mg of TiO_2 is contained in the bicomponent film, a much higher degradation ratio is achieved. This means both TiO_2 and SnO_2 play important roles in the photocatalytic reaction. When the mass of TiO_2 increases to 5.20 mg, the specific photocatalytic activity of the bicomponent film is reduced to 1.64×10^{-4} mol/(g·h). This value is approximately the same as that of the one-component TiO_2 film. This suggests that the SnO_2 layer contributes little to the photocatalytic reaction due to more TiO_2 deposited on its surface.

Figure 3 shows the surface photovoltaic spectrum (SPS) of a bicomponent film in which 3.06 mg of TiO_2

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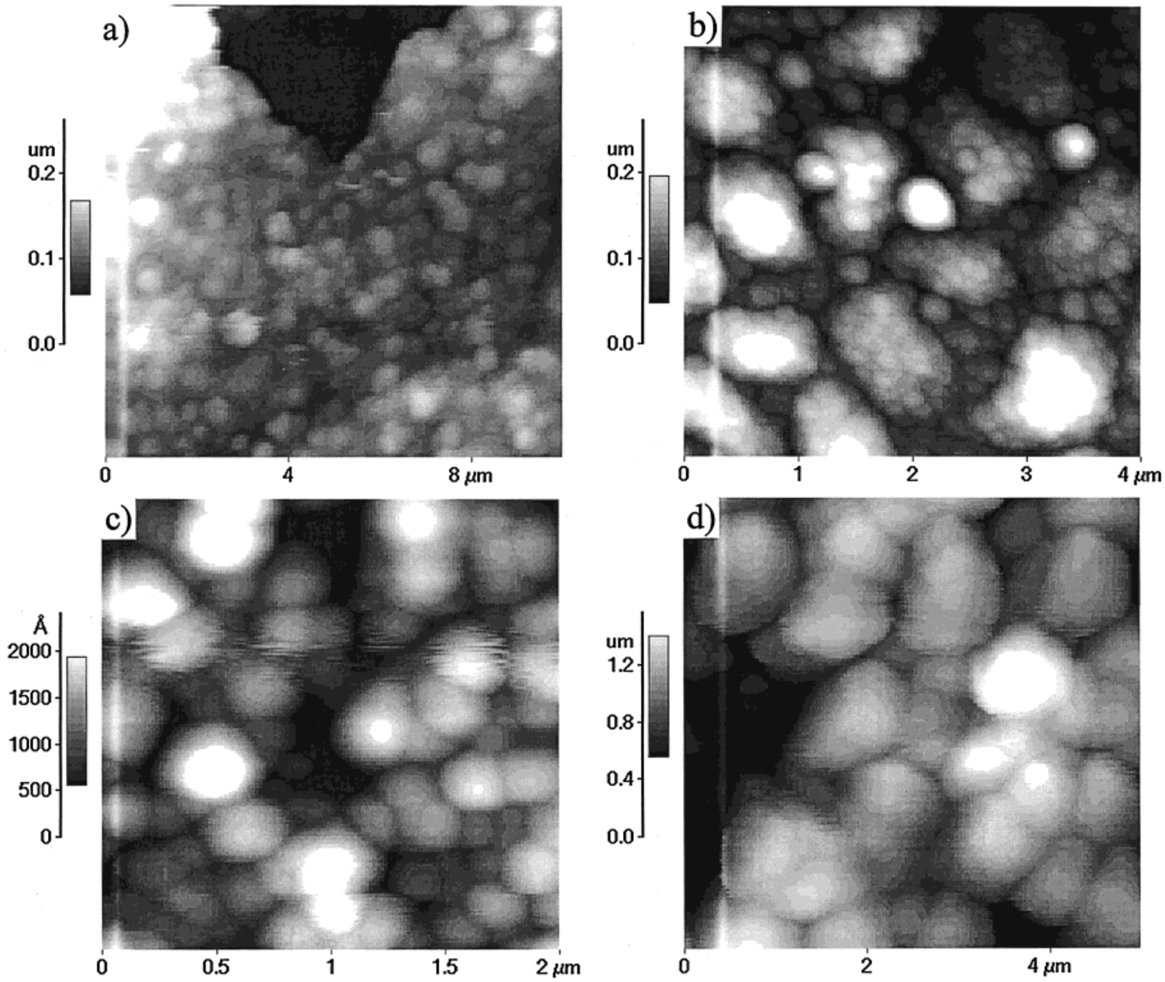

Figure 2. AFM images of double-layered TiO_2/SnO_2 films prepared at different deposition times of TiO_2: (a) 0 min; (b) 10 min; (c) 20 min; (d) 30 min.

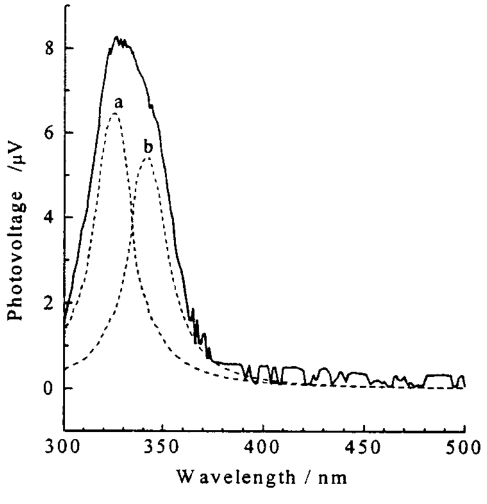

Figure 3. SPS of a TiO_2/SnO_2 bicomponent film deposited on ITO glass. The deposition time is 10 min. The light was irradiated on the SnO_2 side.

was deposited on a SnO_2 layer. The SPS measurements were taken with a sandwich-type photovoltaic cell of ITO/film/ITO.[17] After the curve was fit, two photovoltaic responses at 325 and 340 nm could be identified, corresponding to band-to-band transitions of SnO_2 and TiO_2, respectively. This suggests that a charge-transfer process, similar to that observed from a colloidal TiO_2/SnO_2 double-layered film, as shown in Figure 1, also occurs with these PECVD deposited bicomponent TiO_2/SnO_2 films.[7]

In discussions of photodegradation processes, photogenerated holes in TiO_2 are considered capable of directly oxidizing many organic pollutants. Photogenerated electrons have also been shown to be capable of contributing to the oxidization process through reduction of absorbed O_2 to the superoxide radical ion, $O_2^{\cdot-}$,[2] which can take part in the oxidation of phenol, possibly via a "Russell-like" mechanism.[18,19] The two components, TiO_2 and SnO_2, in the PECVD film act in a cooperative manner. Both photogenerated electrons accumulated on SnO_2 and holes accumulated on TiO_2 contribute to the overall reaction by formation of $O_2^{\cdot-}$ and radical phenol intermediates, respectively, followed by their interactions. As proposed by Levy et al., the overall reaction efficiency of such photodegradation might be improved if the radical phenol intermediates and $O_2^{\cdot-}$ are formed in close proximity on the catalyst surface.[19] This is just the case in our PECVD-deposited TiO_2/SnO_2 bicomponent films, since there exists a vast

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boundary between the two components. Thus, high photocatalytic activity is achieved. It is noted that when the deposition time of TiO_2 on a SnO_2 layer is as long as 30 min, the photoactivity of the resulting bicomponent film is almost the same as that of a one-component film. This means that the SnO_2 layer has little chance to contact with the absorbed oxygen molecules; thus, the charge transfer between them is blocked by the deposited TiO_2 layer and the photocatalytic activity of the composite film is similar to that of the one-component TiO_2 film.

Conclusion

In summary, the results presented here suggest that it is possible to allow both the TiO_2 and SnO_2 components to be present simultaneously at the surface of the TiO_2/SnO_2 bicomponent film prepared via the PECVD approach. This surface heterojunction structure promotes an increase in the charge separation of the photogenerated electrons and holes within the system, suppressing recombination and allowing charge carrier reaction intermediates to participate in the overall photodegradation process.[7,19] It can be expected that the activity of the bicomponent film can be further improved by optimizing the deposition conditions.

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