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Photochromic and photocatalytic behaviors on immobilized TiO_2 particulate films

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Abstract

Transparent TiO_2 films are prepared by sintering colloids on a conducting glass support. TiO_2 particulate film exhibits reversible photochromic and n-type semiconductor properties. The recombination between the photogenerated charge carriers can be suppressed by applying an external anodic bias. Thin semiconductor films provide a convenient way to enhance the efficiency of the photocatalytic degradation. The electrochemically assisted photocatalysis can be applied to photocatalytic reactors with immobilized semiconductor particles. © 1997 Elsevier Science S.A.

Keywords: TiO_2; Photochromism; Photocatalytic degradation

1. Introduction

Photoelectrochemical conversion and photocatalytic degradation using semiconductor colloids have attracted considerable interest in recent years [1–6]. The approach of using semiconductor colloids for the design of optically transparent thin films [7–10] has also been fascinating in the sense that this technique is relatively simple and inexpensive compared with other commonly employed technique such as molecular beam epitaxy or chemical vapor deposition (CVD). The most striking feature of such a particulate film is the ability to retain the photophysical and photochemical properties of individual semiconductor particles and thus to carry out the photocatalytic reactions with similar selectivity and efficiency as in the semiconductor particle suspensions. Recently, we have employed TiO_2 colloids for preparing optically transparent thin films on conducting glass plates, and have investigated their photochromic and photocatalytic properties.

2. Experimental

Preparation of TiO_2 film: titanium tetraethoxide was slowly added to an aqueous solution of alcohol containing nitric acid under continuous stirring with a magnetic stirrer, and the resulting sol was further stirred for 2 h at room temperature. Titania gel film was obtained by dipping an ITO substrate in the TiO_2 sol and subsequently pulling it up at a constant speed (0.1 mm s^{-1}). The resulting TiO_2 gel film was dried at 100 °C for 15 min and then sintered at 550 °C for 1 h. The films were transparent in the visible region. TiO_2 particles have an average diameter of 50 nm (Fig. 1; the photograph was taken at a magnification of 30 000×).

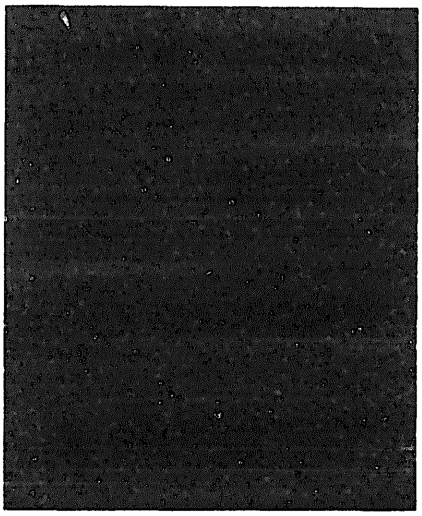
Fig. 1. SEM photograph of TiO_2 particulate film.

Spectroelectrochemical measurements were carried out with a standard three compartment cell consisting a Pt wire counter electrode and a SCE reference electrode. A potentiostat was employed for spectroelectrochemical measure-

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ments. Steady state photocatalysis was carried out by irradiating the TiO_2 film with UV light from a 150 W xenon lamp. The experiments were carried out at room temperature.

3. Results and discussion

3.1. Photochromic effects

The spectral response a TiO_2 particulate film upon bandgap illumination is shown in Fig. 2. The TiO_2 particulate film exhibits strong absorption in the UV region with an absorption onset at around 380 nm. This onset of absorption, which is blue shifted compared with its bulk bandgap of 3.2 eV, indicates size quantization effects in these particles. When a TiO_2 particulate film was illuminated for 4 min in the absence of oxygen an intense color developed. The effect was attributed to the generation of Ti^{3+} species within the particulate film via

$$TiO_2 + h\nu \rightarrow TiO_2(e \ldots h)$$

$$TiO_2(e) \rightarrow TiO_2(Ti^{3+})$$

$$TiO_2(h) + \text{alcohol} \rightarrow TiO_2 + \text{products}$$

where e and h refer to electrons and holes, respectively. Efficient scavenging of holes by alcohol facilitates trapping of electrons in the TiO_2 particulate film. This significant accumulation of electrons occurs in the TiO_2 particulate film. The result is reflected in the blue color developing. When air is admitted to the solution for 1 min after stopping the illumination, the intense blue color disappears. Oxygen absorbed on the TiO_2 surface is a good scavenger for the photogenerated electrons,

$$TiO_2(e) + O_2 \rightarrow TiO_2 + O_2^-$$

and as a result of this no significant accumulation of electrons occurs in the TiO_2 particulate film. Once all the stored electrons are consumed, this electron scavenging effect is also reflected in the intense blue color disappearing. Both effects are completely reversible.

Fig. 3 shows the absorption change (700 nm) vs. time of photocatalysis. With increasing duration of UV photocatalysis an increase of the absorbance was observed. Thus with increasing irradiation time, we are able to trap more electrons within the film.

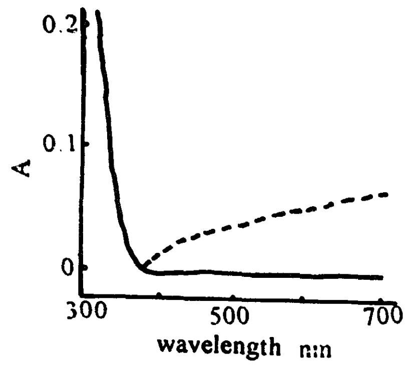

Fig. 2. Spectral changes of illuminated TiO_2 film in 0.1 mol l^{-1} alcohol + 0.5 mol l^{-1} Na_2SO_4 solution: ———, before illumination; - - -, after illumination with UV light for 4 min.

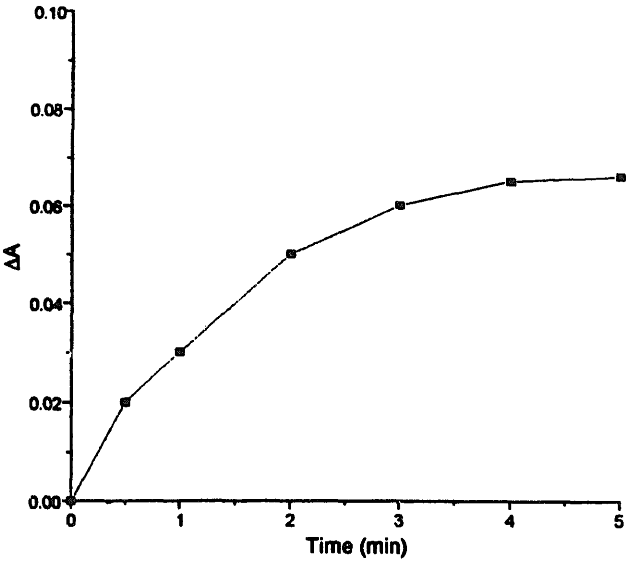

Fig. 3. The absorption changes at 700 nm at different photolysis time in 0.1 mol l^{-1} alcohol + 0.5 mol l^{-1} Na_2SO_4 solution.

3.2. Photocurrent action spectra

Bandgap excitation of TiO_2 electrode in 0.1 mol l^{-1} alcohol + 0.5 mol l^{-1} Na_2SO_4 solution leads to the oxidation of alcohol by photogenerated holes. This process can be quantified, for example in terms of incident photon-to-current conversion efficiency (IPCE) [9].

$$\text{IPCE} = \frac{ihc}{\lambda pe}$$

where i is the short circuit photocurrent density, h Planck's constant, c the velocity of light, λ the wavelength, p the light power density and e the elemental charge. The light power density p is considered in front of the window of the electrochemical cell, i.e. it is not corrected for losses in the window, solution or electrode. We shall further define photocurrent efficiencies of an electrode illuminated from the side of the electrolyte/film interface as IPCE_a, and that for a back side illumination(through the quartz glass/ITO support) as IPCE_b. Fig. 4 shows the photocurrent action spectra. The quantum yield of the TiO_2 electrode increases as the film is biased to a more positive potential. When an anodic bias is applied to the working electrode, the efficiency of the charge separation in the TiO_2 particulate film is increased. One observes a higher quantum yield. For the photoresponse a much higher quantum yield is achieved for back side illumination than for front side illumination. Front side illumination yield, besides a general lowering of the quantum yield, has a clear maximum point of the photoresponse. This shows that the most efficient current generation takes place close to the back contact. The lower quantum yield for front side illumination is explained by recombination losses during

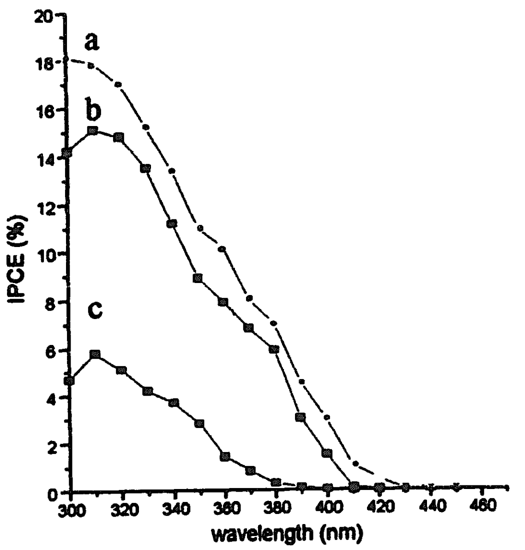

Fig. 4. Photocurrent action spectra of the TiO_2 electrode in 0.1 mol l^{-1} alcohol + 0.5 mol l^{-1} Na_2SO_4 solution: curve a, 0.6 V, back illumination; curve b, 0.6 V, front illumination; curve c, 0 V, front illumination.

transport of electrons in the outer part of the particulate film on their way to the back contact. The maximum in the front side action spectrum, $IPCE_{a,max}$, can be understood in terms of the longer wavelength light penetrating more deeply into the particulate film. The high quantum efficiencies for back side illumination can be explained by the fact that the charge carriers that efficiently contribute to the photocurrent are generated close to the back contact.

3.3. Photocatalysis with TIO₂ particulate film

In order to assess the ability of the TiO_2 particulate electrode to promote the photocatalytic process, we monitored the degradation of 4-chlorophenol (4-CP) in a photoelectrochemical operation. The schematic diagram of the photoelectrochemical cell used to carry out the degradation of 4-chlorophenol is shown in Fig. 5. By separating the working and counter-electrode compartments with a fine glass frit, it was possible to control the oxidation and reduction processes in separate compartments. Nitrogen was bubbled continuously into the working electrode compartment so that the oxidation of 4-CP is initiated only by the photogenerated holes. The absorption spectra of a 4-CP solution recorded following the excitation of an TiO_2 electrode are shown in Fig. 6. An anodic bias of 0.6 V vs. SCE was applied to the TiO_2 electrode. The absorption peaks corresponding to 4-CP disappear completely following the photolysis, thereby indicating complete disappearance of 4-CP. The observation of increased absorbance in the 240–280 nm region at short illumination time is attributed to the formation of reaction intermediates. These observations are similar to those observed during the photolysis of TiO_2 suspension containing 4-CP [11,12]. The intermediates detected by HPLC during the course of the degradation were hydroquinone (major component), 4-chlorocatechol, and benzoquinone. It should be noted that 4-CP alone does not undergo oxidation reaction at an anodic potential of 0.6 V. When the photolysis is carried out with an ITO electrode, negligibly small changes of the 4-CP concentration are seen.

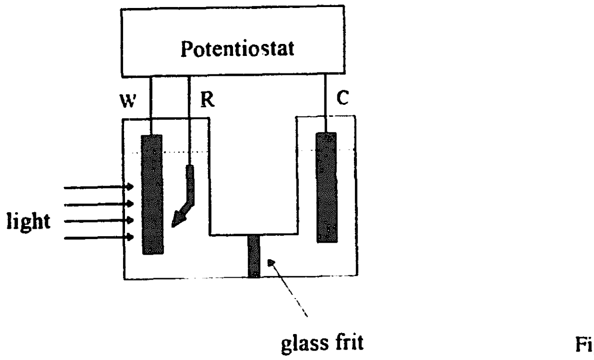

Fig. 5. Schematic diagram of electrochemically assisted degradation: W, semiconductor electrode; C, counter electrode; R, reference electrode.

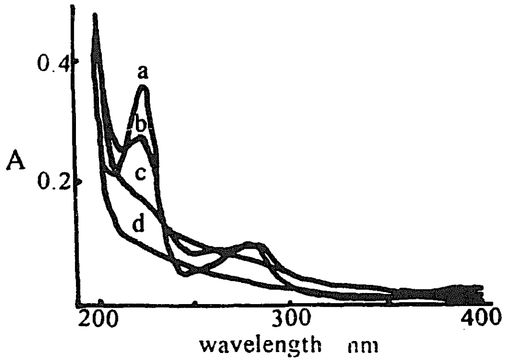

Fig. 6. Absorption spectra of 0.4 mmol l^{-1} 4-CP pH = 9) recorded at different time intervals. TiO_2 electrode is biased at 0.6 V. (a) 0 min, (b) 30 min, (c) 60 min and (d) 140 min.

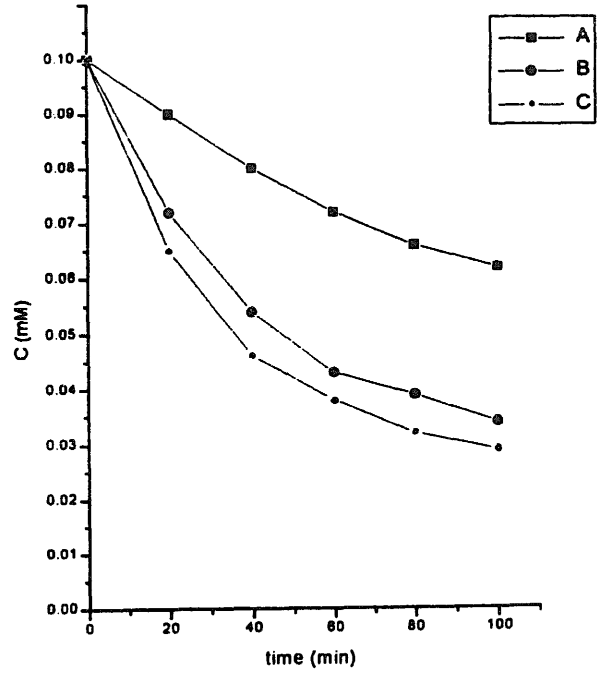

Fig. 7. Dependence of 4-CP degradation rate on the bias: curve A, 0 V bias, front illumination; curve B, 0.6 V bias, front illumination; curve C, 0.6 V bias, back illumination.

The dependence of rate of photocatalytic degradation of 4-CP on the applied potential is shown in Fig. 7. The degradation of 4-CP was monitored from the decrease of the absorbance at 225 nm with illumination time. It is evident from these measurements that the photocatalytic degradation occurs at a faster rate when the applied potential is maintained at 0.6 V than that at 0 V applied bias. In a slurry system, the illuminated particles behave as short circuited microelectrodes, and thus the charge recombination competes with the interfacial charge transfer process. This situation closely resembles the experimental condition in which the TiO_2 electrode is maintained at 0 V. When an anodic bias is applied to the working electrode, the efficiency of the charge separation in the TiO_2 particulate film is increased. One observes a higher efficiency for photocatalytic degradation. The electrochemically assisted photocatalysis overcomes the limitation of electron scavenging process that is encountered in the slurry system. It is also evident that the photocatalytic degradation occurs at a lower rate for front side illumination (through the electrolyte–film interface) than that for back side illumination (through the quartz glass/ITO support) when the applied potential is maintained at 0.6 V. This is explained by recombination losses during transport of electrons in the outer part of the particulate film on their way to the back contact. The charge carriers that most efficiently contribute to the degradation are generated close to the back contact.

4. Conclusions

TiO_2 particulate films have been found to exhibit reversible photochromic effects. Thin semiconductor films provide a convenient way to enhance the efficiency of the photocatalytic degradation. The electrochemically assisted photocatalysis can be applied to photocatalytic reactors with immobilized semiconductor particles.

Acknowledgements

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