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TiO_2 and WO_3 semiconductor particles in contact: photochemical reduction of WO_3 to the non-stoichiometric blue form

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Abstract. Hydrated tungsten oxide $WO_3.xH_2O$ in contact with TiO_2 grains suspended in water is found to reduce to $WO_{2.96}.xH_2O$ upon irradiation with uv light. Measurement of the band position of $WO_3.xH_2O$ suggests that electron transfer from TiO_2 to $WO_3.xH_2O$ is responsible for the reduction.

1. Introduction

Recently, the properties of semiconductor particles and their photocatalytic activity has aroused much interest. The photocatalytic activity of semiconductor particles depends on injection of photogenerated carriers to the solution. It is known that the reduction in size of the particle, surface modifications, deposition of noble metals and other semiconducting materials enhance the charge separation, improving the catalytic activity [1–3]. A composite catalyst consisting of two semiconductor particles in contact is of special interest because of the availability of a large number of semiconducting materials with different band gaps and band positions. Several authors have noted the catalytic properties of such composite systems and attributed this activity to the enhanced charge separation [4–6]. In this note we give an example that vividly demonstrates light-induced charge separation in a composite semiconductor particle. Tungsten oxides of oxygen stoichiometry less than WO_3 are known to possess a deep blue colour [7]. We have found that when WO_3 oxide particles in contact with TiO_2 are irradiated in the presence of water, a deep blue colour is developed as a result of electron transfer from TiO_2 to $WO_3.xH_2O$.

2. Experimental details

Composite particles (where TiO_2 and WO_3 are in contact) were prepared as follows. TiO_2 (2 g) is dispersed in 0.1M sodium tungstate solution (50 ml). When excess dilute HCl is gradually added, tungstic acid (H_2WO_4) is precipitated around the TiO_2 grains. The precipitate is filtered, washed and dried in air at 250, 500, 750 and 1000 °C for 2 h giving a product that is yellow in appearance. The $TiO_2/WO_3.xH_2O$ (200 mg) was suspended in 150 ml distilled water in an immersion well-type photochemical reactor (Applied Photophysics). The dispersion was purged with N_2 to remove dissolved oxygen and then irradiated by a 125 W medium pressure Hg arc lamp. $WO_3.xH_2O$ (prepared by heating H_2WO_4 to 250 °C for 2 h) was compacted into pellets (diameter 13 mm; thickness ~1 mm; pressure 40 MPa) which were used to obtain the Mott–Schottky plots (the plot of C^{-2} against V). The Hewlett Packard LCR meter 4192A and Kenwood DL 707 Digital multimeter were used to measure capacitance and voltage respectively. X-ray diffractometry studies were made to characterize the catalyst (Shimadzu XD 7A model diffractometer with Cu Kα radiation).

3. Results and discussions

When the lamp was switched on for about 0.5 h, the originally white suspension acquired a deep blue colour. The spectra (Shimadzu UV-3000 UV-Vis spectrophotometer) of the suspension before and after irradiation are compared in figure 1. X-ray diffractometry data revealed that the blue colour corresponds to the non-stoichiometric compound $WO_{2.96}.xH_2O$. The maximum reduction of $WO_3.xH_2O$ to $WO_{2.96}.xH_2O$ was observed with the powder mixture heated up to 250 °C for 2 h. This is probably due to the formation of good surface contacts between TiO_2 and WO_3. The physically mixed TiO_2 (anatase) and WO_3 powders heated to 250 °C for 2 h did not show the reduction. This observation indicates the necessity of efficient surface contacts.

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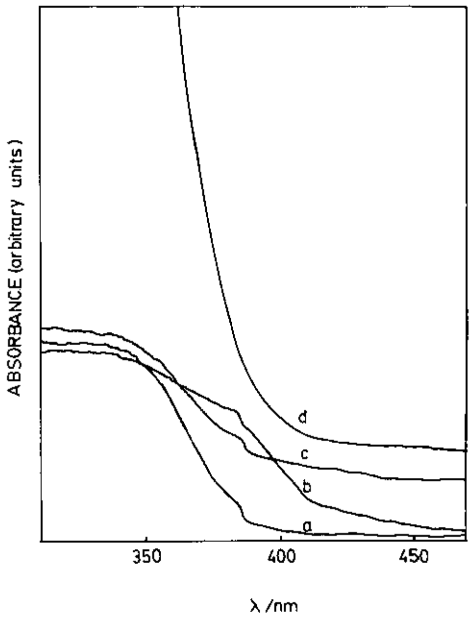

Figure 1. The diffuse reflectance spectra of (*a*) TiO_2, (*b*) TiO_2/WO_3, (*c*) $TiO_2/WO_{2.96}$ and (*d*) $WO_3.xH_2O$.

X-ray diffractometry data showed that drying at 250 °C for 2 h produces amorphous $WO_3.xH_2O$, while differential thermal analysis (Shimadzu model DT 40) data confirmed that the water bound in $WO_3.xH_2O$ begins to loosen at about 415 °C. The materials (heated up to 500, 750 and 1000 °C for 2 h) formed crystalline WO_3 that is lemon yellow in colour [8].

The diffuse reflectance spectra of $WO_3.xH_2O$ (figure 1) suggested that the band gap of the material is ~ 3.15 eV. The flat-band potential of $WO_3.xH_2O$ derived from the Mott–Schottky plots is -0.45 (V against SCE) at pH 5.5 (for 1 and 0.5 kHz, straight line plots with a common intercept at -0.45 V were obtained). The relative band positions of the TiO_2 and $WO_3.xH_2O$ is shown in figure 2. The band position of TiO_2 at pH 5.5 known to be -0.7 V (V against SCE) [9]. Since the conduction band of $WO_3.xH_2O$ is situated below the conduction band of TiO_2, photogenerated electrons will be transferred to the conduction band of WO_3, while holes accumulate in TiO_2. In the presence of water electrons could participate in the reaction:

$$\begin{array}{l} 25WO_3.xH_2O + H_2O \\ \quad \underset{\substack{\uparrow \\ \text{CB } WO_3}}{+\,2e^-} \longrightarrow 2OH^- + 25WO_{2.96}.xH_2O \qquad (1) \end{array}$$

Holes that accumulate on TiO_2 will generate $OH^\bullet$ free radicals at the surface of TiO_2 grains

$$OH^- + \underset{\substack{\uparrow \\ \text{VB } TiO_2}}{h^+} \longrightarrow OH^\bullet \qquad (2)$$

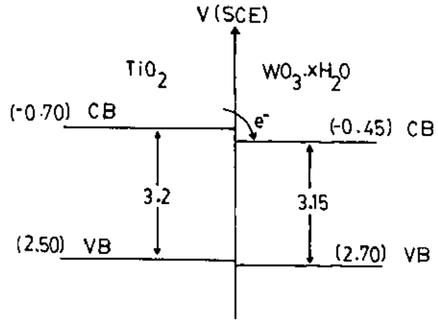

Figure 2. The relative band positions of TiO_2 and $WO_3.xH_2O$ at pH 7. Energies are given in eV with respect to the standard calomel electrode (SCE).

Oxygen evolution is not detected, as expected. This could result from the formation of peroxo- complexes of titanium [10]. When the photo-produced blue compound is exposed to oxygen rapid bleaching is observed as a result of oxidation to the stoichiometric oxide.

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References

[1] Kamat P V, Dimitrijevic N M and Fessenden R W 1987 *J. Phys. Chem.* **91** 396

[2] Miyoshi H, Yamachika M, Yoneama Y and Mori H 1990 *J. Chem. Soc. Faraday Trans.* **86** 1815

[3] Miyoshi H, Tanaka K, Uchida H, Yoneama Y, Mori H and Sakata T 1990 *J. Electroanal. Chem.* **71** 295

[4] Tennakone K, Fernando C N N, Wickramanayake S, Damayanthi M W P, Silva L H K, Wijerathne W, Ileperuma O A and Punchihewa S 1988 *Solar Energy Material* **17** 47

[5] Harry D, Thewissen M W, Timmer K, van der Zouwen-Assink E A, Tinnemans A H A and Macor S 1985 *J. Chem. Soc. Chem. Commun.* 1485

[6] Henglein A, Gutierrez M, Weller H, Fogtik A and Jirkovosky J 1989 *Ber. Bunsenges. Phys. Chem.* **93** 593

[7] Endoh E, Leland J K and Bard A J 1986 *J. Phys. Chem.* **90** 6223

[8] Wells A F 1962 *Structural Inorganic Chemistry* 3rd edn (London: Oxford University Press) p 468

[9] Bolts J M and Wrighton M S 1976 *J. Phys. Chem.* **80** 2641

[10] Gratzel M (ed) 1988 *Energy Resources through Photochemistry and Catalysis* (New York: Academic) pp 218–53