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The influence of transition metal doping on the physical and photocatalytic properties of titania

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Abstract

Titanium dioxide is one of the most efficient photocatalysts for the detoxification of organically charged waste water. However, this material suffers from the drawback of poor absorption properties because of a band gap of 3.2 eV. Thus, wavelengths shorter than 400 nm are needed for light induced generation of electron–hole pairs. Therefore, doping with transition metal ions is interesting for inducing a batho-chromic shift of the band gap. However, this doping changes other physical properties such as lifetime of electron–hole pairs and adsorption characteristics. This paper deals with doping titania by Cr^{3+} and Mo^{5+} ions. We want to show the complex interactions between variations in lifetime of charge carriers, adsorption properties and photocatalytic behaviour. © 1999 Elsevier Science S.A. All rights reserved.

Keywords: Semiconductor photocatalysis; Doped titania; Photophysical properties; Charge carriers; Adsorption

1. Introduction

The principles of photocatalysis of organic pollutants are well known [1–4,6]: by illumination of the catalyst electron–hole pairs are generated. These charge carries can diffuse to the surface of the catalyst and initiate redox reactions. Since the band gap of the most efficient photocatalyst, titania, is about 3.2 eV [5], wavelengths below 380 nm are necessary for this process. Thus, if natural sunlight should be used for the photoexcitation of this material only about 5% of the incident radiation has sufficient energy for this process. A possibility to overcome this obstacle is doping of titanium dioxide by transition metal ions. Several papers deal with this subject and titania was already doped by various transition metal ions using different preparation techniques [7–13]. Therefore, many controversial results are reported in literature since even the method of doping determines the properties of the resulting catalyst. In the present work doping is done during the sol–gel process. This method of preparation leads to the greatest possible homogeneous distribution of the dopant in the host matrix.

In this paper, we want to focus the attention on doping titania with Cr^{3+} and Mo^{5+} in order to investigate the different behaviour of n- and p-dopants. These ions have nearly the same radius [14] as Ti^{4+}.

The modification of the doped titania is investigated by X-ray diffraction. We use photoacoustic spectroscopy to follow the red-shift of the band gap. Since the doping ions act as trapping sites they can influence the lifetime of charge carriers. Therefore, we use the time resolved photocharge method (TRPC) to observe this effect. Since surface sites are also occupied by transition metal ions the surface properties may be changed as well. Therefore, adsorption measurements were performed with the same model compound as for the degradation experiments. Because of two reasons Rhodamine B was chosen as a model compound: on the one hand the complete mineralization of this group of compounds is well understood. On the other hand the Rhodamine B concentration can easily be monitored by UV–Vis spectroscopy.

1.1. Experimental

1.1.1. Preparation of doped titania powders

6.95 ml (6.7 g, 23.55 mmol) tetra-isopropylorthotitanate (>99%, Fluka) is diluted in 30 g (0.6 mol) isopropanol. For stabilisation purposes 9 g (8.77 ml, 68.85 mmol) ethyl acetonate and 1 ml (1.4 g, 14.44 mmol) nitric acid are added to the solution and stirred for 24 h at room temperature. In case of doped titania the synthesis starts with the dissolving of the respective amount of chromium (III) nitrate or molybdenum (V) nitrate.

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For the preparation of the powders the sol is evaporated to dryness at 100°C and calcinated at 400°C for 24 h. By this procedure powders with dopant concentrations from 0.1 to 10 at.% were obtained. Using the Scherrer [15] approximation the particle size of the different powders is in the range of 10–18 nm, the BET surface area is about 40–50 $m^2 g^{-1}$.

The X-ray investigations were recorded by a Siemens diffractometer using copper Cu $K\alpha_1$ and Cu $K\alpha_2$ radiations.

The absorption spectra and the band gap shifts are detected by a home-built photoacoustic spectrometer.

The lifetime of the photogenerated charge carriers (electrons and holes) is determined by time resolved photocharge (TRPC) measurements. The experimental set-up is closely related to that used for the Dember effect [22–24]. Due to the different mobilities of electrons and holes an electric field is generated. The observed voltage is proportional to the separation of the charge carriers. The lifetime is a function of the recombination and trapping rate. Irradiation by a 600 ps pulse of a N_2-laser leads to a monoexponential decay of the voltage versus time curve. From this curve the lifetime of the charge carriers can be calculated. Since decay times are in the μs region no deconvolution is necessary. Details of the TRPC measurements can be found elsewhere [16–21].

1.2. Adsorption experiments

A stock solution of 1.5 mmol Rhodamine B in deionized water was prepared. Ten mg of the titania powder are added in 50 ml of the Rhodamine B solution. The solutions are kept in the dark and mixed regularly. After a setting time of 20 h the Rhodamine B concentration in the solution was determined photometrically using a Perkin–Elmer Lambda 5 spectrometer.

1.3. Photodegradation experiments

The light source for the photodegradation experiments was a metal vapour lamp (Osram, HMI 1200). This lamp emits a quasi continuous spectrum from 315 to 2200 nm. The intensity is determined by a potassium ferrioxalate actinometer [25] to be 4.5×10^{13} quanta $s^{-1}cm^{-2}$ in the range from 254 to 436 nm. The radiation power in the wave length region from 315 to 400 nm is determined to be 29.5 $W m^{-2}$ using a HD9021 Quantum Photo/Radiometer (Delta Ohm).

The degradation experiments were performed in a slurry reactor. At a distance of 15 cm below the lamp a quartz vessel containing the reaction solution (100 ml of a 1.5 mmol solution of Rhodamine B and 20 mg of the catalyst) is rotating with constant velocity. The quartz vessel is immersed in a cooling bath in order to obtain a constant temperature of 30°C. The concentration of the dye is determined photometrically ever 10 min.

2. Results and discussion

2.1. Crystal structure and electronic structure

Incorporation of transition metal ions may distort the crystal structure of the host compound. Since anatase exhibits the most effective photocatalytical properties, we compare in Fig. 1 the X-ray diffraction patterns of undoped TiO_2 with those of chromium doped titania samples. In all cases the observed reflections can be attributed to anatase. Even at the highest Cr^{3+} concentrations there are no reflections originating from chromium oxides or chromium titanate. Furthermore, no shifts in lattice parameters are observed which might be expected according to Vegard's law. So, variations in the photocatalytical response cannot be explained by variations in the crystal structure. The same results are obtained by doping with Mo^{5+}.

The effect of introducing transition metal ions on the electronic structure of titania is demonstrated in Fig. 2. Here, the spectral position of the interband transition as obtained from the photoacoustic absorption spectra is plotted against the transition metal ion concentration. The band gap energy is apparently shifted from about 400 nm for pure titania to 435 nm (2.85 eV) with molybdenum doping and to 620 nm (2.00 eV) in the case of chromium doping. In both cases the most dramatic effect occurs at dopant concentrations as low as about 0.1 at.%. The extension of the spectral response of TiO_2 into the visible by substituting Cr^{3+} for Ti^{4+} has been observed at chromium concentrations as low as 570 ppm [28]. It can be explained by the excitation of an electron of Cr^{3+} into the conduction band of TiO_2.

2.2. Charge carrier lifetimes

On illumination, electrons and holes can be generated in a semiconductor. Recombination of these charge carriers can

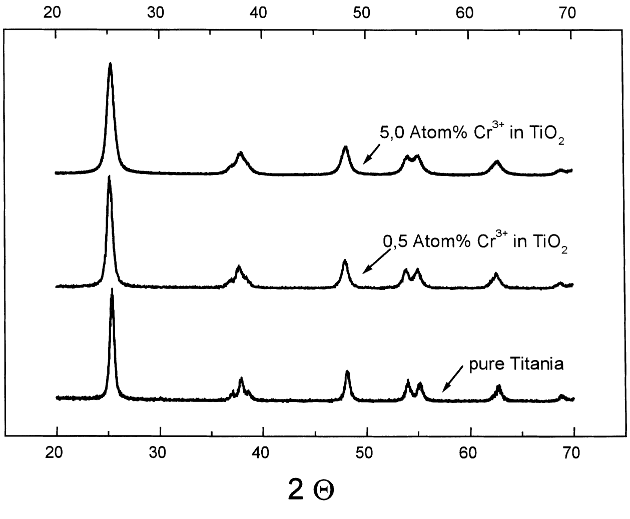

Fig. 1. X-ray diffraction: (a) pure TiO_2, (b) 1 at.% Cr^{3+}, (c) 5 at.% Cr^{3+}; vertical bars correspond to anatase reflexes.

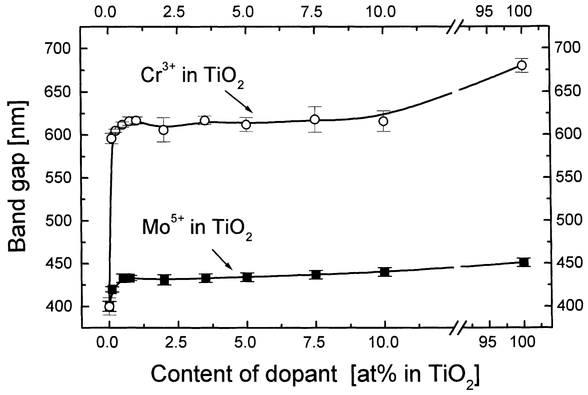

Fig. 2. Band gap shift as a function of dopant concentration.

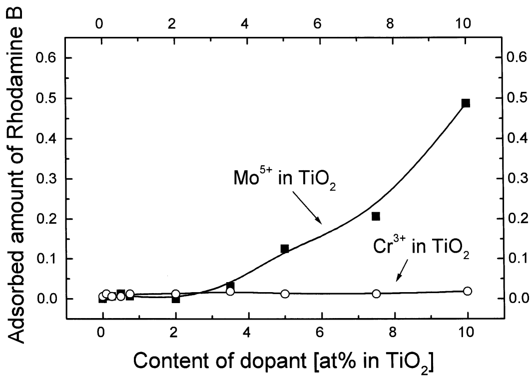

Fig. 4. Adsorption of Rhodamine B on chromium and molybdenum doped titania.

occur in the bulk or at the surface. At the surface, photogenerated electrons can reduce an electron acceptor and photogenerated holes can oxidise an electron donor. For any photocatalytic reaction the lifetimes of electrons and holes must be long enough to allow them to reach the surface of the photocatalyst. By incorporation of transition metal ions new trapping sites are introduced which affect the lifetime of the charge carriers as is demonstrated in Fig. 3. For pure titania we observe a lifetime of 89.3 μs. Doping reduces this lifetime to about 30 μs in the case of Cr^{3+} and about 20 μs with Mo^{5+}. Similar to what we observe with the variations of the band gap, the greatest changes occur at low-transition metal concentrations. In a first step, Cr^{3+} or Mo^{5+} are oxidised by holes:

$$Cr^{3+} + h^+ \rightarrow Cr^{4+}$$

$$Mo^{5+} + h^+ \rightarrow Mo^{6+}$$

These immobilised holes are then reduced by free electrons:

$$Cr^{4+} + e^- \rightarrow Cr^{3+}$$

$$Mo^{6+} + e^- \rightarrow Mo^{5+}$$

This reaction can occur since the potential of the redox pair Cr^{3+}/Cr^{4+} is higher than the potential of the valence band of titania. In the case of molybdenum it has been shown by ESR that Mo^{5+} and Mo^{6+} can exist simultaneously during illumination [26,27].

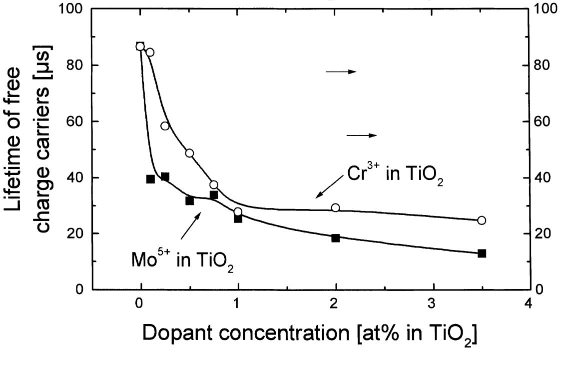

Fig. 3. Lifetime of electron hole-pairs as a function of dopant concentration.

2.3. Adsorption properties of doped titania

An indispensable step in any catalytic reaction is the adsorption of at least one of the reacting species at the surface of the catalyst. Any variation in the electronic structure of the surface is reflected in the adsorption characteristics as can be seen in Fig. 4. Due to the five-fold positive charge on Mo^{5+} there is a strong electrostatic interaction with the electron-rich centres of the dye by which the adsorption of Rhodamine B is markedly increased, whereas Cr^{3+} does not alter the generally poor adsorption properties of TiO_2.

2.4. Photodegradation of Rhodamine B

The photocatalytic activity of the doped titania catalysts has been tested by the photodegradation of Rhodamine B. Identical experimental conditions have been established throughout. For comparison the relative amount of degraded Rhodamine B after an illumination period of 60 min is plotted. The results are shown in Fig. 5. Again, there is a marked difference between the two dopants. For both ions the photocatalytic activity decreases at low dopant concentrations. While for Cr^{3+} the activity remains low (about 20% of the initial value) there is an increase of the activity for Mo^{5+} at higher concentrations. However, even at the highest Mo^{5+} concentration there is no improvement compared to undoped titania.

3. Conclusion

These results obtained for the two different transition metal ions are summarised in- Figs. 6 and 7. Here, the lifetimes of the charge carriers, the adsorbed amount of Rhodamine B, and the photodegradation results are plotted

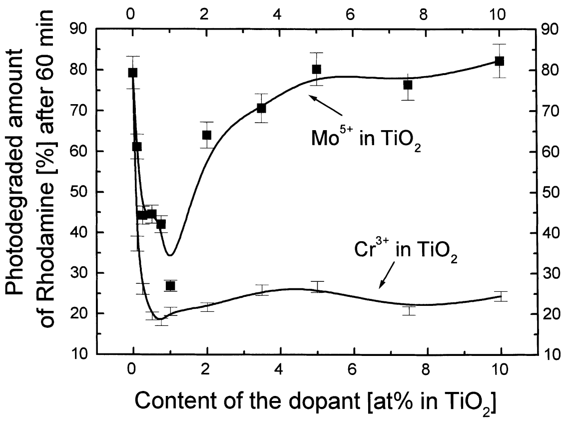

Fig. 5. Relative amounts of degraded Rhodamine B after 60 min illumination as a function of dopant concentration.

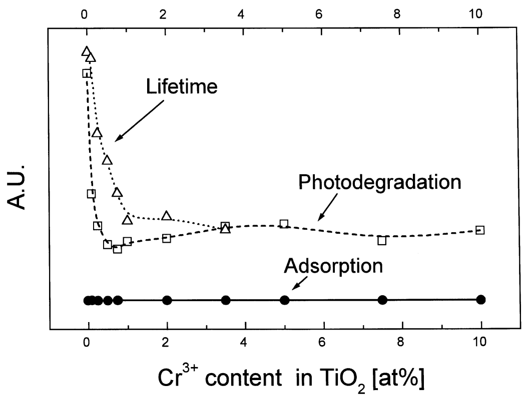

Fig. 6. Charge carrier lifetime, the adsorbed and the photodegraded amount of Rhodamine B vs. concentration Cr^{3+}.

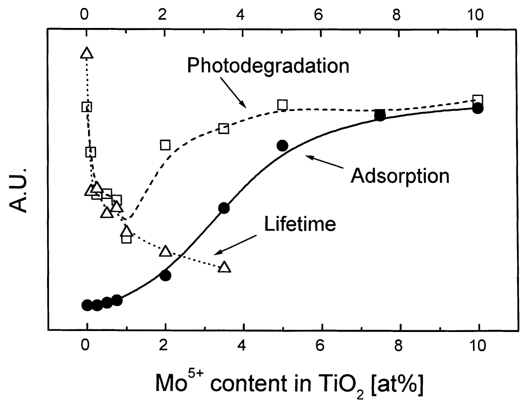

Fig. 7. Charge carrier lifetime, the adsorbed and the photodegraded amount of Rhodamine B vs. concentration of Mo^{5+}.

in arbitrary units against the concentration of the transition metal ions.

3.1. Doping with Cr^{3+}

The adsorption Rhodamine B on titania is not influenced by the incorporation of Cr^{3+} ions. No improvement over undoped titania is observed. There is, however, a clear correlation between the lifetime of the charge carriers and the photocatalytic activity. At chromium concentrations below 1 at.% both the lifetime and photocatalytical activity decrease drastically to remain nearly constant at a low level. The reason for this is that a low concentrations Cr^{3+} ions can occupy regular lattice sites and act as traps. At higher ion concentrations interstitial sites are filled up which obviously do not contribute to the recombination. Due to the reduced lifetime fewer charge carriers can reach the surface and hence initiate degradation of the dye.

3.2. Doping with Mo^{5+}

At low molybdenum concentrations the course of photodegradation and charge carrier lifetime is similar to that observed with the chromium doped samples. However, if the molybdenum concentration is increased beyond 1 at.% the influence of adsorption becomes predominant. Both adsorption and photodegradation increase. Since there is a higher surface coverage of the dye more charge carriers reaching the surface can contribute to the degradation process.

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References

[1] E. Pelizetti, M. Schiavello (Eds.), Photochemical Conversion and Storage of Solar Energy, Kluwer Academic Publishers, Dordrecht, 1991.
[2] Schiavello (Ed.), Photocatalysis and Environment, Kluwer Academic Publishers, Dordrecht, 1988.
[3] N. Serpone, E. Pelizetti (Eds.), Photocatalysis, Fundamentals and Applications, Wiley, New York.
[4] D.F. Ollis, H. Al-Ekabi (Eds.), Photocatalytic Purification of Water and Air, Elsevier, Amsterdam, The Netherlands, 1993.
[5] K.E. Karakitsou, X.E. Verykios, J. Phys. Chem. 97 (1993) 118.
[6] D.W. Bahnemann, Nachr. Chem. Tech. Lab. 42 (1994) 378.
[7] M.I. Litter, J.A. Navio, J. Photochem. Photobiol. A: Chem. 98 (1996) 171.
[8] M.I. Litter, J.A. Navio, J. Photochem. Photobiol. A: Chem. 84 (1994) 183.
[9] A. Sclafani, L. Palmisano, M. Schiavello, Res. Chem. Interm. 18 (1992) 211.
[10] L. Palmisano, V. Augugliaro, A. Sclafani, M. Schiavello, J. Phys. Chem. 92 (1988) 6710.
[11] Z. Luo, Q.H. Gao, J. Photochem. Photobiol. A: Chem. 63 (1992) 367.
[12] W. Choi, A. Termin, M.R. Hoffmann, J. Phys. Chem. 98 (1994) 13669.
[13] N. Serpone, D. Lawless, J. Disdier, J.M. Hermann, Langmuir 10 (1994) 643.

[14] J.E. Huheey, Inorganic Chemistry, Principles of Structure and Reactivity, Harper & Row, New York, 1983.
[15] D. Scherrer, Göttinger Nachrichten 2 (1918) 98.
[16] M. Sadeghi, W. Liu, T.-G. Zhang, P. Stavropoulos, B. Levy, J. Phys. Chem. 100 (1996) 19446.
[17] B. Levy, Photogr. Sci. Eng. 15 (1971) 27.
[18] B. Levy, in: E. Pelizetti, M. Schiavello (Eds.), Photochemical Conversion and Storage of Solar Energy, Kluwer Academic Publishers, Dordrecht, 1991, p. 337.
[19] C. Zou, M.R.V. Sahyun, M.E. Mueller, B. Levy, T.-G. Zhang, J. Imag. Sci. Technol. 39 (1995) 106.
[20] Y. Wang, A. Suna, J. Phys. Chem. 101 (1997) 5627.
[21] C. Paulus, K. Wilke, H.D. Breuer, Inform. Proc., in press.
[22] H. Dember, Physik. Z. 32 (1931) 55.
[23] H. Dember, Physik. Z. 32 (1931) 856.
[24] H. Dember, Physik. Z. 33 (1932) 207.
[25] C.A. Parker, C.G. Hatchard, Proc. Roy. Soc. 235 (1956) 518.
[26] M. Grätzel, R. Howe, J. Phys. Chem. 94 (1990) 2566.
[27] P. Meriaudeau, Chem. Phys. Lett. 72 (1980) 551.
[28] E. Borgarello, J. Kiwi, M. Grätzel, E. Pelizetti, M. Visca, J. Am. Chem. Soc. 104 (1982) 2996.