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Dinitrogen photofixation at ruthenium-modified titania films

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Titania thin films modified with 0.5, 1.0 and 2.5 wt% ruthenium(III) chloride possess *n*-type semiconductor behaviour and enable the photofixation of dinitrogen to ammonia and nitrate in the presence of ethanol or humic acid.

Inspired by the early observation of Schrauzer and Guth[1] that rutile powder doped with 0.2% Fe_2O_3 upon UV irradiation in the presence of water vapour is able to reduce dinitrogen to small amounts of ammonia, we recently employed the sol–gel technique to prepare titania thin films on glass containing various amounts of iron. A 1:1 mixture of iron(III) chloride and titanium(IV) isopropoxide afforded a thin film producing the highest yields of ammonia. Upon UV or visible light irradiation in the presence of air or dinitrogen and ethanol or humic acid as a reducing agent, this system produced initially ammonia (10–15 μM) followed by subsequent thermal air-oxidation to nitrate. When the atomic ratio Fe:Ti was < 1, the yield of ammonia strongly decreased.[2–4] To find out if the homologous ruthenium system may also afford photoactive thin films, anhydrous ruthenium(III) chloride was employed instead of the iron salt in the film preparation.

Following the preparation procedure described for iron modification,[3,9] films were obtained using 1.0, 2.5, 5.0, 50 and 75% of ruthenium relative to titanium; they are designated as TiO_2-1, TiO_2-2.5 *etc.*, respectively. After calcination at 200 °C, the resulting films TiO_2-*x*(200) had a brown colour, whereas black films TiO_2-*x*(600) were formed upon calcination at 600 °C.

The reducing agent solution containing the film and bubbling nitrogen gas were subjected to irradiation with an Osram XBO 150 W xenon arc lamp using a Pyrex filter filled with water to cut off IR radiation at room temperature. Ammonia and nitrate concentrations were monitored as described elsewhere.[4]

The transmission electron micrography of TiO_2-5(200) revealed the presence of a homogeneous film 50–60 nm in thickness exhibiting no structured areas excepting a few small pores at the glass interface (Figure 1).

In the XRD spectrum of TiO_2-5(200) powder scratched off the film peaks at 2θ values of 35.73, 43.04, 47.40, 51.06 and 64.54 can be attributed to α-$RuCl_3$,[5] whereas the values of 25.10, 37.80 and 48.43 degrees clearly indicate the presence of anatase

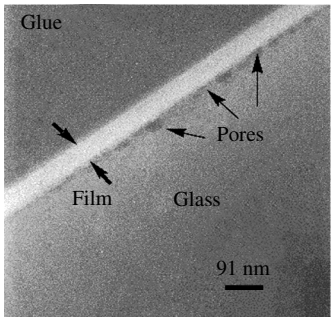

Figure 1 TEM micrograph of TiO_2-5(200).

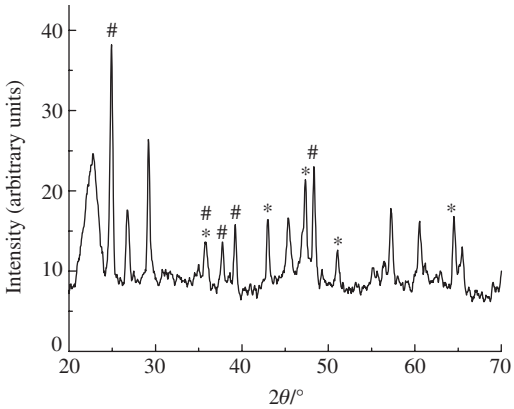

Figure 2 XRD spectrum of TiO_2-5(200): (#) TiO_2, (*) $RuCl_3$.

(Figure 2). In general, the anatase phase starts to be formed only at 400 °C in the case of unmodified titania powders. However, metal ions are known to lower this temperature,[6–8] as also observed in this work. No evidence for the presence of RuO_2 can be found. This is in agreement with published data,[6] according to which temperatures of 400–450 °C are necessary to oxidise Ru^{3+} to Ru^{4+}. The presence of ruthenium chloride indicates incomplete hydrolysis as also observed in the case of iron modification.[4] The films calcined at 600 °C adhered strongly to the glass substrate so that only small amounts of powder could be scratched off (insufficient for XRD analysis).

Figure 3(*a*),(*b*) displays the absorption spectra of films obtained by calcination at 200 and 600 °C, respectively. For comparison, the spectrum of ruthenium(III) chloride in water is also shown exhibiting a maximum at 380 nm. In agreement with the XRD results the presence of $RuCl_3$ can be clearly deduced from the spectrum of TiO_2-5(200), which has a strong shoulder at about 390 nm [Figure 3(*a*), curve *1*], in addition to a maximum at 450 nm, present in all other films [Figure 3(*a*), curves *2* and *3*].

The spectra of the films calcined at 600 °C do not exhibit any distinct maximum although they strongly absorb throughout the visible. A shoulder at about 400 nm can be recognised for TiO_2-50(600) and TiO_2-75(600) [Figure 3(*b*), curves *2*, *3*].

To test if these films have a semiconductor behaviour, as found for the corresponding iron-based systems,[3,9] electrodes were analogously prepared employing conducting indium tin oxide glass (ITO) as the substrate. The ITO glass (10×15 mm) was cleaned by treatment with sodium hydrogencarbonate followed by rinsing with distilled water before dipping into a titanium isopropoxide–ruthenium chloride solution. Although the incident photon-to-current efficiency (IPCE) is low, the appearance of an anodic photocurrent indicates that films treated

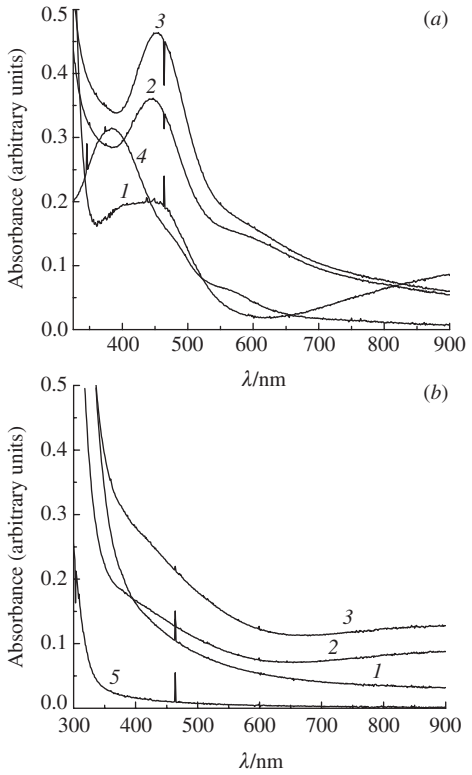

Figure 3 Absorption spectra of TiO_2–Ru films calcined at (*a*) 200 and (*b*) 600 °C. (*1*) TiO_2-5, (*2*) TiO_2-50, (*3*) TiO_2-75, (4) $RuCl_3$ in water and (*5*) TiO_2 film.

at 200 and 600 °C both behave like *n*-type semiconductors. Upon the addition of MeOH to the electrolyte, a current-doubling effect was observable only for the film calcined at 600 rather than 200 °C. Films containing 5% ruthenium did not exhibit a current-doubling effect, irrespective if treated at the lower or higher temperature.

Dinitrogen fixation experiments were performed in the presence of ethanol or humic acid as a reducing agent, as reported for the iron titanate system[2,3] employing unfiltered light of wavelengths larger than 290 nm. The films annealed at 150, 500 and 600 °C were inactive. Only the films obtained at 200 °C exhibited a weak reactivity as indicated by the samples TiO_2-1(200), TiO_2-2.5(200) and TiO_2-5(200). Out of these the latter turned out to be the most active producing 5 μM ammonia in a 75% aqueous ethanol solution (Figure 5). Unlike the iron titanate film reported previously,[2,3] the yield does not significantly decrease when the ethanol content was decreased to 25%. No ammonia was observable when aqueous isopropanol or methanol was employed as the reducing agent.

When humic acid is the reducing agent, its concentration should not exceed 0.01 g dm^{-3}, since otherwise it becomes the more efficient light absorbing species resulting in a strong decrease of ammonia yield (Figure 6).

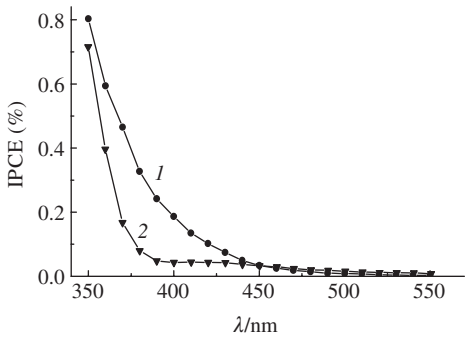

Figure 4 Incident photon-to-current efficiency as a function of irradiation wavelength. (*1*) TiO_2-1(200), (*2*) TiO_2-1(600). In 0.1 M NaOH, applied potential of 0.6 V *vs.* Ag/AgCl.

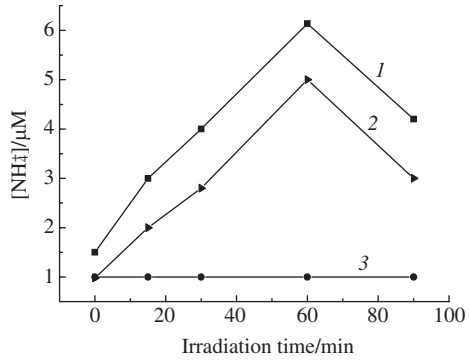

Figure 5 Ammonium ion concentration *vs.* irradiation time for TiO_2-5(200) under N_2 bubbling: (*1*) 0.01 g dm^{-3} humic acid, (*2*) 75% EtOH, (*3*) under Ar bubbling.

Prolonged irradiation for 6 h in the presence of humic acid, as in the iron titanate system,[2,3] afforded nitrate (16 μM) through oxidation by oxygen traces.[4]

These results resemble those of iron-modified titania; therefore, a similar mechanism[4] is suggested for the present system. Accordingly, it is proposed that photogenerated holes most likely oxidise first chloride ions of the metal chloride to adsorbed chlorine atoms, which subsequently oxidise ethanol to the hydroxyethyl radical. The latter is expected to inject an electron into the titania conduction band resulting in the generation of two electrons per absorbed photon. These are required to reduce dinitrogen to diazene, a first plausible intermediate. Disproportionation produces hydrazine, which is photoreduced by a second absorbed photon to ammonia. Oxidation of the latter by the traces of oxygen is a thermal reaction catalysed by the film.

In summary, ruthenium(III) chloride-modified titania films on glass exhibit *n*-type semiconducting properties and are able to photochemically fix dinitrogen. However, their activity is much lower than that of the corresponding iron–titania systems.

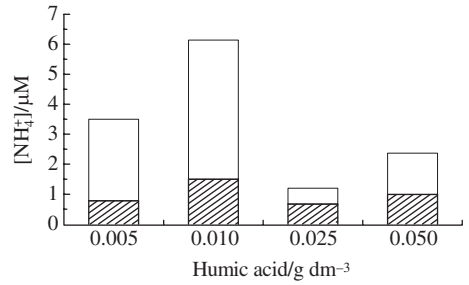

Figure 6 Ammonia concentration *vs.* amount of humic acid: TiO_2-5(200), N_2 bubbling. The dash-filled and unfilled parts represent ammonia concentrations before and after 60 min of irradiation, respectively.

References

1 G. N. Schrauzer and T. D. Guth, *J. Am. Chem. Soc*., 1977, **99**, 7189.
2 O. Rusina, A. Eremenko, G. Frank, H. P. Strunk and H. Kisch, *Angew. Chem., Int. Ed. Engl.*, 2001, **40**, 3993.
3 O. Rusina, O. Linnik, A. Eremenko and H. Kisch, *Chem. Eur. J*., 2003, **9**, 561.
4 O. Linnik and H. Kisch, *Photochem. Photobiol. Sci*., 2006, **5**, 938.
5 *JCPDS* (*Joint Committee on Powder Diffraction Standards)*, 37-1227.
6 M. Egal, M. Conrad, D. L. MacDonald, W. L. Maloy, M. Motley, C. A. Genko, V. V. Panic, A. Dekanski, S. K. Milonjic, R. T. Atanasoski and B. Z. Nikolic, *Colloids Surf., A*, 1999, **157**, 269.
7 M. J. Alam and D. C. Cameron, *Sol-Gel Sci. Technol*., 2002, **25**, 137.
8 J. A. Wang, R. Limas-Ballesteros, T. López, A. Moreno, R. Gómez, O. Novaro and X. Bokhimi, *J. Phys. Chem. B*, 2001, **105**, 9692.
9 O. Rusina, W. Macyk and H. Kisch, *J. Phys. Chem. B*, 2005, **109**, 10858.

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