USA **2001**, *98*, 3750–3755; d) A. D. Keefe, J. W. Szostak, *Nature* **2001**, *410*, 715–718.

[5] a) M. Famulok, G. Mayer, *Curr. Top. Microbiol. Immunol.* **1999**, *243*, 123–136; b) M. Famulok, G. Mayer, M. Blind, *Acc. Chem. Res.* **2000**, *33*, 591–599; c) M. Famulok, M. Blind, G. Mayer, *Chem. Biol.* **2001**, *8*, 931–939.

[6] M. Famulok, A. Jenne, *Top. Curr. Chem.* **1999**, *202*, 101–131.

[7] a) K. Sakthivel, C. F. Barbas III, *Angew. Chem.* **1998**, *110*, 2998–3002; *Angew. Chem. Int. Ed.* **1998**, *37*, 2872–2875; b) D. M. Perrin, T. Garestier, C. Hélène, *Nucleosides Nucleotides* **1999**, *18*, 377–391; c) S. Brakmann, S. Löbermann, *Angew. Chem.* **2001**, *113*, 1473–1476; *Angew. Chem. Int. Ed.* **2001**, *40*, 1427–1429; d) T. Gorlain, A. Sidorov, N. Mignet, S. J. Thorpe, S. E. Lee, J. A. Grasby, D. M. Williams, *Nucleic Acids Res.* **2001**, *29*, 1989–1905.

[8] a) S. W. Santoro, G. F. Joyce, K. Sakthivel, S. Gramatikova, C. F. Barbas III, *J. Am. Chem. Soc.* **2000**, *122*, 2433–2439; b) D. M. Perrin, T. Gerestier, C. Hélène, *J. Am. Chem. Soc.* **2001**, *123*, 1556–1563.

[9] M. A. Augustin, W. Ankenbauer, B. Angerer, *J. Biotechnol.* **2001**, *86*, 289–301.

[10] a) C. A. Stein, J. S. Cohen, *Cancer Res.* **1988**, *48*, 2659–2668; b) B. N. Trawick, A. T. Daniher, J. K. Bashkin, *Chem. Rev.* **1998**, *98*, 939–960.

[11] We use “fDNA” as an abbreviation for the term “functionalized DNA”.

[12] S. W. Santoro, G. F. Joyce, *Proc. Natl. Acad. Sci. USA* **1997**, *94*, 4262–4266.

[13] S. E. Lee, A. Sidorov, T. Gourlain, N. Mignet, S. J. Thorpe, J. A. Brazier, M. J. Dickman, D. F. Hornby, J. A. Grasby, D. M. Williams, *Nucleic Acids Res.* **2001**, *29*, 1565–1573.

[14] The synthesis of **1**–**4** will be published in a forthcoming full-paper.

[15] We used excess of template to ensure quantitative hybridization of the primer.

[16] a) F. Seela, M. Zulauf, *Helv. Chim. Acta* **1999**, *82*, 1878–1898; b) N. Ramzaeva, C. Mittelbach, F. Seela, *Nucleosides Nucleotides* **1999**, *18*, 1439–1440.

Nitrogen Photofixation at Nanostructured Iron Titanate Films[**]

Olga Rusina, Anna Eremenko, Gerhard Frank,
Horst P. Strunk, and Horst Kisch[*]

Dedicated to Professor Günter Hauska
on the occasion of his 60th birthday

Next to photosynthesis nitrogen fixation is the second most important chemical process of the biosphere. The mild reaction conditions of the enzymatic reaction compared to the Haber–Bosch synthesis stimulated a large variety of investigations on the formation and reactivity of N_2 transition metal complexes under thermal reaction conditions. Comparably little work is known on photofixation, especially in regard to a sunlight-induced nonenzymatic nitrogen fixation at a simple inorganic photocatalyst.

Schrauzer and Guth first reported that the electron–hole pairs generated by the absorption of light by a semiconductor powder can reduce molecular nitrogen to ammonia. Water vapor acted as the reducing agent, being oxidized to molecular oxygen during the process. Photoreduction occurred only when rutile-containing titanium dioxide powder was doped with 0.2% of Fe_2O_3 and when it was exposed to humid dinitrogen. No ammonia was formed when dinitrogen was bubbled through an aqueous suspension of this powder. Higher iron contents resulted in inactive materials.[1] Subsequent work confirmed these results, although the nature of the reducing agent was unknown in most cases, since the oxygen produced was only rarely characterized.[2–14] Ammonia concentrations were in the range of 1–10 μM, and excitation by UV light was, in general, necessary. Very recently it was reported that an electrochemically formed titanium dioxide layer is also active without iron doping.[15] These partly contradictory results induced adverse discussions, particularly by Edwards and co-workers, and culminated in the conclusion that all the previously published values resulted from traces of the ubiquitous ammonia.[16] Since, however, it is well known that the photocatalytic properties of semiconductors are strongly influenced by the presence of impurities, the contradictory results may stem from difficulties in preparing the catalyst.

To clarify these adverse results we have prepared mixed iron titanium oxides by a simple and highly reproducible sol–gel method. In contrast to the previously employed titanium dioxide photocatalysts, the new materials were applied as nanostructured thin films containing up to 50% iron. They also photocatalyze the formation of ammonia and nitrate under visible light.

The films were obtained by immersing a glass slide first into an alcoholic solution of iron(III) chloride and titanium tetraisopropylate (1:1), followed by hydrolysis in humid air and annealing at 600 °C; only an inactive film was produced at 500 °C. The iron-free titanium dioxide film was prepared in an analogous manner. Electron microscopy on the iron titanate film indicated the presence of a nanostructured matrix of about 300 nm thickness. It contains 15–20 vol% of cubic crystals with an average diameter of 150 nm (Figure 1). The ratio of Fe:Ti:O was found by energy-dispesive X-ray spectroscopy (EDAX) to be 1:1:3.5 for both the matrix and the crystals. This composition suggests that the compound $Fe_2Ti_2O_7$ is present, which was previously only obtained as an intermediary phase by heating ilmenite ($FeTiO_3$) minerals in an oxygen atmosphere to 700 °C.[17] This assignment is corroborated by the good agreement between the published and measured X-ray diffraction (XRD) spectra. The doublet at $\delta = 0.462\ \mathrm{mm\,s^{-1}}$ (relative to α-Fe), $\Delta E_Q = 0.910\ \mathrm{mm\,s^{-1}}$, line widths: $0.294\ \mathrm{mm\,s^{-1}}$)[18] in the Moessbauer spectrum points to the presence of a six-coordinated Fe^{III} ion. The UV/Vis spectrum reveals extended absorbance down to 800 nm (Figure 2).

---

[*] Prof. Dr. H. Kisch, Dipl.-Chem. O. Rusina
Institut für Anorganische Chemie
der Universität Erlangen-Nürnberg
Egerlandstrasse 1, 91058 Erlangen (Germany)
Fax:(+49) 9131-8527363
E-mail: kisch@chemie.uni-erlangen.de

Prof. Dr. A. Eremenko
Institute of Surface Chemistry
National Ukrainian Academy of Sciences
Prospect Nauki 31, 252022 Kiev (Ukraine)

Dr. G. Frank, Prof. Dr. H. P. Strunk
Institut für Werkstoffwissenschaften
der Universität Erlangen-Nürnberg
Cauerstrasse 6, 91058 Erlangen (Germany)

[**] This work was supported by the Deutsche Forschungsgemeinschaft and Fonds der Chemischen Industrie. Experimental help by Dipl.-Chem. Harald Weiß is gratefully acknowledged.

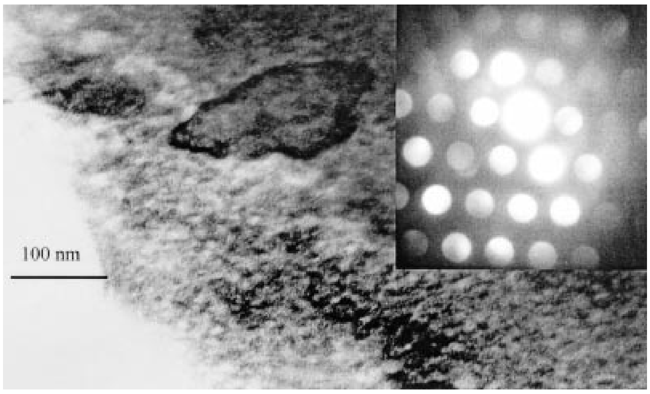

Figure 1. Electron micrograph of the iron titanate film.

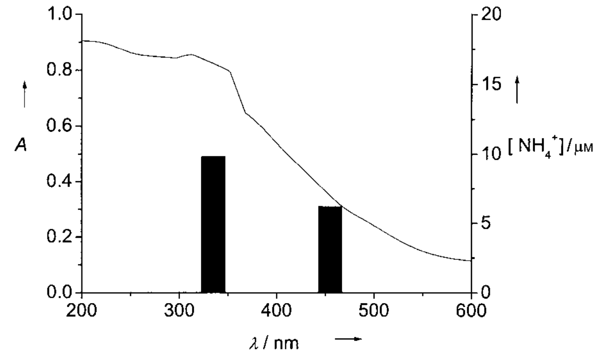

Figure 2. UV/Vis spectrum of the iron titanate film and the wavelength dependence of ammonia formation; the vertical bars indicate the cut-off wavelengths of the filters ($\lambda \geq 335$ and 455 nm); in 75 vol% EtOH; 90 min of irradiation.

Irradiation ($\lambda \geq 320$ nm) of the $Fe_2Ti_2O_7$ film in N_2-bubbled 75 vol% aqueous EtOH induced the formation of ammonia in concentrations of 3–17 µM (Figure 3). The ammonia concentration decreased to the background value of 2 µM when carbon monoxide was present or when dinitrogen was replaced by argon. A decrease of 60% was observed when air was used instead of dinitrogen. Ethanol concentrations above or below 75 vol% led to partial inhibition, which became complete in pure water or pure alcohol. The film is an efficient photocatalyst even upon excitation with visible light ($\lambda \geq$ 455 nm, Figure 2).

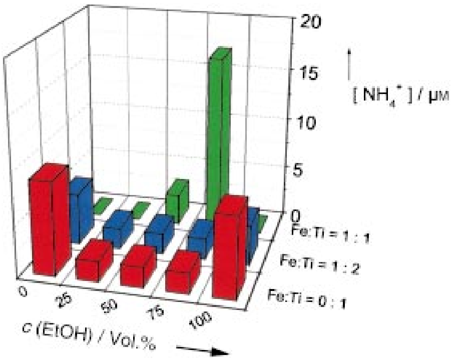

Figure 3. Dependence of the ammonia concentration on the alcohol content of water and on the Fe/Ti ratio employed in the preparation of the thin film; $\lambda \geq 320$ nm; 90 min of irradiation.

An iron titanate film with an Fe:Ti ratio of 1:2 exhibited a pronounced lower reactivity. The iron-free titanium dioxide film induced formation of ammonia at a concentration of 5 µM (Figure 3).[19]

The ammonia concentration reaches a maximum after 90 min of irradiation and decreases to the background value after 180 min (Figure 4). This effect does not originate from catalyst deactivation since the ammonia concentration was lowered by only 15% after washing the film with water and reirradiation. Since it is known that ammonia is photooxidized at titanium dioxide[20] the solution and film were tested for nitrite/nitrate. Whereas only traces of nitrite were detectable, the nitrate concentration reached 45 µM in the film and 7 µM in the solution (Figure 4). When dinitrogen was substituted by air, the total concentration of nitrate was 30 µM. Nitrate was formed in appreciable amounts only when ammonia had reached its maximum concentration. This observation suggests that nitrate is formed through an ammonia intermediate rather than by direct oxidation of dinitrogen. In accordance with this postulate, no nitrite/nitrate was formed in the absence of ethanol. However, nitrate was produced in comparable concentrations (4 µM in the solution, after 90 min) when the reaction was conducted under oxygen or air in 75% EtOH in the presence of ammonium chloride (50 µM).

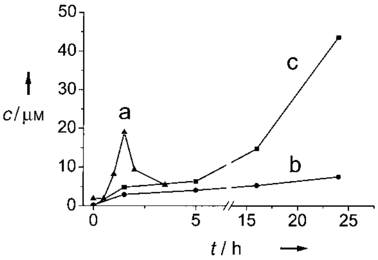

Figure 4. Concentrations of ammonia (a) and nitrate (b: in the solution, c: in the film) as a function of the irradiation time; 75 vol% EtOH; $\lambda \geq 320$ nm.

Initial photoelectrochemical experiments with a $Fe_2Ti_2O_7$ thin film electrode of conducting glass revealed that the anodic photocurrent was amplified by methanol addition only when the electrode was annealed at 600 °C. When the electrode was annealed at 200 °C the film was inactive and the electrode did not exhibit the current-doubling effect.[21] This effect is based upon the injection of an electron from the hydroxyethyl radical, which is formed by primary hole oxidation, into the semiconductor conduction band.

On the basis of these photoelectrochemical properties of the iron titanate film we postulate that the photofixation proceeds according to a semiconductor photocatalysis scheme. Photogenerated conduction band electrons reduce water to adsorbed hydrogen atoms[1, 5a, 8, 10, 22] which then reduce dinitrogen. Holes formed simultaneously in the valence band oxidize the ethanol to the hydroxyethyl radical. The faster these reaction steps are, the less efficient is the undesired recombination of the charge carriers. The increasing catalytic activity upon increasing the alcohol concentration up to 75 vol% is in accordance with this assumption, and arises as a result of an acceleration in the oxidative part of the process. The decreasing activity at larger alcohol concentrations may originate from the concomitant decrease in the water concentration. Consequently, the reductive reaction step may become too slow to efficiently compete with recombination of the charge carriers. The ammonia produced is further photooxidized to nitrate through traces of oxygen present in the system.

Aqueous solutions of sodium formate and humic acids of proper concentration also function as reducing agents. Since the latter compounds are ubiquitous in nature and $Fe_2Ti_2O_7$ phases could be formed through oxidative weathering of ilmenite in sunlight, this novel reaction may be an example of a light-driven nonenzymatic nitrogen fixation under natural conditions.[23]

Experimental Section

After fast immersing a glass slide (26 × 76 mm) into an ethanolic solution of $Ti(OiPr)_4$ and $FeCl_3$ (Fe:Ti = 1:1 or 2:1) it was pulled out at a speed of 6 cm min^{-1} and left in air for 15 min. The film was subsequently tempered for 20 min at 600 °C. Irradiations were performed on an optical train equipped with a high-pressure Hg lamp (HBO 200) mounted at a distance of 35 cm from the solidex glass cuvette ($\lambda \geq 320$ nm, 80 × 40 × 10 mm) which contained the glass slide. Unless otherwise noted, a film with a Fe:Ti ratio of 1:1 was employed and unpurified dinitrogen was permanently bubbled through the suspension. The concentration of NH_4^+ ions was determined colorimetrically according to the method of Kruse and Mellon;[24] the resulting absorbancies at 450 nm were in the range of 0.01 to 2.10. Blank experiments in the absence of the glass slide did not induce the formation of significant amounts of ammonia. The reproducibility of the film preparation was excellent as evident by the ammonia concentrations agreeing within ± 10 %. Nitrite and nitrate were measured by ion chromatography (Dionex-120, Ion Pac AS 14 column, conductivity detector, $NaHCO_3$:Na_2CO_3 = 0.001:0.0035 mol L^{-1} as eluting agent).

Received: November 27, 2000
Revised: June 7, 2001 [Z 16176]

[1] G. N. Schrauzer, T. D. Guth, *J. Am. Chem. Soc.* **1977**, *99*, 7189.
[2] P. P. Radford, C. G. Francis, *J. Chem. Soc. Chem. Commun.* **1983**, 1520.
[3] a) E. Endoh, A. J. Bard, *Nouv. J. Chim.* **1987**, *11*, 217; b) E. Endoh, J. K. Leland, A. J. Bard, *J. Phys. Chem.* **1986**, *90*, 6223.
[4] N. N. Lichtin, K. M. Vijayakumar, *J. Indian Chem. Soc.* **1986**, *63*, 29.
[5] a) V. Augugliaro, A. Lauricella, L. Rizzuti, M. Schiavello, A. Sclafani, *Int. J. Hydrogen Energy* **1982**, *7*, 845; b) V. Augugliaro, F. D'Alba, L. Rizzuti, M. Schiavello, A. Sclafani, *Int. J. Hydrogen Energy* **1982**, *7*, 851.
[6] M. M. Khader, N. N. Lichtin, G. H. Vurens, M. Salmeron, G. A. Somorjai, *Langmuir* **1987**, *3*, 303.
[7] H. Miyama, N. Fujii, Y. Nagae, *Chem. Phys. Lett.* **1980**, *74*, 523.
[8] a) N. N. Rao, S. Dub, Manjubala, P. Natarajan, *Appl. Catal. B* **1994**, *5*, 33; b) M. I. Litter, J. A. Navio, *J. Photochem. Photobiol. A* **1996**, *98*, 171.
[9] a) P. L. Yue, F. Khan, L. Rizzuti, *Chem. Eng. Sci.* **1983**, *38*, 1893; b) M. M. Taqui Khan, D. Chatterjee, M. Bala, *J. Photochem. Photobiol. A* **1992**, *67*, 349.
[10] J. Soria, J. C. Conesa, V. Augugliaro, L. Palmisano, M. Schiavello, A. Sclafani, *J. Phys. Chem.* **1991**, *95*, 274.
[11] A. Sclafani, L. Palmisano, M. Schiavello, *Res. Chem. Intermed.* **1992**, *18*, 211.
[12] L. Palmisano, V. Augugliaro, A. Sclafani, M. Schiavello, *J. Phys. Chem.* **1988**, *92*, 6710.
[13] V. Augugliaro, J. Soria, *Angew. Chem.* **1993**, *32*, 579; *Angew. Chem. Int. Ed. Engl.* **1993**, *105*, 550.
[14] L. Palmisano, M. Schiavello, A. Sclafani, *Angew. Chem.* **1993**, *105*, 579; *Angew. Chem. Int. Ed. Engl.* **1993**, *32*, 550.
[15] K. Hoshino, M. Inui, T. Kitamura, H. Kokado, *Angew. Chem.* **2000**, *112*, 2558; *Angew. Chem. Int. Ed.* **2000**, *39*, 2509.
[16] a) D. L. Boucher, J. A. Davies, J. G. Edwards, A. Mennad, *J. Photochem. Photobiol. A* **1995**, *88*, 53; b) J. G. Edwards, J. A. Davies, D. L. Boucher, A. Mennad, *Angew. Chem.* **1992**, *104*, 489; *Angew. Chem. Int. Ed. Engl.* **1992**, *31*, 480.
[17] S. K. Gupta, V. Rajakumar, P. Grieveson, *Metall. Trans. B* **1991**, *22*, 711.
[18] V. Schünnemann, A. X. Trautwein, O. Rusina, A. Eremenko, H. Kisch, unpublished results.
[19] Unless otherwise noted all the following data correspond to the $Fe_2Ti_2O_7$ film.
[20] a) O. A. Ileperuma, W. C. B. Kiriden, W. D. D. P. Dissanayake, *J. Photochem. Photobiol. A* **1991**, *59*, 191; b) G. N. Schrauzer, T. D. Guth, J. Salehi, N. Strampach, N.-H. Liu, M. R. Palmer in *Homogeneous and Heterogeneous Photocatalysis* (Eds.: E. Pelizzetti, N. Serpone), Reidel, Dordrecht, **1986**, p. 509; c) W. R. McLean, M. Ritchie, *J. Appl. Chem.* **1965**, *15*, 452; d) H. Mozzanega, J.-M. Herrmann, P. Pichat, *J. Phys. Chem.* **1979**, *83*, 2251; e) P. Pichat, J.-M. Herrmann, H. Courbon, J. Disdier, M.-N. Mozzanega, *Can. J. Chem. Eng.* **1982**, *60*, 27; f) C. H. Pollema, E. B. Milosavljevich, J. L. Hendrix, L. Solujic, J. H. Nelson, *Monatsh. Chem.* **1992**, *123*, 333.
[21] O. Rusina, A. Eremenko, W. Macyk, H. Kisch, unpublished results.
[22] V. Augugliaro, L. Palmisano, M. Schiavello, *Photocatalysis and Environment. Trends and Applications*, Kluwer, Amsterdam, **1988**, p. 425.
[23] G. N. Schrauzer, N. Strampach, H.-N. Liu, M. R. Palmer, J. Salehi, *Proc. Natl. Acad. Sci. USA* **1983**, *80*, 3873.
[24] J. Kruse, M. G. Mellon, *Sewage Ind. Wastes* **1952**, *24*, 1098.

PASSflow Syntheses Using Functionalized Monolithic Polymer/Glass Composites in Flow-Through Microreactors**

Andreas Kirschning,* Carsten Altwicker,
Gerald Dräger, Jan Harders, Nora Hoffmann,
Ulrich Hoffmann, Hagen Schönfeld,
Wladimir Solodenko, and Ulrich Kunz*

After an "incubation time" of more than 25 years interest in polymer-supported reagents for the solid-supported synthesis in solution has increased dramatically of late.[1] In this technique reagents or catalysts are immobilized on a solid

---

[*] Prof. Dr. A. Kirschning, Dr. G. Dräger, N. Hoffmann,
Dr. W. Solodenko
Institut für Organische Chemie der Universität Hannover
Schneiderberg 1B
30167 Hannover (Germany)
Fax: (+49) 511-762-3011
E-mail: andreas.kirschning@oci.uni-hannover.de

Dr.-Ing. U. Kunz, Dr.-Ing. C. Altwicker, Prof. Dr.-Ing. U. Hoffmann,
H. Schönfeld
Institut für Chemische Verfahrenstechnik der Technischen Universität Clausthal
Leibnizstrasse 17, 38678 Clausthal-Zellerfeld (Germany)
Fax: (+49) 5323-72-2182
E-mail: kunz@icvt.tu-clausthal.de

Dr. J. Harders
Institut für Organische Chemie der Technischen Universität Clausthal
Leibnizstrasse 6, 38678 Clausthal-Zellerfeld (Germany)

[**] Part of these studies were supported by the Fonds der Chemischen Industrie and the European Community (EC project number HPRI-CT-1999-00085) for which we are grateful. PASSflow = *P*olymer *A*ssisted *S*olution-*P*hase *S*ynthesis technique in flow-through mode.