Nitrogen Photofixation on Nanostructured Iron Titanate Films

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Dedicated to Professor Gerhard N. Schrauzer on the occasion of his 70th birthday

Abstract: A nanostructured iron titanate thin film has been prepared by a sol–gel method from iron(III) chloride and titanium tetraisopropylate. Energy-dispersive X-ray analysis and Mößbauer spectroscopy suggest the presence of a $Fe_2Ti_2O_7$ phase, which was previously obtained as an intermediary phase upon heating ilmenite. In the presence of ethanol or humic acids and traces of oxygen, the novel film photocatalyzes the fixation of dinitrogen to ammonia (17 μM) and nitrate (45 μM). In the first observable reaction step, hydrazine is produced and then undergoes further photoreduction to ammonia. Oxidation of the latter by oxygen affords nitrate as the final product. Since the reaction occurs also in air and with visible light ($\lambda > 455$ nm), and since the iron titanate phase may be formed by the weathering of ilmenite minerals, it may be a model for mutual nonenzymatic nitrogen fixation in nature.

Keywords: nanostructures • nitrogen fixation • photochemistry • thin films • titanates

Introduction

Nitrogen fixation is the second most important chemical process in nature next to photosynthesis. The mild reaction conditions of the enzymatic reaction as compared with the Haber–Bosch synthesis stimulated a large variety of investigations into the synthesis and reactivity of N_2 transition metal complexes under thermal reaction conditions. Relevant examples are reductive protonation to ammonia under concomitant oxidation of the central metal, oxidative alkylation with alkyl halogenides affording alkyldiazenido complexes, and successive addition of methyl lithium and trimethyloxonium tetrafluoroborate leading to a 1,2-dimethyldiazene complex.[1] Comparably little work is known on photofixation, especially with respect to sunlight-induced nonenzymatic nitrogen fixation at a simple inorganic photocatalyst. In 1977 Schrauzer and Guth reported for the first time that the electron–hole pairs generated by light absorption of a semiconductor powder reduce molecular nitrogen to ammonia. Water vapor acted as reducing agent and was oxidized to molecular oxygen. Photoreduction occurred only when rutile-containing titania powder was doped with 0.2% of Fe_2O_3 and when it was exposed to humid nitrogen. No ammonia was formed when nitrogen was bubbled through an aqueous suspension of this powder. Higher iron contents resulted in inactive materials.[2] Subsequent work of other authors confirmed these results, although the nature of the reducing agent was unknown in most cases, since oxygen was only rarely identified.[3–15] In general, ammonia concentrations were in the range of 1–10 μM, and excitation by UV light was necessary. Very recently it was reported that an electrochemically formed titania layer is also active without iron doping.[16] These partly contradictory results induced contrary discussions, particularly by Edwards et al., and culminated in the conclusion that all the previously published values resulted from traces of the ubiquitous ammonia.[17] Since, however, it is well known that the photocatalytic properties of semiconductors are strongly influenced by the presence of impurities, the contrary 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 well-reproducible sol–gel method. Contrary to the previously employed titania photocatalyst powders, the new materials were applied as nanostructured thin films containing up to 50 mol% of iron. They photocatalyze formation of ammonia and nitrate also with visible light. Part of this work has been recently communicated.[18]

Results and Discussion

Film preparation and characterization: The thin films were prepared by dip-coating glass slides in an alcoholic solution of iron(III) chloride and titanium tetraisopropylate in the ratio of

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Fe/Ti = 1:1 or 1:2, followed by hydrolysis in humid air and annealing at 600 °C; at 500 °C and 700 °C only inactive films were produced. The iron-free titania and titania-free iron oxide films were prepared analogously. Electron microscopy of the iron titanate film as obtained from a 1:1 substrate ratio indicated the presence of a nanostructured matrix of about 300 nm thickness. It contained 15–20 % vol of cubic crystals with an average diameter of 150 nm (Figure 1). The ratio of Fe/Ti/O was determined by EDX (energy dispersive X-ray analysis) as 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 obtained only as an intermediary phase by heating ilmenite minerals ($FeTiO_3$) in an oxygen atmosphere at 700 °C.[19] This assignment is corroborated by the good agreement between the published and measured XRD spectra (Figure 2). Though some of the XRD peaks at 2Θ values of 18.15, 25.49, 32.59, 37.33, 46.15, 48.96, 59.85 (corresponding to $d = 4.97, 3.50, 2.75, 2.41, 1.97, 1.86, 1.54$ Å) may be assigned to the pseudobrookite phase Fe_2TiO_5 ($d = 4.90, 3.49, 2.75, 2.41, 1.97, 1.87, 1.54$ Å) and traces of anatase,[20] the remaining peaks at 2Θ values of 26.53, 31.63, 41.19, 54.01, and 56.17 (corresponding to $d = 3.36, 2.85, 2.23, 1.70, 1.64$ Å) do not fit either rutile or hematite, but rather with d values 3.37, 2.87, 2.20, 1.70, 1.64 of the $Fe_2Ti_2O_7$ phase.[19] The iron-free titania film exhibited only anatase peaks.

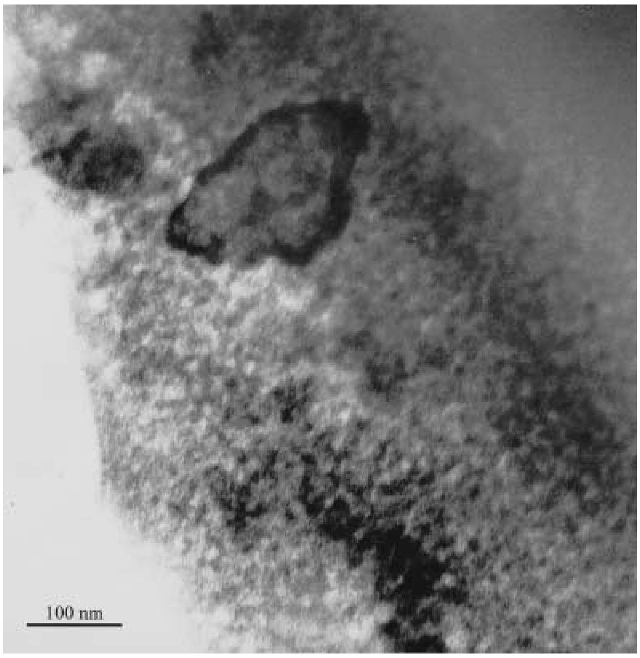

Figure 1. Electron micrograph of the iron titanate film calcined at 600 °C (Fe/Ti = 1:1).

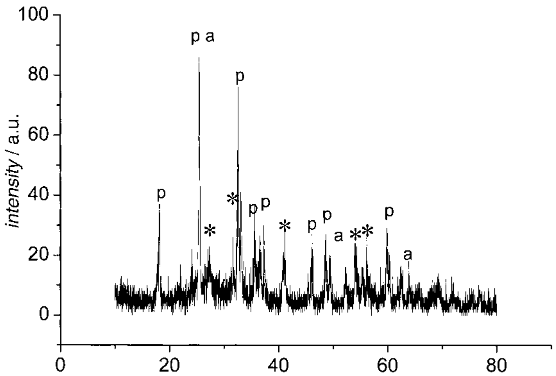

Figure 2. Characteristic XRD pattern of the iron titanate film (Fe/Ti = 1:1); (*) new $Fe_2Ti_2O_7$ phase, (p) pseudobrookite, (a) anatase.

In the Mößbauer spectrum, the doublet at δ (relative to α-Fe) = 0.462 mm s^{-1}, $\Delta E_Q = 0.910$ mm s^{-1} (line widths of 0.294 mm s^{-1}), points to the presence of hexacoordinated Fe^{III} (Figure 3). Although these values are almost identical to those of pseudobrookite, they cannot originate from this phase since the Fe/Ti ratio of the film is 1:1. There is no indication of the presence of an iron(III) oxide phase, which would have a similar isomer shift but a much smaller quadrupole splitting (0.24 mm s^{-1}).[21] The UV/Vis spectrum of titania (Figure 4, curve a) is red-shifted down to 600 nm upon increasing the Fe/Ti ratio from 0:1 to 1:2 and 1:1 (Figure 4, curves b and c, respectively).

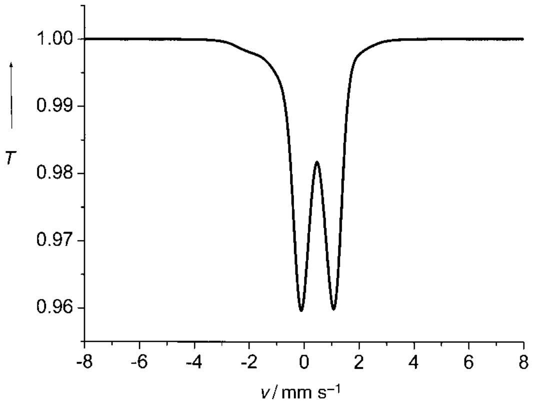

Figure 3. Mößbauer spectrum of the iron titanate film (Fe/Ti = 1:1) recorded at 100 K.

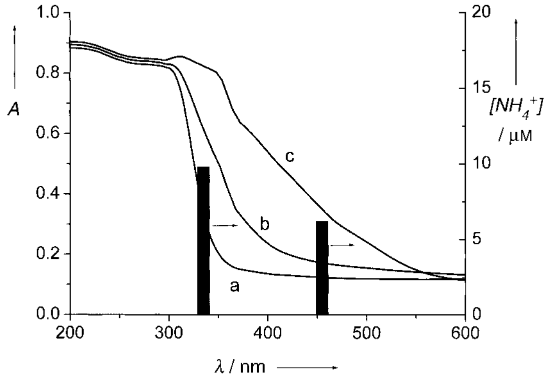

Figure 4. UV/Vis spectra of the various films (in air) and wavelength dependence of ammonia formation; the vertical bars indicate ammonia concentrations when cut-off filters were employed ($\lambda \leq 335$ and 455 nm); in EtOH (75 % vol); 90 min of irradiation time. a) TiO_2, b) Fe/Ti = 1:2, c) Fe/Ti = 1:1.

Nitrogen photofixation: Irradiation ($\lambda \geq 320$ nm) of the iron–titania films in $EtOH/H_2O$ solutions was performed under N_2 bubbling. The background concentration of ammonia was measured before each experiment; this afforded values in the range of up to 2 µM. Depending on the solvent composition, ammonia concentrations of 3–17 µM were observed (Figure 5). The two iron titanate films produced the largest amounts of ammonia when the alcohol content was 75% (*v*/*v*). Whereas the 1:1 phase was inactive both in pure water and pure ethanol, the 1:2 phase afforded small amounts of ammonia in pure ethanol. This differs significantly from the solvent dependence of the iron-free titania phase, which was active both in pure water and pure alcohol and did not exhibit a maximum ammonia yield at 75% alcohol content. From these differences it is very likely that the 1:2 film is a mixture of the new $Fe_2Ti_2O_7$ phase and anatase. It is noted that an analogously prepared titania-free iron oxide film did not produce ammonia. Since the 1:1 film afforded the highest yield of ammonia in 75% EtOH, all of the following experiments were performed with this reaction system. Under these experimental conditions acetaldehyde was detected after 90 min of irradiation and reached a concentration of 13 mM after 24 h.

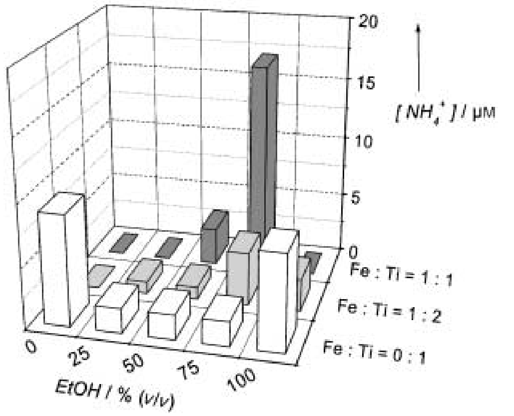

Figure 5. Dependence of ammonia concentration on alcohol content of water and on the Fe/Ti ratio employed in the thin film preparation; $\lambda \geq 320$ nm, 90 min of irradiation time.

Figure 6 displays the time evolution of ammonia concentration under various reaction conditions. Line a represents the values measured for the solution containing the immersed film before irradiation and before N_2 bubbling. Line b corresponds to the values observed upon purging this system with nitrogen in the dark, and line c represents the system under irradiation and purging with argon. In all these blank experiments the ammonia concentration never exceeded 2 µM. When the irradiation was performed under N_2 bubbling, formation of ammonia started after an induction period of 30 min and passed through a maximum at 90 min irradiation time (Figure 6, curve d). By using air instead of nitrogen purging, the ammonia concentration was decreased by about 60%. The film was an efficient photocatalyst even upon excitation with visible light ($\lambda \geq 455$ nm, Figure 4).

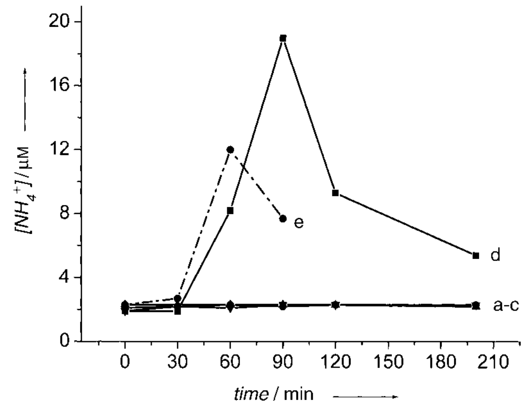

Figure 6. Ammonia formation against time in EtOH (75% vol): a) solution with immersed film prior to nitrogen bubbling and irradiation, b) subsequent nitrogen purging in the dark, c) irradiation under argon bubbling, d) irradiation under N_2 bubbling, e) ammonia formation in the presence of aqueous humic acid (10^{-2} g L^{-1}) under irradiation and N_2 bubbling.

Since it is known that carbon monoxide inhibits thermal nitrogen fixation,[22] a mutual influence on the photofixation was tested. Upon bubbling with a mixture of N_2/CO (10:1), complete inhibition was observed (Figure 7, line b). The effect is reversible since the same film induced ammonia formation after it had been washed with water and irradiated under N_2 purging (Figure 7, curve c).

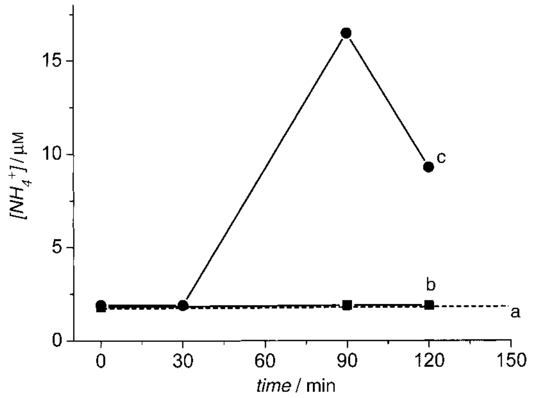

Figure 7. Ammonia formation against irradiation time in EtOH (75% vol). a) background concentration of ammonia, b) under bubbling a mixture of CO and N_2 (1:10), c) under N_2 bubbling after washing the same film.

To check if the induction period of ammonia formation may be related to generation of a plausible intermediate, the reaction solution was analyzed for hydrazine. It was found that hydrazine is formed during the first 15–30 min, having a concentration maximum at about 20 min (Figure 8, curve a). This result clearly suggests that in the induction period nitrogen is photoreduced to hydrazine. No hydrazine was detectable when nitrogen was replaced by argon bubbling. The further reduction to ammonia is a photochemical process, as indicated by the result that upon irradiating the film for 90 min in 75% EtOH in the presence of 15 µM hydrazine ammonia was obtained in a concentration of 25 µM. No ammonia was formed when this reaction was performed in the dark at room temperature or at 50 °C.

Photoelectrochemical experiments with a $Fe_2Ti_2O_7$ thin-film electrode of conducting glass revealed that the observed

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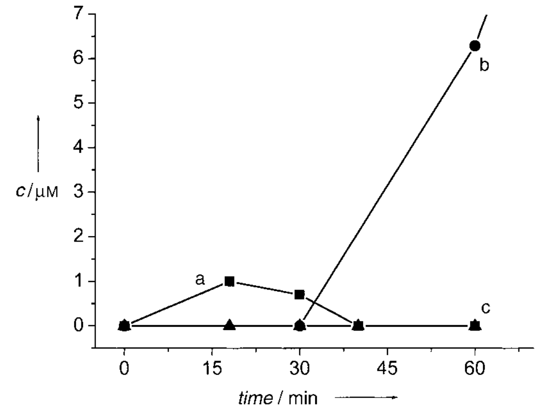

Figure 8. Concentration of a) hydrazine and b) ammonia as a function of irradiation time under bubbling N_2, c) under Ar, EtOH (75 % vol), $\lambda \geq 320$ nm.

anodic photocurrent was amplified by methanol addition only when the electrode was annealed at 600 °C. In the case of annealing at 500 °C, the film was inactive and the electrode did not exhibit this current-doubling effect.[23] The effect is based on electron injection of the hydroxyethyl radical, formed by primary hole oxidation, into the semiconductor conduction band (vide infra).

From the experimental results presented above, a semiconductor photocatalysis mechanism is proposed as working hypothesis. According to this, absorption of a photon by the $Fe_2Ti_2O_7$ phase (SC) generates a reactive electron–hole pair at the surface [Eq. (1)]. The electron reduces water to an adsorbed hydrogen atom [Eq. (2)].[2, 6a, 9, 11, 24] The simultaneously formed valence-band hole oxidizes ethanol to the hydroxyethyl radical [Eq. (3)], which then injects an electron into the conduction band affording acetaldehyde as oxidation product [Eq. (4)],[25] which in turn reduces a second molecule of water [Eq. (5)]. Reduction of N_2 by adsorbed hydrogen atoms leads to diazene as a first plausible intermediate [Eq. (6)]. Thus, absorption of one quantum of light affords the two electrons necessary for the first reduction step. The faster the reactions steps according to Equations (2) and (3), the less efficient is the undesired recombination of the reactive electron–hole pair [Eq. (7)]. Further $2e^-/2H^+$ reductions afford hydrazine and finally ammonia, as known from homogeneous nitrogenase models.[26]

$$\mathrm{SC} + h\nu \rightarrow \mathrm{SC}(e_r^-, h_r^+) \tag{1}$$

$$\mathrm{SC}(e_r^-, h_r^+) + H_2O \rightarrow \mathrm{SC}(h_r^+) + H_{ad} + OH^- \tag{2}$$

$$\mathrm{SC}(h_r^+) + CH_3CH_2OH \rightarrow \mathrm{SC} + CH_3\dot{C}HOH + H^+ \tag{3}$$

$$\mathrm{SC} + CH_3\dot{C}HOH \rightarrow \mathrm{SC}(e_r^-) + CH_3CHO + H^+ \tag{4}$$

$$\mathrm{SC}(e_r^-) + H_2O \rightarrow \mathrm{SC} + H_{ad} + OH^- \tag{5}$$

$$N_2 + 2H_{ad} \rightarrow N_2H_2 \tag{6}$$

$$\mathrm{SC}(e_r^-, h_r^+) \rightarrow \mathrm{SC} + \mathrm{heat} \tag{7}$$

In accordance with this mechanistic proposal is the increasing catalytic activity upon increasing the alcohol concentration up to 75 % vol, due to an acceleration of the oxidative reaction part [Eq. (3)]. The decreasing activity at higher alcohol concentrations may originate from the concomitant decrease of the water concentration, rendering the reductive reaction part [Eq. (2)] too slow to efficiently compete with charge carrier recombination [Eq. (7)].

The strong decrease in ammonia formation at reaction times above 120 min does not originate from catalyst deactivation, since after repeatedly washing the film with water, reirradiation afforded ammonia in a concentration only 15 % lower. Furthermore, no iron ions could be detected in the solution after 24 h of irradiation. These observations suggested that ammonia may be oxidized to nitrite/nitrate by traces of oxygen, a photoreaction known to be catalyzed by titania.[27] Whereas only traces of nitrite were detectable, the nitrate concentration on the film reached 45 μM and 7 μM in the solution (Figure 9). When nitrogen 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 suggests that nitrate is formed via intermediary ammonia rather than by direct oxidation of nitrogen. In accordance with this postulate, no nitrite/nitrate was formed in the absence of EtOH.

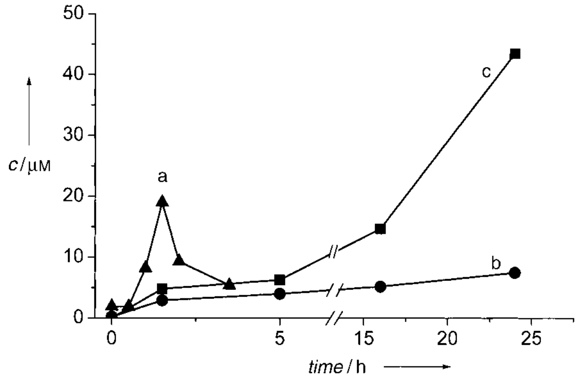

Figure 9. Concentrations of a) ammonia, and nitrate b) in the solution, c) in the film as function of irradiation time, EtOH (75 % vol), $\lambda \geq 320$ nm.

Aqueous solutions of humic acids of proper concentration ($10^{-2}\,gL^{-3}$) also functioned as reducing agents (Figure 6, curve e). Since the latter compounds are ubiquitous in nature, and $Fe_2Ti_2O_7$ phases may be formed through solar oxidative weathering of ilmenite, this novel nitrogen photofixation may be an example for a light-driven nonenzymatic nitrogen fixation under natural conditions.[28]

Experimental Section

$FeCl_3$ (Aldrich) was dissolved in absolute EtOH (15 mL, Riedel–de Haen) in amounts corresponding to Fe/Ti molar ratios of 1:1 and 1:2. After the mixture had been stirred for 10 min, Ti(O*i*Pr)$_4$ (5 mL) was added slowly while the temperature was kept at 30–35 °C. After 10 min of intensive stirring, the sol was ready for dip-coating. A glass slide (26 × 76 mm) was immersed into the sol and pulled out at a speed of 6 cm min^{-1}. After being left in air for hydrolysis for 15–20 min, the Fe/Ti = 1:2 and titania films were calcined for 20 min at 600 °C and 500 °C, respectively, whereas 400, 500, 600, and 700 °C were employed for the Fe/Ti = 1:1 film. The Fe_2O_3 thin film was prepared from $FeCl_3$ with 2 % gelatine[29] and heated at 600 °C.

After the final temperature had been reached (about 1 h), the heating was turned off and the film was left to cool down to room temperature.

Electronic absorption spectra were recorded on a Shimadzu UV-3101 PC, a Philips X'Pert (PW 3040/60) diffractometer was used for XRD measurements. The sample for the latter was prepared by scratching off the film from the glass substrate. A Philips Microscope CM 200 (200 kV) was used for TEM measurements.

Irradiations were performed on an optical train equipped with a high-pressure HBO 200 Hg lamp ($\lambda \geq 320$ nm) mounted at a distance of 35 cm from the solidex glass cuvette, which contained the glass slide. Unless otherwise noted, an Fe/Ti (1:1) film was employed, and nitrogen was permanently bubbled through the reactor in the standard experiment. Argon was used instead of nitrogen for the blank experiments. Appropriate cut-off filters were placed in front of the cuvette. The procedure described above was also applied to the experiments with different solvents.

The concentration of NH_4^+ was determined colorimetrically according to Kruse–Mellon.[30] 20 mL aliquots of the reaction solution were diluted to 50 mL before adding the reagents. Resulting absorbencies at 450 nm were in the range of 0.01 to 0.10. Blank experiments in the absence of the glass slides did not produce ammonia concentrations higher than 2 μM. The reproducibility of the film preparation was excellent, since the ammonia concentrations obtained agreed within ±10%. The concentration of hydrazine was determined spectrophotometrically[31] by withdrawing 10 mL aliquots of the reaction solution and diluting them to 25 mL. Absorbencies at $\lambda = 458$ nm were in the range of 0.001 to 0.020. Nitrite and nitrate were measured by ion chromatography (Dionex-120, Ion Pac AS 14 column, conductivity detector, and $NaHCO_3$ (0.001 M)/Na_2CO_3 (0.0035 M) (1:1) as eluting agent) by withdrawing 1 mL from the reaction solution. For the determination of adsorbed species, the film was washed with water (20 mL), and the solution was dried in an oven at 70–85 °C. After dissolving in of water (1 mL), the sample was injected. Acetaldehyde was measured by GC (Shimadzu GC17A, Supelcowax-10 column, FID detector, N_2) from 1 mL aliquots withdrawn from the reacting solution. Iron concentrations of the reaction solutions were determined by atomic absorption spectroscopy (Shimadzu AA 6200, flame type: air/C_2H_2) after immersing the film in water or EtOH in the dark for 24 h and irradiating it for a further 24 h.

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