Photocatalysis

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The Nature of Nitrogen-Modified Titanium Dioxide Photocatalysts Active in Visible Light[**]

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Semiconductor photocatalysis is developing into the most promising method for basic and applied chemical utilization of solar energy. In addition to the "holy grail" of water cleavage, which is presently limited to the laboratory, the photocatalytic removal of pollutants from the air has already been applied technically.[1] The most commonly employed photocatalyst, titanium dioxide, suffers from the fact that, owing to the large bandgap of 3.2 eV (387 nm), it can utilize only the very small part (about 3 %) of UV solar radiation. Therefore, strong efforts are being made to shift its photocatalytic activity to the visible spectral region. One of the more efficient methods is doping or surface modification with nonmetals, such as carbon and nitrogen. N-modified titania (TiO_2-N) in particular has received great attention.[2,3] The three most important methods for the synthesis of TiO_2-N are 1) sputtering and implantation techniques, 2) high-temperature sintering of TiO_2 under nitrogen-containing atmospheres generated by nitrogen compounds such as ammonia and urea, and 3) by sol–gel methods.[3] The nature of the nitrogen species in the resulting TiO_2-N materials, however, is a matter of controversial discussions. NO_x and various other nitrogen oxide species were proposed by Sato,[4] our group,[5] and others.[6] Nitridic and amidic (NH_x) species were also suggested;[7] in some cases even the presence of several oxidation states of nitrogen was reported.[8] Depending on the preparation methods, the resulting TiO_2-N samples most likely contain diverse nitrogen species and therefore may have different photocatalytic activities. A significant example is the unique difference between TiO_2-N obtained from ammonia[9] or urea[7] as nitrogen source. The latter material photocatalyzes the visible-light mineralization of formic acid to carbon dioxide and water, whereas the former is inactive.

Contrary to the generally made assumption that the nitrogen species is the origin of visible-light photocatalysis, it was proposed that the nitrogen precursor during the modification procedure induces formation of oxygen vacancies and color centers, which themselves are responsible for the visible light activity.[10] In an attempt to experimentally decide between the two proposals, we investigated the nature of the photoactive species in a TiO_2-N sample obtained from urea.[6,7,11] Various N1s binding energies for urea-derived TiO_2-N have been reported in the literature. Peaks at 396–397 eV were assigned to nitridic nitrogen such as in titanium nitride (N−Ti−N),[11b,d,e,f,h,l] peaks at 399 eV to nitridic nitrogen in modified titania (O−Ti−N),[11n] signals at 400–401 eV possibly to N−N, N−O or N−C groups,[7,11b,e,f,n,o] and chemisorbed N_2,[11h,l] and peaks at 407–408 eV were proposed to correspond to nitrite.[8]

Slightly yellow nitrogen-modified titania was prepared by calcining a 1:2 w/w mixture of titania/urea at 400 °C. Elemental analysis revealed the presence of nitrogen and considerable amounts of carbon (Table 1), and therefore the powders are abbreviated in the following as TiO_2-N,C. As-obtained TiO_2-N,C has the anatase structure, and induced about 80 % mineralization of formic acid upon irradiating for 3 h with visible light ($\lambda \geq 455$ nm).[12] When the calcination temperatures were 300 °C and 500/600 °C, mineralization decreased to 60 % and 0 %, respectively.

Table 1: N/C atomic ratio,[a] quasi Fermi potentials (${}_nE_F^*$),[b] bandgap energies (E_{bg}), and initial mineralization rates (r_i) of formic acid for various TiO_2-N/C samples.

Photokatalysator	N/C	E_{bg} [eV]	${}_nE_F^*$ [V, NHE]	r_i [10^{-4} $M^{-1}s^{-1}$]
TiO_2	0	3.23	−0.56	0.80
TiO_2-N,C/CA,NH_3	1.80	2.90	−0.48	4.70
TiO_2-N,C	1.66	2.90	−0.48	3.60
TiO_2-N,C/melamine	1.67	3.02	−0.48	2.70
TiO_2-N,C/melem,melon	1.53	3.07	−0.51	3.50
TiO_2-N,C/CA	1.50	3.07	−0.51	3.50

[a] From elemental analysis. [b] Measured according to ref. [16] and calculated for pH 7.

As it is known that urea is converted into ammonia and isocyanic acid at 300–420 °C,[13] this gas mixture was simulated by heating the isocyanic acid precursor cyanuric acid in the presence of ammonia and titania at 400 °C. The resulting photocatalyst TiO_2-N,C/CA,NH_3 was very active, and induced 92 % degradation within 3 h (Figure 1). To establish whether ammonia is essential to this modification process, TiO_2 was calcined at the same temperature in the presence of only cyanuric acid. The obtained material, TiO_2-N,C/CA, degraded 80 % of formic acid after 3 h of irradiation. As it is known that isocyanic acid in the presence of an hydroxy-group-containing heterogeneous catalyst is converted via cyanamide into melamine in the same temperature range, the latter could also be produced during the urea modification process,

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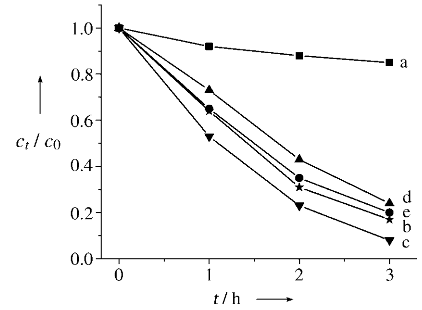
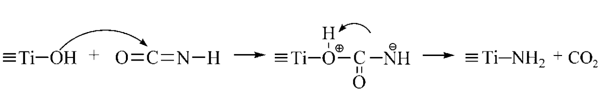


Figure 1. Photomineralization of formic acid ($c = 1 \times 10^{-3}$ mol L^{-1}); c_0, c_t are concentrations at times 0 and t. a) TiO_2, b) TiO_2-N,C, c) TiO_2-N,C/CA,NH_3, d) TiO_2-N,C/melamine, e) TiO_2-N,C/melem,melon. $\lambda \geq 455$ nm.

assuming that titania surface OH groups act as catalysts [Eq. (1), (2)]. Thus, melamine could be produced according to the overall reaction depicted in Equation (3).[13]

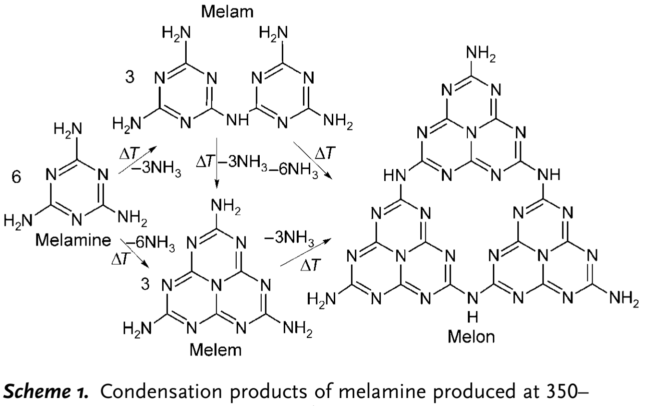
 (1)

$$\equiv\mathrm{Ti{-}OH} + \mathrm{O{=}C{=}N{-}H} \longrightarrow \equiv\mathrm{Ti{-}}\overset{\mathrm{H}}{\overset{|}{\mathrm{O}}}{}^{\oplus}{-}\underset{\mathrm{O}}{\underset{\|}{\mathrm{C}}}{-}\overset{\ominus}{\mathrm{N}}\mathrm{H} \longrightarrow \equiv\mathrm{Ti{-}NH_2} + \mathrm{CO_2} \quad (1)$$

$$\equiv\mathrm{Ti{-}NH_2} + \mathrm{H{-}O{-}C{\equiv}N} \longrightarrow \equiv\mathrm{Ti{-}OH} + \mathrm{H_2N{-}C{\equiv}N} \quad (2)$$

$$6\,(\mathrm{NH_2})_2\mathrm{CO} \xrightarrow{400\,^{\circ}\mathrm{C/TiO_2}} \mathrm{C_3H_6N_6} + 6\,\mathrm{NH_3} + 3\,\mathrm{CO_2} \quad (3)$$

In agreement with this rationalization, efficient photocatalysts were also obtained when urea was replaced by melamine in the modification procedure. The highest photocatalytic activity was achieved (Figure 1) when the calcination was performed at 400 °C, whereas only an inactive material was obtained at 600 °C, which resembles the temperature dependence of the urea modification. As at 400 °C melamine undergoes polycondensation to white melam, white melem, and yellow melon, it appeared likely that melem and melon are present in "N-doped" photocatalysts obtained from urea and titania at about 400 °C (Scheme 1).[14]



Scheme 1. Condensation products of melamine produced at 350–500 °C in the absence of titania.[14a,b]

To further test this hypothesis, melamine was heated at 450 °C, producing a yellow mixture of melem and melon, which did not change when kept in air for 1 h at 400 °C as indicated by IR and elemental analysis. The mixture before and after calcination at 400 °C was inactive in visible-light induced formic acid degradation. However, when the mixture was treated at 400 °C in the presence of an equal amount of titania, the resulting yellowish powder TiO_2-N,C/melem,melon induced 80 % degradation, as also observed for TiO_2-N,C obtained from urea (Figure 1). Grinding the melem/melon mixture with titania at room temperature produced only an inactive material. Thus, the same photocatalyst seems to be obtained, irrespective if urea or melem/melon is used as modifier. To further corroborate this assumption, the N1s binding energies of both photocatalysts were measured by X-ray photoelectron spectroscopy (XPS). The values of 399.2 and 400.5 eV for TiO_2-N,C and 399.1 and 400.6 eV for TiO_2-N,C/melem,melon compare well with corresponding data for carbon nitrides (399–400 eV, C=N−C),[15a,d] and similar graphite-like phases (400.6 eV, N−C_{sp^2}),[15b,c] and of polycyanogen (399.0 eV, 400.5 eV, $(\text{-C=N-})_x$).[15e] Corresponding values for the as-obtained mixture of melem/melon are 399.2 eV and 398.4 eV. For TiO_2-N,C and TiO_2-N,C/melem,melon, the absence of a peak at 398.5 eV[15a] suggests that during calcination, almost all the amino groups of melem/melon had reacted with surface Ti(OH) groups. Analogous to the XPS data, the optical absorptions, quasi Fermi energies, and photocatalytic activities of TiO_2-N,C and TiO_2-N,C/melem,melon are also very similar. Assuming the materials TiO_2-N,C to be indirect semiconductors, as is TiO_2, a plot of the modified Kubelka–Munk function $[F(R_\infty)E]^{1/2}$ vs. $h\nu$ (Figure 2) afforded the bandgap energies summarized in Table 1. As compared to unmodified titania, the new materials exhibited a bandgap-narrowing of 0.16–0.33 eV and a slight anodic shift of the quasi Fermi level of 0.05–0.08 V. Values of 6, 4, 4, 4, 3, and 1 were observed for the relative initial rates (r_i) of formic acid degradation (relative to $r_i = 1$ for TiO_2) for TiO_2-N,C/CA,NH_3, TiO_2-N,C/CA, TiO_2-N,C, TiO_2-N,C/melem,melon, TiO_2-N,C/melamine, respectively.

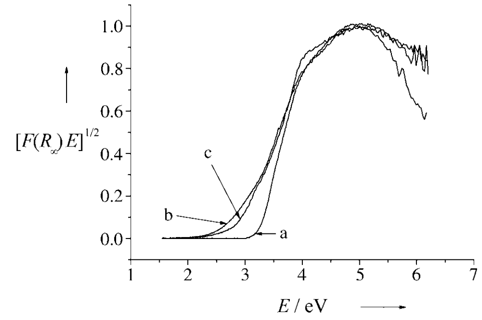
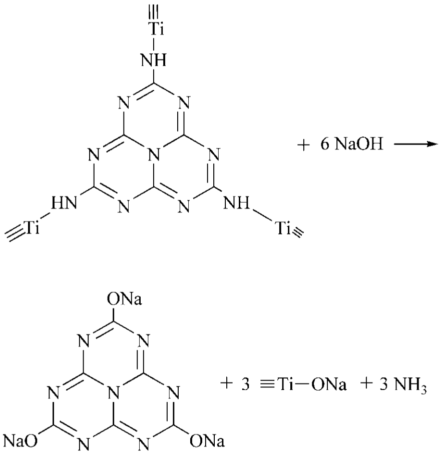


Figure 2. Plot of transformed Kubelka–Munk function vs. energy of light for a) TiO_2, b) TiO_2-N/C, c) TiO_2-N,C/melem,melon.

The results presented above strongly suggest that during the preparation of nitrogen-modified visible-light photocatalysts from titanium dioxide and urea, a key step is the titania-catalyzed formation of melamine. Subsequent condensation affords a mixture of oligonuclear aromatic amines, which are predominantly melam, melem, and melon as indicated by the N/C ratios of 1.80 for TiO_2-N,C/CA,NH_3, 1.66 for TiO_2-N,C, and 1.50 for TiO_2-N,C/CA or 1.53 for TiO_2-N,C/melem,melon. Calculated values for melam, melem, and melon are 1.83, 1.66, and 1.50, respectively. Thereafter, condensation between the triazine amino and titania hydroxy groups generates Ti–N bonds. Thus, the visible-light-absorbing triazine derivative is covalently attached to the semiconductor.

As it is known that the amino groups in melem can be replaced by OH through nucleophilic attack of hydroxide,[17] TiO_2-N,C/melamine was treated with sodium hydroxide solution under reflux. The expected cyamelurate and ammonia were obtained (Scheme 2). Both the titania residue and the evaporated extract did not photocatalyze visible-light mineralization of formic acid. The material obtained by heating titania and the extract at 400 °C afforded a photocatalyst of only low activity (19 % degradation in 3 h) due to the absence of aminotriazine groups in the extract.



Scheme 2. Extraction of cyamelurate from TiO_2-N,C/melamine.

Although the results presented above exclude the possibility that urea-derived TiO_2-N is active in visible light owing to the presence of oxygen vacancies,[10] they do not exclude the possibility that non-stoichiometric titania that is active in visible light may be formed when titania is calcined in vacuo at 400 °C in the absence of urea. The generation of surface defects by annealing in vacuo is well documented in the literature.[18] However, both the resulting TiO_{2-x} and the materials obtained from it by calcining with urea or melamine at 400 °C were inactive in formic acid mineralization. The inactivity of the latter materials is understandable, as the as prepared TiO_{2-x} should have a surface OH group concentration that is too low to enable the crucial addition of isocyanic acid according to Equation (1) or condensation with aminotriazine groups. As established above, without this precalcination, titania and urea or melamine afford highly active TiO_2-N,C photocatalysts.

In summary, these findings show that neither nitridic nor NO_x species nor defect states are responsible for the visible-light photocatalytic activity of N-doped or N-modified titania prepared from urea, but higher melamine condensation products acting as visible-light sensitizers.

Experimental Section

Titania (Hombikat UV-100, 100 % anatase, Sachtleben Chemie), urea, cyanuric acid (CA; Fluka Chemicals), and melamine (Acros Organics) were used as received.

Preparation of photocatalysts: Modified powders were prepared by grinding titania (1 g) with urea or CA in a ratio of 1:2 w/w or with CA/NH_3 gas, melamine, or melem/melon (1:1 w/w), followed by calcination in air at 400 °C for 1 h in an open rotating flask.

Preparation of TiO_{2-x}: Titania (2 g) was calcined at 400 °C for 3 h in an evacuated Schlenk tube.

All the materials were washed six times with of doubly distilled water (ca. 40 mL) by centrifugation. The mixture of melem/melon was prepared by heating melamine (5 g) in an open Schlenk tube for 5 h at 450 °C.

Extraction of cyamelurate acid: TiO_2-N,C/melamine (0.8 g) was refluxed overnight with NaOH (0.01 mol L^{-1}, 80 mL). The liquid was separated from a white solid and evaporated to give a beige powder.

Photodegradation experiments were carried out in a jacketed cylindrical 20 mL glass cuvette attached to an optical train (Osram XBO 150 W xenon arc lamp installed in a light-condensing lamp housing). A water filter and a 455 nm cutoff filter were placed in front of the cuvette. 20 mL of a 1 g L^{-1} powder suspension in 10^{-3} mol L^{-1} formic acid was sonicated for 15 min prior to illumination. Samples withdrawn were filtered through a syringe filter and subjected to ion chromatography analysis (Dionex DX120, Ion Pac 14 column, conductivity detector; $NaHCO_3/NaCO_3 = 0.001{:}0.0035$ mol L^{-1} as eluent); no oxalate was detectable. All activity data correspond to degradation observed after 3 h of irradiation time. Initial rates were calculated from formic acid concentration measured after one hour irradiation time.

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