DOI: 10.1002/chem.200901646

# On the Mechanism of Urea-Induced Titania Modification

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**Abstract:** The mechanism of surface modification of titania by calcination with urea at 400 °C was investigated by substituting urea by its thermal decomposition products. It was found that during the urea-induced process titania acts as a thermal catalyst for the conversion of intermediate isocyanic acid to cyanamide. Trimerization of the latter produces melamine followed by polycondensation to melem- and melon-based poly(aminotri-*s*-triazine) derivatives. Subsequently, amino groups of the latter finish the process by formation of Ti−N bonds through condensation with the OH-terminated titania surface. When the density of these groups is too low, like in substoichiometric titania, no corresponding modification occurs. The mechanistic role of the polytriazine component depends on its concentration. If present in only a small amount, it acts as a molecular photosensitizer. At higher amounts it forms a crystalline semiconducting organic layer, chemically bound to titania. In this case the system represents a unique example of a covalently coupled inorganic–organic semiconductor photocatalyst. Both types of material exhibit the quasi-Fermi level of electrons slightly anodically shifted relative to that of titania. They are all active in the visible-light mineralization of formic acid, whereas nitrogen-modified titania prepared from ammonia is inactive.

**Keywords:** Fermi potential • heterogeneous catalysis • photochemistry • semiconductors • titanium

## Introduction

Semiconductor photocatalysis has become the most important method for basic and applied chemical utilization of solar energy. Whereas the “holy grail” of water cleavage has not yet reached practical application, this is the case for “green” photooxidation reactions like the cleaning of water and air.[1] The most commonly employed photocatalyst, titanium dioxide, suffers from its large band gap of 3.2 eV (387 nm), which allows the utilization of only about 3 % of solar radiation capable of inducing photochemical reactions. It is therefore a central topic of semiconductor photocatalysis to shift the photocatalytic activity of titania to the visible spectral region. Doping with main-group metals such as carbon, nitrogen, and sulfur has turned out to be one of the most promising methods. In particular, “N-doped” titania has received great attention.[2–4]

The nature of the nitrogen species in the resulting materials is a matter of intense discussions. $NO_x$ and various other nitrogen oxide fragments were proposed by Sato,[5] our group,[6–8] and others.[9,10] But also nitridic and amidic ($NH_x$) species were suggested;[11] in some cases there was evidence of the presence of several oxidation states of nitrogen.[12] Contrary to the generally made assumption that the nitrogen species itself is the origin of visible-light photocatalysis, it was proposed that during the modification procedure the nitrogen precursor just induces the formation of crystal lattice defects, which themselves are responsible for the visible-light activity.[13–16] Since in most cases it is not known whether the nitrogen species is a true dopant or just part of a modified titania surface layer, we prefer the more general term “N-modified” instead of “N-doped”. It should also be noted that all photoreactions cited in this paper were conducted with visible light unless stated otherwise.

There is disagreement in the literature as to whether N-doping causes band-gap narrowing by an anodically shifted valence band edge[17–19] or by novel intra-band-gap states. For the latter case most of the papers postulated the existence of nitrogen-centered energy levels located just above the valence band edge as suggested from both theoretical[3,20–25] and experimental investigations like UV photoelectron spectroscopy,[26] electron paramagnetic resonance,[22] deep-level optical spectroscopy,[19,27] analysis of photocata-

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Supporting information for this article is available on the WWW under http://dx.doi.org/10.1002/chem.200901646.

lytic reactions,[6] and photocurrent measurements.[28–31] Contrary to this, even band-gap widening was postulated.[24,32]

Nitrogen-modified titania may be prepared by three methods consisting of 1) sputtering and implantation techniques, 2) calcination of $TiO_2$ or $Ti(OH)_4$ under N-containing atmospheres generated by nitrogen compounds like ammonia, amines, or urea, and 3) by sol–gel methods.[2–4] A convenient and easy to handle nitrogen source for the last two methods turned out to be urea, which is known to afford ammonia and isocyanic acid upon heating to about 400 °C. A typical example for the sol–gel route is stirring a solution of urea and tetraisopropyl titanate in ethanol at room temperature followed by calcination of the produced precipitate at 300–550 °C. The resulting yellow material photocatalyzed the oxidation of phosphatidylethanolamine lipids.[12] Surprisingly, even when the calcination temperature was increased to 800 °C, the anatase phase was still present at 97 %, whereas it decreased to 11 % at 900 °C, but the resulting material exhibited the highest photoactivity in rhodamine 6G degradation.[33] Results from XRD analysis suggested that urea may prevent the phase transition to rutile.[34] When urea was replaced by thiourea, visible-light activity of the obtained titania sample was due to nitrogen- but not to sulfur-modification as reported before in the literature.[7,35] Employing tetra-*n*-butyl titanate and calcination at 450 °C[36] and 500 °C[34] gave a material active in methyl orange degradation. Application of a microemulsion–hydrothermal method on the tetra-*n*-butyl titanate/urea system afforded photocatalysts active in 2,4-dichlorophenol and rhodamine B degradation.[10,37] When tetrabutylammonium halides were also present in the titanate solution in addition to urea, a carbon–nitrogen-modified titania was obtained. After calcination at 400 °C this material exhibited a high photocatalytic activity in methylene blue degradation.[38]

Instead of alkoxides as titania precursors, corresponding halides and sulfates were also employed. In this case urea or guanidine carbonate and the titanium salt were dissolved in ethanol or water. The hydroxide precipitated with water is subsequently calcined at temperatures of 400–900 °C. The oxidation of 1,2-trichloroethylene[39,40] and acetaldehyde[40] was catalyzed by the resulting materials. Solvothermal treatment of aqueous $TiCl_3$ with urea in methanol at 190 °C afforded violet titania due to the presence of oxygen vacancies. The color changed to bright yellow after calcination in air at 400 °C.[41,42] This material photocatalyzed the degradation of nitrogen monoxide. Upon thermal decomposition of $[Ti\{OC(NH)_2\}Cl_3]$ at 200–600 °C a C-, N-, and Cl-containing titania material was obtained. It catalyzed the photodegradation of methyl orange.[43]

A series of papers reported on the calcination of titania or titanium hydroxide in the presence of urea. Calcining the hydroxide at about 400 °C resulted in the most active photocatalysts, which enabled the oxidation of 4-chlorophenol,[11] iodide,[44] and gaseous toluene.[45] Impregnating meso-/macroporous and zeolite-encapsulated $TiO_2$ with aqueous urea followed by calcination at 350–550 °C produced yellow materials photoactive in the degradation of rhodamine B[46] and phenol,[47] respectively. Pristine $TiO_2$ and urea were calcined under various conditions at temperatures of 300–600 °C. Depending on the titania-to-urea ratio and on details of the calcination apparatus, different products may be obtained. To our knowledge the first visible-light-active N-modified titania prepared from titanium dioxide and urea was obtained in 2003 by ball-milling of a commercial $TiO_2$ (P25) with 10 wt % urea and subsequent calcination in air at 400 °C.[48] The bright yellow powder photocatalyzed the oxidation of NO with visible light.[48–50] A similar mechanochemical treatment of anatase was performed with 5 wt % urea.[9] Impregnating anatase with an aqueous solution of urea or guanidine carbonate followed by calcination at 350–400 °C in air afforded modified titania that was active in the oxidation of 2-propanol to acetone.[51] Modification by the gaseous decomposition products of urea was conducted at 350 °C. Electrodes obtained from this material enabled the photooxidation of iodide.[52] When thiourea and titania were treated at 400–500 °C, the resulting powder was photoactive in methylene blue degradation. As indicated by X-ray photoelectron spectroscopy (XPS) analysis, neither nitrogen nor sulfur was present in the material. The XPS C1s binding energy at 288 eV was attributed to carbonate species.[53]

Urea as a nitrogen source has been employed in the preparation of “co-doped” $TiO_2$ with ions of B,[54] Ce,[55] Cu,[56] Nb,[57] and Pt.[58] The combination of urea and titanium dioxide was also investigated in a nonphotocatalytic context, like electrorheological properties,[59,60] nanocomposite electrodes for application in lithium ion batteries,[61] and new resins with high stability.[62]

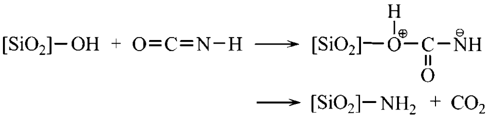
As mentioned above, the nature of the nitrogen species responsible for the visible-light activity of urea-derived titania is still under debate. Most proposals are based on the results of the XPS measurement of N1s binding energies. Values of 396–397 and 399 eV were assumed to be evidence of the presence of nitridic nitrogen, such as that in titanium nitride (N-Ti-N)[38,41,44,49,51,63] or in modified titania (O-Ti-N),[10,37,46] or of N−H groups.[12] Higher energies of 400–401, 402–403, and even 407–408 eV were proposed to correspond to N−N, N−O, or N−C groups,[10,11,37,41,42,49,51,52] chemisorbed $N_2$,[38,63] or $NO_x$ ($x<2$) and $NO_2^-$ groups,[12] respectively. EPR and solid-state NMR spectra suggested the existence of interstitial $NO_2^{2-}$[9] or $NO_x$ species[39] and nitrate,[39] respectively. Both FTIR and solid-state NMR experiments indicated the presence of Ti−$NH_2$ groups.[47] Based on a detailed curve analysis of diffuse reflectance spectra of all so-called “nitrogen-doped” titania materials it was concluded that irrespective of the chemical nature of the nitrogen precursor, not nitrogen species but lattice defects are the origin of visible-light activity.[13–16] Diffuse reflectance spectra in general exhibit a weak shoulder on the low-energy onset of the steep band-to-band absorption. An exception is a low-band-gap material obtained by a modified-urea treatment. This new material has an intense band-to-band absorption in the range of 400–500 nm, which results in corresponding band gaps of 2.46 and 2.20 eV.[11]

Only a few papers report on the photocatalytic degradation of formic acid over N-doped $TiO_2$.[64,65] Photocatalysts prepared from titanium isopropoxide and triethylamine at room temperature or by nitridation of anatase powder under $NH_3$/Ar at 600 °C were inactive under visible light ($\lambda > 400$ nm). It was concluded that valence-band holes are thermodynamically or kinetically unable to oxidize $HCOO^-$.[64] However, in a later report the material obtained by nitridation exhibited a very weak activity.[65]

It is known that upon fast heating from 300 to 420 °C under atmospheric pressure, urea exclusively decomposes to ammonia and isocyanic acid [Eq. (1)] with a rate maximum at 370–400 °C. Isocyanic acid can also be prepared by heating cyanuric acid to 370–400 °C [Eq. 2].[66] Furthermore, isocyanic acid in the presence of OH groups containing a catalyst like silica is converted to cyanamide, which can trimerize to melamine [Eqs. (3)–(5)]. In the absence of the heterogeneous catalyst, melamine is formed only under high-pressure conditions. Thus, the overall thermolysis of urea in the presence of silica affords melamine, ammonia, and carbon dioxide [Eq. (6)].

$$(NH_2)_2CO \xrightarrow{300-420\,^{\circ}C} HNCO + NH_3 \tag{1}$$

$$C_3N_3(OH)_3 \xrightarrow{370-400\,^{\circ}C} 3\,HNCO \tag{2}$$



$$[SiO_2]{-}OH + O{=}C{=}N{-}H \longrightarrow [SiO_2]{-}\overset{H}{\overset{|}{O^{\oplus}}}{-}\underset{\underset{O}{\|}}{C}{-}\overset{\ominus}{N}H \longrightarrow [SiO_2]{-}NH_2 + CO_2 \tag{3}$$

$$[SiO_2]{-}NH_2 + H\text{-}O\text{-}C{\equiv}N \rightarrow H_2N\text{-}C{\equiv}N + [SiO_2]{-}OH \tag{4}$$

$$3\,H_2N\text{-}C{\equiv}N \rightarrow C_3N_3(NH_2)_3 \tag{5}$$

$$6\,(NH_2)_2CO \xrightarrow{400\,^{\circ}C/SiO_2} C_3N_3(NH_2)_3 + 6\,NH_3 + 3\,CO_2 \tag{6}$$

Furthermore it is known that upon thermal treatment at 450 °C, melamine is converted under condensation to white melam, white-beige melem, and yellow melon (Scheme 1). Prolonged heating at 550 °C produces polycondensed *s*-triazines of graphitic structure.[67–69] These compounds are very likely the first organic polymers reported.[70]

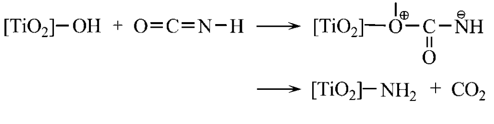
In summary, although an enormous amount of experimental data is available on the urea-induced preparation of "N-modified" titania, no information is available on the mechanism of the modification reaction. In addition, the nature of the nitrogen species responsible for visible-light activity is still a matter of intense discussion. Herein we report on experimental results that answer these basic questions.

## Results and Discussion

$TiO_2$-N/C was obtained by calcining a 2:1 (w/w) mixture of urea/titania in a rotating open flask at 400 °C followed by washing with water.[74] Whereas this material under standard irradiation conditions (180 min of irradiation time; see the Experimental Section) induced 82 % mineralization of formic acid, this activity decreased to 60 and 2–3 % when the thermal treatment was conducted at 300 and 500–600 °C, respectively. All the powders had a slightly yellow color. Varying the reaction time at 400 °C from 30 to 60 and 180 min afforded the photocatalysts $TiO_2$-N,C30, $TiO_2$-N,C, and $TiO_2$-N,C180 exhibiting a formic acid mineralization of 93, 82, and 40 %, respectively (Figure 1). However, since the calcination time of 1 h led to the best reproducibility of mineralization rates, it was employed throughout this work.

Formic acid was selected as a model organic acid pollutant because 1) it does not form colored charge-transfer complexes with titania that would prevent visible-light absorption by the photocatalyst, 2) it is oxidized without generation of long-lived and light-absorbing intermediates, 3) almost all organic pollutants are mineralized via formic acid, which also represents the final and most likely rate-determining reaction step.[75]

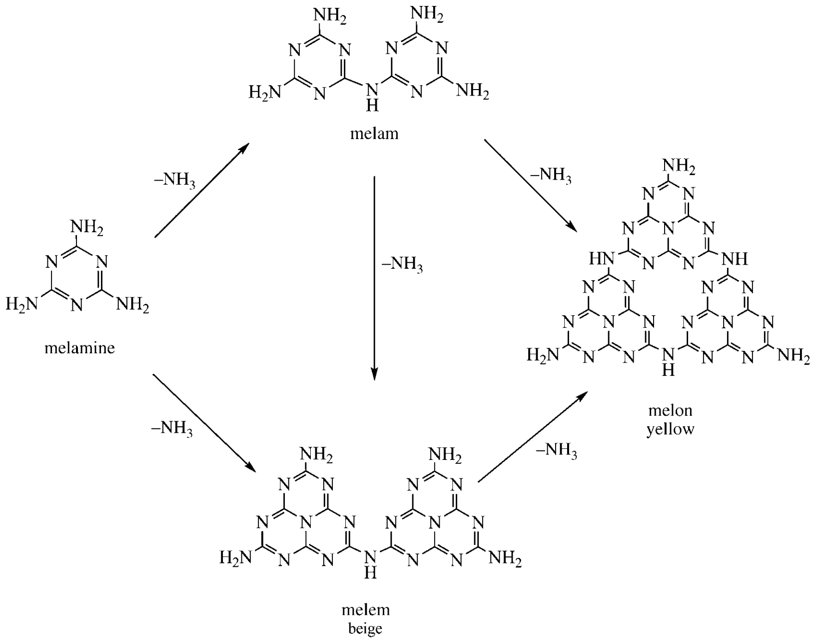
To find out which decomposition product of urea may be responsible for formation of the final nitrogen species, titania was treated at 400 °C with an equal weight amount of isocyanic acid, cyanamide, melamine or a melem/melon mixture. To simulate the initial urea decomposition products [Eq. (1)] isocyanic acid was generated [Eq. (2)] from a mixture of cyanuric acid and $TiO_2$ under a flow of ammonia. It is known that the highest decomposition rate of cyanuric acid is in the range of 395–400 °C.[72] The resulting photocatalyst $TiO_2$-N,C/CA,$NH_3$ exhibited 92 % mineralization of formic acid (Figure 2, curve b). To examine if ammonia is essential for a successful modification process, cyanuric acid was employed in the absence of ammonia. The obtained photocatalyst $TiO_2$-N,C/CA mineralized 80 % of formic acid (Figure 2, curve c). Notice, that the material $TiO_2$-N produced with only ammonia according to Asahi et al.[17] is inactive (Figure 3, curve d).[76] Since surface OH groups on titania, like in the case of silica,[66] may also be able to catalyze cyanamide formation according to Equations (7) and (8), titania was treated with the precursor guanidine carbonate under the standard modification conditions.[77,51,40] In addition to cyanamide only carbon dioxide, ammonia, and water are formed in this reaction.[78] A formic acid mineralization yield of 79 % was observed with this material ($TiO_2$-N,C/GU; Figure 3, curve b). As next mutual intermediate of the modification process, melamine, the cyclotrimer of cyanamide [Eq. (5)], was employed as the modifier. The obtained slightly yellow photocatalyst $TiO_2$-N,C/MA induced 75 % mineralization of formic acid (Figure 3, curve c).



$$[TiO_2]{-}OH + O{=}C{=}N{-}H \longrightarrow [TiO_2]{-}\overset{H}{\overset{|}{O^{\oplus}}}{-}\underset{\underset{O}{\|}}{C}{-}\overset{\ominus}{N}H \longrightarrow [TiO_2]{-}NH_2 + CO_2 \tag{7}$$

$$[TiO_2]{-}NH_2 + H\text{-}O\text{-}C{\equiv}N \rightarrow H_2N{-}C{\equiv}N + [TiO_2]{-}OH \tag{8}$$

These as well as further results (vide infra) strongly suggest that during modification with urea, analogously to silica,[66] titania acts as a heterogeneous catalyst for the formation of cyanamide from isocyanic acid. To find out which final carbon/nitrogen compounds are produced, melamine was first thermally treated at 450 °C under standard modification conditions but in the absence of titania.[71–73] In the obtained yellow melem/melon mixture (ME,MO) the major component melem changed to melon as indicated by elemental analysis when kept thereafter for 1 h in air at 400 °C (see the Experimental Section).



Scheme 1. Condensation products of melamine produced at 350–500 °C.[71–73]

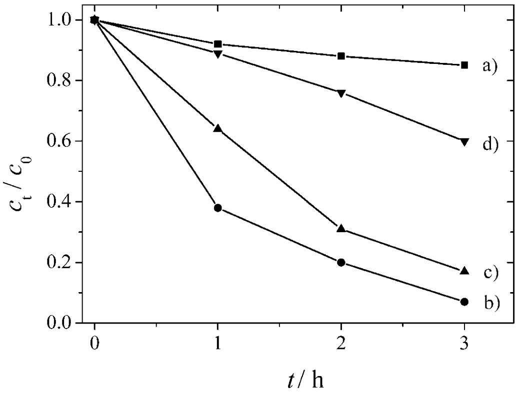


Figure 1. Photomineralization of formic acid ($c = 1\times10^{-3}$ mol L$^{-1}$; $c_0$ and $c_t$ refer to concentrations at times 0 and $t$, respectively): a) $TiO_2$, b) $TiO_2$-N,C30, c) $TiO_2$-N,C, d) $TiO_2$-N,C180.

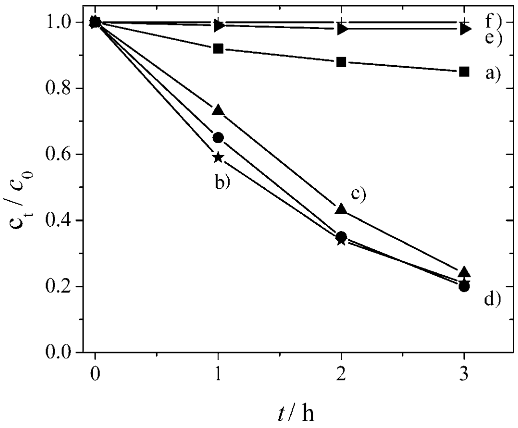


Figure 3. Photomineralization of formic acid ($c = 1\times10^{-3}$ mol L$^{-1}$; $c_0$ and $c_t$ refer to concentrations at times 0 and $t$, respectively): a) $TiO_2$, b) $TiO_2$-N,C/GU, c) $TiO_2$-N,C/MA, d) $TiO_2$-N,C/ME,MO, e) ME,MO, f) $TiO_2$/ME,MO.

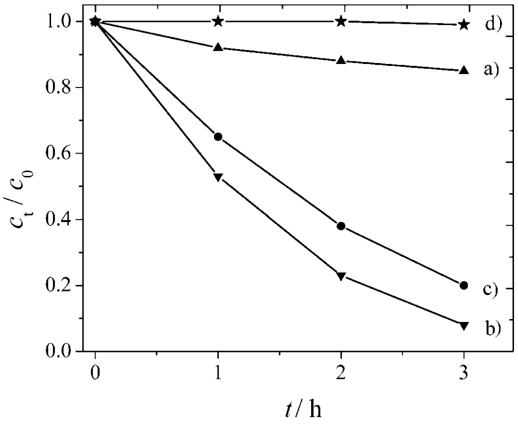


Figure 2. Photomineralization of formic acid ($c = 1\times10^{-3}$ mol L$^{-1}$; $c_0$ and $c_t$ refer to concentrations at times 0 and $t$, respectively): a) $TiO_2$, b) $TiO_2$-N,C/CA,$NH_3$, c) $TiO_2$-N,C/CA, d) $TiO_2$-N.

No significant changes are observable in the IR spectra (Figure 4). Peaks at 805, 1325, 1463, and 1616 cm$^{-1}$ are tentatively assigned to the heteroaromatic *s*-triazine nucleus (vide infra),[73] whereas signals at 1206, 1246, and 1325 cm$^{-1}$ most likely correspond to the central C-N(-C)-C fragment and/or bridging C-NH-C units.[79] The small peak at 714 cm$^{-1}$ is assigned to the ring bending modes of melem and melon, but there is no band at 681 cm$^{-1}$, which is known for melamine.[80] Absence of the latter is also indicated by the absence of the characteristic *s*-triazine signal at 1560 cm$^{-1}$. The broad band around 3141 cm$^{-1}$ is due to the presence of NH and/or $NH_2$ groups.

The as-prepared ME,MO mixture before and after calcination at 400 °C was inactive. However, when treated with an equal amount of titania under standard conditions, the

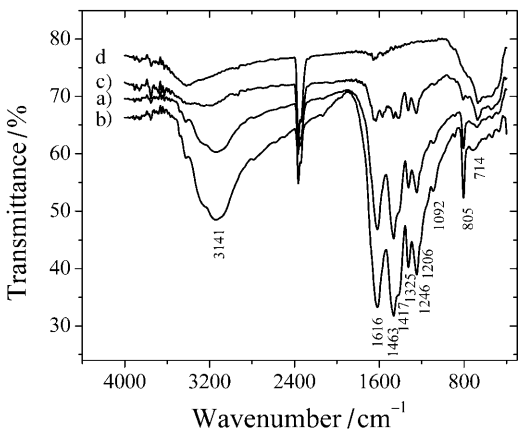
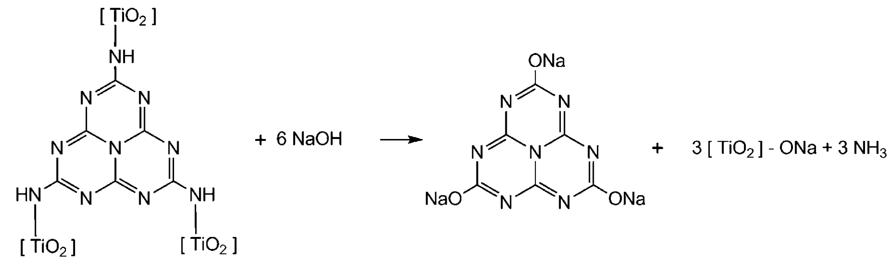


Figure 4. FTIR spectra of the melem/melon mixture a) before and b) after heating at 400 °C; and of c) TiO$_2$-N,C/ME,MO and d) TiO$_2$.

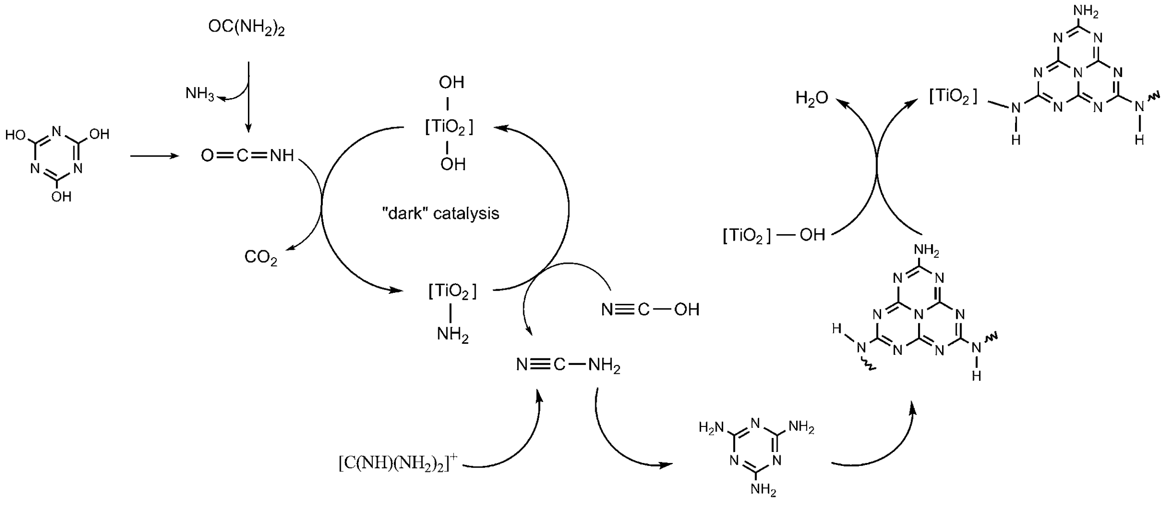
resulting yellowish powder TiO$_2$-N,C/ME,MO induced 80% degradation, as also observed for TiO$_2$-N,C obtained from urea (Figure 3). Since grinding the melem/melon mixture with titania at room temperature produced only an inactive material TiO$_2$/ME,MO (Figure 3, curve f), it seemed likely that during the thermal treatment melem/melon reacted with the titania surface to form Ti–N bonds. This is further corroborated by the reaction of TiO$_2$-N,C/MA with sodium hydroxide at 100 °C affording cyamelurate [Eq. (9)]. It is known that the amino groups in melem can be replaced by OH through nucleophilic attack of hydroxide.[81] The remaining white material TiO$_2$-R did not exhibit the characteristic weak absorption shoulder above 400 nm (see Figure S1 in the Supporting Information) and was inactive in formic acid degradation.



(9)

The results presented above clearly suggest that irrespective of using urea, cyanuric acid, guanidine carbonate, or melamine, the same type of modified titania photocatalyst is obtained. In contrast to previous proposals[9–12,37–39,41,42,44,46,47,49,51,52,63] the visible-light activity is therefore not caused by small nitrogen species or lattice defects but by polycondensation products of intermediate melamine produced in a titania-catalyzed transformation of urea (Scheme 2).

The resulting poly-*s*-triazine surface-modified photocatalysts contain melem/melon fragments having nitrogen and carbon contents of 0.49–2.34 and 0.28–1.20%, respectively (see Table S1 in the Supporting Information). Nitrogen 1s binding energies of 399.2 and 400.5 eV as measured for TiO$_2$-N,C are in agreement with literature values reported for carbon nitrides (399–400 eV, C=N-C)[82,83] and similar graphite-like phases (400.6 eV, N–C$_{sp^2}$),[84,85] and of polycyanogen (399.0, 400.5 eV (-C=N-)$_x$).[86] Corresponding values for the as-obtained mixture of melem/melon are 399.2 and 398.4 eV. The absence of the latter peak, which corresponds to *s*-triazinylamino groups,[82] suggests that during the modi-



Scheme 2. Proposed mechanism of urea-induced titania modification.

fication process almost all the amino groups of the relevant intermediates reacted with surface Ti(OH) fragments.

According to X-ray powder diffraction analysis all powders have retained the anatase structure of the starting material (Figure 5) and consist of 10–13 nm-sized crystallites.

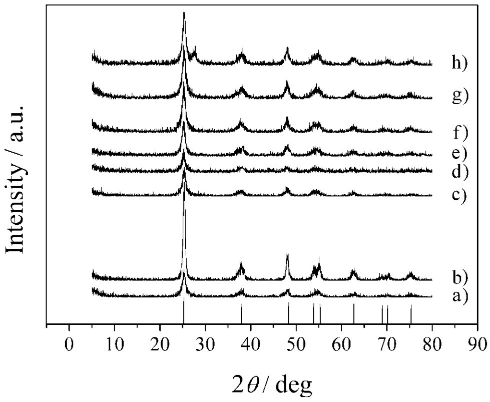


Figure 5. XRD patterns of a) $TiO_2$, b) $TiO_{2-x}$, c) $TiO_2$-N/C, d) $TiO_2$-N,C/CA,$NH_3$, e) $TiO_2$-N,C/CA, f) $TiO_2$-N,C/GU, g) $TiO_2$-N,C/MA, h) $TiO_2$-N,C/ME,MO. Vertical lines represent the literature values for anatase (ASTM file card no. 01-0562).

Electron microscopy indicated that the latter form a few large, micrometer-sized aggregates. A specific surface area of $180\,m^2g^{-1}$ was measured for $TiO_2$, $TiO_2$-N/C, $TiO_2$-N,C/CA,$NH_3$, and $TiO_2$-N,C/CA, whereas $125\,m^2g^{-1}$ was found for $TiO_2$-N,C/MA. The quasi-Fermi level of electrons at pH 7 as obtained form the Roy slurry method is −0.48 V for $TiO_2$-N/C, $TiO_2$-N,C/CA,$NH_3$,$TiO_2$-N,C/MA and −0.51 V for $TiO_2$-N,C/CA, $TiO_2$-N,C/GU, and $TiO_2$-N,C/ME,MO (see Figure S2 in the Supporting Information; Table 1). A value of −0.56 V was measured for unmodified titania. This slight anodic shift found for the modified samples may be due to a higher positive surface charge induced by protonation of the more basic $TiO_2$-NH- groups absent in pristine titania.

The photocatalyst $TiO_2$-N,C/ME,MO as obtained from titania and a melem/melon mixture exhibits nitrogen and carbon contents of 19.41 and 10.86%, respectively, which are about 10 times higher than those found for the $TiO_2$-N,C materials discussed above. The observed N/C ratio of 1.53 is close to the melon value of 1.50, which was also found for $TiO_2$-N,C/CA and $TiO_2$-N,C/GU, whereas 1.67–1.80 was measured for the other powders. The lower this ratio the higher condensation products of melamine are expected to be present. This is also evidenced by the N1s binding energies of 399.1 and 400.6 eV for $TiO_2$-N,C/ME,MO, and indicates the presence of melon and higher polycondensation products (vide supra). Due to the relative high content of the organic component all peaks attributed to the melem/melon mixture (vide supra) are also observed in the FTIR spectrum of $TiO_2$-N,C/ME,MO (Figure 4). The XRD peak at a $2\theta$ value of 27.4° found for $TiO_2$-N,C/ME,MO (Figure 5) can be attributed to the stacked aromatic system of carbon nitrides.[67–69] Together with the high nitrogen and carbon contents it strongly suggests the presence of a thick layer of polymeric melon. Accordingly, this XRD peak is not present in other modified titania samples that have a much smaller fraction of polycondensed triazines. The surprisingly low specific surface area of $34\,m^2g^{-1}$ measured by $N_2$ adsorption for $TiO_2$-N,C/ME,MO is in accord with the presence of a dense organic shell preventing access of dinitrogen (see the Experimental Section) to a porous unmodified titania core. This postulate of a core–shell structure is also corroborated by the inactivity of the white residue remaining after extraction of cyameluric acid.

Table 1. Nitrogen-to-carbon atomic ratios (N/C),[a] quasi-Fermi potentials of electrons (${}_nE_F^*$),[b] apparent band-gap energies ($E_{bg}$), and initial mineralization rates ($r_i$) of formic acid.

| Photocatalyst | N/C | $E_{bg}$ [eV] | ${}_nE_F^*$ [V][c] | $r_i$ [$10^{-4}\,mol\,L^{-1}s^{-1}$] |
|---|---|---|---|---|
| $TiO_2$ | – | 3.23 | −0.56 | 0.80 |
| $TiO_2$-N,C/CA | 1.50 | 3.07 | −0.51 | 3.50 |
| $TiO_2$-N,C/GU | 1.50 | 3.07 | −0.51 | 3.66 |
| $TiO_2$-N,C/ME,MO | 1.53 | 3.07 | −0.51 | 3.50 |
| $TiO_2$-N,C/MA | 1.67 | 3.02 | −0.48 | 2.70 |
| $TiO_2$-N,C | 1.66 | 2.90 | −0.48 | 3.60 |
| $TiO_2$-N,C/CA,$NH_3$ | 1.80 | 2.90 | −0.48 | 4.70 |

[a] From elemental analysis. [b] Measured according to ref. [88] and calculated for pH 7. [c] Versus NHE.

The diffuse reflectance spectra of all modified samples are almost identical exhibiting a weak absorption shoulder in the range of 400–450 nm as exemplified in Figure 6 for $TiO_2$-N,C and $TiO_2$-N,C/ME,MO. If this visible absorbance originates from a local excitation of the polytriazine sensitizer, it should be higher in the melem/melon-modified material that is present in about a tenfold higher concentration. However, this is not the case as evidenced by the spectra depicted in the figure.[87] The very low absorbance of the pristine melem/melon mixture also disfavors the possibility of a local excitation. It is therefore proposed that the absorption shoulder in the visible region is a charge-transfer band enabling an optical electron transfer from the polytriazine component to titania. Since in the case of $TiO_2$-N,C/ME,MO the polytriazine is present as a crystalline layer, this material

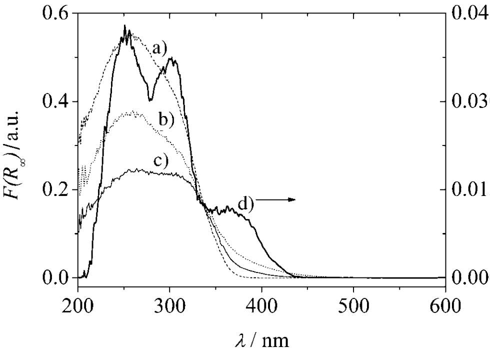


Figure 6. Diffuse reflectance spectra of a) $TiO_2$, b) $TiO_2$-N,C, c) $TiO_2$-N,C/ME,MO, and d) melem/melon. The Kubelka–Munk function $F(R_\infty)$ is equivalent to absorbance.

represents an unique combination of an inorganic with an organic semiconductor connected through Ti-N-C bonds.

By assuming that all the materials are indirect semiconductors, the band gap was obtained from the extrapolation of the linear part of the modified Kubelka–Munk function $(F(R_\infty)h\nu)^{1/2}$ versus $h\nu$. Considering that in the critical spectral range the band-to-band and charge-transfer absorptions are superimposed, a discussion of these apparent band gaps summarized in Table 1 is presently not possible (see Figure S3 in the Supporting Information). This does not apply for the pristine melem/melon mixture exhibiting a band gap of 2.76 eV in excellent agreement with the value of 2.7 recently reported for semiconducting polymeric melon of graphitic structure.[67–69]

As mentioned in the Introduction, it was proposed that the nitrogen precursor during the modification procedure induces the formation of lattice defects, which themselves are responsible for the visible-light activity. This was based on the similarities of the optical properties of all "anion-doped" titania photocatalysts.[89,90,13–16] The results presented above exclude the possibility that urea-derived catalysts are active in visible light due to the presence of such defects. However, our results do not exclude the possibility that non-stoichiometric visible-light-active titania may be formed upon calcination 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.[91–93] However, both the resulting $TiO_{2-x}$ and the materials obtained from it by calcining with melamine at 400 °C were inactive in formic acid mineralization. Therefore, oxygen vacancies and/or other lattice defects generated during $TiO_2$ annealing in the absence or presence of melamine are not responsible for visible-light photoactivity. It is recalled that the photocatalyst $TiO_2$-N,C/MA prepared from $TiO_2$ and melamine without thermal pretreatment exhibited excellent activity. Furthermore, and contrary to samples $TiO_{2-x}$ and $TiO_{2-x}$/MA, only $TiO_2$-N,C/MA exhibits a visible-light absorption shoulder (Figure 7). The same results were obtained when urea instead of melamine was used for the modification of $TiO_{2-x}$.

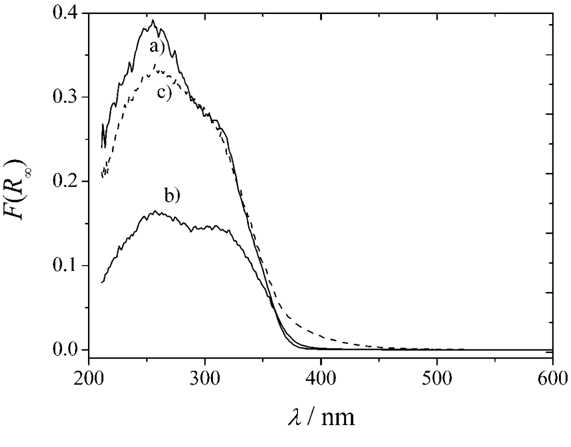


Figure 7. Diffuse reflectance spectra of a) $TiO_{2-x}$, b) $TiO_{2-x}$/MA, and c) $TiO_2$-N,C/MA.

Since the thermal pretreatment of $TiO_2$ results in removal of adsorbed water and surface OH groups from the titania surface, the density of surface OH groups should decrease. As expected, after annealing unmodified $TiO_2$ at 400 °C for 3 h under reduced pressure 51 % of the OH groups were removed, which corresponds to a lowering of the surface OH density from 9 to 4 (OH) $nm^{-2}$. This may be too low for catalyzing cyanamide formation and condensation with aminotriazine groups.

## Conclusion

In summary, the results presented above clearly reveal that calcining a mixture of urea and $TiO_2$ at 400 °C produces poly(aminotri-*s*-triazine) derivatives covalently attached to the semiconductor. Therefore, and contrary to previous reports, visible-light photocatalytic activity of "N-doped" or "N-modified" titania prepared from urea does not originate from the presence of nitridic, amidic, and nitrogen oxide species or lattice defects. It arises from condensed aromatic *s*-triazine compounds containing melem and melon units. Their specific structure depends on the amount produced in the modification process. If present only in a small fraction they act as a molecular photosensitizer for titania. At higher amounts they form a semiconducting organic layer chemically bound to titania, which represents a unique example of a covalently coupled inorganic–organic semiconductor photocatalyst. Both types of materials are active in the visible-light mineralization of formic acid, whereas nitrogen-modified titania prepared from ammonia is inactive. During the modification process with urea at 400 °C titania acts as thermal catalyst for the conversion of intermediate isocyanic acid to cyanamide. Trimerization of the latter produces melamine followed by polycondensation to melem- and melam-based heteroaromatic compounds. Subsequently, amino groups of the latter finish the process by formation of Ti–N bonds through condensation with titania surface OH groups. When the density of these groups is too low, like in substoichiometric titania obtained by preheating titania at 400 °C, no corresponding modification occurs.

## Experimental Section

**Materials**: Commercially available $TiO_2$ powder (100 % anatase; Hombikat UV-100, Sachtleben, Germany), urea, cyanuric acid (CA; Fluka Chemicals), melamine (MA; Acros Organics), guanidine carbonate (GU; Acros Organics), formic acid (Merck), and methyl viologen (1,1′-dimethyl-4,4′-bipyridinium dichloride; Acros Organics) were used as received.

**Standard modification procedure**: Modified powders were prepared by grinding a 2:1 (w/w) mixture of urea or cyanuric acid/titania or a 1:1 (wt/wt) mixture of titania with guanidine carbonate, melamine, or a melem/melon mixture, followed by calcination in air at 400 °C for 1 h in an open rotating flask (250 mL). In the case of cyanuric acid, in an additional experiment air was replaced by ammonia gas. Subsequently, all the materials were ground up and washed six times with portions (40 mL) of doubly distilled water by centrifugation. Finally, the materials were dried at 80 °C for approximately 1 h followed by grinding. In all cases grinding was performed in an agate mortar.

When urea, cyanuric acid (ammonia gas), guanidine carbonate, melamine, and melem/melon were used as precursors the resulting materials are denoted as $TiO_2$-N,C, $TiO_2$-N,C/CA ($TiO_2$-N,C/CA,$NH_3$), $TiO_2$-N,C/GU, $TiO_2$-N,C/MA, and $TiO_2$-N,C/ME,MO, respectively.

$TiO_2$-N was prepared according to the literature[17] by treatment of $TiO_2$ (1 g) for 3 h at 600 °C in a $NH_3$(67 %)/Ar atmosphere. The material was washed and dried as described above.

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

**Preparation of the melem/melon mixture**: The mixture of melem/melon was prepared by heating melamine (5 g) in an open Schlenk tube for 5 h at 450 °C. The elemental analysis of the resulting material revealed the presence of nitrogen (64.2 %), carbon (33.6 %), and hydrogen (2.3 %). After a second calcination in air for 1 h at 400 °C in an open rotating flask the N, C, and H contents had changed to 62.7, 33.3, and 2.3 %, respectively. The theoretical values (%) for melem are N 64.2, C 33.0, H 2.8 and for melon are N 62.7, C 35.8, H 1.5.

**Instruments**: Elemental analyses (EuroVector, CHNSO, E.A.3000 equipped with a GC detector) were conducted by dynamic spontaneous combustion. FTIR transmission spectra were obtained using a Perkin–Elmer PE-16PC FTIR spectrometer against an air background. The samples were pressed pellets of a mixture of the titania powder with KBr. Diffuse reflectance spectra of samples in the form of pressed pellets of a mixture of the powder (0.025 g) with $BaSO_4$ (2 g) were recorded relative to barium sulfate using a Shimadzu UV-2401 UV/Vis spectrophotometer equipped with a diffuse reflectance accessory. X-ray difractometry measurements were performed with a Philips X'Pert PW 3040/60 diffractometer. Surface area was determined by the BET (Brunauer–Emmett–Teller) method using a Gemini 2370 V.01 instrument. Thermal gravimetric analysis (TGA) was performed using a Universal V2.6D TA instrument in a nitrogen atmosphere in the temperature range of 33–900 °C and a heating rate of 10 °C $min^{-1}$ with a 60 min isothermal step at 150 °C. The density of surface OH groups was determined by TGA analysis assuming that the weight loss between 150 and 1000 °C is due to the desorption of surface OH groups. For analysis by X-ray photoelectron spectroscopy (XPS) (PHI 5600) samples were prepared as pressed powder pellets attached to aluminum foil by silver lacquer. Binding energies are referenced to the C1s peak at 284.8 eV originating from adventitious hydrocarbon contamination. Fitting of the data was accomplished using XPSPEAK41 software; a Shirley-type background subtraction was used.

**Extraction of cyamelurate acid**: $TiO_2$-N,C/MA (0.8 g) was heated at reflux at 100 °C for 1 h with NaOH (0.01 mol $L^{-1}$, 80 mL) followed by overnight stirring at room temperature. The liquid was separated from a white solid and evaporated to give a beige powder.

**Standard degradation procedure**: Photomineralization experiments were carried out in a jacketed cylindrical 20 mL cuvette attached to an optical train. Irradiation was performed with an Osram XBO 150 W xenon arc lamp installed in a light-condensing lamp housing (PTI, A1010S). A water filter and a 455 nm cutoff filter were placed in front of the cuvette. An air stream was directed to the cuvette to ensure constant temperature of the reaction mixture, which was stirred magnetically. A powder suspension (1 g $L^{-1}$, 20 mL) in formic acid ($10^{-3}$ mol $L^{-1}$) 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. Initial rates were calculated from formic acid concentration measured after 1 h of irradiation.

**Quasi-Fermi potentials of electrons ($_{n}E_{F}^{*}$)**: $_{n}E_{F}^{*}$ values were measured according to the literature[88] using methyl viologen dichloride ($E^{\circ}_{MV^{2+/+\bullet}}$ = –0.445 V vs. normal hydrogen electrode (NHE)) as the pH-independent redox system. In a typical experiment, the catalyst (50 mg) and methyl viologen dichloride (10 mg) were suspended and sonicated for 15 min prior to illumination in a 100 mL two-necked flask in $KNO_3$ (0.1 mol $L^{-1}$, 50 mL). A platinum flag and Ag/AgCl served as the working and reference electrodes and a pH meter was used for recording the proton concentration. Initially the pH of the suspension was adjusted using $HNO_3$ to pH 2.5 before measurement. Stable photovoltages were recorded about 30 min after changing the pH value. The suspension was magnetically stirred and purged with nitrogen gas about 30 min prior to and throughout the experiment. A water filter was placed in front of the flask. The tests were performed in the presence or absence of various electron donors, such as 2-propanol (10 %, v/v), 4-chlorophenol ($2.5 \times 10^{-4}$ and $2.5 \times 10^{-3}$ mol $L^{-1}$ afforded the same $pH_0$ value), NaBr (0.1 mol $L^{-1}$), and formic acid ($10^{-3}$ mol $L^{-1}$). Titration was performed using NaOH (0.1, 0.01, and 0.001 mol $L^{-1}$) also purged with nitrogen gas. The obtained $pH_0$ values were converted to the quasi-Fermi potential at pH 7 by the equation $_{n}E_{F}^{*}\ (\mathrm{pH}\ 7) = E^{\circ}_{MV^{2+/+\bullet}} + 0.059\,(\mathrm{pH}_0 - 7)$.[88] The light source was the same as that used in photomineralization.

## Acknowledgements

The authors are highly indebted to Dr. R. Beránek for helpful discussions and to H. Hildebrand and S. Smolny for measuring XPS spectra and specific surface areas, respectively. This work was supported by the Deutsche Forschungsgemeinschaft.

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Received: June 16, 2009