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LETTERS

Oxidative Power of Nitrogen-Doped TiO₂ Photocatalysts under Visible Illumination

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Nitrogen doping was recently shown to extend the absorptivity of TiO₂ photocatalysts into the visible. We find that N-doped TiO₂ materials fail, however, to catalyze the oxidation of HCOO[−] into CO₂^{•−}, or of NH₃-OH⁺ into NO₃[−], under visible illumination. By N-doping anatase at ambient or high temperature according to the literature we obtained yellow powders *A* and *H*, respectively, that absorb up to ~520 nm. Aqueous *H* suspensions (pH ~ 6, 1 atm O₂) photocatalyze the oxidation of HCOO[−] into CO₂^{•−} radicals at λ ~ 330 nm, but the quantum yield of CO₂^{•−} formation at λ > 400 nm remains below ~2 × 10^{−5} and is probably zero. *A* is similarly inert toward HCOO[−] in the visible region and, moreover, unstable in the UV range. Thus, the holes generated on N-doped TiO₂ by visible photons are unable to oxidize HCOO[−] either by direct means or via intermediate species produced in the oxidation of water or the catalyst. Reports of the bleaching of methylene blue (MB) on N-doped TiO₂, which may proceed by direct oxidative or reductive photocatalytic pathways and also by indirect photocatalysis (i.e., induced by light absorbed by MB rather than by the catalyst) even under aerobic conditions are, therefore, rather uninformative about the title issue.

Introduction

Outstanding stability and oxidative power make TiO₂ the best semiconductor photocatalyst for environmental remediation and energy conversion purposes.^{1–6} However, its wide band gap (3.2 eV ≡ 380 nm for anatase) can only capture less than 3% of the solar irradiance at the Earth's surface.⁷ Large scale technological applications would require a stable photocatalyst absorbing in the visible that could simultaneously reduce O₂ and oxidize most saturated organic substrates. The ideal semiconductor photocatalysts should have, therefore, a flatband potential similar to, and a slightly less positive (vs NHE) valence band potential than TiO₂.

The band gap of TiO₂ has been narrowed by doping with transition metal cations,^{8–12} by creating oxygen vacancies¹³ and, more recently, by replacing lattice oxygen with B, C, N, or S dopants.^{14–19} Substitutional N-doping was found to be particularly effective in decreasing the band gap of anatase through the mixing of N and O 2p states.²⁰ Asahi et al. and Irie et al. prepared N-doped TiO₂ by treating anatase powders with NH₃ gas at 550–600 °C followed by partial reoxidation in air.^{20–22} Diwald et al. doped TiO₂(110) single crystals with NH₃ at 870 K.^{23,24} Intriguingly, Gole et al. reported on the photocatalytic activity of the material obtained via “nitridation” of TiO₂ colloidal nanoparticles with alkylammonium salts at room temperature,⁷ in contrast with most wet syntheses that are followed by calcination of the resulting materials.^{25–27}

The various N-doped TiO₂ catalysts proved to bleach methylene blue (MB), reduce Ag⁺,^{7,20,24} and oxidatively degrade 2-propanol^{22,28} and acetone²⁵ vapors, as well as NO_x,²⁶ upon

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irradiation with visible light. However, the possibility that N-doped TiO₂ would catalyze the photooxidation of typical aqueous organic contaminants remains conjectural because (1) MB can be bleached via oxidation by valence band holes into MB^{•+} ($E_{\text{MB}^{•+}/\text{MB}}^0 = 1.08$ V), by reduction into MB^{•-} by conduction band electrons ($E_{\text{MB}/\text{MB}^{•-}}^0 = -0.23$ V) followed by MB^{•-} disproportionation into *leuco*-MB ($E_{\text{MB}/\text{LMB}}^0 \sim 0$ V) even under aerobic conditions,^{29,30} or even by light absorbed by the dye rather than by the catalyst,^{18,30–34} (2) the favorable reduction of Ag⁺ ($E_{\text{Ag}^+/\text{Ag}}^0 = 0.8$ V) is only a weak indicator that the conduction band of anatase ($E_{\text{CB}} = -0.5$ V) is not significantly shifted toward a more positive potential by band gap narrowing, and (3) it is unwarranted to extrapolate photocatalytic activity for gas/solid reactions to aqueous media.

Recently, Nakato et al. addressed some of these issues and found that methanol did not enhance the photocurrents induced by visible light on N-doped TiO₂ in aqueous media,³⁵ i.e., that methanol is not directly oxidized by holes. Although the establishment of steady photocurrents under visible irradiation implies that water and/or the catalyst undergo faradaic oxidation, Nakato's experiments are silent about whether methanol or other substrates could be oxidized by the products formed in such processes. Here we report that the N-TiO₂ photocatalysts described in the literature cannot oxidize formate, HCOO⁻, into carbon dioxide radical anion, CO₂^{•-}, as monitored by electron spin resonance spectrometry in the presence of the 5,5-dimethyl-1-pyrroline *N*-oxide (DMPO) spin trap, when illuminated with $\lambda > 400$ nm light.³⁶ N-TiO₂ is also unable to oxidize the cationic donor NH₃OH⁺ into NO₃⁻ under the same conditions.

Experimental Section

All chemicals used in the experiments were of analytical reagent grade. Titanium (IV) tetraisopropoxide (Aldrich), triethylamine (Aldrich), anatase TiO₂ (Aldrich), TiO₂ (Degussa P25; 25% rutile, 75% anatase), formic acid (Aldrich), methylene blue (Baker Analyzed), hydroxylamine (Aldrich), 5,5-dimethyl-1-pyrroline *N*-oxide (DMPO, Aldrich), and 2,2,6,6-Tetramethylpiperidin-1-oxyl (TEMPO, Aldrich, purified by sublimation 99%) were used as received. Stock solutions of DMPO in deaerated water were prepared under argon and stored in dark bottles at 253 K. Milli-Q water (Millipore) was used throughout. Solutions were adjusted at pH ~ 6 using NaOH, HClO₄ or HNO₃, as measured with a PHM84 Research pHmeter (Radiometer Copenhagen).

Two different nitrogen-doped titanium dioxide photocatalysts were used in these experiments: one, A, obtained by the room-temperature procedure described by Gole et al.,⁷ and another, H, by high-temperature nitridation of anatase TiO₂.^{20,22} Preparation of the A N-doped TiO₂ material was based on colloidal TiO₂ obtained by hydrolyzing Ti[OCH(CH₃)₂]₄ in water at pH 2, and stirring the suspension overnight.³⁷ Ten milliliters of triethylamine were added to 5 mL of this suspension under continuous stirring. The resulting mixture yielded an intense yellow powder upon vacuum-drying. The high-temperature preparation involved treating commercial anatase TiO₂ powder at 550 °C under a NH₃(80%)/Ar gas flow at 1 atm for 3 h, and then under air for 1 h, a procedure that optimizes the photocatalytic activity of the resulting material toward HCOO⁻ photocatalytic degradation under $\lambda = 330$ nm illumination. A pale yellow powder was obtained. Both photocatalysts were characterized by X-ray photoelectron (M-probe surface spectrometer VG Instruments), UV-vis absorption (HP 8452A diode array spectrophotometer), and diffuse reflectance UV-vis absorption spectroscopy (Shimadzu UV-2101 PC UV-scanning spectrophotometer).

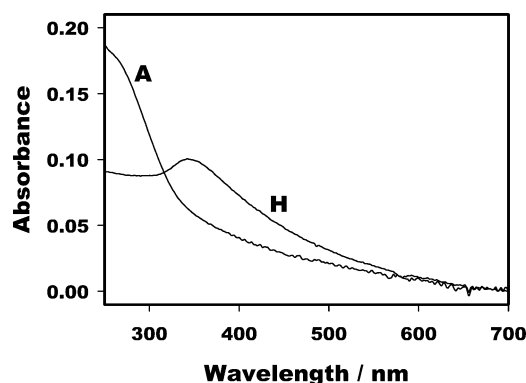


Figure 1. Ultraviolet absorption spectra of the clear aqueous N-doped TiO₂ (~ 500 ppb Ti) suspensions used in these experiments: (A) doped at ambient temperature according to ref 7; (H) doped at high-temperature according to ref 20. See text for details.

Clear, aqueous suspensions of the photocatalysts were prepared by suspending the synthesized A nanoparticles (0.15 or 1.5 g L⁻¹), or by centrifugation (5–10 min at 5000 rpm) of 0.15 g L⁻¹ H or Degussa P25 TiO₂ slurries previously sonicated in a Branson 1210 Sonic Bath for 30 min, before each photochemical experiment. The actual Ti concentration in the centrifuged suspensions was determined by ICP-MS analysis (HP 4500 inductively coupled plasma mass spectrometer). The ultraviolet absorption spectra of these suspensions are shown in Figure 1.

Continuously stirred, clear solutions of photocatalyst 0.1 or 1 mM in formate, or 1 mM in hydroxylamine, or spiked with ~ 10 μ M MB, were suspended in fused silica cuvettes (1 cm optical path) kept at 10 ± 0.1 °C under 1 atm O₂ and irradiated for variable periods. The light source was an ozone-free 1000 W xenon arc lamp (Oriel) whose output traversed 10 cm of water (to remove IR radiation), a focusing lens and a suitable spectral filter. Oriel band-pass (330 ± 10 nm), and long-wave ($\lambda > 400$ nm or $\lambda > 500$ nm) pass filters were used. Light fluxes were determined using the potassium ferrioxalate actinometer.³⁸ The photon rate incident on the cell was $I_0 = 4.58 \times 10^{-7}$ einsteins L⁻¹ s⁻¹ in the presence of the band-pass filter at 330 nm, and $I_0 = 3.04 \times 10^{-5}$ einsteins L⁻¹ s⁻¹ between 400 and 500 nm (a range obtained by using a long-wave $\lambda > 400$ nm pass filter in tandem with a short-wave $\lambda < 500$ nm pass filter). Aliquots of the irradiated solutions were withdrawn at appropriate intervals and analyzed. HCOO⁻ decay, or NO₃⁻ formation in the photocatalytic oxidation of HN₂OH, were followed using a Dionex DX500 ion chromatograph (Dionex IonPac AS11 column) equipped with a conductivity detector. The bleaching of MB (initial absorbance 0.8–1.0) was followed spectrophotometrically at $\lambda = 665$ nm.

The formation of the carbon dioxide radical anion, CO₂^{•-}, during the photocatalytic oxidation of HCOO⁻ was monitored by detecting its adduct with DMPO via electron spin resonance spectrometry at room temperature (Bruker EMX spectrometer, Bruker BioSpin GMBH, Germany). Typical instrumental conditions were as follows: central field, 0.349 T; sweep width, 10.0 mT; scans, 10–40; microwave power, 12.75 mW; microwave frequency, 9.8 GHz; receiver gain, 7.10×10^3 ; modulation frequency, 100 kHz; modulation amplitude, 0.2 mT; time constant, 10.24 ms; sweep time, 20.97 s. Formate (6.5 mM) + DMPO (1.5 mM) suspensions were photolyzed in the experimental setup previously described, and periodically transferred to a flat ESR cell for spectral analysis.³⁹ This procedure was chosen, over in situ irradiation in the flat EPR cell, to ensure oxygen saturation throughout. Radical concentrations were

estimated by comparing doubly integrated first derivative $\text{DMPO}-\text{CO}_2^{\bullet-}$ signals with those obtained using TEMPO solutions of known concentration at the same spectrometer settings.⁴⁰

Results and Discussion

Nitrogen doping at ambient or high-temperature conditions led to yellow powders absorbing into the visible up to 520 nm (Figure 1).^{7,20} The UV-vis diffuse reflectance spectra of the *H* powders revealed a shoulder at 451 nm, which is apparently associated with the Ti-N bond.⁴¹ The X-ray photoelectron spectra (XPS) of *A* surfaces revealed intense peaks at 399.6 and 404.5 eV in the N 1s region, as reported by Gole et al.⁷ In contrast, the peak at 396 eV in the XPS of *H* powders^{20,22} was weak and diffuse, even after Ar^+ -sputtering for variable periods (60–90 s, 4 keV), probably due to their low (<1%) nitrogen content.^{22,35}

We investigated the photocatalytic activity of *A* nanoparticles for aqueous formate degradation at $\lambda > 200$ nm and at $\lambda > 400$ nm. Undetectable degradation of HCOO^- (0.1 or 1 mM) was registered after 2 h of irradiation at $\lambda > 400$ nm in the presence of 0.15 g L^{-1} or 1.5 g L^{-1} of *A*. Exposure of the clear, yellowish colloidal *A* solutions to $\lambda > 200$ nm radiation irreversibly transformed them into opaque, white suspensions. The positive detection of C-H bond absorptions in the 2800–3000 cm^{-1} region of the FTIR spectra of fluorolube mulls of *A* powders reveals that TiO_2 "nitridation" leaves residual organic groups. We infer that the reaction between colloidal titanium dioxide and triethylamine at 298 K likely leads to the formation of surficial organotitanium complexes, rather than to substitutional N-doped TiO_2 , that are readily degraded by UV light.

The discoloration of methylene blue in the presence of *A* has been previously interpreted as evidence of photocatalytic activity in the visible.^{7,20} In our hands, the absorbance ($\lambda_{\text{max}} = 665$ nm) of MB solutions is reduced by 73% after 15 min exposure to $\lambda > 400$ nm radiation in the presence of 0.15 g L^{-1} of *A*, and by 15% in the presence of the same concentration of undoped colloidal TiO_2 (see Experimental Section). Extensive (72%) MB bleaching also occurs in N-doped TiO_2 suspensions upon 15 min irradiation at $\lambda > 500$ nm, i.e., beyond the absorption range of the photocatalyst. The comparable effects of $\lambda > 400$ nm and $\lambda > 500$ nm radiation suggest that the photocatalyst could be directly and indirectly involved in the mechanism of bleaching.^{18,31–34} It should be emphasized that the bleaching of MB in the visible ($\lambda > 500$ nm) may be partially driven by light absorbed by the dye (MB absorbs weakly in the 350–520 nm range)³⁰ rather than by the photocatalyst. The excited triplet $^3\text{MB}^*$ state thus created can inject an electron into the conduction band of N-doped TiO_2 ($E_{\text{MB}^*}^0/3\text{MB} = 0.71$ V).³⁴ If O_2 is present to scavenge the injected electrons and prevent back recombination, the degradation of $\text{MB}^{\bullet+}$ will ensue. Considering that at 10 μM MB can compete with O_2 for conduction band electrons under aerobic conditions,³⁰ and because neither Gole et al.⁷ nor Asahi et al.²⁰ provide information about O_2 levels in their experiments, it is impossible to assess the actual mechanism for the bleaching processes they observe, or the relevance of their results on the issue of the oxidative power of N-doped TiO_2 under visible illumination. Notably, we found that the absorbance of aqueous MB in the 500–600 nm range is unaffected by the presence of 0.15 g L^{-1} undoped colloidal TiO_2 , but decreases by $\sim 40\%$ in the presence of the same concentration of *A* in the dark, a fact that reveals strong interactions between ground-state MB and *A*. The higher affinity of MB for *A* surfaces may play a key role in the photosensitized mechanism of degradation.⁴²

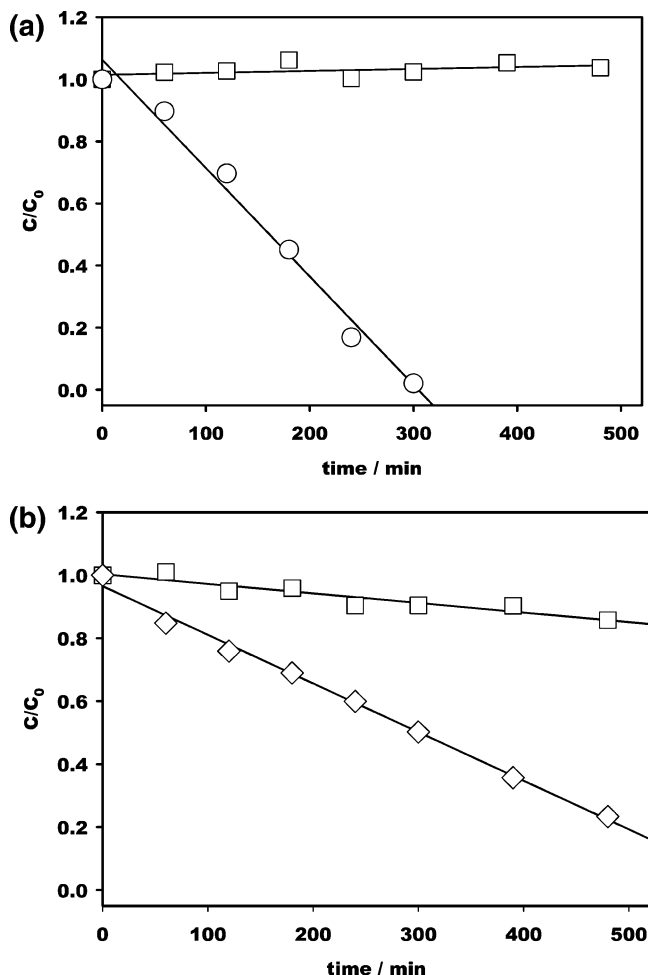


Figure 2. (A) Photocatalytic degradation of HCOO^- ($C_0 = 1$ mM) at pH ~ 6 , 10 $^\circ\text{C}$ in the presence of TiO_2 N-doped at high-temperature (*H*) under (□) $\lambda > 400$ nm and (○) $\lambda > 200$ nm irradiation. (B) Photocatalytic degradation of HCOO^- ($C_0 = 1$ mM) at pH ~ 6 , 10 $^\circ\text{C}$, in the presence of (□) *H* and (◇) Degussa P25 TiO_2 , under $\lambda = 330$ nm irradiation.

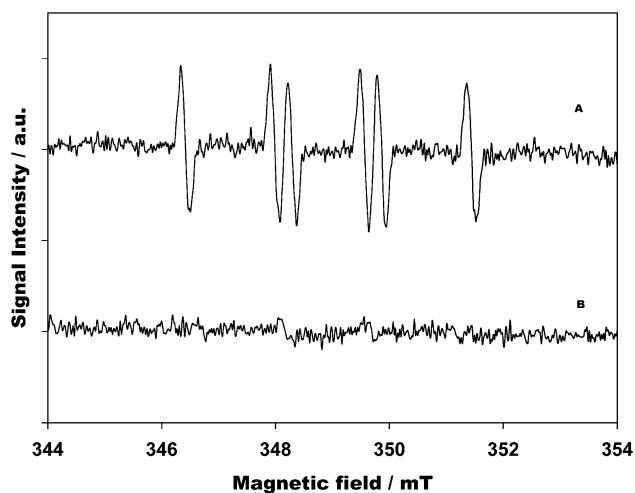
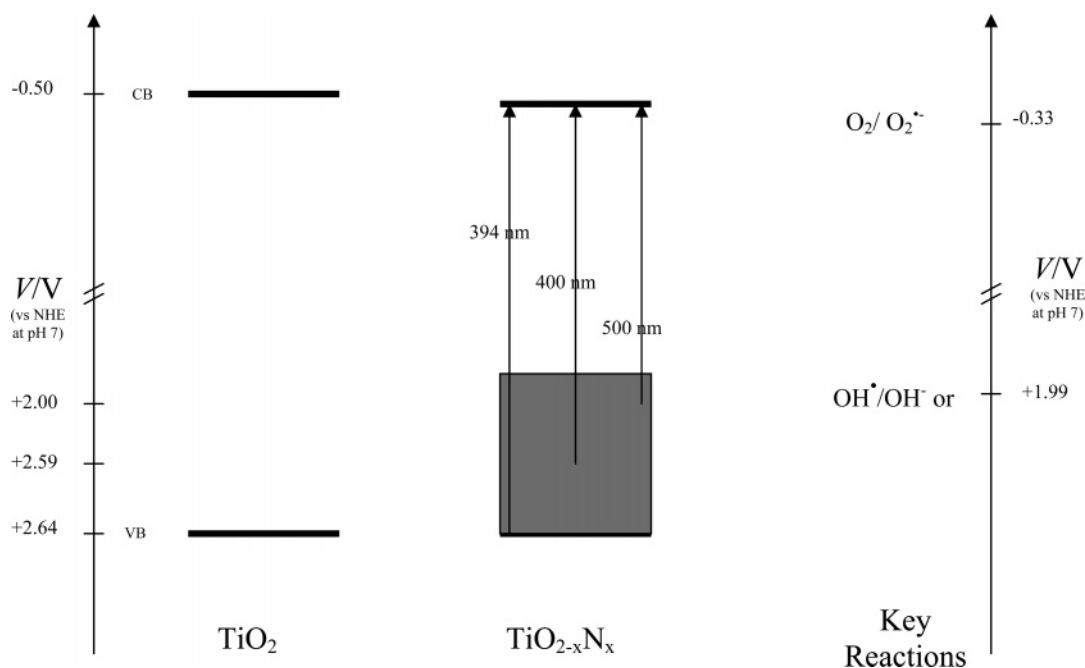


Figure 3. ESR spectra of $\text{DMPO}-\text{CO}_2^{\bullet-}$ formed in HCOO^- (6.5 mM) + DMPO (1.5 mM) solutions in the presence of TiO_2 N-doped at high-temperature (*H*) after 15 min irradiation at (A) $\lambda = 330$ nm and (B) $\lambda > 400$ nm.

Figure 2A shows the photocatalytic degradation of 1 mM HCOO^- in *H* suspensions exposed to $\lambda > 400$ nm and $\lambda > 200$ nm. These experiments provide clear evidence that *H* is an active photocatalyst for the oxidation of HCOO^- at $\lambda > 200$ nm, and

SCHEME 1: Electric Potential Diagram for TiO₂ and N-Doped TiO₂ in Aqueous Solutions at pH 7.0^a

^a Holes thermodynamically able to oxidize OH⁻ into •OH, or HCOO⁻ into CO₂^{•-} ($E^0_{\text{HCOO}^-/\text{CO}_2^{\bullet-}} \sim 1.9 \text{ V}$)⁴⁸ can be potentially generated on N-doped TiO₂ by $\lambda = 500 \text{ nm}$ photons. However, no free radicals were detected ($[\text{DMPO}-\text{CO}_2^{\bullet-}] < 2 \times 10^{-8} \text{ M}$) after 15 min irradiation with $\lambda > 400 \text{ nm}$ light.

an inactive one at $\lambda > 400 \text{ nm}$. Because formate only absorbs at $\lambda < 240 \text{ nm}$, the significant degradation of HCOO⁻ at $\lambda = 330 \pm 10 \text{ nm}$ in the presence of *H* and Degussa P25 TiO₂ suspensions (both suspensions were $\sim 500 \text{ ppb Ti}$, as determined by ICP-MS), see Figure 2B, is even more compelling. From the data of Figure 2B, the measured incident photon fluxes at $\lambda = 330 \text{ nm}$, and the corresponding suspensions absorbances, we were able to evaluate quantum yields for the oxidation of HCOO⁻:³⁶ $\varphi_F(H) = 0.056 \pm 0.019$, $\varphi_F(\text{TiO}_2) = 0.118 \pm 0.009$.

Because Miyauchi et al.²⁸ found that nitrogen doping shifts the zero charge point of TiO₂ to higher pH values, we also investigated the oxidation of hydroxylammonium, NH₃OH⁺, $pK_b = 8.04$, as a representative of a cationic (vs HCOO⁻) donor, into NO₃⁻ in *H* suspensions under visible light.⁴³ The reversal of substrate polarity could influence adsorption, and hence degradation rates, but we found that, similarly to the HCOO⁻ case, NH₃OH⁺ is readily oxidized to NO₃⁻ at $\lambda > 200 \text{ nm}$, but not at all at $\lambda > 400 \text{ nm}$.

Because the preceding assertions about the negligible photocatalytic activity of N-doped TiO₂ for HCOO⁻ degradation at $\lambda > 400 \text{ nm}$ are strictly statements about a small upper bound to φ_F , we sought to lower this bound by spin-trapping the CO₂^{•-} radical produced in the one-electron oxidation of HCOO⁻.⁴⁴ Direct HCOO⁻ oxidation by holes, reaction 1, or mediated by OH-radicals, reaction 2, should produce the carboxyl radical anion, CO₂^{•-}, which can be trapped by 5,5-dimethyl-1-pyrroline *N*-oxide (DMPO) as DMPO-CO₂^{•-}, reaction 3:^{39,45,46}

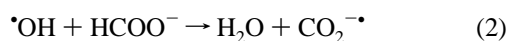
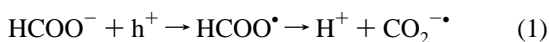


Figure 3 shows the electron spin resonance (ESR) spectra of HCOO⁻ (6.5 mM) + DMPO (1.5 mM) + *H* N-doped TiO₂ suspensions exposed for 30 min to $\lambda = 330 \text{ nm}$ (A), and $\lambda >$

400 nm (B). The species produced by UV irradiation can be assigned to a DMPO-CO₂^{•-} adduct possessing $a^N = 1.58 \text{ mT}$, $a^H = 1.91 \text{ mT}$ hyperfine splittings and a *g*-factor of 2.0062, as reported in the literature.^{39,45,46} The intensity of the signal corresponds to $[\text{DMPO}-\text{CO}_2^{\bullet-}] \sim 5 \mu\text{M}$, as determined by calibrations made with TEMPO solutions of known concentration under identical instrumental settings.⁴⁰ No DMPO-CO₂^{•-} was formed in solutions kept in the dark. By assuming that any DMPO-CO₂^{•-} signals generated in experiments performed with $\lambda > 400 \text{ nm}$ irradiation fail to exceed the noise, i.e., by assuming a threshold signal-to-noise ratio $S/N \sim 2$, we estimate a quantum yield of $\varphi_F \leq 2 \times 10^{-5}$.

The above results unequivocally show that the illumination of aqueous N-doped TiO₂ suspensions with $\lambda > 400 \text{ nm}$ light does not produce oxidizing species powerful enough to oxidize formate or hydroxylamine. Scheme 1 depicts the inferred effect of nitrogen doping on the band system of titanium dioxide. The conduction band level in TiO_{2-x}N_{0.67x} materials is negligibly shifted relative to anatase:²⁷ the flatband potential of N-doped TiO₂ at pH 7.0 was found to be $-0.48 \pm 0.01 \text{ V}$ vs $-0.52 \pm 0.01 \text{ V}$ for TiO₂. A small shift in the conduction band energy should have been particularly consequential because the reduction potential of O₂, the key electron scavenger: $E^0_{\text{O}_2/\text{O}_2^{\bullet-}} = -0.33 \text{ V}$,⁴⁷ is critically close to the flatband potential. Our experiments therefore imply that band gap narrowing by N-doping is largely due to the creation of occupied states above the valence band of TiO₂ ($E_{\text{VB}} = 2.64 \text{ V}$ at pH 7)²⁷ and that the oxidizing species ultimately generated at the interface after the promotion of such states by means of visible illumination are thermodynamically or kinetically unable to oxidize weak, albeit typical, donors such as HCOO⁻ ($E^0_{\text{CO}_2^{\bullet-}/\text{HCOO}^-} \sim 1.9 \text{ V}$),⁴⁸ despite that absorption of $\lambda = 500 \text{ nm}$ photons creates vacancies at $+2.0 \text{ V}$.^{14,27} In other words, the faradaic electrochemical processes responsible for the photocurrents observed by Nakato et al.,^{35,49} in N-doped TiO₂/0.1 M HClO₄ interfaces under visible light produce neither free nor adsorbed OH-radical intermediates, nor any other species that could have oxidized HCOO⁻ into

$\text{CO}_2^{\bullet-}$ under present conditions.⁵⁰ These irreversible processes involve water and TiO_2 , efficiently compete with the direct oxidation of potential donors, and degrade the oxidative power of the photogenerated holes in aqueous media at all wavelengths, particularly those produced by visible illumination. The fact that acetone vapor, with $E^0_{\text{Ac}^{\bullet}/\text{AcH}} \sim E^0_{\text{CO}_2^{\bullet-}/\text{HCOO}^-} \sim 1.9 \text{ V}$



is readily oxidized on N-doped TiO_2 under visible illumination,^{22,28} whereas aqueous HCOO^- does not, actually confirms the conclusion that water impairs the efficiency of TiO_2 photocatalysts. Present results are consistent with the fact that the N-doped TiO_2 photocatalyzed hydroxylation of benzoic acid into salicylic acid at $\lambda > 400 \text{ nm}$ is blocked by substituting tetranitromethane for O_2 as electron scavenger²⁷ but eliminates OH radicals as the hydroxylating agent.

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