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Selective Photocatalytic Oxidation of NH_3 to N_2 on Platinized TiO_2 in Water

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Selective photocatalytic oxidation of NH_3 to N_2 is proposed as a new treatment method for controlling the levels of ammonia in water. The photocatalytic oxidation of ammonia on naked and metallized TiO_2 in water saturated with air, nitrogen, or N_2O gas was investigated. While the slow photocatalytic oxidation of NH_3 to $\text{NO}_2^-/\text{NO}_3^-$ is the only pathway for decomposition of NH_3 on naked TiO_2 and Au/TiO_2 , a new pathway, that of selective oxidation of ammonia to dinitrogen, opens up on Pt/TiO_2 . The formation of dinitrogen from the oxidation of $^{15}\text{NH}_3$ was confirmed by mass spectrometric detection of $^{15}\text{N}_2$. The photocatalytic conversion of NH_3 to N_2 greatly increases when the Pt/TiO_2 suspension is saturated with N_2O gas, whereas N_2O itself shows little reactivity with naked TiO_2 and Au/TiO_2 . Over 80% of the total nitrogen available in ammonia (0.1 mM) is converted into N_2 within 40 min illumination of the N_2O -saturated Pt/TiO_2 suspension. The ability of N_2O to accept the conduction band electrons of Pt/TiO_2 was verified by photoelectrochemical measurements. N_2O reductively decomposes to generate OH radicals on Pt/TiO_2 ; the rate of ammonia degradation in the N_2O -saturated Pt/TiO_2 suspension significantly decreases in the presence of excess *tert*-butyl alcohol, an OH radical scavenger. The presence of Pt deposits on the TiO_2 particles changes the photocatalytic pathway of ammonia conversion by both enhancing OH radical production from N_2O and stabilizing intermediate NH_x ($x=0,1,2$) species to facilitate their recombination into N_2 .

Introduction

Ammonia is one of the major nitrogen-containing pollutants in wastewater; it is a source of nutrients that may accelerate the eutrophication of and algal growth in natural waters and is a common product of the chemical/biological transformation of organic nitrogenous pollutants (1). High concentrations of ammonia in wastewater effluents deplete dissolved oxygen, reduce chlorine disinfection efficiency, and exhibit acute toxicity to aquatic life. The World Health Organization also recommends that the total amount of ammonia in drinking water should not exceed 1.5 mg/L since it causes a disagreeable taste and smell at trace levels. To cope with the deterioration of water quality produced by the discharge of ammonia into aquatic systems, several chemical and physical methods have been developed and applied in the field such as air stripping, ion exchange, and breakpoint

chlorination (1, 2). Among these methods, the biological nitrification/denitrification process is generally regarded as the most efficient method for remediating high concentrations of ammonia in wastewater (1).

The increasing interest in advanced oxidation processes (AOPs) has encouraged researchers to investigate their applicability to the removal of ammonia from water (3–10). In the 1970s, the ozonation process was proposed as a method for oxidation of ammonia in wastewater (5, 6). A few studies also reported the photocatalytic oxidation of ammonia using titanium dioxide (3, 4, 8–10). These oxidation processes, which involve hydroxyl radicals as a primary oxidant, transform ammonia into nitrite/nitrate quantitatively. However, since nitrite/nitrate is more toxic than ammonia, a better remediation process would be to convert ammonia into dinitrogen. In fact, there are electrochemical oxidation processes that have been reported as converting ammonia into dinitrogen on platinum electrodes (11, 12).

Semiconductor photocatalysis has been made use of in a variety of chemical conversion systems (13). While much research has been directed toward achieving nitrogen fixation ($\text{N}_2 \rightarrow \text{NH}_3$) using photocatalysis as a part of solar energy conversion technology (14–16), the reverse photocatalytic conversion has not been reported. Since most photocatalytic remedial action is enabled by the strong oxidizing power of OH radicals (10, 17, 18), it is very difficult to attain selectivity in TiO_2 photocatalytic reactions. In the case of the oxidation of ammonia, the problem is how to convert ammonia [$\text{N}(-\text{III})$] selectively to dinitrogen [$\text{N}(0)$], not to completely oxidized nitrate [$\text{N}(+\text{V})$]. Among the many possible methods of modifying photocatalyst reactivities, metallization has been frequently tried. Deposition of noble metals such as Pt, Pd, Au, and Ag on semiconductor surfaces enhances their photocatalytic efficiency by retarding electron–hole recombination (19, 20). Semiconductors coated with these metal deposits have been used successfully in various systems for remediation of polluted water and air and have exhibited high efficiency in photocatalytic reduction processes (19–23). The presence of metal deposits not only enhances photocatalytic activity but also in general changes reaction pathways.

In this work, we demonstrate that NH_3 can be selectively converted to N_2 on platinized TiO_2 under UV illumination. Pt deposits on TiO_2 stabilize the intermediate atomic nitrogen species and thus facilitate their recombination into dinitrogen. The conversion of NH_3 to N_2 is particularly effective when the system is saturated with N_2O . In contrast to biological ammonia conversion which is a two-step process (nitrification/denitrification), the present photocatalytic transformation proceeds in a single step.

Experimental Section

Chemicals and Materials. NH_4Cl (Aldrich), $^{15}\text{NH}_4\text{Cl}$ (Aldrich), NaNO_2 (Aldrich), NaNO_3 (Aldrich), N_2H_4 (Aldrich), NH_2OH (Aldrich), HAuCl_4 (Sigma), H_2PtCl_6 (Aldrich), and *tert*-butyl alcohol (*t*-BuOH) (Shinyo) were used as received. For the analysis of hydroxylamine levels, FerroZine reagent, $\text{NH}_4(\text{CH}_3\text{CO}_2)$, and $\text{Fe}(\text{ClO}_4)_3$ were purchased from Aldrich. The gases (air, Ar, N_2 , and N_2O) used were of > 99% purity. Air, Ar, and N_2 were obtained from BOC–Gases and N_2O was obtained from Dongbang Inc. The water used was ultrapure (18 $\text{M}\Omega\cdot\text{cm}$) and prepared with a Barnstead purification system. Titanium dioxide (Degussa P25), a mixture of 80% anatase and 20% rutile, was used as the photocatalyst. Other chemicals used were of the highest purity available.

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Preparation of Metallized TiO₂. Metallization of TiO₂ was carried out using a photodeposition method. Platinization was carried out by irradiating (with a 200 W medium-pressure mercury lamp) an aqueous suspension of TiO₂ (0.5 g/L) for 30 min in the presence of 1 M methanol (electron donor) and 0.1 mM chloroplatinic acid (H₂PtCl₆). After irradiation, the filtered Pt/TiO₂ sample was collected and washed with distilled water. The concentration of unused chloroplatinic acid remaining in the filtrate solution after photodeposition was determined by inductively coupled plasma-atomic emission spectroscopy (ICP-AES, Thermo Jarrell Ash Cooperation IRIS/AP) in order to quantify the amount of deposited Pt. A typical Pt loading on the TiO₂ particles was estimated to be ca. 0.2 wt %. Au was photodeposited from chloroauric acid onto the TiO₂ particles by following a similar procedure. Transmission electron micrographic images of Pt/TiO₂ showed that the resulting Pt particles were in the size range 1–2 nm and were well dispersed on the TiO₂ particles (20–30 nm).

Photolysis and Analysis. All naked or metallized TiO₂ suspensions were prepared in water at a concentration of 0.5 g/L and were dispersed by simultaneous sonication and shaking for 30 s in an ultrasonic cleaning bath. The substrate NH₃ stock solution (10 mM) was added to the suspensions to make the desired concentration (typically 0.1 mM), and then the pH of the suspensions was adjusted to pH 10.0 with 1 M NaOH standard solution. For the experiments in the presence of various dissolved gases such as air, Ar, N₂, and N₂O, the reactor was continuously purged with the corresponding gas. Assuming saturation at room temperature, the concentration of dissolved O₂ (under air-saturation), N₂, and N₂O in the suspensions was 0.26, 0.66, and 24 mM, respectively. Loss of ammonia due to volatilization and adsorption onto TiO₂ surfaces was minimal within the time scale of the present experiments. After gas bubbling for 30 min, photolysis was commenced using a 300 W Xe-arc lamp (Oriol). The light was passed through a 10 cm IR water filter and a UV cutoff filter ($\lambda > 300$ nm). The filtered light was focused onto a 200 mL Pyrex reactor with a quartz window. The photocatalytic reactor was filled with minimized headspace, sealed with a rubber septum, and stirred magnetically. Sample aliquots of 1.5 mL were withdrawn from the illuminated reactor with a 2 mL syringe, filtered through a 0.45 μ m PTFE filter (Millipore), and injected into a 4 mL glass vial. More than a duplicate set of photolysis experiments were carried out for a given condition.

Quantitative analyses of the ionic intermediates and products were performed using an ion chromatograph (IC, Dionex DX-120). The IC system was equipped with a Dionex IonPac AS-14 for detection of anions, a Dionex IonPac CS-12A for detection of cations, and a conductivity detector. The possible formation of NH₂OH as an intermediate was checked colorimetrically using a FerroZine method in which hydroxylamine reduces Fe(III) species to Fe(II) species whose complexes with FerroZine can be detected by visible light absorption (24, 25). Aliquots (each of 0.5 mL) of Fe(III) (0.5 mM), ammonium acetate buffer, and FerroZine (10 mM) were mixed with 3.5 mL of sample solution. After 1 h of color development, the concentration of NH₂OH in the samples was determined by monitoring the absorbance at 562 nm. The detection limit for NH₂OH with the FerroZine method is less than 10 μ M, according to the literature (25).

GC/MS Analysis for Detecting ¹⁵N₂. Qualitative identification of the N-containing gas products evolved from the ammonia oxidation was carried out by using gas chromatography/mass spectrometry (GC/MS). To distinguish atmospheric N₂ from the dinitrogen produced by the photocatalytic oxidation of ammonia, ¹⁵NH₄Cl (98% atom ¹⁵N, Aldrich) was used as the source of ammonia. A much higher ammonia concentration (1 mM) was employed for this

purpose. A Pyrex reactor with a quartz window and a sampling port was purged with ultrapure Ar gas for 30 min prior to the photolysis, and then the sampling port was sealed. The gas trapped in the reactor headspace during the photolysis was sampled by a 500 μ L gastight syringe and analyzed by injection into a GC/MS. The GC/MS system consisted of a gas chromatograph (HP 6890) equipped with a HP-5DB column and a mass selective detector (HP 5973 MSD). The electron impact energy for ionization was 70 eV.

Photoelectrochemical Measurements. The effects of the purging gases on the photoelectrochemical characteristics of the TiO₂ and Pt/TiO₂ electrodes were compared. TiO₂ electrodes were prepared as described previously (26). One milliliter of TiO₂ suspension (5 wt %) was spread over indium tin oxide (ITO) glass (1 \times 1 cm²; Samsung) and dried. This TiO₂/ITO electrode was then heated at 450 $^{\circ}$ C for 30 min. For Pt deposition onto a TiO₂ electrode, the electrode was immersed in an aqueous solution of 0.4 g/L H₂PtCl₆ and 0.1 M methanol and illuminated with a 200 W Hg lamp for 2 h. The photoelectrochemical reactor was cylindrical and had a working electrode (TiO₂ or Pt/TiO₂), a reference saturated calomel electrode (SCE), a counter Pt-gauze electrode, and a gas injection port. The electrolyte used was distilled water or 0.1 mM NH₄Cl at pH 10 and the purging gas was O₂, N₂, or N₂O. The UV light source was three 10 W black-light lamps (Sankyo Denki) and the UV intensity was 0.13 mW \cdot cm⁻² at 30 W. Open-circuit potentials and short-circuit currents were measured by a potentiostat (EG&G, Model 263A) that was connected to a computer.

Results and Discussion

The Photocatalytic Degradation of NH₃ under Air and N₂ Saturation. The removal of ammonia and the formation of intermediates and products during the course of photocatalytic degradation on naked and metallized TiO₂ in air-saturated conditions are compared in Figure 1. Ammonium ions (NH₄⁺) have little reactivity with OH radicals (27, 28) and do not degrade at all in the UV/TiO₂ system (3, 4, 8–10), whereas neutral ammonia degrades on TiO₂ photocatalytically (4, 8–10). Therefore, all the photolysis experiments in the present work were carried out at pH 10–11 (above ammonia's pK_a=9.3). The photocatalytic degradation of ammonia on naked TiO₂ (Figure 1a) is slow and results in its stoichiometric conversion to NO₂⁻ and NO₃⁻, which agrees with previous results (8–10). The total N-mass balance could be satisfactorily accounted for throughout the photolysis, which indicates that there were no other products. The slight decrease in total-N shown in Figure 1a,b could be due to volatile loss or adsorption of ammonia. Au/TiO₂ showed a similar reactivity to naked TiO₂, except that NO₂⁻ production was higher than that of NO₃⁻ (Figure 1b). On the other hand, the photocatalytic degradation of ammonia on Pt/TiO₂ (Figure 1c) was much faster and was accompanied by a significant reduction in the total N-mass, which implies the presence of other products. Hydrazine (N₂H₄) might be produced through the dimerization of the amino radicals (NH₂•) that form from the reaction of NH₃ with OH radicals. Although N₂H₄ has not been reported as an intermediate of ammonia degradation in photocatalytic systems (8–10), its formation has been suggested by a pulse radiolytic study of the oxidation of Ni^{II}(NH₃)_n complexes by NH₂• radicals (27). In this study, however, IC analysis detected no sign of hydrazine formation. The presence or otherwise of hydroxylamine (NH₂OH) was also checked according to the method described in the Experimental Section but was produced only at concentrations beneath the detection limit (<10 μ M), if at all.

Figure 2 shows the results of the photocatalytic degradation of ammonia under N₂ saturation. In the absence of dissolved oxygen, NH₃ degradation on naked TiO₂ was

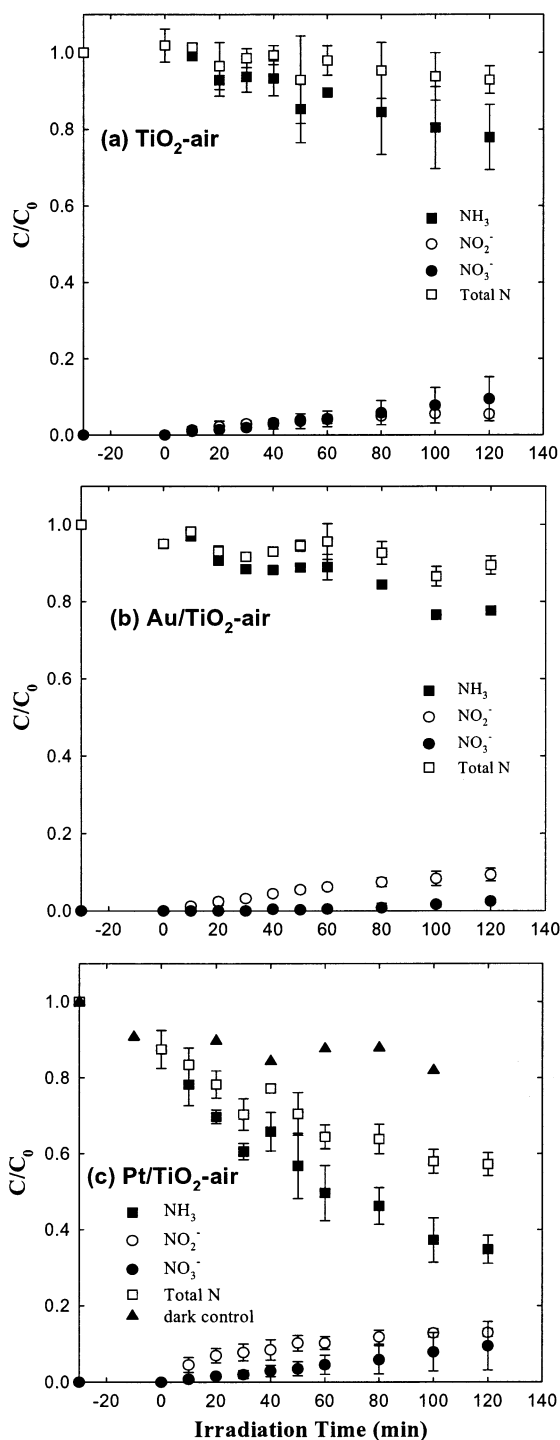


FIGURE 1. Photocatalytic conversion of NH_3 ($C_0 = 0.1 \text{ mM}$) with (a) naked TiO_2 , (b) Au/TiO_2 , and (c) Pt/TiO_2 under air-equilibrated conditions. The irradiation was started at time "zero" after 30 min equilibration. The ordinate scale, C/C_0 , refers to concentrations normalized with respect to the initial ammonia concentration. The reactor was open to the air during irradiation. The loss of NH_3 through volatilization was insignificant. Other experimental conditions were $\text{pH} = 10$; $[\text{TiO}_2] = 0.5 \text{ g/L}$.

negligible, whereas its degradation was slightly enhanced on Au/TiO_2 and much enhanced on Pt/TiO_2 . It is interesting to note that the kinetics of ammonia oxidation on metallized TiO_2 (for both Au/TiO_2 and Pt/TiO_2) showed little dependence on whether dioxygen was present (compare Figures 1 and 2). Ammonia oxidation on Pt/TiO_2 in the anoxic suspension also showed a significant mass deficit in the total N balance.

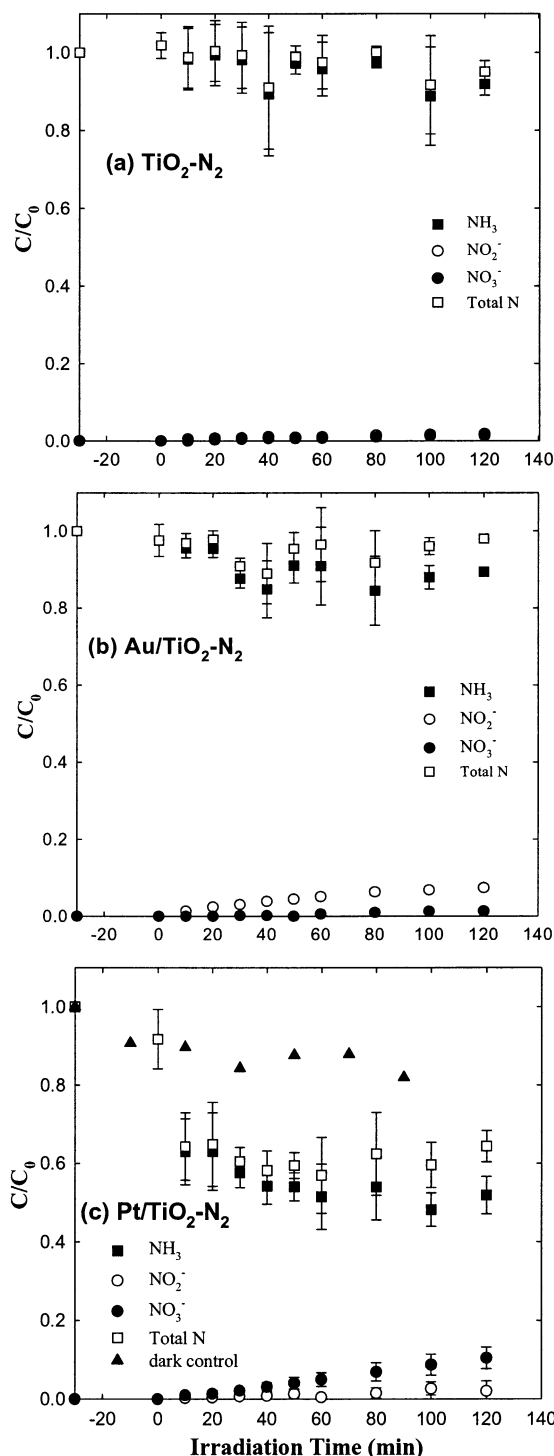


FIGURE 2. Photocatalytic conversion of NH_3 ($C_0 = 0.1 \text{ mM}$) with (a) naked TiO_2 , (b) Au/TiO_2 , and (c) Pt/TiO_2 under N_2 -saturated conditions. The suspension was continuously purged with N_2 during irradiation. The loss of NH_3 through volatilization was insignificant. Other experimental conditions were the same as those for Figure 1.

This implies that gaseous products such as N_2 , NO , and N_2O are generated as a result of NH_3 degradation.

The Photocatalytic Degradation of NH_3 under N_2O -Saturation. Figure 3 shows the influence of N_2O on the photocatalytic oxidation of ammonia on naked TiO_2 , Au/TiO_2 , and Pt/TiO_2 . Nitrous oxide, which scavenges the aqueous electrons produced by the γ -radiolysis of water (27, 29), has often been used as an alternative to dioxygen as a conduction band (CB) electron acceptor in semiconductor

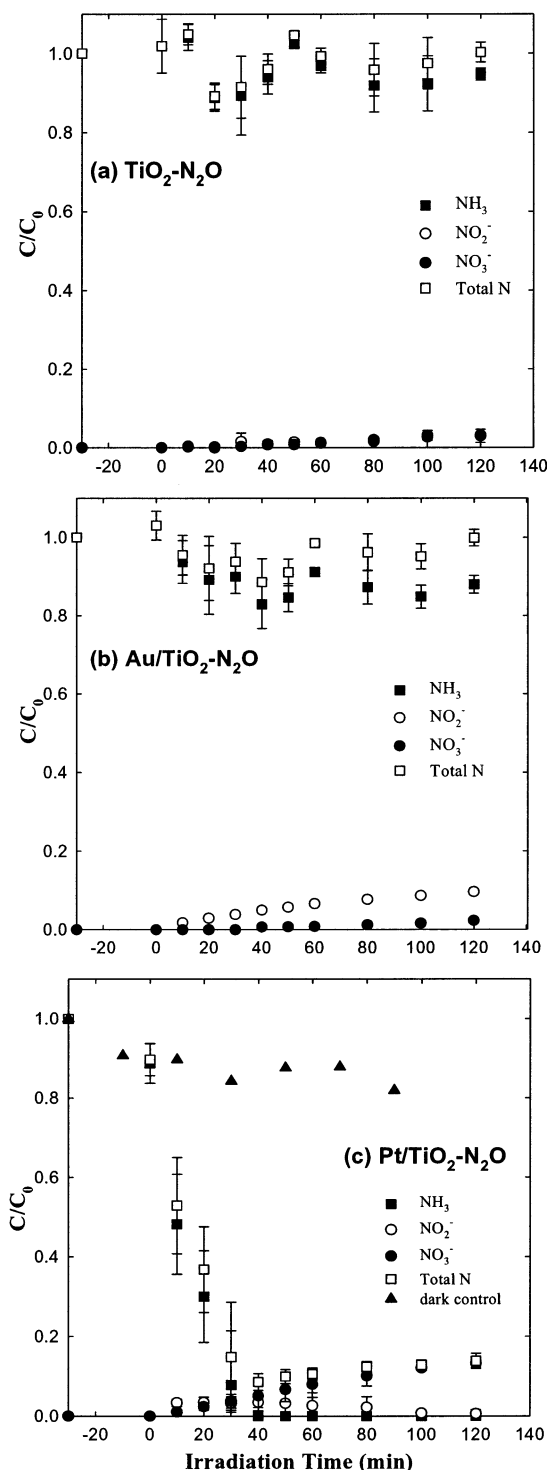
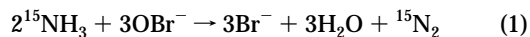


FIGURE 3. Photocatalytic conversion of NH_3 ($C_0 = 0.1 \text{ mM}$) with (a) naked TiO_2 , (b) Au/TiO_2 , and (c) Pt/TiO_2 under N_2O -saturated conditions. Other experimental conditions were the same as those for Figure 1.

photocatalytic reactions (30–36). N_2O has been shown to scavenge CB electrons trapped on ZnO (30–34) and TiO_2 (34, 35). However, N_2O has been reported to have little activity on TiO_2 surfaces as an electron acceptor with respect to enhancing the self-decomposition of N_2O (36) and to the photocatalytic degradation of organic compounds (33, 34), although it has shown activity in photocatalytic reactions on ZnO surfaces (30–34). In accordance with these previous observations, we found that N_2O activity differed little from N_2 activity in inducing the photooxidation of NH_3 on naked

TiO_2 and Au/TiO_2 (Figure 3a,b). However, N_2O on Pt/TiO_2 produced a dramatically enhanced effect (Figure 3c): the NH_3 in the Pt/TiO_2 suspension disappeared completely within 40 min, and less than 20% of the total NH_3 depleted was converted into $\text{NO}_2^-/\text{NO}_3^-$, which reassured the presence of gaseous products generated on Pt/TiO_2 . The different reactivities of N_2O with the TiO_2 and Pt/TiO_2 surfaces have been previously recognized: decomposition of N_2O into N_2 and O_2 does not occur on naked TiO_2 but does on Pt/TiO_2 (36). The high efficiency of N_2O as an electron acceptor should be responsible for the complete removal of NH_3 on Pt/TiO_2 . We checked the possibility that N_2O decomposition might produce $\text{NO}_2^-/\text{NO}_3^-$ by carrying out an N_2O photolysis in a Pt/TiO_2 suspension in the absence of NH_3 . No NO_2^- and NO_3^- were detected throughout the N_2O photolysis. Any further UV irradiation beyond the point of complete removal of NH_3 increased the concentration of NO_3^- (Figure 3c) only marginally, which indicates that no other intermediate that could be oxidized to NO_3^- was produced in the N_2O – Pt/TiO_2 system. Most of the ammonia removed by photocatalysis on Pt/TiO_2 seemed to have been converted into gaseous products.

Analysis of Gas Products by GC/MS. In the mass spectra obtained from the GC/MS analysis we detected a peak at $m/e = 30$ ($^{15}\text{N}_2$), produced by the photocatalytic oxidation of $^{15}\text{NH}_3$ on Pt/TiO_2 . A similar experiment using naked TiO_2 did not produce any $m/e = 30$ signal. Mass peaks corresponding to other gaseous nitrogen compounds such as $^{15}\text{-NO}$ and $^{15}\text{N}_2\text{O}$ also could not be detected. Although a direct quantification of the amount of evolved $^{15}\text{N}_2$ could not be achieved in this experiment, a relative abundance comparison of the $^{15}\text{N}_2$ generated from the photocatalytic oxidation of $^{15}\text{NH}_3$ on Pt/TiO_2 and the $^{15}\text{N}_2$ produced by a chemical oxidation of $^{15}\text{NH}_3$ was carried out. The chemical oxidant used was hypobromite (OBr^-), which has been reported as transforming ammonia into dinitrogen through the following reaction (37):

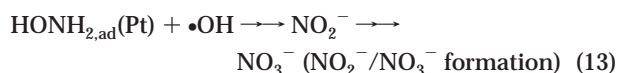
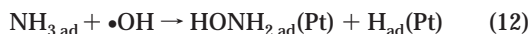
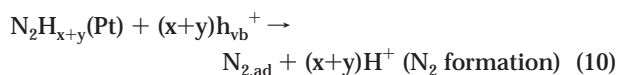
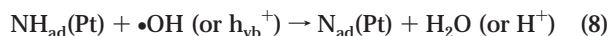
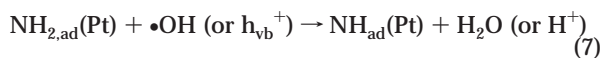
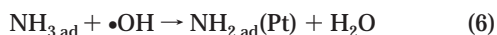
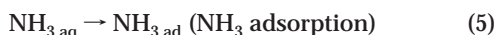
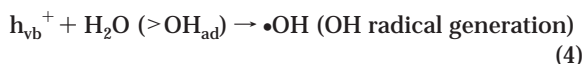


Hypobromite was prepared by adding bromine to a solution of lithium hydroxide. Under conditions similar to those of the photocatalytic experiment, the oxidation of $^{15}\text{-NH}_3$ was initiated by injecting excess hypobromite into an ammonia solution after 30 min of Ar gas purging. The IC analysis showed that the complete chemical oxidation of the ammonia was achieved without formation of ionic products such as NO_2^- and NO_3^- . GC/MS analysis of the headspace gas after the completion of chemical oxidation also detected a mass peak of $m/e = 30$, whose intensity was a little higher than that obtained from the photocatalytic oxidation of $^{15}\text{NH}_3$ on Pt/TiO_2 . This confirms that most of the NH_3 on Pt/TiO_2 was photocatalytically transformed into N_2 in this study. Since the nitrite, nitrate, and dinitrogen are the observed products of the photocatalytic conversion of ammonia, the N-mass deficits shown in Figures 1c, 2c, and 3c should be ascribed to dinitrogen. Based on this fact, the conversion efficiency of NH_3 to N_2 on Pt/TiO_2 after 2 h irradiation is estimated to be 65–70% in air- or nitrogen-saturated suspensions and over 80% under N_2O saturation.

The Effects of Pt on the Dinitrogen Formation Mechanism. While group VIII metals on semiconductors are known to trap CB electrons and subsequently to enhance interfacial electron transfers through a Schottky barrier, their catalytic effects on photoinduced reactions should also be considered. Platinum has been used as a catalyst in various heterogeneous reactions such as hydrogen–deuterium exchange, hydrogenation of ethylene, and oxidation of carbon monoxide (20, 38). The transition metals such as Pt, Pd, and Rh have been reported to have a stronger affinity for ammonia than the

coinage metals (Cu, Ag, and Au) (12). Computed adsorption energies of atomic nitrogen on noble metals have shown that the Pt surface (-394 kJ mol^{-1}) has an optimal moderate atomic nitrogen affinity for the production of dinitrogen in comparison with the affinities of Ru (-525 kJ mol^{-1}) and Rh (-448 kJ mol^{-1}), on which N atoms are too tightly bound to recombine; Au (-162 kJ mol^{-1}) and Ag (-156 kJ mol^{-1}) bond with N atoms too weakly to produce active intermediates (12).

Due to this unique property of Pt as a catalyst, ammonia can be transformed into dinitrogen on platinum electrodes by electrochemical oxidation (11, 12): NH_3 adsorbed on a Pt electrode is oxidized to NH_x radical species ($x = 1, 2$) that are subsequently transformed into N_2 through their diffusion and recombination. In accordance with this scheme, N, NH, and NH_2 radical species formed by thermally activated oxidation of NH_3 have been shown using surface spectroscopic techniques to be stabilized on the Pt (111) and Pt (100) surface (39, 40). On the other hand, a similar electrochemical oxidation study (12) reported that NH_3 conversion to N_2 was inactive on Cu, Ag, and Au electrodes, which agrees with our observation that Au/TiO₂ is inactive. Judging from our results and these previous findings, dinitrogen formation seems to be enabled by the stabilization of the intermediate NH_x species on Pt deposited on TiO₂. Based upon an electrochemical mechanism proposed by Gerischer and Mauerer (11), the following reaction steps are suggested here as a plausible mechanism for the selective photocatalytic conversion of NH_3 to N_2 on Pt/TiO₂. However, it should be noted that the photocatalytic mechanism could be different from the electrochemical mechanism and thus needs further experimental verification.



Gerischer and Mauerer (11) proposed that the active intermediates for dinitrogen formation were NH_x ($x=1,2$) species and that the formation of N_{ad} deactivated the electrode surface. The formation of active intermediates NH_x on the naked TiO₂ surface is not favored so reaction 13 should be dominant, as we observed.

The favorable adsorption of nitrogen species such as NH_3 and NH_x ($x=0,1,2$) onto the Pt surface is a prerequisite for the selective photocatalytic oxidation of NH_3 to N_2 . Figure 4 shows that NH_3 adsorption characteristics are notably different between naked TiO₂, Au/TiO₂ and Pt/TiO₂ surfaces. Although the volatile loss of NH_3 is negligible at $[\text{NH}_3]_0 = 0.1$

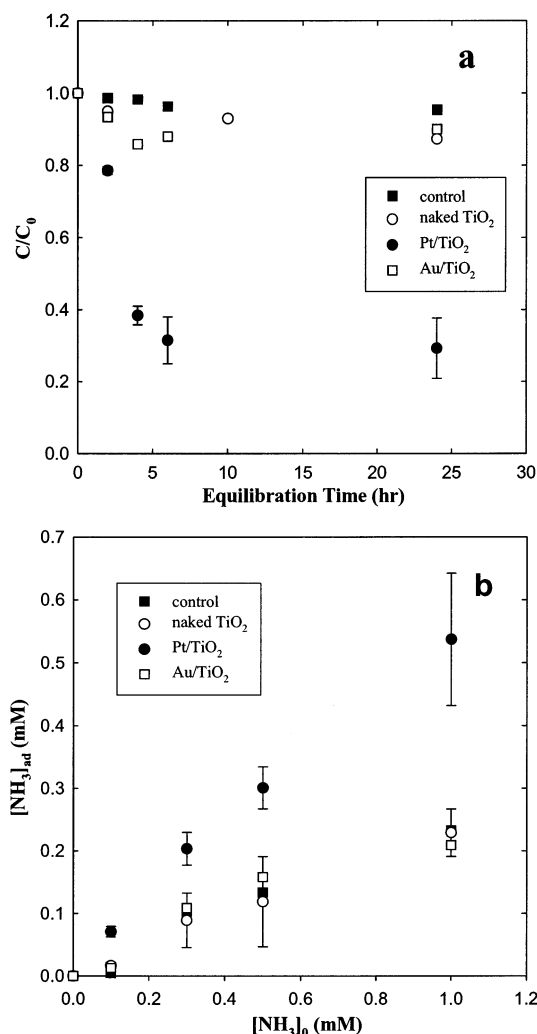


FIGURE 4. Dark adsorption of NH_3 on naked TiO₂, Au/TiO₂, and Pt/TiO₂. (a) The adsorptive removal of NH_3 ($C_0 = 0.1 \text{ mM}$) on naked TiO₂, Au/TiO₂, and Pt/TiO₂ as a function of the equilibration time and (b) the adsorption isotherms of NH_3 on naked TiO₂, Au/TiO₂, and Pt/TiO₂ ($[\text{NH}_3]_{\text{ad}}$ measured after 24 h equilibration). The control experiments were done in the absence of photocatalysts in order to estimate the volatile loss. The experimental conditions were $\text{pH} = 10$; $[\text{TiO}_2] = 0.5 \text{ g/L}$; air-equilibrated.

mM, it becomes significant at higher concentrations (Figure 4b). The isotherms of naked TiO₂ and Au/TiO₂ are almost identical with the control data, which indicates that the adsorption of NH_3 onto naked TiO₂ and Au/TiO₂ is negligible. On the other hand, Pt/TiO₂ exhibits a much higher adsorption affinity for NH_3 . The adsorption of ammonia onto Pt/TiO₂ proceeded gradually over 6 h and further equilibration produced little change (Figure 4a). The slow adsorption kinetics of ammonia on Pt/TiO₂ implies that the photocatalytic conversion process could be limited by diffusion effects. The markedly decelerating rates of ammonia removal shown in Figures 1c and 2c reflect the fact that the initial surface concentration of ammonia on Pt/TiO₂ was rapidly depleted but only slowly replenished from the bulk aqueous phase. Although the present photolysis experiments were performed after 30 min equilibration, a much longer preirradiation equilibration should yield higher conversion rates of ammonia on Pt/TiO₂. The adsorption isotherm of ammonia on Pt/TiO₂ (Figure 4b) shows no sign of saturation up to $[\text{NH}_3]_0 = 1 \text{ mM}$, which implies that all the experiments in this work were performed at surface concentrations of NH_3 that are far below monolayer coverage.

TABLE 1. Effects of Purging Gases on the Open-Circuit Voltage (E_{OC}) and Short-Circuit Current (I_{SC}) in a Photoelectrochemical Cell with TiO_2 or Pt/TiO_2 Electrode

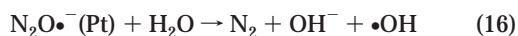
electrode/ electrolyte	ΔE_{OC} (mV) ^a			ΔI_{SC} ($\mu A/cm^2$) ^b		
	O ₂	N ₂	N ₂ O	O ₂	N ₂	N ₂ O
TiO_2/H_2O^c	-51	-252	-230	22.4	39.4	27.3
TiO_2/NH_4Cl^d	-187	-322	-310	21.3	34.3	33.6
$Pt-TiO_2/H_2O^c$	-39	-120	-32	3.6	8.0	3.3
$Pt-TiO_2/NH_4Cl^d$	-21	-163	-56	4.0	10.1	5.4

^a ΔE_{OC} = illuminated E_{OC} - dark E_{OC} . ^b ΔI_{SC} = illuminated I_{SC} - dark I_{SC} . ^c Distilled water at pH 10. ^d 0.1 mM NH_4Cl at pH 10.

The Role of N_2O on Pt/TiO_2 . In terms of energetics, N_2O should not be a better electron acceptor than O_2 since the electron affinity (EA) of the former is much lower than that of the latter [$EA(N_2O) = 0.22$ eV; $EA(O_2) = 0.45$ eV] (41). Although Anpo et al. (35) verified that N_2O could trap CB electrons of TiO_2 by detecting $N_2O^{\bullet-}$ in an electron spin resonance study, its subsequent decomposition into N_2 and O_2 did not take place on naked TiO_2 (36). In this study, N_2O did not enhance the photocatalytic oxidation of NH_3 on naked TiO_2 and Au/TiO_2 . On the other hand, the fact that N_2O can degrade on Pt/TiO_2 (36) is in accord with our results. However, the highly enhanced photocatalytic conversion of NH_3 on Pt/TiO_2 in the presence of N_2O should not be ascribed to the electron scavenging action of N_2O because the ammonia removal efficiency with Pt/TiO_2 is lower in the presence of the more powerful electron acceptor, dioxygen.

To confirm the ability of N_2O to accept CB electrons from Pt/TiO_2 , we compare the steady-state open-circuit voltages (E_{OC}) and short-circuit currents (I_{SC}) in a photoelectrochemical cell with a TiO_2 or Pt/TiO_2 electrode in O_2 -, N_2 -, or N_2O -saturated solutions in Table 1. If the dissolved gases can accept CB electrons from the electrode surface, the voltage (or current) difference between the illuminated and dark condition, ΔE_{OC} (or ΔI_{SC}), should decrease. Table 1 shows that both ΔE_{OC} and ΔI_{SC} for the TiO_2 electrode under O_2 -saturation were much smaller than for N_2 - and N_2O -saturation, which implies that O_2 readily accepts CB electrons from the TiO_2 electrode whereas N_2O and N_2 do not. On the other hand, the Pt/TiO_2 electrode under N_2O -saturation exhibited comparable ΔE_{OC} and ΔI_{SC} values to those for O_2 saturation, indicating that N_2O accepts CB electrons from Pt/TiO_2 to a similar degree to O_2 .

The most plausible role of N_2O in this system is the production of OH radicals on Pt/TiO_2 . On the Pt surface, N_2O accepts CB electrons (reaction 14) and subsequently dissociates to yield OH radicals (reactions 15–17)



The resulting hydroxyl radicals react with NH_3 to generate N_2 through reactions 5–11. To verify the involvement of OH radicals in the oxidation of NH_3 in the N_2O -saturated suspension, the effect of adding excess t -BuOH, an OH radical scavenger (10), was investigated (Figure 5). Given the reported rate constants and concentrations employed [$k(t\text{-BuOH} + OH\bullet) = 5 \times 10^8 \text{ M}^{-1}\text{s}^{-1}$ (42), $k(NH_3 + OH\bullet) = 1.7 \times 10^7 \text{ M}^{-1}\text{s}^{-1}$ (27); $[t\text{-BuOH}]_0 = 10^{-2} \text{ M}$, $[NH_3]_0 = 10^{-4} \text{ M}$], it is expected that all OH radicals should be scavenged by t -BuOH. As shown in Figure 5, the presence of excess t -BuOH significantly

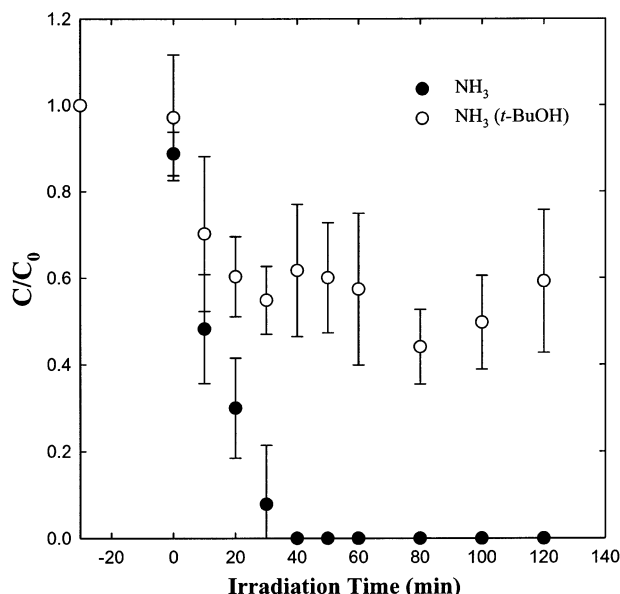


FIGURE 5. Photocatalytic removal of NH_3 on Pt/TiO_2 in the presence or absence of t -BuOH. The experimental conditions were $[NH_3]_0 = 0.1 \text{ mM}$; $[TiO_2] = 0.5 \text{ g/L}$; $[t\text{-BuOH}]_0 = 10 \text{ mM}$; N_2O -saturated.

inhibited the removal of NH_3 from the N_2O -saturated Pt/TiO_2 suspension. This confirms that N_2O serves as a precursor of OH radicals on Pt/TiO_2 .

The heterogeneous electron scavenging ability of N_2O seems to sensitively depend on the kind of semiconductor surface that is used. N_2O scavenged trapped electrons from a ZnO surface in a similar way to O_2 (30–34) and assisted the photodecomposition of organic compounds on ZnO (34), whereas N_2O is much less efficient in scavenging CB electrons from TiO_2 . Serpone et al. (33) speculated that trapped electrons on TiO_2 might be much more strongly bound than those on ZnO . The presence of Pt on TiO_2 could release trapped electrons from tightly bound Ti^{III} sites into the platinum phase where electrons are much more mobile. As a result, trapped electrons on Pt could be easily transferred to N_2O . The Pt deposits on TiO_2 enable the selective oxidation of NH_3 to N_2 in two ways: (1) by trapping CB electrons and reductively dissociating N_2O into OH radicals that initiate NH_3 oxidation and (2) by stabilizing intermediate NH_x species on Pt and facilitating their recombination to dinitrogen.

Using a Pt/TiO_2 suspension may not in general be economical as a practical water treatment technology. Catalyst immobilization or recovery processes should be considered for practical applications. It should be also noted that this selective photocatalytic conversion of ammonia to N_2 is applicable only to NH_3 , not to NH_4^+ . The present method could be viable when dealing with low concentration levels of ammonia (less than a few ppm) in water.

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