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Simultaneous removal of nitrite and ammonia as dinitrogen in aqueous suspensions of a titanium(IV) oxide photocatalyst under reagent-free and metal-free conditions at room temperature

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Photocatalytic reduction of nitrite (NO_2^-) in an aqueous suspension of metal-free titanium(IV) oxide in the presence of ammonia (NH_3) as a hole scavenger gave dinitrogen (N_2), indicating that NO_2^- and NH_3 are simultaneously removed from water as N_2 at room temperature without the use of an extra reagent.

In nature, nitrite ion (NO_2^-) is a product formed in the process of ammonia (NH_3) oxidation by nitrite bacteria. Since NO_2^- reacts with secondary amines to yield nitrosoamines, which are carcinogens, ingestion of a large amount of NO_2^- should be avoided. Nitrite ion is often formed as a relatively stable intermediate in the processes of nitrate ion (NO_3^-) reduction by catalysis,[1-9] electrocatalysis[10-17] and photocatalysis[9,18-33] using dihydrogen (H_2), electrically supplied electrons and photogenerated electrons, respectively. However, reduction of NO_3^- and NO_2^- by the above methods has mainly or partially yielded NH_3 or ammonium ion (NH_4^+), in which nitrogen is over-reduced.

In our previous study, photocatalytic reaction of NO_2^- in aqueous suspensions of bare and metal-loaded titanium(IV) oxide (TiO_2) particles was examined in the absence of electron and hole scavengers under irradiation of UV light.[34] In the bare TiO_2 system, disproportionation of NO_2^- to dinitrogen (N_2) and nitrate (NO_3^-) with both nitrogen balance (NB) and redox balance (ROB) close to 100% within experimental errors was observed (Equation (1)), although the reaction was slow. Equation (1) consists of two half reactions caused by photogenerated electrons and holes as shown in Equations (2) and (3), respectively. Palladium-loaded TiO_2 (Pd-TiO_2) particles exhibited an extraordinarily large rate of disproportionation of NO_2^- in their aqueous suspension, i.e., NO_2^- was almost completely converted to N_2 and NO_3^-, both the values of NB and ROB being close to unity.[34]

$$5NO_2^- + 2H^+ \rightarrow N_2 + 3NO_3^- + H_2O \quad (1)$$

$$2NO_2^- + 8H^+ + 6e^- \rightarrow N_2 + 4H_2O \quad (2)$$

$$3NO_2^- + 3H_2O + 6h^+ \rightarrow 3NO_3^- + 6H^+ \quad (3)$$

From the point of view of denitrification of waste water, conversion of NO_2^- to N_2 without formation of NO_3^- is most favorable.

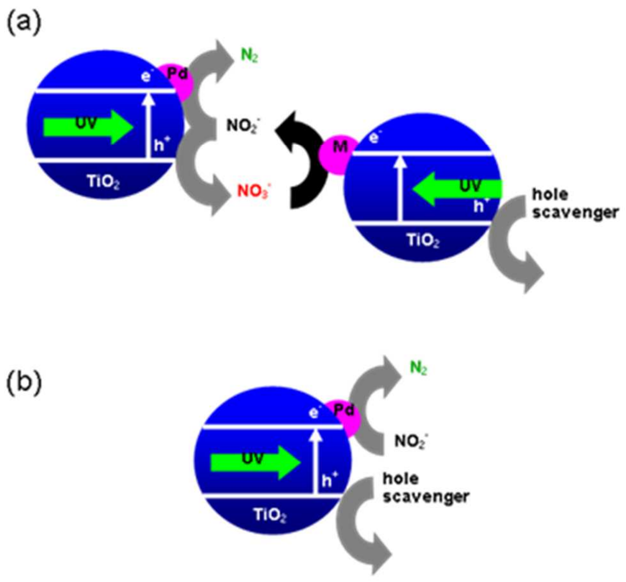


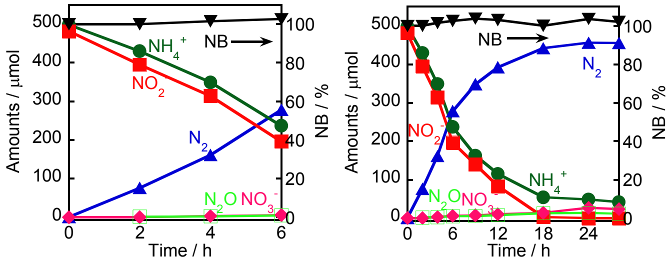
Fig 1 Photocatalytic reduction of NO_2^- to N_2 in an aqueous suspension of metal-loaded TiO_2 in the presence of a hole scavenger. (a) Combination of two photocatalytic systems: disproportionation of NO_2^- to N_2 and NO_3^- catalyzed by Pd-TiO_2 and selective reduction of NO_3^- to NO_2^- catalyzed by another metal-loaded TiO_2 in the presence of a hole scavenger and (b) simple photocatalytic system: hole scavenging with a sacrificial reagent and reduction of NO_2^- to N_2 by photogenerated electrons on Pd particles

Two feasible methods for photocatalysis of TiO_2 for conversion of NO_2^- to N_2 in aqueous suspensions are shown in Fig. 1. As shown in Fig. 1(a), NO_3^- was selectively reduced back to NO_2^- over Ag-TiO_2 in the presence of a hole scavenger (HS) (Equations (4) and (5)), and NO_2^- was totally reduced to N_2 by combination with disproportionation of NO_2^- catalyzed by Pd-TiO_2.[35]

$$e^- – h^+ + HS \rightarrow e^- + HSox^+ \quad (4)$$

$$NO_3^- + 2e^- + 2H^+ \rightarrow NO_2^- + H_2O \quad (5)$$

If HS is added together with NO_2^- to an aqueous suspension of TiO_2 or Pd-TiO_2 and holes are consumed by the hole scavenger (Equation (4)), the oxidation aspect of disproportionation of NO_2^- (Equation (3)) may be suppressed and only N_2 can be obtained without formation of NO_3^- as shown in Fig. 1(b). However, oxidation of NO_2^- by holes partly occurred (Equation (3)) even in the presence of HS (sodium oxalate), and ideal selective conversion of NO_2^- to N_2 in an aqueous suspension of Pd-TiO_2 as shown in Fig. 1(b) was not achieved.[35] From the point of view of practical application, metal-free reaction and the use of a cheap HS are highly desired in addition to high product selectivity to N_2 in NO_2^- conversion. In the present study, we investigated various kinds of HSs enabling us to achieve selective conversion of NO_2^- to N_2 and found that NH_3 was an excellent HS for conversion of NO_2^- to N_2.



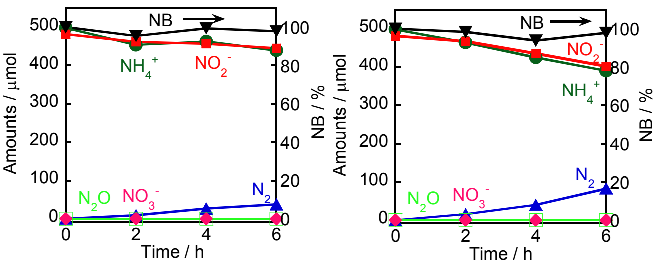
(a) (b)

Fig. 2 Time courses of photocatalytic conversions of NO_2^- (squares) and NH_4^+ (circles) in aqueous suspensions of bare TiO_2 particles at pH 7 under irradiation of UV light for (a) 6 h and (b) 28 h at 298 K. Triangles: N_2, Diamonds: NO_3^-, Open squares: N_2O, Reversed triangles: NB.

Results of photoirradiation of UV light to NO_2^- in an aqueous suspension of bare TiO_2 (AEROXIDE® TiO_2 P25, Evonik) in the presence of NH_3 (as NH_4^+) for 6 h are shown in Fig. 2(a). Only sodium nitrite ($NaNO_2$), ammonium sulfate ($(NH_4)_2SO_4$), water, TiO_2 and argon were present before the reaction. The amounts of NO_2^- and NH_4^+ (both 500 µmol) were gradually decreased with photoirradiation, and NO_2^- (285 µmol) and NH_4^+ (260 µmol) were removed from the liquid phase after photoirradiation for 6 h. Corresponding to the decreases in NO_2^- and NH_4^+, N_2 (278 µmol, corresponding to 556 µmol nitrogen) was formed. During the reaction, NB was close to 100% within experimental errors as also shown in Fig. 2(a). The amounts of other detectable species with GC (NO, H_2 and O_2) were under their detection limits. After photoirradiation for 28 h, almost 100% of NO_2^- and 92% of NH_4^+ were removed and 455 µmol of N_2 was evolved, the values of NB being close to unity (Fig. 2(b)). These results indicate that NO_2^- and NH_4^+ reacted with almost 1:1, forming N_2. The oxidation states of nitrogen in NO_2^-, NH_3 and N_2 are +3, –3 and 0, respectively. Therefore, this reaction includes change in the oxidation states of nitrogen in NO_2^- and NH_4^+ (+3 and –3, respectively) to the same oxidation state (zero), i.e., redox reaction between NO_2^- and NH_4^+, and formation of an N_2 product. We used various commercially available metal (double) oxides for photocatalytic reaction of NO_2^- and NH_4^+ under the same conditions, and results obtained after 5-h photoirradiation are shown in Fig. S1 (†ESI), indicating that TiO_2 (P 25) exhibited the highest N_2 yield among the metal oxides used in this study.

It is known that $NaNO_2$ in a concentrated and boiling aqueous solution reacts with ammonium chloride in the solution to form N_2. Based on the thermal reaction of NO_2^- and NH_4^+ in an aqueous solution, the simultaneous removal of NO_2^- and NH_4^+ and formation of N_2 observed under the present conditions can be shown by Equation (6).

$$NO_2^- + NH_4^+ \rightarrow N_2 + 2H_2O \quad (6)$$



(a) (b)

Fig. 3 Time courses of (a) thermal conversions of NO_2^- (squares) and NH_4^+ (circles) at pH 7 and at 348 K in the absence of TiO_2 in the dark and (b) photochemical conversions of NO_2^- (squares) and NH_4^+ (circles) in the absence of TiO_2 at pH 7 and at 298 K under irradiation of UV light. Triangles: N_2, Diamonds: NO_3^-, Open squares: N_2O, Reversed triangles: NB.

A large molar heat capacity at constant pressure of liquid water (75 J K^{-1} mol^{-1} at 298 K) means that removal of NO_2^- and NH_4^+ in waste water by boiling needs a large amount of energy. Therefore, the thermal reaction cannot be applied for the removal of NO_2^- and NH_4^+ in waste water from the point of view of practical application. Since a moderate supply of heat to waste water would be possible by using exhaust heat in factories, thermal reaction of NO_2^- and NH_4^+ in the dark at 348 K was examined to compare with the results of photocatalytic reaction at 298 K, and the results are shown in Fig. 3(a). Concentrations of NO_2^- and NH_4^+ slightly decreased and a small amount of N_2 was evolved, indicating that thermal reaction of NO_2^- and NH_4^+ occurs at 348 K. However, the reaction rate was much smaller than that of the photocatalytic reaction (Fig. 2(a)). Since NO_2^- absorbs UV light, photochemical reaction (not photocatalytic reaction) might occur under the present conditions. To elucidate the effect of photochemical reaction, a solution containing NO_2^- and NH_4^+ was irradiated by UV light in the absence of TiO_2 at 298 K, and the results are shown in Fig. 3(b). Only a small decreases in NO_2^- and NH_4^+ and formation of N_2 were observed, indicating that the contribution of photochemical reaction was negligible under the present conditions. From results of control experiments shown in Fig. 3, it can be concluded that a photocatalyst (TiO_2) and UV light were essential for the reaction of NO_2^- and NH_4^+ to N_2 with a sufficient reaction rate. In factories producing and re-producing precious metals, a large amount of waste water containing NH_3 is formed in another process and should be denitrificated as well as waste water containing NO_2^-. Therefore, simultaneous removal of NO_2^- and NH_4^+ to N_2 over a bare TiO_2 photocatalyst by appropriate mixing of two kinds of waste water is an ideal method from the point of view of practical application for the following reasons: 1) Since NH_3, which should be detoxificated, can be used as a reducing reagent (hole scavenger), an extra reagent for NO_2^- reduction such as methanol in a biochemical process is not required, 2) TiO_2 is a safe, stable and cheap catalyst material, 3) extra precious metals such as platinum and Pd are not required, 4) the reaction occurs under atmospheric pressure at room temperature, and 5) sunlight can be used as the energy source.

Tanaka and co-workers reported that photo-assisted gas-phase selective catalytic reduction of nitrogen oxide (NO) with NH_3 (photo-SCR) in the presence of oxygen (O_2) proceeded over a TiO_2

photocatalyst at room temperature[36–43] and that the process of decomposition of NH_2NO intermediates was a rate-determining step at room temperature in the presence of excess O_2 gas.[40] As well as their proposed reaction mechanism for the gas-phase photo-SCR of NO with NH_3 over TiO_2,[42] the present NO_2^--NH_4^+ reaction over TiO_2 would occur via reduction of NO_2^- and oxidation of NH_4^+ (or NH_3) followed by the formation of NH_2NO intermediates as shown in Equation (7), although we did not observe NH_2NO intermediates and related compounds because of the difficulty in detection of these species in water.

$$NO_2^- + NH_4^+ + (e^-\text{-}h^+) \rightarrow [NH_2NO + H_2O] \rightarrow N_2 + 2H_2O \quad (7)$$

Equation (7) means that only one electron-hole pair contributes to N_2 formation. Therefore, apparent quantum efficiency (AQE) was calculated from Equation (8).

$$AQE = \frac{amount\ of\ N_2}{number\ of\ incident\ photons} \times 100. \quad (8)$$

The value of AQE in this reaction under irradiation of relatively intense light at 366 nm (3.23 mW cm^{-2}) at room temperature was determined to be 1.9%. Since there are various parameters controlling the reaction rate and AQE in this reaction system, we are now investigating a decisive parameter among them.

In summary, we succeeded in conversion of NO_2^- to N_2 in an aqueous suspension of a metal-free TiO_2 photocatalyst under irradiation of UV light in the presence of NH_3. Since NH_3, which should be detoxificated, works as a reducing reagent (hole scavenger) and an extra reagent for NO_2^- reduction is not required, this reaction system is ideal from the point of view of practical application.

Notes and references

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† Electronic Supplementary Information (ESI) available: Experimental procedure and Fig. S1. See DOI: 10.1039/c000000x/

1 S. Horold, K. D. Vorlop, T. Tacke and M. Sell, *Catal. Today*, 1993, **17**, 21-30.

2 H. Berndt, I. Monnich, B. Lucke and M. Menzel, *Appl. Catal. B: Environ.*, 2001, **30**, 111-122.

3 F. Gauthard, F. Epron and J. Barbier, *J. Catal.*, 2003, **220**, 182-191.

4 O. Salome, G. P. Soares, J. J. M. Orfao and M. F. R. Pereira, *Catal. Lett.*, 2008, **126**, 253-260.

5 Y. Wang, Y. Sakamoto and Y. Kamiya, *Appl. Catal. A: General*, 2009, **361**, 123-129.

6 O. Salome, G. P. Soares, J. J. M. Orfao and M. F. R. Pereira, *Appl. Catal. B: Environ.*, 2009, **91**, 441-448.

7 K. A. Guy, H. Xu, J. C. Yang, C. J. Werth and J. R. Shapley, J. Phys. Chem. C, 2009, **113**, 8177-8185.

8 C. Neyertz, F. A. Marchesini, A. Boix, E. Miro and C. A. Querini, *Appl. Catal. A: General*, 2010, **372**, 40-47.

9 N. Wehbe, M. Jaafar, C. Guillard, J.-M. Hermann, S. Miachon, E. Puzenat and N. Guilhaume, *Appl. Catal. A: General.*, 2009, **368**, 1-8.

10 K. Shimazu, R. Goto and K. Tada, *Chem. Lett.*, 2002, 204-205.

11 K. Tada, T. Kawaguchi and K. Shimazu, *J. Electroanal. Chem.*, 2004, **572**, 93-99.

12 P. M. Tucker, M. J. Waite and B. E. Hyyden, *J. Appl. Electrochem.*, 2004, **34**, 781-796.

13 O. Brylev, M. Sarrazin, D. Belanger and L. Roue, *Appl. Catal. B; Environ.*, 2006, **64**, 243-253.

14 F. V. Andrade, L. J. Deiner, H. Varela, J. F. R de Castro, *J. Electrothermal Sci.*, 2007, **154**, F159-F164.

15 M. A. Hasnat, R. Augi, S. Hinokuma, T. Yamaguchi and M. Machida, *Catal. Commun.*, 2009, **10**, 1132-1135.

16 G. E. Badea, *Electrochmica Acta*, 2009, **54**, 996-1001.

17 S. Piao, Y. Kayama, Y. Nakano, K. Nakata, Y. Yoshinaga, K. Shimazu, *J. Eleectyroanalytical Chem.*, 2009, **629**, 110-116.

18 A. Kudo, K. Domen, K. Maruya and T. Ohnishi, *Chem. Lett.*, 1987, 1019-1022.

19 B. Ohtani, M. Kakimoto, H. Miyadzu, S.-i. Nishimoto and T. Kagiya, *J. Phys Chem.*, 1988, **92**, 5773-5777.

20 A. Kudo, K. Domen, K. Maruya and T. Ohnishi, *J. Catal.*, 1992, **135**, 300-303.

21 K. T. Ranjit, T. K. Varadarajan and B. Viswanathan, *J. Photochem. Photobio. A: Chem.*, 1995, **89**, 67-68.

22 Y. Li and F. Wasgestian, *J. Photochem. Photobio. A: Chem.*, 1998, **112**, 255-259.

23 B. Bems, F. C. Jentoft and R. Schlogl, *Appl. Catal. B. Environ.*, 1999, **20**, 155-163.

24 T. Mori, J. Suzuki, K. Fujimoto, M. Watanabe and Y. Hasegawa, *J. Sol-Gel Sci. Tech.*, 2000, **19**, 505-510.

25 H. Kominami, A. Furusho, S.-y. Murakami, H. Inoue, Y. Kera and B. Ohtani, *Catal. Lett.*, 2001, **76**, 31-34.

26 H. Kato and A. Kudo, *Phys. Chem. Chem. Phys.*, 2002, **4**, 2833-2838.

27 R. Jin, W. Gao, J. Chen, H. Zeng, F. Zhang, Z. Liu and N. Guan, *J. Photochem. Photobio., A: Chem.*, 2004, **162**, 585-590.

28 W. Gao, R. Jin, J. Chen, X. Guan, H. Zeng, F. Zhang and N. Guan, *Catal. Today*, 2004, **90**, 331-336.

29 H. Kominami, T. Nakaseko, Y. Shimada, A. Furusho, H. Inoue, S.-y. Murakami, Y. Kera and B. Ohtani, *Chem. Commun.*, 2005, 2933-2935.

30 F. Zhang, R. Jin, J. Chen, C. Shao, W. Gao, L. Li and N. Guan, *J. Catal.*, 2005, **232**, 424-431.

31 F. Zhang, Y. Pi, J. Cui, Y. Yang, X. Zhang and N. Guan, *J. Phys. Chem. C*, 2007, **111**, 3756-3761.

32 N. Wehbe, M. Jaafar, C. Guillard, J.-M. Herrmann, S. Miachon, E. Puzenat and N. Guilhaume, *Appl. Catal. A*, 2009, **368** 1-8.

33 J. Sa, C. A. Aguera, S. Gross and J. A. Anderson, *Appl. Catal. B: Environ.*, 2009, **85**, 192-200.

34 H. Kominami, H. Gekko and K. Hashimoto, *Phys. Chem. Chem. Phys.*, 2010, **12**, 15423-15427.

35 H. Gekko, K. Hashimoto, H. Kominami, *Phys. Chem. Chem. Phys.* 2012, **14**, 7965-7970.

36 T. Tanaka, K. Teramura and T. Funabiki, *Phys. Chem. Chem. Phys.*, 2000, **2**, 2681-2682.

37 T. Tanaka, K. Teramura, T. Yamamoto, S. Takenaka, S. Yoshida and T. Funabiki, *J. Photochem. Photobiol., A*, 2002, **148**, 277-281.

38 T. Tanaka, K. Teramura, K. Arakaki and T. Funabiki, *Chem. Commun.*, 2002, 2742-2743.

39 S. Yamazoe, T. Okumura, K. Teramura and T. Tanaka, *Catal. Today*, 2006, **111**, 266-270.

40 K. Teramura, T. Tanaka, S. Yamazoe, K. Arakaki and T. Funabiki, *Appl. Catal., B*, 2004, **53**, 29-36.

41 S. Yamazoe, Y. Masutani, K. Teramura, Y. Hitomi, T. Shishido and T. Tanaka, *Appl. Catal., B*, 2008, **83**, 123-130.
42 K. Teramura, T. Tanaka and T. Funabiki, *Langmuir*, 2003, **19**, 1209-1214.
43 A. Yamamoto, Y. Mizuno, K. Teramura, T. Shishido and T. Tanaka, *Catal. Sci. Tech.*, 2013, **3**, 1771-1775.

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