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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 metalfree conditions at room temperature<sup>†</sup>

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Photocatalytic reduction of nitrite (NO<sub>2</sub><sup>-</sup>) in an aqueous suspension of metal-free titanium(IV) oxide in the presence of ammonia (NH<sub>3</sub>) as a hole scavenger gave dinitrogen (N<sub>2</sub>), indicating that NO<sub>2</sub><sup>-</sup> and NH<sub>3</sub> are simultaneously removed from water as N<sub>2</sub> at room temperature without the use of an extra reagent.

In nature, the 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,<sup>1-9</sup> electrocatalysis<sup>10-17</sup> and photocatalysis<sup>9,18-33</sup> 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<sub>2</sub>) particles was examined in the absence of electron and hole scavengers under irradiation of UV light.<sup>34</sup> In the bare TiO<sub>2</sub> 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 (eqn (1)), although the reaction was slow. Eqn (1) consists of two half reactions caused by photogenerated electrons and holes as shown in eqn (2) and (3), respectively. Palladium-loaded TiO<sub>2</sub> (Pd-TiO<sub>2</sub>) 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.<sup>34</sup>

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

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

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

Two feasible methods for photocatalysis of  $\text{TiO}_2$  for conversion of  $\text{NO}_2^-$  to  $\text{N}_2$  in aqueous suspensions are shown in Fig. 1. As shown in Fig. 1(a),  $\text{NO}_3^-$  was selectively reduced back to  $\text{NO}_2^-$  over Ag–TiO<sub>2</sub> in the presence of a hole scavenger (HS) (eqn (4) and (5)), and  $\text{NO}_2^-$  was totally reduced to  $\text{N}_2$  by combination with disproportionation of  $\text{NO}_2^-$  catalyzed by Pd-TiO<sub>2</sub>.<sup>35</sup>

$$e^{-} - h^{+} + HS \rightarrow e^{-} + HSox^{+}$$
(4)

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

If HS is added together with NO<sub>2</sub><sup>-</sup> to an aqueous suspension of TiO<sub>2</sub> or Pd-TiO<sub>2</sub> and holes are consumed by the hole scavenger (eqn (4)), the oxidation aspect of disproportionation of NO<sub>2</sub><sup>-</sup> (eqn (3)) may be suppressed and only N<sub>2</sub> can be obtained without formation of NO<sub>3</sub><sup>-</sup> as shown in Fig. 1(b). However, oxidation of NO<sub>2</sub><sup>-</sup> by holes partly occurred (eqn (3)) even in the presence of HS (sodium oxalate), and ideal selective conversion of NO<sub>2</sub><sup>-</sup> to N<sub>2</sub> in an aqueous suspension of Pd-TiO<sub>2</sub> as shown in Fig. 1(b) was not achieved.<sup>35</sup> From the point of view of practical application, metalfree reaction and the use of a cheap HS are highly desired in addition to high product selectivity to N<sub>2</sub> in NO<sub>2</sub><sup>-</sup> conversion. In the present study, we investigated various kinds of HSs enabling us to achieve selective conversion of NO<sub>2</sub><sup>-</sup> to N<sub>2</sub> and found that NH<sub>3</sub> was an excellent HS for conversion of NO<sub>2</sub><sup>-</sup> to N<sub>2</sub>.

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Fig. 1 Photocatalytic reduction of NO<sub>2</sub><sup>-</sup> to N<sub>2</sub> in an aqueous suspension of metal-loaded TiO<sub>2</sub> in the presence of a hole scavenger. (a) Combination of two photocatalytic systems: disproportionation of NO<sub>2</sub><sup>-</sup> to N<sub>2</sub> and NO<sub>3</sub><sup>-</sup> catalyzed by Pd-TiO<sub>2</sub> and selective reduction of NO<sub>3</sub><sup>-</sup> to NO<sub>2</sub><sup>-</sup> catalyzed by another metal-loaded TiO<sub>2</sub> in the presence of a hole scavenger and (b) simple photocatalytic system: hole scavenging with a sacrificial reagent and reduction of NO<sub>2</sub><sup>-</sup> to N<sub>2</sub> by photogenerated electrons on Pd particles.

Results of photoirradiation of UV light to  $NO_2^-$  in an aqueous suspension of bare TiO<sub>2</sub> (AEROXIDE® TiO<sub>2</sub> P25, Evonik) in the presence of NH<sub>3</sub> (as NH<sub>4</sub><sup>+</sup>) for 6 h are shown in Fig. 2(a). Only sodium nitrite (NaNO<sub>2</sub>), ammonium sulfate ((NH<sub>4</sub>)<sub>2</sub>SO<sub>4</sub>), water, TiO<sub>2</sub> and argon were present before the reaction. The amounts of NO<sub>2</sub><sup>-</sup> and NH<sub>4</sub><sup>+</sup> (both 500 µmol) were gradually decreased with photoirradiation, and NO<sub>2</sub><sup>-</sup> (285 µmol) and NH<sub>4</sub><sup>+</sup> (260 µmol) were removed from the liquid phase after photoirradiation for 6 h. Corresponding to the decreases in NO<sub>2</sub><sup>-</sup> and NH<sub>4</sub><sup>+</sup>, N<sub>2</sub> (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<sub>2</sub> and O<sub>2</sub>)

500

400

300

200

100

Amounts / µmol

NB / %

20

100

80

60 🕺

40 <sup>m</sup>

20

12 18 Time / h

(b)

00

NB

N<sub>2</sub>O NO

4

Time / h

(a)

Fig. 2 Time courses of photocatalytic conversions of  $NO_2^-$  (squares) and  $NH_4^+$  (circles) in aqueous suspensions of bare TiO<sub>2</sub> particles at pH 7 under irradiation of UV light for (a) 6 h and (b) 28 h at 298 K. Triangles: N<sub>2</sub>, diamonds:  $NO_3^-$ , open squares: N<sub>2</sub>O, reversed triangles: NB.

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<sub>2</sub> (P 25) exhibited the highest  $N_2$  yield among the metal oxides used in this study.

It is known that NaNO<sub>2</sub> in a concentrated and boiling aqueous solution reacts with ammonium chloride in the solution to form N<sub>2</sub>. Based on the thermal reaction of NO<sub>2</sub><sup>-</sup> and NH<sub>4</sub><sup>+</sup> in an aqueous solution, the simultaneous removal of NO<sub>2</sub><sup>-</sup> and NH<sub>4</sub><sup>+</sup> and formation of N<sub>2</sub> observed under the present conditions can be shown by eqn (6).

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

A large molar heat capacity at constant pressure of liquid water (75 J K<sup>-1</sup> mol<sup>-1</sup> at 298 K) means that removal of NO<sub>2</sub><sup>-</sup> and NH<sub>4</sub><sup>+</sup> 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 NO2<sup>-</sup> and NH4<sup>+</sup> slightly decreased and a small amount of N2 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<sub>2</sub><sup>-</sup> 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<sub>2</sub><sup>-</sup> and NH<sub>4</sub><sup>+</sup> was irradiated by UV light in the absence of TiO2 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<sub>2</sub> 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<sub>2</sub>) 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<sub>3</sub> is formed in another process and should be denitrificated as well as waste water containing NO2<sup>-</sup>. Therefore, simultaneous removal of NO<sub>2</sub><sup>-</sup> and NH<sub>4</sub><sup>+</sup> to N<sub>2</sub> over a bare TiO<sub>2</sub> 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<sub>3</sub>, which should be detoxificated,

500

400

300

200

100

Amounts / µmo

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Fig. 3 Time courses of (a) thermal conversions of NO<sub>2</sub><sup>-</sup> (squares) and NH<sub>4</sub><sup>+</sup> (circles) at pH 7 and at 348 K in the absence of TiO<sub>2</sub> in the dark and (b) photochemical conversions of NO<sub>2</sub><sup>-</sup> (squares) and NH<sub>4</sub><sup>+</sup> (circles) in the absence of TiO<sub>2</sub> at pH 7 and at 298 K under irradiation of UV light. Triangles: N<sub>2</sub>, diamonds: NO<sub>3</sub><sup>-</sup>, open squares: N<sub>2</sub>O, reversed triangles: NB.

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<sub>2</sub> 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 gasphase selective catalytic reduction of nitrogen oxide (NO) with NH<sub>3</sub> (photo-SCR) in the presence of oxygen (O<sub>2</sub>) proceeded over a TiO<sub>2</sub> photocatalyst at room temperature<sup>36-43</sup> and that the process of decomposition of NH<sub>2</sub>NO intermediates was a ratedetermining step at room temperature in the presence of excess O<sub>2</sub> gas.<sup>40</sup> As well as their proposed reaction mechanism for the gas-phase photo-SCR of NO with NH<sub>3</sub> over TiO<sub>2</sub>,<sup>42</sup> the present NO<sub>2</sub><sup>-</sup>-NH<sub>4</sub><sup>+</sup> reaction over TiO<sub>2</sub> would occur *via* reduction of NO<sub>2</sub><sup>-</sup> and oxidation of NH<sub>4</sub><sup>+</sup> (or NH<sub>3</sub>) followed by the formation of NH<sub>2</sub>NO intermediates as shown in eqn (7), although we did not observe NH<sub>2</sub>NO intermediates and related compounds because of the difficulty in detection of these species in water.

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

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

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

The value of AQE in this reaction under irradiation of relatively intense light at 366 nm (3.23 mW cm<sup>-2</sup>) 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<sub>2</sub> 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.

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