

# Unexpected Selective Photocatalytic Reduction of Nitrite to Nitrogen on Silver-Doped Titanium Dioxide

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Photocatalytic reduction of nitrite ions on silver-doped titania catalysts prepared by photodeposition and chemical reduction methods was investigated. With respect to the Ag/TiO<sub>2</sub> (C) catalyst prepared by the conventional chemical reduction method, the photoinduced synthesized Ag/TiO<sub>2</sub> (P) samples showed a more homogeneous silver morphology and narrow size distribution. For the first time, selective conversion of nitrite ions to nitrogen instead of ammonia was achieved on the Ag/TiO<sub>2</sub> (P) catalysts. A great influence of hole scavengers on the catalytic activity was observed and can be described as follows: H<sub>2</sub>C<sub>2</sub>O<sub>4</sub> > HCOONa > C<sub>2</sub>H<sub>3</sub>OOH > C<sub>2</sub>H<sub>5</sub>OH > C<sub>2</sub>H<sub>3</sub>OONa > Na<sub>2</sub>C<sub>2</sub>O<sub>4</sub>. The optimal average activity of approximately 19 mmol<sub>N</sub>·g<sub>Ag</sub><sup>-1</sup>·min<sup>-1</sup> was achieved on the 1 wt % Ag/TiO<sub>2</sub> (P) sample under the modification of 0.04 mol/L oxalic acid, which was greatly higher than that on most of the previously supported noble metal catalysts (1–3 mmol<sub>N</sub>·g<sub>metal</sub><sup>-1</sup>·min<sup>-1</sup>) in terms of metal usage. It is interesting that slight influences of other anions such as SO<sub>4</sub><sup>2-</sup>, CO<sub>3</sub><sup>2-</sup>, or HCO<sub>3</sub><sup>-</sup> coexisting in drinking water were observed, which is different from previous works. Meanwhile, the effect of silver morphology as well as the photocatalytic mechanism of nitrite was discussed.

## 1. Introduction

With the development of modern industry and agriculture, the concentration of nitrite ions in drinking water is significantly rising because of excessive industrial effluents, overuse of nitrogenous fertilizer, and incomplete abiotic denitrification process in the soil.<sup>1,2</sup> Excessive nitrite in the body can form methemoglobin and, as a result, lead to “blue baby syndrome”; furthermore, nitrite can be converted into carcinogenic nitrosamine resulting in cancer and hypertension. Therefore, it is very necessary and desirable to eliminate the nitrite ions in drinking water for satisfying the requirement of health.

Although the reduction of nitrogen oxides and oxyanions has been extensively studied electrochemically,<sup>3–6</sup> biochemically,<sup>7,8</sup> and catalytically,<sup>8,9</sup> reports of photocatalytic reduction of nitrite ions are scarce.<sup>10–15</sup> Recently, photocatalytic conversion has been extensively developed in controlling the concentration of inorganic and organic compounds in drinking and industrial water.<sup>14–19</sup> Various semiconductor materials such as TiO<sub>2</sub>, CdS, ZnS, and ZnO have been employed, among which TiO<sub>2</sub> has been considered to be the most potential material for photocatalytic purposes, owing to its exceptional optical and electronic properties, chemical stability, nontoxicity, and low cost.<sup>20</sup> It has been proved<sup>21,22</sup> that metal loading and addition of so-called hole scavengers instead of photochemically produced hydrogen are essential to improve the catalytic performance of catalysts.

Many metals such as Pd,<sup>22,12</sup> Pt,<sup>22,12</sup> Rh,<sup>22,12</sup> Ru,<sup>12</sup> and Ag<sup>17,30,31</sup> and hole scavengers such as methanol,<sup>12,23,24</sup> ethanol,<sup>12</sup> EDTA,<sup>12</sup> oxalic acid,<sup>25,26</sup> sodium oxalate,<sup>19</sup> formic acid,<sup>17,27,28</sup> sucrose,<sup>29</sup> and humic acid<sup>16</sup> have been commonly employed to enhance photocatalytic efficiencies. Kominami and co-workers<sup>25</sup> compared the photocatalytic performance of various metal-doped

(such as Pt, Pd, Co, Ni, Au, Ag, Cu, etc.) titanium dioxide catalysts and found that the silver deposition on the surface of titania exhibited the optimal activity and nitrogen selectivity of photocatalytic nitrate ions, close to 86% and 47%, respectively, after 3 h of irradiation. Although such reductants were found easier to handle than hydrogen, unfortunately, the photocatalytic efficiency of the catalyst was still unsatisfying, and highly concentrated toxic ammonium byproducts instead of desired nitrogen were observed in previous de-nitrification processes.<sup>19–21</sup>

In this study, Ag/TiO<sub>2</sub> catalysts were prepared by photodeposition and the chemical reduction method and used for the photocatalytic purification of nitrite ions. Unexpectedly, nitrite ions were first found to be selectively reduced into nitrogen as a desirable product without the byproduct of ammonium ions, and the residual oxalic acid can be completely decomposed into the harmless compound CO<sub>2</sub> by further irradiation. The activities of nitrite reduction on these samples were compared, and the effects of doped silver and hole scavengers were mainly discussed.

## 2. Experimental Section

**2.1. Preparation and Characterization of Catalysts.** Ag/TiO<sub>2</sub> catalysts were prepared by photodeposition and the conventional chemical reduction method. Typically, during the photodeposition process, a suspension of TiO<sub>2</sub> was first prepared by mixing 500 mg of TiO<sub>2</sub> (Degussa P-25 with anatase/rutile crystalline ratio of 8:2 and a surface area of 50 m<sup>2</sup>/g) and a pre-calculated amount of AgNO<sub>3</sub> with 120 mL of twice-distilled water in a round-bottom flask. The suspension was purged with a stream of nitrogen for 15 min and then irradiated for 2 h using a high-pressure mercury lamp (250 W with a major emission wavelength at ca. 365 nm). The suspension was then centrifuged, and the supernatant was removed for atomic absorption spec-

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trometry (AAS) analysis. The particles were washed with distilled water and centrifuged (7000 rpm for 10 min) five times before transmission electron microscopy (TEM) analysis without drying. Other analyses (see below) were conducted on samples that were dried in an N<sub>2</sub> flow at 473 K for 6 h. The as-prepared catalysts were denoted as Ag/TiO<sub>2</sub> (P).

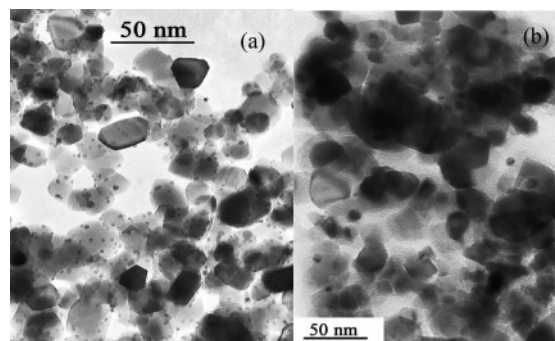
Comparatively, the Ag/TiO<sub>2</sub> (C) catalyst was synthesized by the conventional chemical reduction method employing KBH<sub>4</sub> (1.0 M) as the reductant under nitrogen atmosphere. Typically, 500 mg of titania and 8.4 mg of AgNO<sub>3</sub> were added to 25 mL of twice-distilled water under stirring for 30 min and subsequently ultrasonically dispersed for 20 min. After that, more than five times the stoichiometric amounts of 1 M KBH<sub>4</sub> and 1 M NaOH were mixed and slowly added into the above mixture. The reduced particles were finally filtrated and washed by ethanol or water and dried at ambient conditions. The metal weight content was 1 wt % analyzed by AAS.

TEM was carried out on a Philips EM-120 TEM instrument with accelerating voltage of 100 keV. X-ray diffraction (XRD) patterns were collected on a D/max-2500 commercial instrument (Cu K $\alpha$ ,  $\lambda = 1.54178 \text{ \AA}$ ) with a scan speed of  $2\theta = 8.0^\circ/\text{min}$ . X-ray photoelectron spectroscopy (XPS) was performed using a PHI 5300 ESCA commercial instrument (PHI, Inc., Mg K $\alpha$  radiation, 1253.6 eV,  $10^{-7}$  Pa) using a C 1s photoelectron peak (binding energy at 284.6 eV) as the energy reference. UV-vis spectra were collected on a V-570 spectrometer from JASCO Corporation.

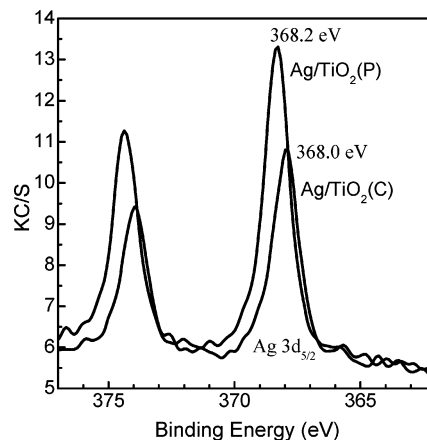
**2.2. Photocatalytic Reduction Tests.** A photocatalytic reaction was carried out in a double-wall quartz cell cooled by water with a 125 W high-pressure Hg lamp (main wavelength around 365 nm) as the light source. In order to maintain a constant temperature and filter IR light, one water circulation system was set up in the middle of the columniform reactor (diameter, 78 mm; height, 92 mm), into which the UV lamp was placed. Namely, it is an inner irradiation quartz reactor. The UV intensity was determined with a UV meter (Spectroline DRC-100X) as approximately 4 mW/cm<sup>2</sup>. The initial concentration of nitrite ions was calculated from the nitrogen weight (the same as ammonium in this study) as 100 mg<sub>N</sub>/L. No treatment was carried out to drive out the dissolved oxygen. During irradiation, a small part of the solution was withdrawn periodically, the powder catalyst was immediately separated by centrifugation, and the supernatant was analyzed to determine the residual concentration of nitrite and ammonium ions with a UV-vis spectrophotometer (Shimadzu, UV-240), which has been described in the literature.<sup>17</sup> Generally, nitrite and ammonium ions were colored by color reactions, and then their absorption intensities were measured at 540 and 697 nm separately. No notable catalytic ability was found without illumination in this reaction system.

The catalytic activity for the reduction of nitrite ions was commonly defined as the amount of nitrite anions reduced per minute and active metal weight ( $\text{mol}_{\text{NO}_2} \cdot \text{min}^{-1} \cdot \text{g}_{\text{metal}}^{-1}$ ). The selectivity to nitrogen was defined as the ratio between the concentration of nitrite reduced to form nitrogen ( $M_{\text{N}_2}$ ) and the total concentration of nitrite reduced ( $M_{\text{Total}}$ ), provided that no byproducts were formed other than ammonium ( $S_{\text{N}_2} = M_{\text{N}_2}/M_{\text{Total}} \cdot 100\%$ ). If it is not specifically stated, the selectivity in this study is an integral result of a 40 min reaction, not a differential or stable one.

To identify the gaseous products during nitrite photocatalytic reduction, one separate experiment was done with 1 wt % Ag/TiO<sub>2</sub> (P) catalyst in the presence of 0.04 mol/L oxalic acid. Before irradiation, the solution and the reactor volume were



**Figure 1.** Representative TEM images of Ag/TiO<sub>2</sub> catalysts (a) Ag/TiO<sub>2</sub> (P) and (b) Ag/TiO<sub>2</sub> (C).



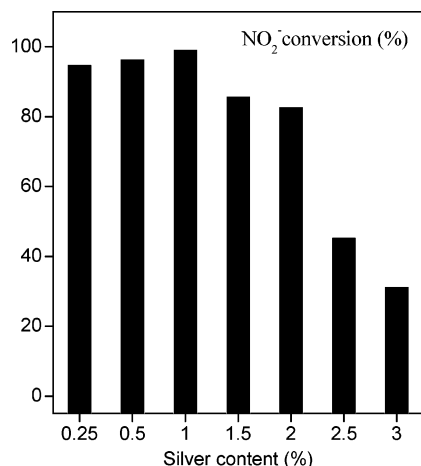
**Figure 2.** Typical XPS spectra of catalysts Ag/TiO<sub>2</sub> (P) and Ag/TiO<sub>2</sub> (C).

saturated with helium. The experimental results showed that the nitrite conversion rate was unchanged compared to the corresponding experimental conditions without helium. Gaseous products were analyzed by gas chromatography equipped with a thermal conductivity detector using helium as a carrier, and a 5A molecular sieve column coupled with a Porapak Q column was used for the gas separation. The experimental results demonstrated that nitrogen was the only gas product which was calculated to have N<sub>2</sub> selectivity of 99.9%.

### 3. Results

Figure 1 compares the typical TEM images of the as-prepared Ag/TiO<sub>2</sub> catalyst with those of photodeposition and the chemical reduction method, respectively. For Ag/TiO<sub>2</sub> (P) shown in Figure 1a, the coated silver nanoclusters are evenly dispersed on the surface of TiO<sub>2</sub> with an average diameter of approximately 2 nm. In contrast to that, the metal particles coated on the Ag/TiO<sub>2</sub> (C) catalyst by chemical reduction are larger and heterogeneously dispersed, as shown in Figure 1b. The preparative mechanism of highly dispersed silver on Ag/TiO<sub>2</sub>(P) was mainly ascribed to the control of stability of titanium dioxide as well as deposition kinetics of silver during preparation, as have been discussed in detail in our previous work.<sup>32</sup> It should be mentioned that, because of the avoidance of calcinations at high temperatures, the morphology of support titanium dioxide shows no obvious changes in both cases.

On the basis of the binding energy of Ag 3d<sub>5/2</sub> XPS spectra shown in Figure 2, the coated silver on both Ag/TiO<sub>2</sub> (P) and Ag/TiO<sub>2</sub> (C) can be deduced to mainly exist as the metal state.<sup>33</sup> This can be further confirmed by the observation of the plasma absorption peak at the region of 400–800 nm shown in the UV-vis spectra (not given).<sup>34</sup> Typical diffraction peaks of the

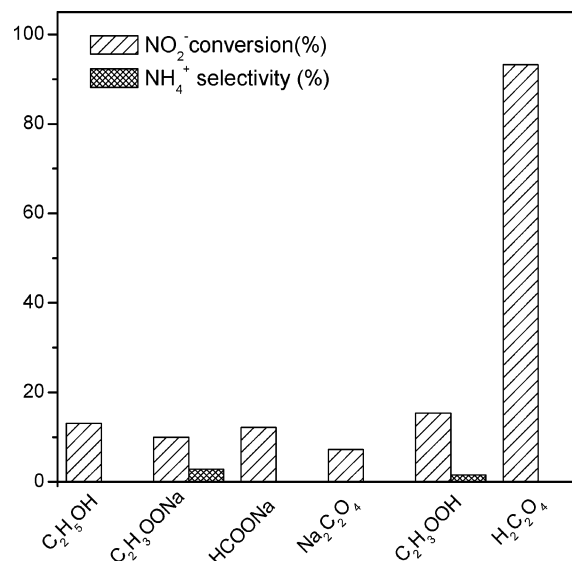


**Figure 3.** Comparison of NO<sub>2</sub><sup>-</sup> conversion on Ag/TiO<sub>2</sub> (P) catalysts with different silver content. Reaction conditions: 0.2 g (1 wt %) of the Ag/TiO<sub>2</sub> (P) catalyst, 200 mL of the NO<sub>2</sub><sup>-</sup> solution (100 mg/L), 0.04 M oxalic acid as the hole scavenger, *T* = 40 min, selectivity of nitrogen 100%.

TiO<sub>2</sub> support corresponding to the anatase (JCPDS 21-1272) and rutile (JCPDS 21-1276) phase can be found in the XRD patterns (not given). With respect to the pure sample, no obvious peaks assigned to silver species are observed on the Ag/TiO<sub>2</sub> (P) and Ag/TiO<sub>2</sub> (C) particles. It should be ascribed to the low content or high dispersion of deposited silver on the surface of titanium dioxide. Compared with the XRD patterns of pure TiO<sub>2</sub>, the crystalline phase of support on the Ag/TiO<sub>2</sub> (P) catalyst was also well-maintained. This indicates that the two preparative methods free of calcinations in this study do not destroy the component of crystalline phase of support that was extensively known to affect the photocatalytic performance greatly.

Similar to most metal-doped photocatalysts, the volcano-type curve of conversion to metal content is found for the Ag/TiO<sub>2</sub> (P) catalysts, as shown in Figure 3. A 1 wt % Ag/TiO<sub>2</sub> (P) catalyst shows the optimal photocatalytic activity under the modification of oxalic acid as a hole scavenger. After 40 min of irradiation, the conversion of nitrite ions to nitrogen reaches 99.5%, much higher than that on 1 wt % Ag/TiO<sub>2</sub>(C) calculated as 55.1% (details not given). Moreover, no ammonium ions are detected for the Ag/TiO<sub>2</sub> (P) catalyst, while the N<sub>2</sub> selectivity on the Ag/TiO<sub>2</sub> (C) catalyst was calculated as 67.5%. The conversion of nitrite ions on pure P-25 TiO<sub>2</sub> was measured as 45%. This reveals that the deposition of silver greatly promotes the photocatalytic conversion of nitrite on Ag/TiO<sub>2</sub> (P) (from 45% to 99.5%) but has a slight enhancement on Ag/TiO<sub>2</sub> (C) (from 45% to 55.1%). It is worthy of being mentioned that the nitrite on Ag/TiO<sub>2</sub> (P) was selectively photoreduced into nitrogen instead of ammonium ions.

Figure 4 exhibits the effects of several typical hole scavengers on the nitrite reduction, in which oxalic acid shows the best promotion effect. The addition of H<sub>2</sub>C<sub>2</sub>O<sub>4</sub> leads to a remarkable enhancement of nitrite conversion, while the favoring effects of other hole scavengers are less remarkable. The promotion effect can be described as H<sub>2</sub>C<sub>2</sub>O<sub>4</sub> > HCOONa > C<sub>2</sub>H<sub>3</sub>OOH > C<sub>2</sub>H<sub>5</sub>OH > C<sub>2</sub>H<sub>3</sub>OONa > Na<sub>2</sub>C<sub>2</sub>O<sub>4</sub>. In addition, the nitrogen selectivity under the effect of the hole scavengers mentioned above is slightly different, and the undesirable product ammonium ions is formed when C<sub>2</sub>H<sub>3</sub>OOH and C<sub>2</sub>H<sub>3</sub>OONa were used as hole scavengers. In this study, no reduction activity can also be observed in water without hole scavengers indicating that a hole scavenger is necessary for the photocatalytic reduction of nitrite ions.



**Figure 4.** Photocatalytic performance of nitrite under the modification of different hole scavengers. Reaction conditions: 0.2 g of the Ag/TiO<sub>2</sub> (P) catalyst, 1 wt % metal content, 200 mL of the NO<sub>2</sub><sup>-</sup> solution (100 mg/L), scavenger concentration of 0.04 mol/L, irradiation time of 40 min.

**TABLE 1: Effect of Oxalic Acid Concentration on the Conversion of Nitrite and pH Changes of Reaction Solution<sup>a</sup>**

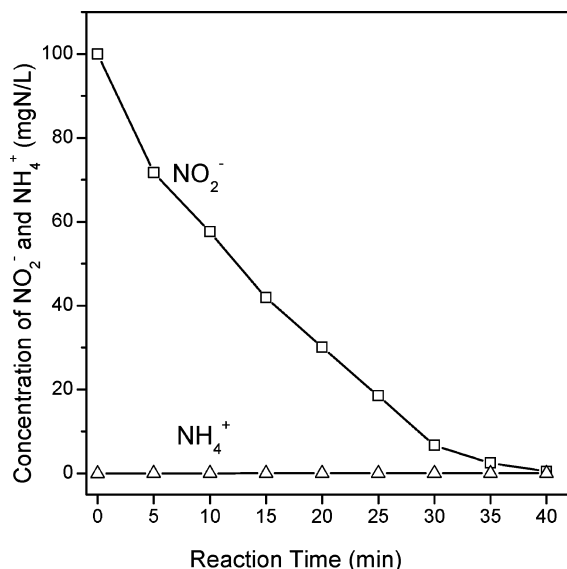
concentration (mol/L)	conversion (%)	pH value
0.02	88.6	2.56–5.54
0.04	99.5	2.34–3.41
0.06	93.2	2.21–3.02
0.08	93.3	2.17–2.76

<sup>a</sup> Reaction conditions: 0.2 g (1 wt %) of the Ag/TiO<sub>2</sub> (P) catalyst, 200 mL of the NO<sub>2</sub><sup>-</sup> solution (100 mg/L), 0.04 M oxalic acid as the hole scavenger, *T* = 40 min.

The effect of the oxalic acid concentration was given in Table 1, in which 0.04 mol/L hole scavengers were found sufficient enough to reduce 100 mg<sub>N</sub>/L (7.14 mmol/L) nitrite. With a further increase of the scavengers' concentration, catalytic activities slightly decrease, as may be attributed to the adsorption competition between nitrite anions and anions of scavengers. All of the pH values simultaneously increase with the consumption of scavengers. It was found that the residual oxalic acid can be efficiently eliminated by further irradiation of about 30 min.

Figure 5 is a plot of the representative time dependence curve of nitrite reduction on the 1 wt % Ag/TiO<sub>2</sub> (P) catalyst under the modification of oxalic acid, in which the concentration of nitrite ions was quasi-linearly decreased with time. The average activity is calculated as 19 mmol·g<sub>Ag</sub><sup>-1</sup>·min<sup>-1</sup> in terms of silver usage. However, for most previously supported metal catalysts, the average activities are usually 1–3 mmol·g<sub>metal</sub><sup>-1</sup>·min<sup>-1</sup>. It is, moreover, worth noting that, under the detection limit of UV–vis spectroscopy, no ammonium ions are found. The analysis of gas product mentioned in the last paragraph of Experimental Section reveals that nitrogen is the only product formed during nitrite reduction.

The effect of three typical anions, HCO<sub>3</sub><sup>-</sup>, CO<sub>3</sub><sup>2-</sup>, and SO<sub>4</sub><sup>2-</sup>, which commonly coexisted in the drinking water, was finally investigated, and all of the experimental results are given in Table 2. It can be seen that the photocatalytic activities of nitrite ions are rarely influenced by the coexisted anions with a concentration below 200 mg/L. This indicates that nitrite ions have a strong adsorption ability on active sites to well compete with the coexisted anions in drinking water mentioned above.



**Figure 5.** Time curve of nitrite photoreduction on the 1 wt % Ag/TiO<sub>2</sub> (P) catalyst with oxalic acid as the hole scavenger. Reaction conditions: 0.2 g (1 wt %) of the Ag/TiO<sub>2</sub> (P) catalyst, 200 mL of the NO<sub>2</sub><sup>-</sup> solution (100 mg/L), 0.04 M oxalic acid as the hole scavenger.

**TABLE 2: Effect of Different Concentrated Coexisted Anions on the Conversion of Nitrite under the Modification of Oxalic Acid<sup>a</sup>**

coexisted anions	concentration (mg/L)	conversion (%)
HCO <sub>3</sub> <sup>-</sup>	0	99.5
	50	98.8
	100	98.7
	200	97.2
CO <sub>3</sub> <sup>2-</sup>	0	99.5
	50	98
	100	97.4
	200	97.2
SO <sub>4</sub> <sup>2-</sup>	0	99.5
	50	97.1
	100	94.1
	200	93.4

<sup>a</sup> Reaction conditions: 0.2 g (1 wt %) of the Ag/TiO<sub>2</sub> (P) catalyst, 200 mL of the NO<sub>2</sub><sup>-</sup> solution (100 mg/L), *T* = 40 min.

#### 4. Discussion

TiO<sub>2</sub> as an effective photocatalyst has been widely studied for its use in environment purification. However, for a practical application, the photocatalytic activity of TiO<sub>2</sub> needs further improvement. Many methods have been designed to enhance its catalytic ability; utilizing doping metals and adding hole scavengers are the most prevalent means.<sup>35</sup>

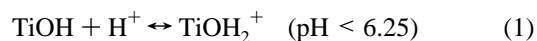
Because the Ag Fermi level is lower than that of TiO<sub>2</sub>, the photogenerated electrons may transfer to the Ag particles deposited on the surface of TiO<sub>2</sub>, and as such, a Schottky barrier is formed at the interface between Ag and TiO<sub>2</sub>. Therefore, the enhancement of photocatalytic efficiency due to the addition of metals like silver (Ag) is commonly attributed to the rapid transfer of the photogenerated electrons from the semiconductors to the metal particles, resulting in the effective separation of the electrons and holes.<sup>36,37</sup> However, it has also been demonstrated that two aspects of these influences should be considered for the metal modification. Superfluous metal doping will cover and occupy more active sites on the surface of semiconductors decreasing the photoinduced efficiency. On the other hand, too big metal particles will enrich more electrons and become new recombination centers of photogenerated electrons and holes.<sup>17,37–39</sup> That is to say, the morphology and size of the coated metals

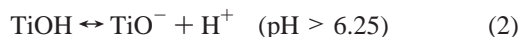
that are commonly influenced by the method of preparation should be considered as other crucial factors in determining catalytic activity.<sup>12</sup> For instance, the activity order of nitrate reduction was Ru > Pt > Pd > Rh for the catalysts prepared by the impregnation method, while the order of activity was Pd > Rh > Pt > Ru for the catalysts prepared by the photodeposition method.<sup>12</sup>

The different catalytic activity and selectivity on Ag/TiO<sub>2</sub> (P) and Ag/TiO<sub>2</sub> (C) may be attributed to their dissimilar morphology and size of deposited silver. Compared with the Ag/TiO<sub>2</sub> (P) catalysts, the deposited silver particles on the Ag/TiO<sub>2</sub> (C) catalyst are typically aggregated and heterogeneously dispersed. The bigger metal particles not only decrease the number of active sites trapping the electrons but also enrich much more photogenerated electrons and become new recombination centers of photogenerated carriers. Comparatively, the coated silver nanoparticles on the Ag/TiO<sub>2</sub> (P) catalysts are much smaller and homogeneously dispersed in favor of the better separation of photogenerated carriers. Therefore, the photocatalytic efficiency on the Ag/TiO<sub>2</sub> (P) catalysts is significantly superior to that on the corresponding Ag/TiO<sub>2</sub> (C) catalyst. However, the size of coated silver on the Ag/TiO<sub>2</sub> (P) catalysts will become larger with the increasing Ag content and will influence the separation efficiency of photogenerated carriers. As a result, the photocatalytic activity curve as a function of silver content exhibits a volcano-type curve and has the optimum level of silver deposition known as approximately 1 wt %.

Since nitrogen, as the desirable product, contains two nitrogen atoms, whereas the substrate nitrite just has one nitrogen atom, a pairing of two nitrogen-containing surface species (N-species) has to occur for the formation of nitrogen. Comparatively, the formation of ammonium commonly results from the meeting of one N-species and reductant species covered on the surface of active sites by a diffusion effect. Therefore, the selectivity of nitrite reduction could be suggested as a function of the ratio of surface coverage of N-species to reductant species (N/reductant ratio) on the silver active sites. The nitrogen selectivity should increase with the enhanced N/reductant ratio. It is reasonable to deduce that the active metals with a bigger size will provide more possibilities for the simultaneous absorption and activation of two N-species and finally produce nitrogen. Hence, the size of the active sites should be an important parameter of influencing the nitrogen selectivity. Since the silver particles (ca. 2 nm) on the Ag/TiO<sub>2</sub> (P) catalyst were more homogeneous with respect to those on the Ag/TiO<sub>2</sub> (C) catalyst, the former could make the more homogeneous simultaneous absorption and activation of two N-species for the final generation of nitrogen. Relatively, the absorption and activation of nitrite ions on the heterogeneously dispersed silver sites on the Ag/TiO<sub>2</sub> (C) catalyst were not uniform, and ammonia, as a side product, was unavoidably formed. Similar discussion on the size and morphology effect of active metals on the nitrogen selectivity was introduced and is now generally accepted in the process of liquid-phase hydrogenation of nitrate and nitrite.<sup>40,41</sup>

The high efficient conversion of nitrite to nitrogen on the Ag/TiO<sub>2</sub> (P) is also related to the suitable acid environment originating from the addition of oxalic acid. It has been indicated<sup>42</sup> that at the surface of titanium dioxide existed a surface group named "titanol", which was amphoteric and could occur in such an acid–base equilibrium:

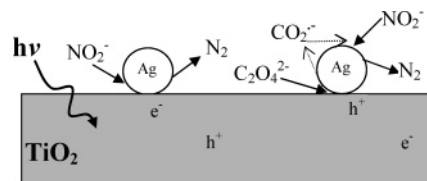




At  $\text{pH} < 6.25$ , the  $\text{TiO}_2$  surface accumulates a net positive charge because of the increasing fraction of total surface sites present as  $\text{TiOH}_2^+$ , and nitrite could be adsorbed quickly into the surface of  $\text{TiO}_2$  in the acidic medium, as has been experimentally testified.<sup>43</sup> Oppositely, at  $\text{pH} > 6.25$ , the surface of titanium dioxide will be negatively charged to inhibit the adsorption of nitrite. Accordingly, the pH environment is very important for the adsorption and reduction of nitrite ions, and the significant effect of the pH value on the reduction of nitrate has been demonstrated in previous literature.<sup>43,44</sup> As to the use of hole scavengers such as  $\text{C}_2\text{H}_3\text{OONa}$ ,  $\text{HCOONa}$ , and  $\text{Na}_2\text{C}_2\text{O}_4$ , in this study, the reaction medium is typically basic with a pH value higher than 7, so the surface of titania is negatively charged and not in favor of the adsorption and conversion of nitrite ions. Since methanol is neutral, close to the isoelectric point (IEP) of titania (IEP = 6.25), the adsorption of nitrite is also unfavorable, and the reduction activity was just slightly improved with respect to the basic medium. Because of the promoted adsorption of nitrite ions in an acidic solution, however, the reduction activity becomes remarkably higher especially for the addition of oxalic acid.

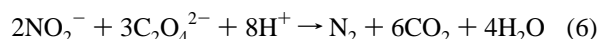
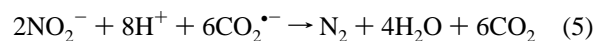
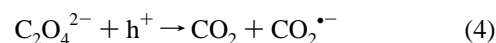
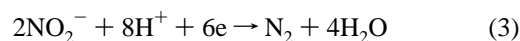
Similar to most of the catalytic processes, the photocatalytic performance of nitrite should be greatly influenced by the ability of the absorption, activation, and desorption of the reaction species on the active sites. The diverse hole scavengers not only influenced the surface charge of titanium dioxide because of the formed dissimilar pH environment but also made a distinct absorption competition with nitrite, both of which together affected the absorption and the activation of nitrite on the active sites. On the other hand, the amount of reductant species originating from the activation of the scavengers is different because of the discrepancies of the absorption and activation ability of various scavengers on the active sites. As a result, the ratio of N-species to reductant species becomes typically different and consequently affects the nitrogen selectivity greatly.<sup>40,41</sup> However, it was demonstrated in Figure 4 that the undesirable ammonia product was just observed during the photocatalytic processes with  $\text{CH}_3\text{COOH}$  or  $\text{CH}_3\text{COONa}$  (containing the  $\text{CH}_3\text{COO}^-$  radical) as hole scavengers, while the nitrogen selectivity of approximately 100% was achieved under the modification of other scavengers. It indicates that other than the scavengers containing the  $\text{CH}_3\text{COO}^-$  radical, the effect of the other hole scavengers on the nitrogen selectivity was much less obvious. Accordingly, it can be deduced that, on the Ag/ $\text{TiO}_2$  (P) catalyst, the homogeneous silver active sites with an average size of approximately 2 nm should have good adaptability to simultaneously activate two N-species and reductant species for the nitrogen formation with most of the scavengers used, which is responsible for the observation of high nitrogen selectivity.

The different reduction activities between oxalic acid and acetic acid demonstrate that a suitable pH value of the reaction solution is desirable for the catalytic performance, where the initial pH value (measured at 3.4) in the solution of acetic acid is comparatively higher than that with the modification of oxalic acid (pH = 2.34). Further proof concerning the suitable pH environment is that less than or more than 0.04 mol/L oxalic acid having different initial pH values leads to the decrease of reduction activity (see Table 1). It should also be pointed out that the dissimilar structure and the adsorption ability among hole scavengers may be other reasons which influence the catalytic performance and should be systemically studied later.



**Figure 6.** Mechanism sketch for photocatalytic reduction of nitrite on the Ag/ $\text{TiO}_2$  (P) catalyst.

It is easy to deduce that photogenerated electrons and holes can be consumed by nitrite and oxalic acid, respectively. Values for the flatband potential ( $V_{fb}$ ) of the conduction band (cb) and valence band (vb) of Degussa P-25 have been calculated as  $-0.3$  V and  $+2.9$  V (pH = 0), respectively.<sup>20</sup> And the position of the flatband of a semiconductor in solution follows Nernstian pH dependence, decreasing 59 mV per pH unit,<sup>45</sup> and consequently, the capability of electrons and holes which are responsible for the redox reaction can be controlled by changes in the pH.<sup>20</sup> It has been demonstrated<sup>44,22</sup> that the oxidation of oxalate ions is to form the  $\text{CO}_2$  and  $\text{CO}_2^{\bullet-}$  species by trapping photogenerated holes. The stronger reductive ability of the  $\text{CO}_2^{\bullet-}$  species ( $E^0(\text{CO}_2/\text{CO}_2^{\bullet-}) = -1.8$  V) tends to reduce nitrite ions ( $E^0(\text{NO}_2^-/\text{N}_2) = 1.45$  V;  $E^0(\text{NO}_2^-/\text{NH}_4^+) = 0.879$  V) into nitrogen or ammonium. Accordingly, the reduction of nitrite ions to nitrogen in this study can be expressed in eq 6, and the proposed reduction mechanisms are as follows:



The reaction mechanism can be described by the sketch shown in Figure 6, where the photogenerated electrons and holes inspired by the UV light with wavelength below 380 nm were first rapidly transferred to the surface of silver deposited on titanium dioxide because of the existence of the Schottky barrier between silver and  $\text{TiO}_2$  mentioned above. The photoelectrons on the silver particles can then be directly used for the reduction of nitrite. On the other hand, the photogenerated holes were to be consumed by  $\text{C}_2\text{O}_4^{2-}$  to form  $\text{CO}_2^{\bullet-}$  for the further conversion of nitrite to nitrogen. Presumably, the latter should make a larger contribution to nitrite conversion because of the fact that the radical  $\text{CO}_2^{\bullet-}$  has a much stronger reduction ability than photogenerated electrons. On the other hand, without the addition of hole scavengers or under the modification of other hole scavengers, the photocatalytic activity of nitrite is much lower.

Summarily, the rapid selective conversion of nitrite to nitrogen instead of ammonia has been achieved on the Ag/ $\text{TiO}_2$  (P) catalyst under the modification of oxalic acid. The unexpected catalytic performance should result from the multiple areas of contributions mainly including (i) homogeneous silver deposition results in the effective separation of the electrons and holes improving the photocatalytic activity, (ii) the suitable size (ca. 2 nm) of deposited silver providing more opportunities to simultaneously adsorb and activate two N-species favoring the formation of nitrogen, and (iii) the oxalic acid which created a

suitable acid pH environment (below IEP of TiO<sub>2</sub>) favoring the absorption and activation of nitrite and oxalic radicals anions.

## 5. Conclusion

For the first time, nitrogen as a desirable product instead of ammonia was only observed during the photocatalytic reduction of nitrite. The best average activity of 19 mmol<sub>NO<sub>2</sub></sub>·g<sub>Ag</sub><sup>-1</sup>·min<sup>-1</sup> has been achieved on the 1 wt % Ag/TiO<sub>2</sub> (P) catalyst with the effect of 0.04 mol/L oxalic acid as the hole scavenger in this study. The unexpected selective reduction of nitrite to nitrogen on Ag/TiO<sub>2</sub> (P) was ascribed to the homogeneous silver morphology on the surface of titanium dioxide and the appropriate pH environment originating from the addition of oxalic acid. The coexisted anions in drinking water show a minor effect on the photocatalytic efficiency. With the development of sunlight catalysts, the photopurification can be expected to be a promising denitrification method.

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