

High photocatalytic activity and selectivity for nitrogen in nitrate reduction on Ag/TiO₂ catalyst with fine silver clusters

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Abstract

Ag/TiO₂ catalyst with fine size and homogeneous dispersion of coated silver clusters was synthesized by a recently developed pH-controlled photocatalytic process and applied to the photocatalytic reduction of nitrate as an environmentally friendly and low-cost catalyst with formic acid as a hole scavenger. Compared with conventional preparation routes, the as-prepared Ag/TiO₂ catalyst in this study shows better catalytic performance: a nitrate conversion of 98% and selectivity for nitrogen of ca. 100%, which can be achieved after 30 min of irradiation. The average activity was calculated to be ca. 24 mmol_{NO₃⁻} g_{Ag}⁻¹ min⁻¹, which is much higher than that of most of Pd–Cu-based nitrate hydrogenation systems in terms of metal usage, demonstrating its application potential. A similar photocatalytic efficiency and selectivity for nitrogen were also observed for nitrite photocatalytic reduction on this catalyst. The effects of Ag content, hole scavengers, concentration of formic acid, and other anions present in drinking water, such as SO₄²⁻, CO₃²⁻, and HCO₃⁻, were systematically investigated.

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1. Introduction

Highly concentrated nitrate and its metabolites are toxic to human health and are particularly harmful to infants, so the World Health Organization (WHO) recommends a maximum nitrate concentration of 10 mg/l (calculated by nitrogen weight, denoted as mg_N/l), a maximum nitrite concentration of 0.03 mg_N/l, and a maximum ammonium concentration of 0.4 mg_N/l in drinking water. It has been reported that the nitrate concentration in groundwater can be as high as 50 mg_N/l in some locations [1]. Biological and physicochemical methods have been developed to treat excess nitrate, but a catalytic process is expected to be more economical and to have ecological advantages [2,3].

Liquid-phase catalytic nitrate hydrogenation has been extensively studied since 1989, when a Pd–Cu bimetal catalyst was found to be active by Tacke and Vorlop [4,5]. Since the water treatment process must be carried out at ambient temperature, noble metals with potential toxicity, such as Pd, Rh, and Pt, had to be used primarily to achieve high activity. Nevertheless, the activity and selectivity for nitrogen have not been simultaneously satisfying, especially for tapwater treatment, until recent studies [2,3,6–16]. Furthermore, the formation of undesired ammonia, the safety of hydrogen, and the efficient contact among three phases are still major problems to be faced in future applications. In view of this, a negative view of the application prospects of liquid-phase catalytic hydrogenation and conventional methods like reverse osmosis as alternatives were expressed by Ruiz-Bevía [17], but they were soon defended by Corma [18].

In recent years, heterogeneous photocatalytic reduction of nitrate over semiconductor materials has also been de-

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veloped as a promising method for controlling the concentration of nitrate in drinking water [19–21]. Among them, TiO_2 was considered to be the material with the most potential for photocatalytic purposes, because of its exceptional optical and electronic properties, chemical stability, nontoxicity, and low cost [22]. It has been proved [23–25] that metal loading and the addition of so-called hole scavengers instead of photochemically produced hydrogen are essential for the effective reduction of NO_3^- . Many metals, such as Pd [24,26], Pt [24,26], Rh [24,26], Ru [26], and sacrificial electron donors, such as methanol [26–28], ethanol [26], EDTA [26], oxalic acid [29,30], sodium oxalate [31], formic acid [32,33], sucrose [34], and humic acid [19], have commonly been used to improve photocatalytic efficiency. Although the reductants were easier to handle than hydrogen, unfortunately, the photocatalytic efficiency of the catalyst was still unsatisfying, and high concentrations of toxic nitrite or ammonium by-products instead of the desired nitrogen were observed in previous studies [19–21,23–34]. Accordingly, it is extremely desirable and exigent to find out an optimal reaction system to improve the activity and selectivity for nitrogen of the reaction, and to produce a quality standard for drinking water.

In our previous work [35–37], a pH-controlled photodeposition process at room temperature was developed to control the size and morphology of coated metals such as silver, platinum, and palladium on the surface of titania, to produce homogeneous dispersion and narrow size dispersion.

In this study, the effect of morphology of coated silver on the photocatalytic activity of nitrate was further investigated. High conversion (98%) and almost 100% selectivity for nitrogen were obtained in nitrate photocatalytic reduction with the use of nontoxic and relatively low-cost fine Ag clusters photodeposited on nanosized titanium dioxide particles as catalyst (denoted as Ag/ TiO_2) and formic acid as an effective hole scavenger. The formation of more deleterious products, nitrite and ammonium, was thereby avoided, and residual formic acid can be completely decomposed into a harmless compound, CO_2 , by further irradiation. Formate has also been reported to be a potential electron donor instead of hydrogen for the biodegradation of nitrate in groundwater [38]. The average activity for nitrate conversion was calculated to be ca. $24 \text{ mmol g}_{\text{Ag}}^{-1} \text{ min}^{-1}$, whereas that of most precious metal-based bimetal catalysts in nitrate hydrogenation is $1\text{--}3 \text{ mmol g}_{\text{Pd/Pt}}^{-1} \text{ min}^{-1}$.

2. Experimental

2.1. Catalyst preparation

Ag/ TiO_2 (A) (P25, Degussa, Japan; anatase 79%, rutile 21%) catalyst was prepared by a pH-controlled photocatalytic process that has been described in our previous work in detail [35]. Ag/ TiO_2 (B) (P25, Degussa) catalyst was synthesized by a conventional chemical reduction method with

KBH_4 (1.0 M) as the reductant under a nitrogen atmosphere. Typically 2 g titania and a certain amount of AgNO_3 was added to 25 ml double-distilled water with stirring for 30 min and subsequently ultrasonically dispersed for 20 min. After that, more than 5 times stoichiometric 1 M KBH_4 and 1 M NaOH were mixed and slowly added to the above mixture. The reduced particles were finally filtrated and washed by ethanol or water and dried under ambient conditions. The metal weight content of both catalysts was 1 wt%, as analyzed by ICP.

2.2. Catalyst characterization

Transmission electron microscopy (TEM) was carried out with a Philips EM-120 TEM instrument with an accelerating voltage of 100 keV.

X-ray photoelectron spectroscopy (XPS) was performed with a PHI 5300 ESCA commercial instrument (PHI Inc.) ($\text{Mg-K}\alpha$ radiation; 1253.6 eV; 10^{-7} Pa), with a C 1s photoelectron peak (binding energy at 284.6 eV) as an energy reference.

2.3. Photocatalytic reduction tests

Photocatalytic reaction was carried out in a double-walled quartz cell cooled by water with a 125-W high-pressure Hg lamp (main wavelength around 365 nm) as a light source (Fig. 1). The initial concentration of nitrate anions was $100 \text{ mg}_\text{N}/\text{l}$ (calculated by nitrogen weight, as done for nitrite and ammonium in this paper). No treatment was carried out to drive out the dissolved oxygen. During irradiation, a small part of the solution was withdrawn periodically, the powdered catalyst was immediately separated by centrifugation, and the supernatant was analyzed to determine the residual concentration of nitrate, nitrite, and ammonium ions with an UV-vis spectrophotometer (Shimadzu; UV-240), which has been described in the literature [39]. Generally, nitrate, nitrite, and ammonium ions were colored by color reactions and then their absorption intensity was measured at 410, 540, and 697 nm separately. No notable

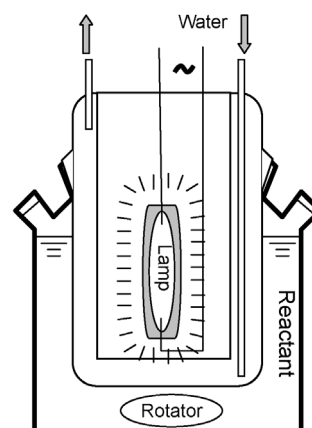


Fig. 1. Scheme of reactor.

catalytic ability was found without illumination in this reaction system.

The catalytic activity for the reduction of nitrate was commonly defined as the amount of nitrate anions reduced per minute and active metal weight ($\text{mol}_{\text{NO}_3^-} \cdot \text{min}^{-1} \cdot \text{g}_{\text{metal}}^{-1}$). The selectivity for nitrogen was defined as the ratio between the concentration of nitrate reduced to form nitrogen (M_{N_2}) and the total concentration of nitrate reduced (M_{total}), provided that no by-products were formed, other than nitrite and ammonium ($S_{\text{N}_2} = (M_{\text{N}_2}/M_{\text{total}}) \times 100\%$). Unless stated otherwise, the selectivity in this study is an integral result of 30 min of reaction, not a differential or stable one.

To identify the gaseous products during nitrate photocatalytic reduction, one separate experiment was done for Ag/TiO₂(A) catalyst in the presence of 0.04 mol/l formic acid. Before irradiation, the solution and the reactor volume were saturated with helium. The experimental results showed that the nitrate conversion rate was unchanged compared with the corresponding experimental conditions without helium. Gaseous products were analyzed with a gas chromatograph equipped with a TCD detector, with helium as a carrier, and a molecular sieve 5A column coupled with a Porapak Q column was used for the gas separation. The experimental results demonstrated that nitrogen was the only gas product and the N₂ selectivity was calculated to be 99.9%.

3. Results and discussion

3.1. Metal modification

It has been reported that noble metal clusters such as Pd, Pt, and Ag of appropriate amount or size can efficiently trap the photoinduced electrons [40–43]. However, metal coating will usually cause some new problems, resulting in a decrease in photocatalytic ability. One is the coverage and occupation of some semiconductor surfaces, decreasing the photoinduction efficiency; the other is that particle that are too large will become new recombination centers of photo-generated electrons and holes [44–47]. Thereby, a volcano-type dependence of metal load was commonly found in many photocatalytic systems.

Modification of semiconductors with metals has been carried out by different techniques, and the resulting efficiency depends on the preparation method and final physicochemical properties of the material [22]. Thermal impregnation, chemical reduction, and photodeposition were the usual methods, and the last was reported to yield more active photocatalytic catalysts [48]. Fig. 2 shows a typical TEM image of Ag/TiO₂(A) in which the coated silver particles, with an average diameter of ca. 2 nm, are evenly dispersed on the surface of TiO₂. In contrast to this, the metal particles coated on a Ag/TiO₂(B) catalyst by chemical reduction are larger and heterogeneously dispersed, which is shown in Fig. 3. Based on the binding energy of silver in XPS spectra

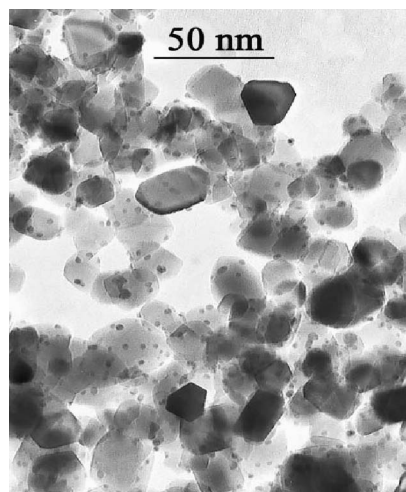


Fig. 2. TEM image of nanosized Ag/TiO₂(A) synthesized by photodeposition.

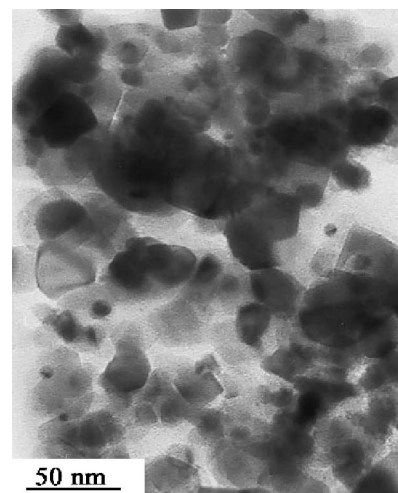
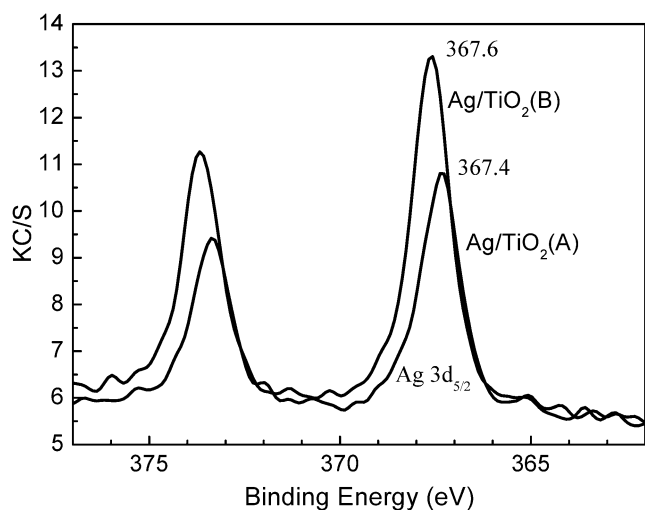
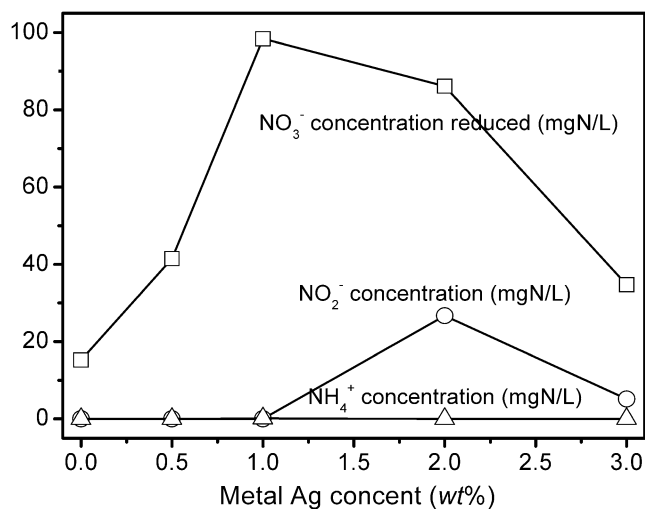


Fig. 3. TEM image of Ag/TiO₂(B) synthesized by chemical reduction.

(Fig. 4), the coated silver on both catalysts can be deduced to be in the metal state. Table 1 exhibits the corresponding experimental results for catalysts TiO₂ (Degussa P-25), Ag/TiO₂(A), and Ag/TiO₂(B). Obviously, proper silver coating inhibits the recombination of photogenerated electrons and holes very well and thus accelerates the conversion of nitrate. In view of the polydispersion of silver nanoparticles coated on Ag/TiO₂(B), the metal modification effect is relatively inferior to catalyst Ag/TiO₂(A), on which a conversion of 98.4% and a selectivity for a desirable product, nitrogen, of 100% are achieved. As discussed above, the main difference between Ag/TiO₂(A) and Ag/TiO₂(B) lies in the morphology of coated silver particles; thus the fine size and even dispersion of coated silver nanoparticles may prolong the lifetime of photogenerated electrons more efficiently and may be responsible for their superior accelerating effect.

A volcano-type curve of metal content to conversion was also found in this study. Fig. 5 plots the conversion of nitrate as a function of silver content, from which 1 wt%

Fig. 4. XPS spectra of Ag/TiO₂.Fig. 5. Concentration curve of reduced NO₃⁻, formed NO₂⁻ and NH₄⁺ after 30 min reaction plotted as a function of silver loaded.

Ag/TiO₂(A) catalyst was found to have optimal activity and selectivity. The distinct modification effect of silver content may be attributed to their dissimilar improvement in the recombination rate of photogenerated electrons and holes. A low level of metal deposition will form fewer electron-accumulated centers, whereas superfluous silver coating will lead to the formation of larger silver nanoparticles, on which a great number of photogenerated electrons will accumulate and which will become new recombination centers of

photogenerated electrons and holes, leading a decrease in photocatalytic efficiency.

To determine the chemical resistance of Ag/TiO₂(A) catalyst, the solution was analyzed by ICP after irradiation to determine the concentration of silver ions. With the detection limitation of ICP, no silver was observed in solution, indicating a good chemical resistance of Ag/TiO₂(A) catalyst.

3.2. Effect of hole scavengers

In addition to the modification of catalysts, another way to promote photocatalytic performance is to add sacrificial electron donors (hole scavengers) to the reaction system. Distinct kinds of sacrificial reagents were commonly found to have a different effect on various systems. Accordingly, choosing a suitable and effective sacrificial reagent becomes especially important for the improvement of catalytic performance. In this study, several hole scavengers were chosen to investigate their effects on the nitrate reduction (Table 2).

Formic acid exhibited the highest ability among seven reagents, as displayed in Table 2. When the initial pH is in a near-neutral region, the reaction activity ranks as HCOONa > CH₃CH₂OH > CH₃CHOONa > Na₂C₂O₄, whereas in an acid region from acidic hole scavengers, the activity is further improved on HCOOH. No catalytic activity was observed in water without a scavenger. It is also found that the selectivity for nitrogen is greatly improved in an acid environment for these hole scavengers (“selectivity” in this article is an integral result of 30 min of reaction, not a differential or stable one).

As far as formic acid was concerned, 0.04 mol/l formic acid was sufficient to reduce 100 mg_N/l (7.14 mmol/l or 443 mg_{NO₃⁻/l) nitrate (Table 3). Although the stoichiometric amount of formic acid is 0.018 mol/l, 0.02 mol/l formic acid resulted in residual nitrite and the formation of ammonia. At the same time, the pH rose from 2.66 to 5.73 with the consumption of formic acid. A further increase of formic acid did not increase the catalytic activity, which may be caused by competition for adsorption between nitrate and formic anions. Thus the consumption of electrons by nitrate was inhibited and finally affected the whole reaction.}

Table 1

Conversion of nitrate, yield of nitrite and ammonium, and selectivity to nitrogen on different catalysts

Catalyst	Conversion of NO ₃ ⁻ (%)	Yield of NO ₂ ⁻ (mg _N /l)	Yield of NH ₄ ⁺ (mg _N /l)	Selectivity to N ₂ (%)
TiO ₂ (P25)	15.2	0	0	100
Ag/TiO ₂ (A)	98.4	0	0	100
Ag/TiO ₂ (B)	71.7	11.5	0.167	83.7

Reaction conditions: 250 ml nitrate solution (100 mg_N/l or 7.14 mmol/l), 0.25 g catalyst, 0.04 mol/l formic acid and 30 min irradiation time. Selectivity to nitrogen was calculated by [(converted nitrate) – nitrite – ammonium]/(converted nitrate).

Table 2

The influences of different hole scavengers on conversion of nitrate, yield of nitrite and ammonium, and selectivity to nitrogen over Ag/TiO₂(A) catalyst

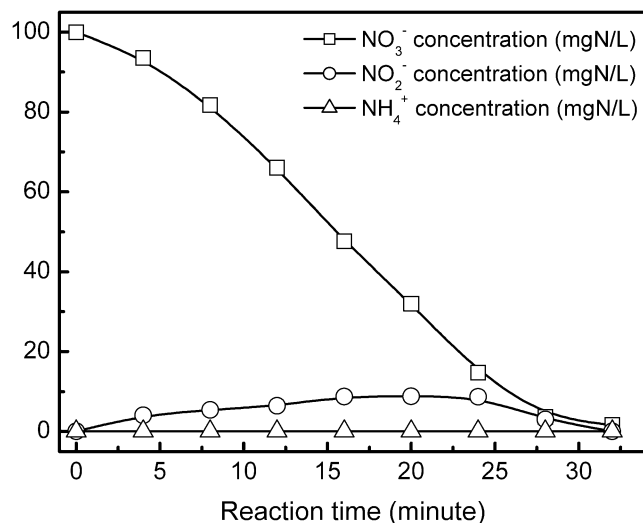
Hole scavengers	Conversion of NO ₃ ⁻ (%)	Yield of NO ₂ ⁻ (mg _N /l)	Yield of NH ₄ ⁺ (mg _N /l)	Selectivity to N ₂ (%)	Initial pH
HCOOH	98.4	0	0	100	2.46
HCOONa	84.5	45.0	3.90	42.2	7.20
CH ₃ CHOOH	9.10	3.50	0	61.5	2.83
CH ₃ CHOONa	11.6	5.99	0	48.4	7.10
H ₂ C ₂ O ₄	16.7	2.20	0.37	84.6	2.34
Na ₂ C ₂ O ₄	7.40	5.26	0	28.4	7.54
CH ₃ CH ₂ OH	28.7	22.20	0	22.6	6.40
Blank (H ₂ O)	0	0	0	0	6.70

Reaction conditions: 250 ml nitrate solution (100 mg_N/l or 7.14 mmol/l), 0.25 g Ag/TiO₂ catalyst, 0.04 mol/l hole scavenger and 30 min irradiation time.

Table 3

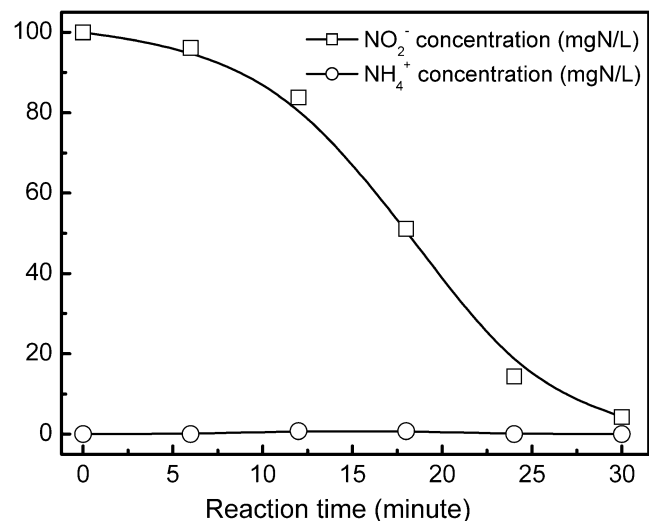
The influence of formic acid concentration on NO₃⁻ conversion, formed NO₂⁻ and NH₄⁺ over Ag/TiO₂(A) catalyst

Formic acid concentration (mol/l)	NO ₃ ⁻ conversion (%)	Formed NO ₂ ⁻ concentration (mg _N /l)	Formed NH ₄ ⁺ concentration (mg _N /l)	pH
0.02	95.4	37.1	4.2	2.66–5.73
0.04	98.4	0.4	0.14	2.46–3.53
0.08	95.2	0.64	2.43	2.28–2.90
0.12	93.5	1.2	0.19	2.28–2.61
0.16	85.2	3.5	0.13	2.15–2.37

Reaction conditions: 250 ml nitrate solution (100 mg_N/l or 7.14 mmol/l), 0.25 g Ag/TiO₂ catalyst, 30 min irradiation time.Fig. 6. Concentration curve of NO₃⁻, formed NO₂⁻ and NH₄⁺ plotted as a function of irradiation time.

3.3. Dependence of irradiation time

Fig. 6 shows the time dependence of the photocatalytic reduction activity of nitrate on Ag/TiO₂(A) catalyst. The conversion of nitrate increases linearly, like most photoinduced reactions, at an average rate of about 24 mmol g_{Ag}⁻¹ min⁻¹, which is superior to rates reported for photocatalytic denitrification systems and even higher than most noble-metal-based hydrogenation systems. During illumination, nitrite was detected but was finally completely converted, and no ammonium ions were found in the whole

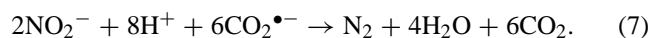
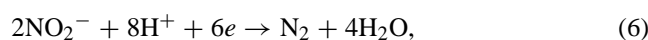
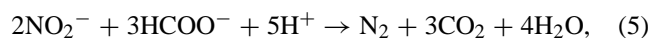
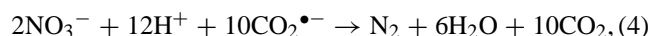
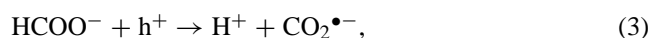
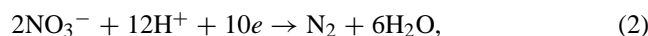
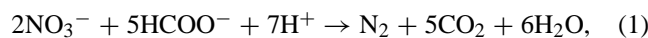
Fig. 7. Concentration curve of NO₂⁻ and formed NH₄⁺ plotted as a function of irradiation time.

process. The conversion of nitrite demonstrates that this catalyst also shows good photocatalytic activity for nitrite reduction, as can be proved by the photoreduction of nitrite under analogous reaction conditions (Fig. 7), where 95.8% nitrite conversion and near-100% selectivity for nitrogen were achieved after 30 min of irradiation at an average activity of 23 mmol g_{Ag}⁻¹ min⁻¹.

3.4. Proposed reduction mechanism of nitrate

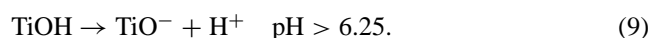
Cox [49] has reported that when a mixture of formate and nitrate at a molar ratio of 3:1 at pH 3.9 was heated for 2 h

at 350 °C and 194 atm, 100% conversion of the nitrate to N₂ occurred, whereas at normal temperature and pressure, the reaction could not happen. This was proved by a dark experiment without UV irradiation. In the presence of formic acid, nitrate and nitrite reduction can be expressed as follows (under UV illumination):



It is easy to deduce that photogenerated electrons and holes can be consumed by nitrate and formic 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 to be -0.3 V and $+2.9$ V (pH = 0), respectively [50]. And the position of the flatband of a semiconductor in solution follows Nernstian pH dependence, decreasing by 59 mV per pH unit [51], and, consequently, the capability of electrons and holes that are responsible for redox reaction can be controlled by changes in the pH [22]. It was reported that the photogenerated holes were consumed by formic anions to form $\text{CO}_2^{\bullet-}$ [52] [Eq. (3)]. Compared with HCOO^- ($E^\circ(\text{CO}_2/\text{HCOO}^-) = -0.2$ V), the $\text{CO}_2^{\bullet-}$ species has a stronger reductive ability [53] ($E^\circ(\text{CO}_2/\text{CO}_2^{\bullet-}) = -1.8$ V) and tends to reduce nitrate ($E^\circ(\text{NO}_3^-/\text{NO}_2^-) = 0.94$ V; $E^\circ(\text{NO}_3^-/\text{N}_2) = 1.25$ V; $E^\circ(\text{NO}_2^-/\text{N}_2) = 1.45$ V) to nitrogen [Eq. (4)]. At the same time, photogenerated electrons also have a relatively weaker ability to reduce nitrate [Eq. (2)]. So the total reaction can be expressed as Eqs. (4) and (7). Because no treatment was taken for the dissolved oxygen, the decomposition of formate by nitrate or nitrite may be competed by oxygen ($E^\circ(\text{O}_2/\text{H}_2\text{O}) = 1.23$ V), and the redox of water can be neglected.

On the surface of TiO₂, “titanol” (Ti–OH) is present, which is amphoteric and occurs in an acid-base equilibrium [54] as in Eqs. (8) and (9), so the absorption properties can be greatly changed for different pH values



In an acidic environment, H⁺ ions will be adsorbed to the surface of P25 TiO₂, which was reported to have a large surface proton exchange capacity (0.46 mmol/g) [55]. The photogenerated electrons can be captured by the adsorbed H⁺ to form H_{ads}[•], which is able to reduce nitrate. And the positively charged titania makes nitrate and formic anions reach the Stern layer near the surface of catalyst and adsorb to active sites easily.

It has been reported [25,29] that noble-metal-loaded catalysts (M/TiO₂) have been used in photocatalytic reactions mainly because (i) they have a high electron affinity and hence increase the lifetime of the excitons, thus slowing the recombination of the charge carriers (i.e., electrons and holes) and (ii) they promote the dissociative adsorption of hydrogen as H_{ads} for metals with low H₂ overpotential (e.g., Pt) or stabilize H_{ads} for metals with high H₂ overpotential (e.g., Ru). Photocatalytic effectiveness was known to depend on how long the photogenerated electrons are trapped on the metal centers and how efficiently they are used in subsequent reduction reactions [25]. Moreover, the morphology and size of coated metals that were commonly influenced by the method of preparation were considered another crucial factor in determining catalytic activity [56]. For instance, the activity order of nitrate reduction was Ru > Pt > Pd > Rh for the catalysts prepared by the impregnation method, and the order of activity was Pd > Rh > Pt > Ru for the catalysts prepared by photodeposition method. In this study, metal silver clusters coated on TiO₂ particles not only should prolong the lifetime of photogenerated electrons very well, but should also act as efficient reduction sites. Since equal numbers of e⁻ and h⁻ must be consumed in the photocatalytic systems, the acceleration of reduction with e⁻ at the homogeneously dispersed metal silver surface enhanced the overall reaction as observed.

Compared with a near-neutral pH region, the catalytic activity was much higher in an acid environment. The results suggested that the reduction of nitrite was greatly increased in the acid region, which resulted in the production of a great quantity of nitrogen, whereas the reduction of nitrate was not as affected by acid. As the reductive ability of photogenerated electrons was improved in the acid region, the consumption of electrons by nitrate or nitrite may be increased.

3.5. Effect of salts

In tapwater, the components were complex, including many anions and cations, which more or less affect the photoreduction of nitrate. In this study, different concentrations of Na₂SO₄, Na₂CO₃, and NaHCO₃ were added to the reaction solution to study their effect on the photoreduction of nitrate. Figs. 8–10 show their experimental results, from which different disturbance effects can be observed. Compared with HCO₃⁻ ions, the presence of SO₄²⁻ or CO₃²⁻ ions produces a more negative effect on the photocatalytic conversion of nitrate. The distinct disturbance effects may be attributed to the dissimilar ability of adsorption competition with nitrate on the surface of the catalyst. Typically, the surface of titania will be positively charged in the formic acid system, so it may be much easier for more negative SO₄²⁻ or CO₃²⁻ anions to stay near the surface than for HCO₃⁻ to produce stronger adsorption competition.

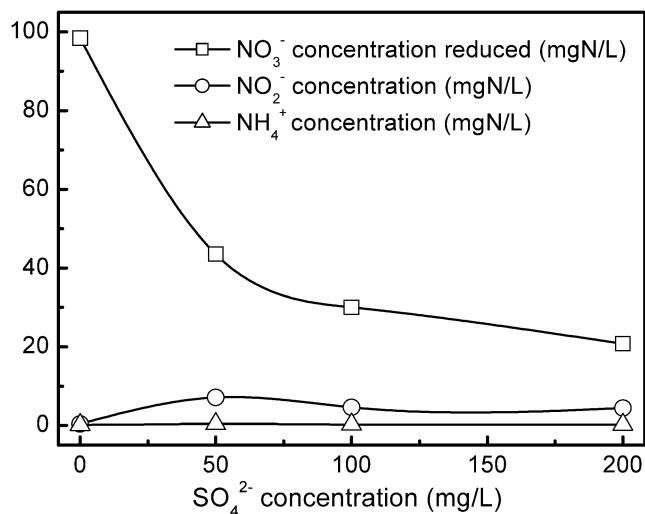


Fig. 8. Concentration curve of reduced NO₃⁻, formed NO₂⁻ and NH₄⁺ plotted as a function of SO₄²⁻ concentration.

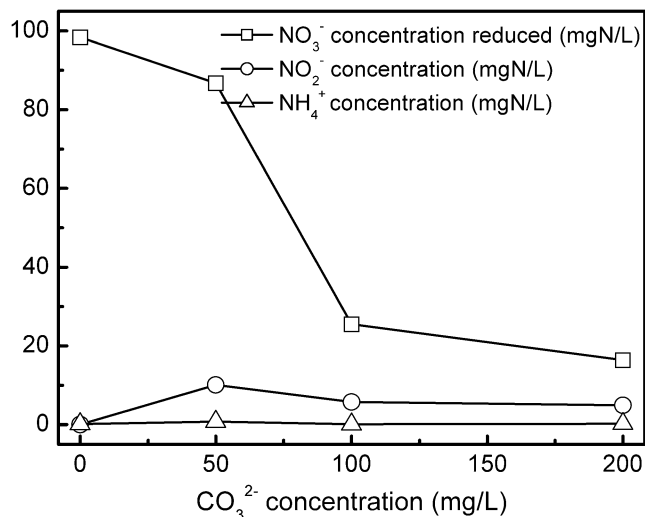


Fig. 9. Concentration curve of reduced NO₃⁻, formed NO₂⁻ and NH₄⁺ plotted as a function of SO₃²⁻ concentration.

4. Conclusions

Photodeposited Ag/TiO₂ with fine silver clusters exhibited better activity for photocatalytic reduction of nitrate anions than Ag/TiO₂ catalyst prepared by a traditional method. Under the modification of 0.04 mol/l formic acid as a hole scavenger, the as-prepared 1 wt% Ag/TiO₂(A) catalyst was found to exhibit as much as 98% nitrate conversion for 443 mg_{NO₃⁻}/l nitrate solution and 100% selectivity for nitrogen after 30 min of UV illumination. The average activity was calculated to be 24 mmol_{NO₃⁻}/g_{Ag} min⁻¹, which is much higher than the average activity for most noble-metal-based nitrate hydrogenation systems. The results demonstrate that the photocatalytic reduction of nitrate in drinking water may be a promising denitrification method, especially with the development of applications involving sunlight.}}

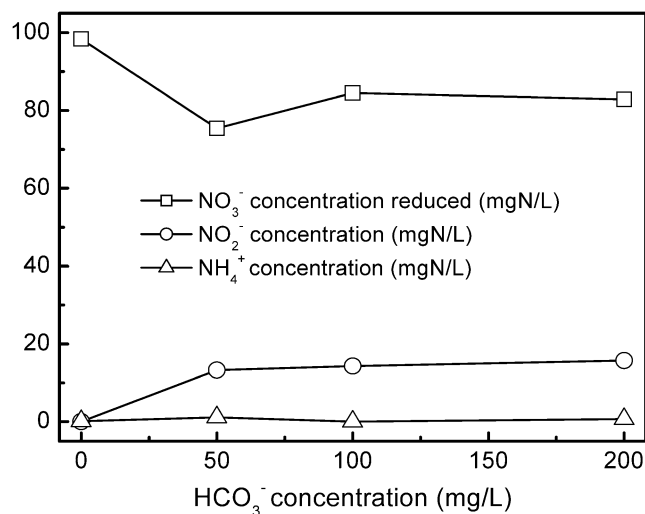


Fig. 10. Concentration curve of reduced NO₃⁻, formed NO₂⁻ and NH₄⁺ plotted as a function of HCO₃⁻ concentration.

Acknowledgments

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