

# Titania-supported bimetallic catalysts for photocatalytic reduction of nitrate

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## Abstract

Photocatalytic reduction of nitrate in the presence of hole scavenger has been studied by using TiO<sub>2</sub>-supported bimetallic catalysts for the first time. Compared with monometallic catalysts, bimetallic catalysts, especially Ni–Cu/TiO<sub>2</sub> catalyst, show more excellent photocatalytic reduction activity. Furthermore, the effects of metal weight ratio, total metal content, different hole scavengers and pH value of the solution are also investigated. It is found that pH value of reaction solution plays an important role in the photocatalytic reduction of nitrate ions. A mechanism is proposed to discuss enhancement effect of the bimetallic catalyst in photocatalytic reduction of nitrate ions in this paper.

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**Keywords:** Ni–Cu/TiO<sub>2</sub> bimetallic catalyst; Drinking water; Photocatalytic reduction; Mechanism

## 1. Introduction

In recent years, nitrate concentration in ground water, which is the main source for drinking water, has been increasing throughout the world because of intensive agricultural activities, especially overusing man-made fertilizers [1]. High concentration of nitrate in drinking water is fatal to infants under 6 months of age, in whose bodies, NO<sub>3</sub><sup>−</sup> is reduced to NO<sub>2</sub><sup>−</sup>, which combines with hemoglobin in the blood to form methaemoglobin, and leads to a condition commonly known as “blue baby syndrome”. Furthermore, nitrate can be converted into nitrosamine, which can cause cancer and hypertension [2]. For these reasons, the US Environmental Protection Agency (EPA) established the maximum permitted level of nitrate to 10 mg NO<sub>3</sub><sup>−</sup> (calculated by nitrogen, N/L) in drinking water. The European Community set the maximum permitted level of nitrate to 11.3 mg/L (N/L) and recommended level of 5.65 mg/L (N/L). So reducing nitrate concentration in drinking water is an imperative task at the present time.

Many methods like ion exchange, reverse osmosis, electrolysis, chemical denitrification and biological denitrification have been used to remove nitrate from drinking water. However, these techniques are costly and cannot be easily performed, and usually need a post-treatment of the produced effluents. More recently, photocatalytic denitrification [3–10] has been developed and proved to be a promising method in controlling the concentration of nitrate in drinking water. It has been reported that pure titania hardly has photocatalytic reduction activity, and loading of metal on titania is necessary for photocatalytic reduction of nitrate. In last two decades, many authors [3,4,7–9] had investigated photocatalytic reduction of nitrate by using monometal-loaded catalysts. Ranjit et al. [7–9] reported the photocatalytic reduction of nitrate ion into ammonia on noble metal-loaded TiO<sub>2</sub> catalyst system and observed that photocatalytic reduction of nitrate was dependent on various experimental factors such as the irradiation time, the pH value of the solution, the nature of the sacrificial agent and the nature of the metal loaded on the semiconductor. An optimum metal content is beneficial for the activity, and beyond this optimum content the activity decreases. Kudo et al. [3,4] studied the photocatalytic reduction of nitrate ions into nitrite and ammonia over some modified TiO<sub>2</sub>, SrTiO<sub>3</sub>, K<sub>4</sub>Nb<sub>6</sub>O<sub>17</sub> photocatalysts and found that ammonia was evolved on metallic

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surface such as Pt, whereas nitrite formation was favored on oxide surfaces such as NiO. Although monometal-loaded catalysts are effective in photocatalytic reduction of nitrate, the activities of these catalysts are still lower. At present, supported bimetallic catalysts have been investigated and applied widely in many industrial fields [11–13], however there has no report on the photocatalytic reduction of nitrate over bimetal-loaded TiO<sub>2</sub> catalyst system up to now. In the presence of hole scavenger oxalic acid, we are of the opinion that photocatalytic reduction of nitrate can be performed successfully over titania-supported bimetal catalysts. The purpose of this paper is to investigate the optimal operating conditions and examine the enhancement effect of bimetals in the course of the photocatalytic reduction of nitrate ion.

## 2. Experimental

### 2.1. Preparation of catalysts

The mono- and bimetallic catalysts were prepared via (co)impregnation of the powdered TiO<sub>2</sub> (80% anatase, 20% rutile) with respective salt aqueous solutions. Copper(II) acetate, nickel(II) nitrate, palladium(II) chloride, and hexachloride platinum(III) acid were selected as precursors for the catalysts preparation. After the solvent in the mixture were completely evaporated in air, the resulting solids were dried in an oven at 353 K, then calcined in air at 773 K for 4 h and finally reduced at 773 K in hydrogen atmosphere for 4 h. The obtained catalysts were labeled as Ni–Cu/TiO<sub>2</sub>, Pd–Cu/TiO<sub>2</sub>, Pt–Cu/TiO<sub>2</sub>, Cu/TiO<sub>2</sub>, Ni/TiO<sub>2</sub>, Pd/TiO<sub>2</sub>, and Pt/TiO<sub>2</sub>.

### 2.2. Photocatalytic reduction tests

The photocatalytic experiments were performed in a Pyrex glass reactor at ambient temperature and atmospheric pressure. The reactor was equipped with water circulation in order to maintain a constant temperature and filter IR light. A 125 W high-pressure mercury lamp was used as light source. The reaction mixture was stirred to make the catalyst maintain in suspension by means of a magnetic stirrer. Before irradiation of the solution, CO<sub>2</sub> gas was purged into the solution for 30 min to remove oxygen and then neutralize the produced hydroxyl ions in the succedent reaction. The sample solution was withdrawn periodically and powdered catalyst was immediately separated from the aqueous phase by centrifugation and the remaining top solution was analyzed to determine the residual contents of nitrate, nitrite, and ammonium ions.

### 2.3. Analysis

The concentration of nitrate, nitrite and ammonium were determined by UV-Vis spectrophotometry (Shimadzu, UV-240) [14].

### 2.4. Characterizations of catalysts

X-ray diffraction (XRD) patterns were carried out in a D/max-2500 powder diffractometer using Cu K $\alpha$  ( $\lambda = 1.54178 \text{ \AA}$ ) radiation from 5° to 90° (in  $2\theta$ ) with the scanning rate of 2.4°/min.

Transmission electron microscopy (TEM) was carried out in a Philips CM-120 model instrument operating at 100 keV. Before photographing, the samples were dropped onto the surface of carbon membrane and dried at ambient conditions.

### 2.5. Determination of catalytic activity and selectivity

The catalytic activity for the reduction of nitrate is defined as the reduced amount of nitrate ions per time and catalyst weight ( $\text{mmol g}_{\text{cat}}^{-1} \text{ h}^{-1}$ ).

The selectivity to nitrogen is defined as the ratio of formed nitrogen amount to the reduced nitrate amount, which is based on the assumption that no other side products are formed other than nitrite and ammonium.

## 3. Results and discussion

### 3.1. Photocatalytic nitrate reduction over different metal-modified catalysts

Various metal-modified catalysts were tested for the reduction of nitrate to nitrogen and the corresponding results are shown in Table 1. It can be seen that under the given conditions, pure titanium dioxide did not show any photocatalytic activity for nitrate reduction. Furthermore, although monometallic photocatalysts, such as Pd/TiO<sub>2</sub>, Pt/TiO<sub>2</sub>, Ni/TiO<sub>2</sub> and Cu/TiO<sub>2</sub>, exhibited much higher selectivity to nitrogen, the activity for nitrate reduction was much lower. Compared with corresponding monometallic catalysts, bimetallic catalysts showed more excellent photocatalytic nitrate reduction activity. Among these catalysts, Ni–Cu/TiO<sub>2</sub> showed the maximum photocatalytic activity and thereby was selected as model catalyst in this study.

### 3.2. Effect of Ni:Cu weight ratio

In general, the weight ratio of two metals in bimetallic catalyst is an important factor for its catalytic activity and selectivity. In this work, by fixing the total metal content (4 wt.%), the molar ratios of Ni to Cu varied from 4:1, 3:1, 2:1, 1:1, 1:2, 1:3 to 1:4 and the results are listed in Fig. 1. The optimum Ni:Cu molar ratio with the highest catalytic activity was found to be at 3:1.

### 3.3. Effect of total metal content

By fixing weight ratio Ni:Cu = 3:1, the influence of total metal content on nitrate reduction has been investigated. As shown in Fig. 2, low metal content (2 wt.%) or high

Table 1  
Photocatalytic reduction of nitrate ions over different catalysts

Catalyst (4 wt.%)	Activity ( $\text{mmol g}_{\text{cat}}^{-1} \text{h}^{-1}$ )	Yield of nitrite (mmol)	Yield of ammonia (mmol)	Selectivity to $\text{N}_2$ (%)
$\text{TiO}_2$	0	0	0	0
$\text{Pd/TiO}_2$	$7.1 \times 10^{-2}$	0	0	100
$\text{Pt/TiO}_2$	$1.7 \times 10^{-1}$	0	$1.3 \times 10^{-2}$	81
$\text{Ni/TiO}_2$	$1.7 \times 10^{-1}$	0	$7.1 \times 10^{-3}$	89
$\text{Cu/TiO}_2$	$2.4 \times 10^{-1}$	$2.0 \times 10^{-3}$	$1.2 \times 10^{-2}$	86
$\text{Pd-Cu/TiO}_2$ (3:1)	$2.3 \times 10^{-1}$	$2.1 \times 10^{-3}$	$9.3 \times 10^{-3}$	88
$\text{Pt-Cu/TiO}_2$ (3:1)	$4.7 \times 10^{-1}$	$1.9 \times 10^{-2}$	$1.1 \times 10^{-1}$	33
$\text{Ni-Cu/TiO}_2$ (3:1)	$6.0 \times 10^{-1}$	$2.8 \times 10^{-2}$	$1.7 \times 10^{-1}$	19

Reaction conditions: 200 ml nitrate solution (100 mg/L), 0.2 g catalyst, 0.005 mol/L oxalic acid solution,  $\text{CO}_2$  flow rate: 100 ml/min, 2 h irradiation time.

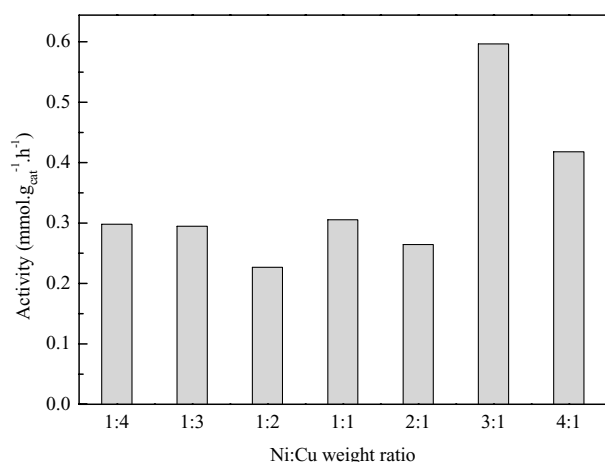


Fig. 1. Influence of Ni:Cu weight ratio on photocatalytic reduction activity of nitrate ions over Ni–Cu/ $\text{TiO}_2$  (4 wt.%) bimetallic catalyst.

metal content (8, 12, 16 wt.%) is not beneficial to the reduction of nitrate and the optimum content is obtained at metal content 4 and 16 wt.%. This suggests that active atomic arrangement and active particles size in the surface of catalyst may have a great influence on the removal of nitrate, rather than the metal loading amount. We select 4 wt.% metal con-

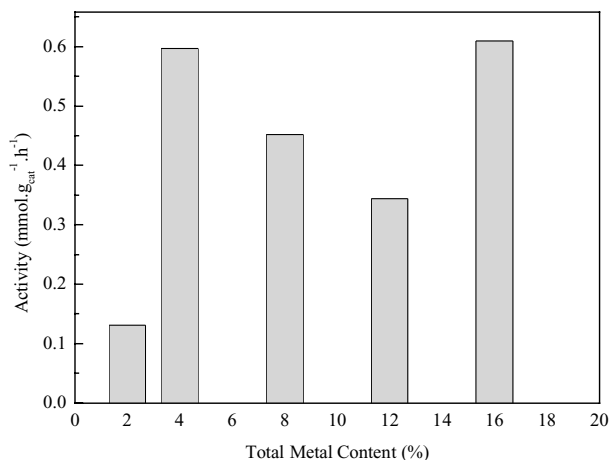


Fig. 2. Influence of total metal content on photocatalytic reduction activity of nitrate ions over Ni–Cu/ $\text{TiO}_2$  (Ni:Cu = 3:1) bimetallic catalyst.

tent rather than 16 wt.% as model catalyst in order to reduce supported metal amount and can make use of these active metal. In order to further observe the morphology of bimetallic Ni–Cu catalyst, TEM of the catalyst (4 wt.%) was taken and one representative photograph is shown in Fig. 3. TEM images shows that the supported active metals clusters are clearly visible and are homogeneously dispersed on the  $\text{TiO}_2$  particles. The size of most of the metal clusters is about 20–30 nm.

### 3.4. Effect of hole scavenger

Two different sacrificial reagents, oxalic acid and sodium oxalate, were used to act as the hole scavenger for the photocatalytic reduction of nitrate, and the results obtained are shown in Fig. 4. It has been proved that sacrificial reagent is necessary for the reduction of nitrate ions, and different sacrificial reagents have distinct redox characteristic [5]. From Fig. 4, it can be seen that nitrate conversion and ammonium

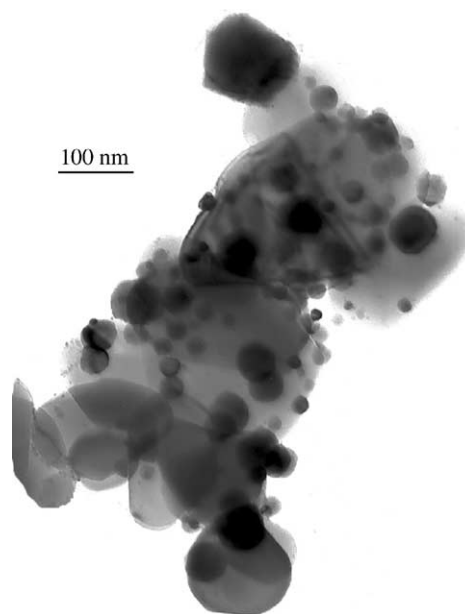


Fig. 3. Transmission electron microscopy of 4 wt.% Ni–Cu/ $\text{TiO}_2$  with a weight ratio Ni:Cu = 3:1. Small particles represent clusters of the active metals; large particles represent  $\text{TiO}_2$  particle.

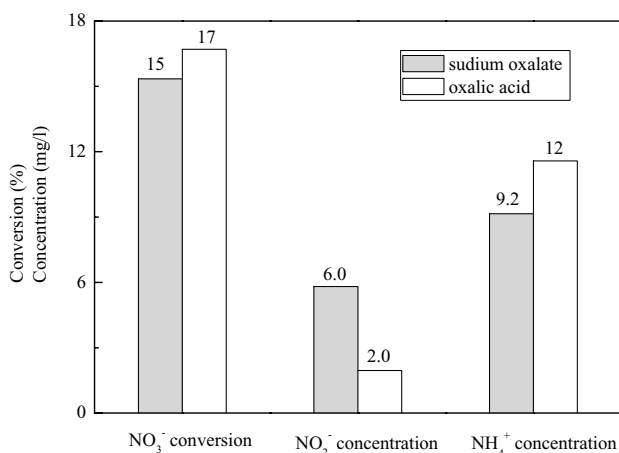
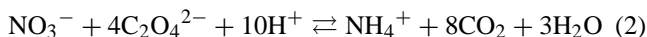
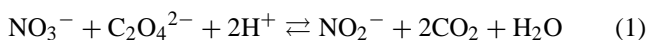


Fig. 4. The effect of hole scavengers (sodium oxalate and oxalic acid) in the photocatalytic reduction of nitrate ions over Ni–Cu/TiO<sub>2</sub> (4 wt.%, Ni:Cu = 3:1) catalyst.

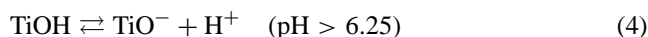
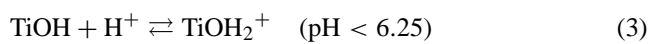
yield were appreciably high when oxalic acid was used as the hole scavenger. In the presence of oxalic acid, nitrate reduction can be expressed as follows:



According to Eqs. (1) and (2), photocatalytic reduction of nitrate is easily performed in a highly acidic medium. But at the same time, only at the higher pH value, a flatband potential is just sufficiently negative for nitrate reduction. So an optimum pH needs to be established in order to achieve maximum reaction rate.

### 3.5. Time dependence of photocatalytic reduction of nitrate ions

Fig. 5 shows the time dependence of the photocatalytic nitrate reduction activity over Ni–Cu/TiO<sub>2</sub> bimetallic catalyst system. As shown in Fig. 5, at the beginning of photocatalytic reaction, the concentration of nitrate decreased rapidly, but only trace of nitrite and ammonium appeared in the solution. With the proceeding of reaction, it had been found that the concentration of the nitrite and ammonium increased sharply, and the pH value of reaction solution also increased accordingly. These results suggested that pH value of the reaction medium played an important role in the photocatalytic nitrate reduction activity and the selectivity to nitrogen; the higher activity and selectivity was favored in the acidic solution. This phenomenon is probably due to specific absorption properties of nitrate and nitrite ions in different pH surroundings. Zhang et al. [15] have reported the acid–basic effects for the photocatalytic reduction reaction of nitrite ions, and found that nitrite could be adsorbed quickly into the surface of TiO<sub>2</sub> in acidic medium, but at higher pH value, the adsorbed nitrite could be desorbed completely. Kormann et al. [16] thought that surface of the titanium dioxide existed a surface group named “titanol”, which was amphoteric and could occur such an acid–base equilibrium:



At pH < 6.25, TiO<sub>2</sub> surface accumulates a net positive charge due to the increasing fraction of total surface sites present as TiOH<sub>2</sub><sup>+</sup>. At high pH, the surface has a net negative charge due to a significant fraction of total surface

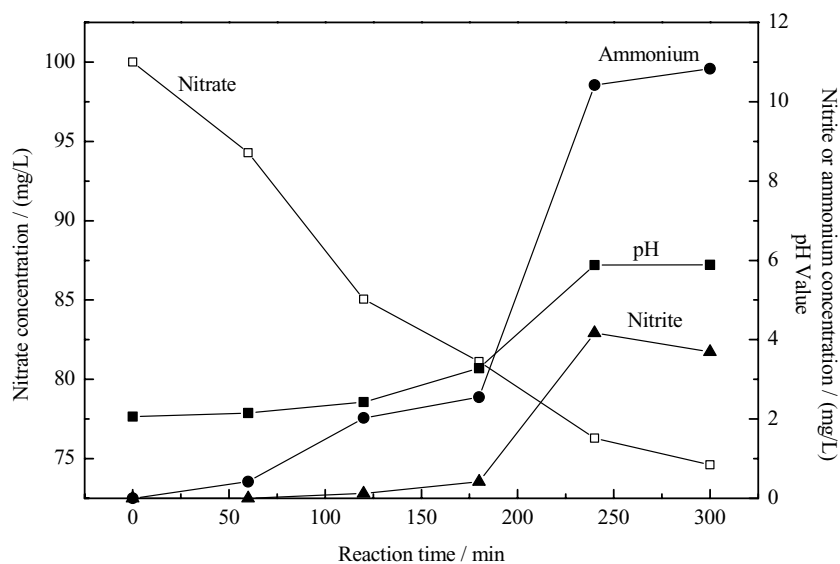


Fig. 5. The concentrations of the nitrate (□), produced nitrite (▲) and ammonium (●), and pH (■) value of the solution as a function of the reaction time over Ni–Cu/TiO<sub>2</sub> (4 wt.%, Ni:Cu = 3:1) catalyst.

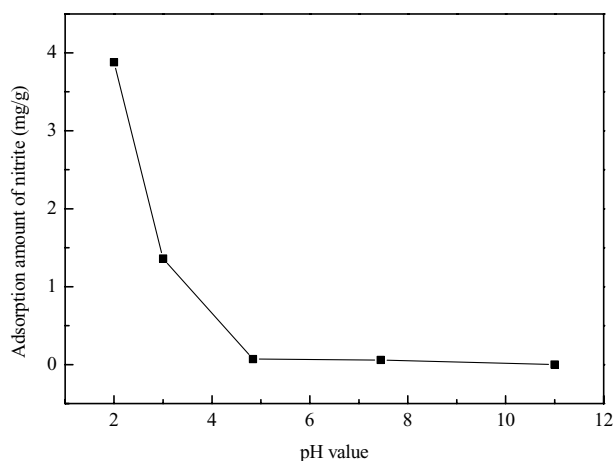


Fig. 6. Influence of pH value on the nitrite adsorption over Ni–Cu/TiO<sub>2</sub> (4 wt.%, Ni:Cu = 3:1) catalyst.

sites present as TiO<sup>-</sup>. Fig. 6 shows the adsorption amount of nitrite on Ni–Cu/TiO<sub>2</sub> catalyst in different pH values. As shown in Fig. 6, with the increasing pH value, the adsorption amount of nitrite decreased sharply. As the pH approached to 5, the adsorption amount of nitrite reached to zero as a whole. It is well recognized that the pre-adsorption of reactants in catalyst surface is an essential step for a catalytic reaction. In our experimental conditions, the reaction was performed in acidic medium, so the surface of titanium dioxide was electropositive and could adsorb anion reversibly. Since the amount of pre-absorbed nitrate and nitrite were determined by pH value of solution, it is much essential to choose a suitable pH environment for the photocatalytic reduction of nitrate ions in this study.

### 3.6. Discussions about photocatalytic nitrate reduction

As mentioned above, bimetallic catalyst Ni–Cu/TiO<sub>2</sub> showed more excellent photocatalytic nitrate reduction activity compared with corresponding monometallic Ni/TiO<sub>2</sub> and Cu/TiO<sub>2</sub> catalysts. It has been generally believed that the conversion of nitrate into nitrite is structure-sensitive and geometric effect of catalyst plays an important role in catalytic hydrogenation of nitrate [6,17], and two metals have probably interacted with support or produced alloy. However, in our study, XRD patterns (Fig. 7) of Ni–Cu/TiO<sub>2</sub> catalyst only showed all the main characteristic peaks of TiO<sub>2</sub> support, no characteristic reflections for Ni, Cu or their Ni–Cu combination (alloy) containing phases are recorded, which indicates that metal particles are well dispersed or interact with TiO<sub>2</sub> support. Although Ni or Cu crystalline phase have not been detected, the enhancement effect between these two metals was much prominent for nitrate reduction. This promoting effect of bimetal is probably attributed to the more effective separation of photogenerated spatial charges in tiny TiO<sub>2</sub> semiconductor particles. For a tiny metal-modified semiconductor particle, supported

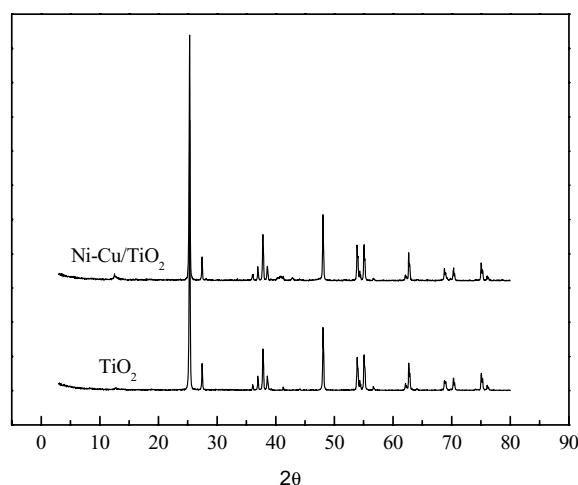
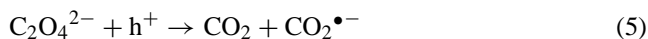


Fig. 7. XRD patterns of TiO<sub>2</sub> and Ni–Cu/TiO<sub>2</sub> (4 wt.%, Ni:Cu = 3:1) catalysts.

bimetal Cu and Ni can behave as short-circuited photoelectrochemical cell, where both cathodic and anodic reactions can occur on the same particle [18]. For photogenerated electrons and holes, metal Ni and Cu in the semiconductor surface can separately trap these reductive electrons and oxidative holes and prevent their combinations, then transfer these trapped electrons or holes to absorbed substances in their surface, thereby increase their existent life and improve the efficiency of a photocatalytic reaction.

In the presence of oxalic acid, nitrate reduction can be expressed as Eqs. (1) and (2). In these processes, the reduction reaction was indirect and began with oxidation of oxalate ions to the species CO<sub>2</sub> and CO<sub>2</sub><sup>•-</sup> by these trapped photogenerated holes [19]:



It was reported [19] that CO<sub>2</sub><sup>•-</sup> species are much active and have stronger reductive ability  $E^0(\text{CO}_2/\text{CO}_2^{\bullet-}) = -1.8 \text{ V}$  and thus can reduce nitrate ( $E^0(\text{NO}_3^-/\text{NH}_4^+) = 1.203 \text{ V}$ ;  $E^0(\text{NO}_2^-/\text{NH}_4^+) = 0.897 \text{ V}$ ) to nitrite or ammonium.

## 4. Conclusions

Studies on the photocatalytic reduction of nitrate on bimetal-loaded TiO<sub>2</sub> catalysts have led to the following conclusions:

1. Compared with monometal-loaded catalysts, bimetal-loaded catalysts have shown more excellent activity in the photocatalytic reduction of nitrate in the presence of oxalic acid. The highest activity is achieved by using Ni–Cu/TiO<sub>2</sub> catalyst with 3:1 metal weight ratio and 4 wt.% total metal content.
2. As the hole scavenger, oxalic acid has appreciably higher photocatalytic reduction activity than sodium oxalate.
3. The pH value of the reaction medium play an important role in the photocatalytic nitrate reduction; the higher

activity and selectivity was favored in the acidic solution. Because the amphoteric property of  $\text{TiO}_2$  support, anion nitrate and nitrite can absorb more effectively in the surface of catalyst in acidic solution. It is the specific adsorption properties of nitrate and nitrite ions that result in the higher activity and the selectivity to nitrogen.

4. The promoting effect of bimetal is probably attributed to the spatial charge separation in tiny  $\text{TiO}_2$  semiconductor. For photogenerated electrons and holes, metal Ni and Cu in the semiconductor surface can separately trap them and prevent their combinations, thereby increase their existent life and improve the efficiency of a photocatalytic reaction.

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