

Photocatalytic reduction of nitrate ion in drinking water by using metal-loaded $\text{MgTiO}_3\text{-TiO}_2$ composite semiconductor catalyst

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Abstract

Photocatalytic reduction of nitrate ions was examined by using $\text{Cu/MgTiO}_3\text{-TiO}_2$ catalyst in the presence of sodium oxalate as hole scavenger. Many factors such as catalyst calcination temperature, Cu:Mg atom molar ratio, different hole scavengers and different concentrations of sodium oxalate were tested to search for the optimal reaction conditions. X-ray diffraction (XRD) and Transmission Electron Micrograph (TEM) were performed to characterize the composite semiconductors catalyst. Our results indicated that $\text{Cu/MgTiO}_3\text{-TiO}_2$ catalyst calcined at 873 K showed the highest photocatalytic activity and nitrate conversion reached 39.2% after 2 h irradiation. The enhanced effect for photocatalytic nitrate reduction activity was most likely to result from the formation of composite semiconductor $\text{MgTiO}_3\text{-TiO}_2$ and the transformation of TiO_2 crystalline phase.

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1. Introduction

In recent years, the intensive agricultural activities, especially overusing man-made nitrogenous substance has made the removal of nitrate ions from drinking water much more attractive [1]. High concentration of nitrate ions in drinking water is deleterious to human bodies because they can be converted into carcinogenic nitrosamine and other *N*-nitroso compounds during nitrate degradation process, and as a result, leads to so-called “blue baby syndrome” [2]. For these reasons, European Drinking Water Directive has introduced maximum admissible concentration for nitrate ions in drinking water to 50 mg/l and the World Health Organization has set 25 mg/l as guide level [3]. Therefore, reducing nitrate concentration in drinking water becomes imperative at the present time.

More recently, photocatalytic nitrate reduction has been developed and proved to be a promising method in controlling the concentration of nitrate in drinking water [4–6]. In these investigations, various semiconductor materials such as TiO_2 , CdS, ZnS, and ZnO have been employed to

study photocatalytic reduction of nitrate in drinking water, among which TiO_2 was proved to be the most efficient photocatalyst due to its exceptional optical, electronic properties, chemical stability, non-toxicity, and low cost [7,8]. In earlier studies, some researchers suggested that the suppression of the recombination of photogenerated electrons and holes in semiconductor particle system is essential to improve the efficiency of net charge transfer in the interface between semiconductor and electrolyte, and a variety of efficient methods such as noble metals modification on TiO_2 surface or coupling two semiconductor particles with different energy levels have been employed for this purpose [9–11]. For example, many authors [12–15] prepared TiO_2 loaded noble metals (Pd, Pt, Ru) catalysts to study the photocatalytic reduction of nitrate in aqueous solution. Results showed that photocatalytic nitrate reduction activity was also dependent on various experimental factors such as pH value of the solution, nature of the sacrificial agent, especially the metal loading on the TiO_2 semiconductor. Reports [16–18] demonstrated that semiconductor systems such as CdS/TiO_2 and CdS/AgI could not only extend the photo-response of large bandgap semiconductors, but also rectify the flow of photogenerated charge carriers and improve the efficiency of dye sensitization. However, photocatalytic reduction of nitrate by using

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composite semiconductor as catalyst has not been reported up to now.

Combined with these concepts and results, it is interesting to load metal on composite semiconductor and study its photocatalytic nitrate reduction performance. In this paper, Cu/MgTiO₃-TiO₂ composite catalyst system was prepared by impregnation/calcination method and its photocatalytic activity for removal of nitrate ions from drinking water was examined.

2. Experimental

2.1. Catalysts preparation

The metal-loaded composite semiconductor catalysts were prepared by means of impregnation/calcination method. First, 2 g TiO₂ powder (P25, Degussa, Japan. Anatase 79%, and rutile 21%) was impregnated with dilute magnesium nitrate solution and Cu(II) acetate solution under stirring at ambient temperature until most of water was evaporated. Second, the resulting mixture was dried in oven at 353 K for 12 h, then ground adequately and calcined in air at 873 K for 4 h. In this stage, a semiconductor MgTiO₃ was formed under given reaction conditions, however, the species copper was only oxidized into CuO. Finally, the obtained powder was reduced in hydrogen at 873 K for 4 h for reducing CuO into metal Cu.

2.2. Photocatalytic reduction tests

Photocatalytic reaction was carried out in a double wall cylindrical Pyrex cell. The initial concentration of nitrate ions was 100 mg/l (calculated by nitrogen weight, denoted as N/L, and the same to nitrite and ammonium). A 125 W high-pressure Hg lamp was used as light resource. CO₂ was bubbled into the reaction solution to control pH value of the reaction solution and remove dissolved oxygen. The sample solution was withdrawn periodically and powdered catalyst was immediately separated from the aqueous phase by centrifugation, then the supernatant was analyzed to determine the residual contents of nitrate, nitrite, and ammonium ions by UV-Vis spectrophotometer (Shimadzu, UV-240). The detailed procedures are described in [19].

2.3. Catalyst characterization

X-ray diffraction (XRD) patterns were carried out in a D/max-2500 powder diffractometer using Cu K α ($\lambda = 1.54178 \text{ \AA}$) radiation in 0.04° steps from 5° to 90° (2θ) with 1 s per step.

Transmission Electron Micrograph (TEM) was carried out on a Philips EM-120 model TEM instrument with the accelerating voltage of 100 keV. Before photographing, the samples were dispersed in ultrasonic for 20 min, then dropped

onto the surface of carbon membrane and dried at ambient conditions.

3. Results and discussion

3.1. Catalyst evaluation

In order to evaluate the performance of Cu loaded composite semiconductor Cu/MgTiO₃-TiO₂ catalyst, other catalysts such as TiO₂, MgTiO₃-TiO₂ and Cu/TiO₂ obtained with the same preparation process were also used as comparison and corresponding results were shown in Table 1.

It could be seen that under the given conditions, pure titanium dioxide did not show any photocatalytic activity for nitrate reduction, moreover, coupled photocatalyst MgTiO₃-TiO₂ also showed little photocatalytic activity. However, we could see that metal Cu loading catalysts, Cu/TiO₂ and Cu/MgTiO₃-TiO₂, exhibited higher photocatalytic activity, which indicated that metal loaded on the catalyst was essential for the reduction of nitrate. As for the Cu/TiO₂ (4 wt.%) catalyst, the conversion of nitrate was 31.4% after 2 h irradiation in the presence of sodium oxalate; but for Cu/MgTiO₃-TiO₂ (4 wt.%, Cu:Mg = 1:3) composite catalyst, nitrate conversion was improved to 39.2% under the same reaction conditions. Although the conversion of nitrate showed no remarkable difference between these two catalysts, the amount of metal Cu as the main active component in this photocatalytic reaction, was 1 wt.% for MgTiO₃-TiO₂ composite semiconductor (nitrate conversion: 39.2%), and 4 wt.% for TiO₂ (nitrate conversion: 31.4%), that is to say, the photocatalytic activity is determined by the appropriate content of metal Cu. So the photocatalytic reduction activity (represented in mol NO₃⁻/(min g_{Cu})) of the former was much higher than the latter due to the more effectively dispersed Cu particles. Furthermore, in order to observe the morphology of prepared catalysts, TEM of Cu/TiO₂ and Cu/MgTiO₃-TiO₂ were taken and their photographs were shown in Fig. 1. TEM of Cu/TiO₂ catalyst (image A, 130,000 times in order to observe the Cu particles very clearly) shows Cu metal clusters are clearly visible and are homogeneously dispersed on the TiO₂ particles. The size of most Cu metal clusters is around 5 nm. But for Cu/MgTiO₃-TiO₂ catalysts (image

Table 1
Photocatalytic reduction of nitrate over different catalysts

Catalyst	Nitrate conversion (%)	Yield of nitrite (mg/l)	Yield of ammonium (mg/l)	pH
TiO ₂	0	0	0	5.15–5.23
MgTiO ₃ -TiO ₂	1.2	0.05	0.27	5.14–5.13
Cu/TiO ₂	31.4	20.7	5.25	5.29–6.18
Cu/MgTiO ₃ -TiO ₂	39.2	29.9	7.2	5.44–6.26

Reaction conditions: 200 ml nitrate solution (100 mg/l), 0.2 g catalyst, 0.005 mol/l sodium oxalate, 2 h irradiation time, bubbled CO₂.

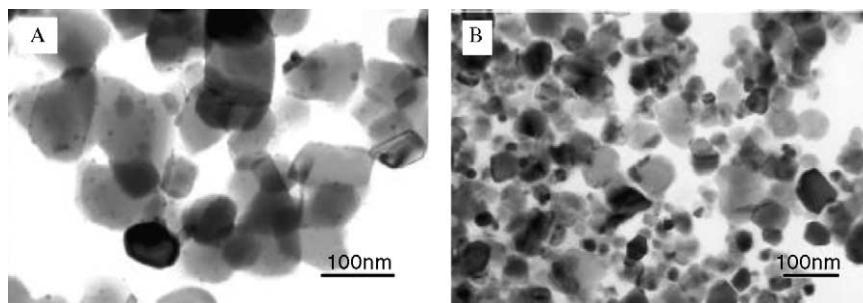


Fig. 1. TEM images of prepared catalysts: (A) Cu/TiO₂; (B) Cu/MgTiO₃-TiO₂.

B, 100,000 times), TEM shows that supported metal Cu doesn't disperse in TEM visible metal cluster form, which indicates that supported metal Cu has interacted with the MgTiO₃ or MgTiO₃-TiO₂ composite semiconductor and dispersed as more tiny particles on the catalyst surface. In the following investigation, many efforts have been tried to optimize the superior activity of Cu/MgTiO₃-TiO₂ and find where the activity was result from.

3.2. Effect of Cu:Mg molar ratio

Cu/MgTiO₃-TiO₂ catalysts were prepared by varying molar ratio of Cu:Mg from 4:0, 3:1, 1:1, 1:3, 1:6, 1:10 to 0:4 (total metal weight content: 4 wt.%), and used for photocatalytic reduction of nitrate ions. From the experimental results (Fig. 2), we can conclude that nitrate conversion reached the maximum value on catalyst with Cu:Mg molar ratio 1:3, and beyond which, nitrate conversion was more or less depressed. This difference in catalytic nitrate activity might be due to the different amount of produced MgTiO₃ semiconductor. So we choose Cu:Mg molar ratio at 1:3 for preparing catalyst in the following experiments.

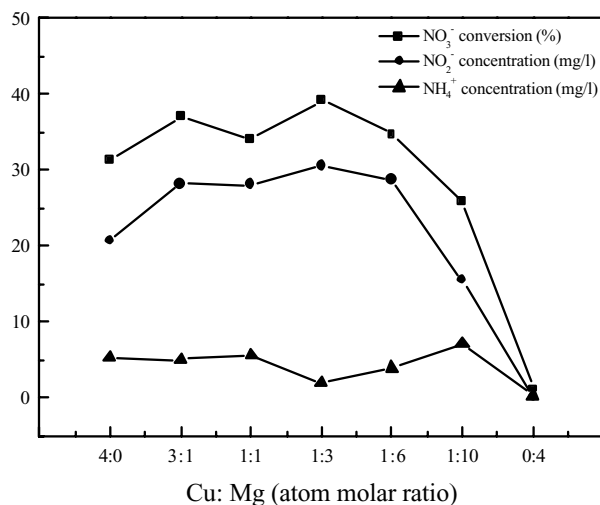


Fig. 2. NO₃⁻ conversion (■), amount of formed NO₂⁻ (●) and NH₄⁺ (▲) as a function of atom molar ratio (Cu:Mg) on Cu/MgTiO₃-TiO₂ catalyst.

3.3. Effect of calcination temperature in catalyst preparation

Results showed that the calcination temperature might strongly affect the formation of MgTiO₃, which was illustrated in Fig. 3, and further influence on the activity of nitrate conversion. As is shown, nitrate conversion increased greatly with the increase of calcination temperature, and then reached the maximum value at $T = 873$ K. After that, nitrate conversion began to decrease with further increase of temperature. In addition, the amount of produced nitrite and ammonium also correlated with this tendency. From our XRD characterization results (Fig. 4), this calcination temperature dependence much likely arose from such two factors: formation of composite semiconductor MgTiO₃-TiO₂ and crystalline phase transformation of TiO₂. At high temperature, loaded Mg(NO₃)₂ compound may react with TiO₂ and form MgTiO₃ compound on the surface of TiO₂, which was observed in XRD patterns (curve 5). Furthermore, these formed MgTiO₃ could couple with TiO₂ and “in situ” formed a composite semiconductor MgTiO₃-TiO₂. This

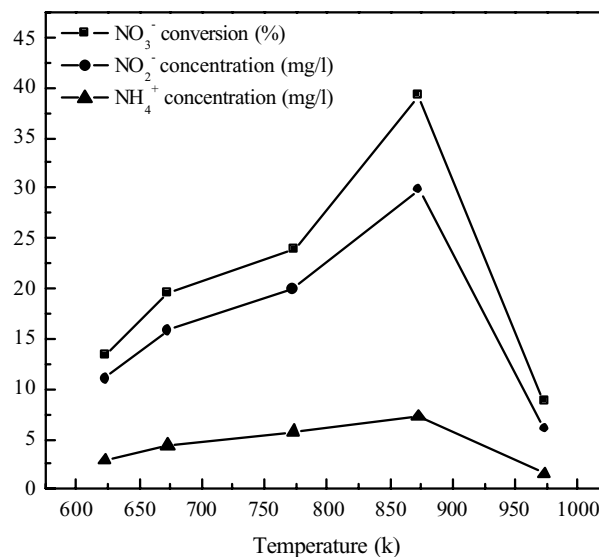


Fig. 3. NO₃⁻ conversion (■), amount of formed NO₂⁻ (●) and NH₄⁺ (▲) as a function of different calcination temperature.

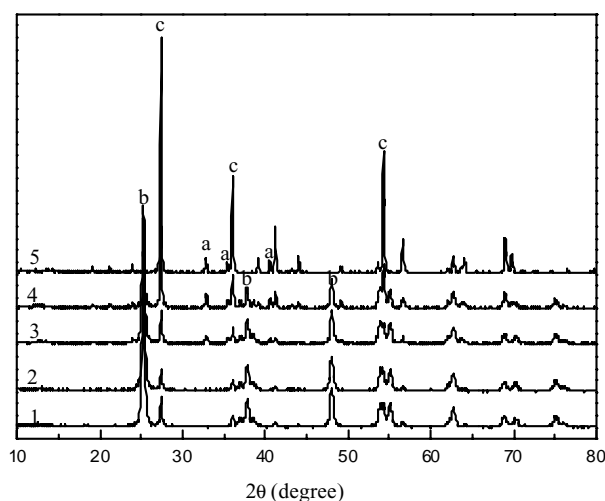


Fig. 4. X-ray diffraction patterns of prepared catalysts treated at different temperature (1) pure TiO_2 , no calcination; (2) calcination at 673 K; (3) calcination at 773 K; (4) calcination at 873 K; (5) calcination at 973 K (a: MgTiO_3 ; b: anatase; c: rutile).

coupled semiconductor photocatalyst increased the efficiency of the photocatalytic process by increasing the charge separation and extending the energy range of photoexcitation, and as a result, the higher conversion of nitrate was achieved.

It is also well known that the crystalline structure of TiO_2 is an important parameter to affect its photocatalytic activity. Although pure anatase has higher photocatalytic activity than rutile structure, however, the maximum photocatalytic activity was usually obtained in the certain crystalline phase ratio of anatase to rutile [20]. In our study, TiO_2 (P25 type) has two main crystalline phase structures (anatase 79% and rutile 21%), however, it was shown that calcination process at high temperature (873 and 973 K) significantly changed its crystalline structure components (Fig. 4). From curve 4 and 5 (Fig. 4), we can observe that the peak intensity of anatase weakened and the peaks intensity of rutile strengthened, which indicated that the transformation of anatase into rutile has occurred and could reasonably explain why the catalyst treated at 973 K exhibited lower catalytic activity than the one treated at 873 K. From our results, we can also determine the optimal crystalline ratio of anatase to rutile for photocatalytic reduction (48:52 wt.%).

3.4. Effect of different hole scavengers

In photocatalytic process, hole scavenger was proved to be an efficient way to enhance the photocatalytic efficiency by baffling the combination of photogenerated holes and electrons [4,5,21,22]. In this study, three different hole scavengers, $\text{H}_2\text{C}_2\text{O}_4$, $\text{Na}_2\text{C}_2\text{O}_4$, and $\text{C}_2\text{H}_5\text{OH}$, were used to investigate the photocatalytic reduction of nitrate ions and the results are shown in Fig. 5. As can be seen, under the same reaction condition, when no hole scavenger was added

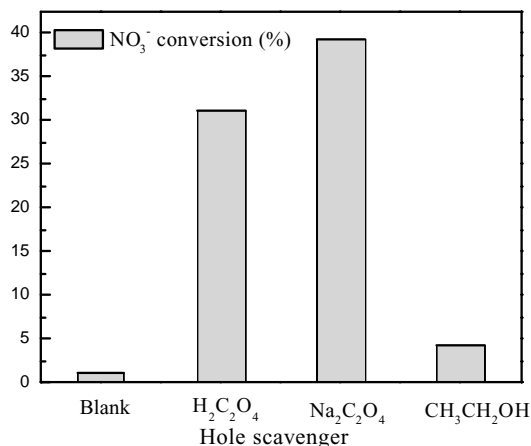
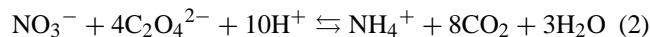
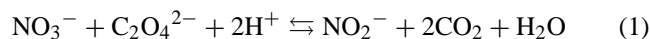
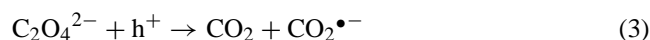


Fig. 5. Nitrate conversion as a function of different hole scavengers.

into the reaction solution, only a small amount of nitrate ions was reduced; this conclusion was accordant with many authors' results [7]. However, when hole scavengers such as $\text{CH}_3\text{CH}_2\text{OH}$, $\text{H}_2\text{C}_2\text{O}_4$, or $\text{Na}_2\text{C}_2\text{O}_4$ was used, the photocatalytic reduction activity were dramatically increased, and the highest conversion of nitrate was obtained by using $\text{Na}_2\text{C}_2\text{O}_4$ as hole scavenger. In the presence of sodium oxalate, nitrate reduction can be expressed as below:



In these processes, this reduction reaction was indirect and began with oxidation of oxalate ions by photogenerated holes to the species CO_2 and $\text{CO}_2^{\bullet-}$ [8]:



It was reported [23] that $\text{CO}_2^{\bullet-}$ species has stronger reductive ability ($E^0(\text{CO}_2/\text{CO}_2^{\bullet-}) = -1.8\text{V}$) and is

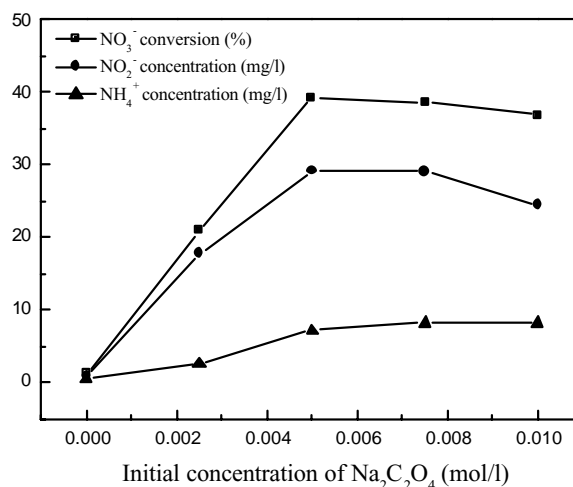


Fig. 6. NO_3^- conversion (■), amount of formed NO_2^- (●) and NH_4^+ (▲) as a function of initial concentration of sodium oxalate.

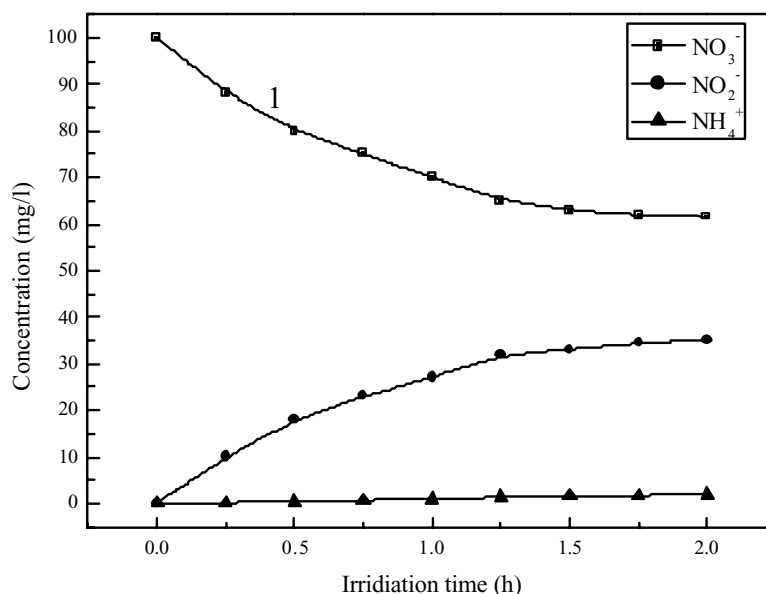


Fig. 7. NO₃⁻ conversion (■), amount of formed NO₂⁻ (●) and NH₄⁺ (▲) as a function of irradiation time.

able to reduce nitrate ($E^0(\text{NO}_3^-/\text{NH}_4^+) = 1.203 \text{ V}$; $E^0(\text{NO}_2^-/\text{NH}_4^+) = 0.897 \text{ V}$ [14]) to nitrite or ammonium.

It has been proved that hole scavengers are necessary to reduce nitrate ions, however, different hole scavengers exhibit the most efficiency only in their proper concentration. From Fig. 6, it was shown that optimum value of initial concentration of Na₂C₂O₄ was 0.005 mol/l. The concentration influence on catalytic activity may ascribe to the adsorption competition between nitrate and sodium oxalate hole scavenger [22]. It is well known that absorption of reductants on the surface of catalyst is an important step for a catalytic reaction. At low concentration, the amount of absorbed oxalate ions is insufficient to trap the photogenerated holes, so nitrate reduction are restricted and cannot be efficiently performed. However, at high concentrations, because of repulsion between same charges (C₂O₄²⁻ and NO₃⁻), excess oxalate ions can adsorb on the surface of catalyst and repulse the adsorption of nitrate ions. As a result, nitrate adsorption is greatly restrained. On the other hand, suitable concentration of Na₂C₂O₄ will promote the adsorption of nitrate ions more sufficiently. Simultaneously, photogenerated holes can be sufficiently trapped by oxalate ions in this case, and then the produced species CO₂^{•-} will reduce pre-adsorbed nitrate ions into other low oxidation nitric compounds.

3.5. Dependence of irradiation time

Fig. 7 shows the time dependence of the photocatalytic nitrate reduction activity of Cu/MgTiO₃-TiO₂ composite catalyst. As shown in the Fig. 7, at the beginning of photocatalytic reaction, the concentration of nitrate decreased rapidly, while the amount of produced nitrite was increasing simultaneously. From the slope of nitrate disappearance

curve (curve 1 in Fig. 7), we can observe that the maximum reaction rate was obtained in the initial reaction steps. However, it was greatly decreased with the proceeding of reaction, and basically diminished to zero after 2 h irradiation. This result was most likely explained by the continuous consumption of sodium oxalate. That was, after 2 h, hole scavenger Na₂(COOH)₂ decomposed completely to CO₂ and H₂O, so the photocatalytic reduction ceased in the absence of sacrificial reagent, which has been discussed in our preceding sections.

4. Conclusions

Studies on the photocatalytic reduction of nitrate over Cu/MgTiO₃-TiO₂ catalyst system have drawn the following conclusions:

The composite semiconductor catalyst (Cu/MgTiO₃-TiO₂) exhibited a superior photocatalytic activity in the reduction of nitrate ions. The formation of composite semiconductor MgTiO₃-TiO₂ and crystalline phase transformation of TiO₂ are important factors to photocatalytic nitrate reduction, which can be obtained at an appropriate calcination temperature. Furthermore, sodium oxalate was testified to be an effective hole scavenger in the study and the optimal initial concentration is 0.005 mol/l.

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References

- [1] L.W. Canter, Nitrates in Ground Water, CRC Press, Boca Raton, FL, 1997.
- [2] World Health Organization (Ed.), Health Hazards from Nitrates in Drinking Water, WHO Regional Office for Europe Copenhagen, 1985.
- [3] L. Bontoux, N. Bournis, D. Papameletiou, IPTS Rep. 6 (1997) 7.
- [4] B. Bems, F.C. Jentoft, R. Schlögl, Appl. Catal. B 20 (1999) 155.
- [5] K.T. Ranjit, R. Krishnamoorthy, T.K. Varadarajan, B. Viswanathan, J. Photochem. Photobiol. A: Chem. 86 (1995) 185.
- [6] K.T. Ranjit, R. Krishnamoorthy, B. Viswanathan, J. Photochem. Photobiol. A: Chem. 81 (1994) 55.
- [7] H. Kominami, A. Furusho, S. Murakami, H. Inoue, Y. Kera, B. Ohtani, Catal. Lett. 76 (2001) 31.
- [8] M.I. Litter, Appl. Catal. B 23 (1999) 89.
- [9] Y. Hiroshi, H. Shigeo, J. Phys. Chem. 93 (1989) 4833.
- [10] H. Gerischer, A. Heller, J. Phys. Chem. 95 (1991) 5261.
- [11] K.R. Gopidas, M. Bohorquez, P.V. Kamat, J. Phys. Chem. 98 (1994) 3822.
- [12] T. Tanaka, A. Tanaka, M. Hara, J.N. Kondo, K. Domen, Catal. Today 44 (1998) 17.
- [13] K.T. Ranjit, R. Krishnamoorthy, T.K. Varadarajan, B. Viswanathan, J. Photochem. Photobiol. A: Chem. 89 (1995) 67.
- [14] K.T. Ranjit, B. Viswanathan, J. Photochem. Photobiol. A: Chem. 108 (1997) 73.
- [15] H. Kato, A. Kudo, Chem. Phys. Lett. 295 (1998) 487.
- [16] A. Sclafani, M.N. Mozzanega, P. Pichat, J. Photochem. Photobiol. A: Chem. 59 (1991) 181.
- [17] K.R. Gopidas, M. Bohorquez, P.V. Kamat, J. Phys. Chem. 94 (1990) 643.
- [18] L. Spanhel, H. Weller, A. Henglein, J. Am. Chem. Soc. 109 (1987) 1216.
- [19] D.F. Boltz, J.A. Howell, Colorimetric Determination of Non-Metal, Wiley, New York, 1978.
- [20] J.F. Porter, Y.G. Li, J. Mater. Sci. 34 (1999) 1523.
- [21] T. Mori, J. Suzudi, K. Fujimoto, M. Watanabe, Y. Hasegawa, Appl. Catal. B 23 (1999) 283.
- [22] Y.X. Li, F. Wasgestian, J. Photochem. Photobiol. A: Chem. 112 (1998) 255.
- [23] D.M. Stanbury, Adv. Inorg. Chem. 33 (1989) 69.