Enhanced photocatalytic reduction reaction over Bi³⁺-TiO₂ nanoparticles in presence of formic acid as a hole scavenger

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11 Abstract

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12 A series of Bi^{3+} -doped TiO₂ (Bi^{3+} -TiO₂) catalysts with a doping concentration up to 2 13 wt% were prepared by a sol-gel method. The prepared photocatalysts were characterized by 14 different means to determine their chemical composition, surface structure and light 15 absorption properties. The photocatalytic activity of different Bi³⁺-TiO₂ catalysts was 16 evaluated in the photocatalytic reduction of nitrate in aqueous solution under UV 17 18 illumination. In the experiments, formic acid was used as a hole scavenger to enhance the 19 photocatalytic reduction reaction. The experiments demonstrated that nitrate was effectively degraded in aqueous Bi³⁺-TiO₂ suspension by more than 83% within 150 min, while the pH 20 of the solution increased from 3.19 to 5.83 due to the consumption of formic acid. The 21 experimental results indicate that the presence of Bi³⁺ in TiO₂ catalysts substantially enhances 22 23 the photocatalytic reaction of nitrate reduction. It was found that the optimal dosage of 1.5 wt% Bi³⁺ in TiO₂ achieved the fastest reaction of nitrate reduction under the experimental 24 25 condition. Bismuth ions deposit on the TiO₂ surface behaves as sites where electrons 26 accumulate. Better separation of electrons and holes on the modified TiO₂ surface allows 27 more efficient channeling of the charge carriers into useful reduction and oxidation reactions 28 rather than recombination reactions. Two intermediate products of nitrite and ammonia 29 during the reaction were also monitored to explore the possible mechanisms of 30 photoluminescence quenching and photocatalytic reduction in the context of donor-acceptor 31 interaction with electron trapping centers.

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33 *Keywords:* Bishmuth; Bi^{3+} -TiO₂; Hole scavenger; Nitrate; Photocatalytic reduction; Titanium dioxide.

1. Introduction

38 In recent years, nitrate concentration in water supply sources has been increasing in many 39 regions because of intensive agricultural activities, especially man-made fertilizers (Gao et 40 al., 2004). High levels of nitrate in domestic water cause cyanosis in young babies (Williams, 41 1979). High concentration of nitrate in drinking water is fatal to infants under 6 months of 42 age, in whose bodies, nitrate is reduced to nitrite, which combines with hemoglobin in the 43 blood to form methaemoglobin, and leads to a condition commonly known a "blue baby 44 syndrome". Furthermore, nitrate can be converted into nitrosamine, which can cause cancer and hypertension (Canter, 1997). For these reasons, the World Health Organization (WHO) 45 46 standards recommend that NO_3^- in drinking water should be less than 45 mg l⁻¹ (WHO, 47 1996). The US Environmental Protection Agency (EPA) established the maximum permitted level of nitrate to 10 mg l⁻¹ in drinking water. The European community set the maximum 48 permitted level of nitrate to 11.3 mg l^{-1} and recommended level of 5.65 mg l^{-1} . So reducing 49 50 nitrate concentration in drinking water is an imperative task at the present time.

51 Many methods like ion exchange, reverse osmosis, electrodialysis, chemical denitrification and biological denitrification have been used to remove nitrate from drinking 52 53 water. However, these techniques are either not cost-effective or need a post-treatment of the 54 produced effluents (Gao et al., 2004). In recent years, heterogeneous photocatalytic reduction 55 of nitrate over semiconductor materials has also been developed as a promising method for 56 controlling the concentration of nitrate in water (Ranjit et al., 1994; Ranjit et al., 1995a; Bems 57 et al., 1999). Among them, TiO₂ was considered to be the material with the most potential for 58 photocatalytic purposes, because of its exceptional optical and electronic properties, chemical 59 stability, non toxicity, and low cost (Litter, 1999). It has been proved that metal loading and the addition of so-called hole scavengers instead of photochemically produced hydrogen are 60 61 essential for the effective reduction of NO_3^- (Ohtani et al., 1988; Zhang et al., 2005). Many metals, such as Pd, Pt, and Rh (Ranjit et al., 1995b), and sacrificial electron donors, such as 62 63 methanol (Ranjit and Viswanathan, 1997; Mori et al., 1999; Tawkaew et al., 2001), ethanol 64 and EDTA (Ranjit and Viswanathan, 1997), oxalic acid (Li and Wasgentian, 1998; 65 Kominami et al., 2001), sodium oxalate (Jin et al., 2004), formic acid (Perissinotti et al., 2001), sucrose (Zhang et al., 2005), and humic acid (Bems et al., 1999) have been commonly 66 67 used to improve photocatalytic efficiency.

68 The present work focuses on the preparation, characterization and application of Bi^{3+} -69 doped TiO₂ photocatalysts (hereafter referred to as Bi^{3+} -TiO₂) for the reductive decomposition of nitrate to form nitrogen in water. In the presence of formic acid as a hole scavenger, we are of the opinion that photocatalytic reduction of nitrate can be performed successfully over Bi^{3+} -TiO₂ catalysts. Not only has the photocatalytic reduction efficiency shown an improvement relative to that for the undoped photocatalyst, but also some understanding of the mechanisms of photoluminescence (PL) and photodegradation is forthcoming.

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77 2. Experimental78

79 2.1. Materials

81 Titanium tetra-n-butoxide (Ti(O-Bu)₄) and bismuth nitrate (Bi(NO₃)₃·5H₂O) with analytic 82 grade from Aldrich, USA were used as titanium and bismuth sources for preparing TiO₂ and 83 Bi³⁺-TiO₂ photocatalysts. Formic acid and sodium nitrate with analytical grade were also 84 obtained from the Aldrich, USA and used without further purification. Demonized doubly-85 distilled water was used for preparing all aqueous solutions.

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87 2.2. Preparation of photocatalysts

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The Bi^{3+} -doped TiO₂ samples (Bi^{3+} -TiO₂) were prepared by a sol-gel method in which 21 89 90 ml of Ti(O-Bu)₄ was dissolved in 80 ml of absolute ethanol (100%), and the resulting 91 solution was stirred vigorously. Then 2 ml of water and 0.5 ml of acetic acid (50%) were 92 added to another 80 ml of ethanol to make an ethanol-water-acetic acid solution. The latter 93 solution was slowly added to the Ti(O-Bu)₄-ethanol solution under vigorous stirring. When 94 the resulting mixture turned to sol, the bismuth nitrate solution was added drop-by-drop. The 95 resulting transparent colloidal suspension was stirred for 1 h and was aged for 2 d at 25 °C 96 until the formation of gel. The gel was dried at 70 °C in vacuo and then ground. The resulting powder was calcined at 500 °C for 4 h. A TiO₂ sample was also prepared by the above same 97 98 procedure without adding bismuth nitrate, and is subsequently referred to as pure TiO₂. The doping concentrations of Bi³⁺ by weight are expressed as wt%. 99

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The crystalline phases of the synthesized TiO_2 and Bi^{3+} - TiO_2 catalysts were analyzed by 104 105 X-ray powder diffraction using a X-ray diffractometer (XRD, Philips PW3020) with Cu K_{α} radiation ($\lambda = 0.15406$ nm), in which an accelerating voltage of 40 kV and an emission 106 107 current of 30 mA were used. The texture and morphology of the prepared samples were 108 measured by environmental scanning electron microscopy (ESEM Phillips XL30), fitted with 109 an energy dispersive X-ray (EDX) accessory. The diffraction pattern and interplanar spacings 110 of the pure and doped catalysts were examined by transmission electron microscope (TEM 111 JEOL JEM-2011) operated at 200 keV. The TEM samples were prepared by dispersion in 112 ethanol by sonication and deposition on a carbon film supported on a copper grid. The PL 113 emission spectra of the samples were measured at room temperature by two 114 spectrofluorometers (Photon Technology International MD502 and Jobin-Yvon Fluoromax-3) using 325 nm xenon lamp excitation. The emission spectra of pure TiO_2 and $Bi^{3+}-TiO_2$ (1) 115 wt%) at low temperature (~10 K) were measured at a resolution of 2-4 cm⁻¹ using a Panther 116 optical parametric oscillator system pumped by the second harmonic of a Surelite Nd-YAG 117 118 laser. The crystals were mounted in an Oxford Instruments closed cycle cryostat. The emission was collected at 90° and passed through an Acton 0.5 m spectrometer equipped with 119 120 a charge-coupled device. To study the optical absorption properties of the photocatalysts, the 121 diffuse reflectance spectra (DRS) of the samples in the wavelength range 250-700 nm were 122 obtained using a spectrophotometer (Shimadzu UV-2101), with MgO as reference. The 123 transmission absorption spectra of TiO₂-Bi (1 wt%) in a KBr disc (0.63 wt%) was recorded in 124 infrared by Fourier transform infrared spectroscopy (FTIR Nicolet Avatar 360) and 125 ultraviolet by a UV spectrometer (Agilent 8453) regions. X-ray photoelectron spectra (XPS) 126 of the catalysts were recorded by a PHI Quantum ESCA Microprobe system using a MgK_{α} 127 excitation source. Calibration of the spectra was done at the C 1s peak of surface 128 contamination taken at 1253.6 eV. The fitting of XPS curves was performed using Multipak 129 6.0A software.

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- 131 2.4. Set up of photocatalytic reactor
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Photocatalytic reduction studies of nitrate were carried out in a photoreactor system as shown in Fig. 1, which consists of a cylindrical borosilicate glass reactor vessel with an effective volume of 250 ml, a cooling water jacket, and a 8 W medium-pressure mercury 136 lamp (Institute of Electric Light Source, Beijing) positioned axially at the center as a 365 nm UV light source. The reaction temperature was kept at 25 °C by cooling water. 137

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139 2.5. Experimental procedure

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In order to investigate the effects of bismuth doping on the photocatalytic activity of 141 142 TiO₂, the photocatalytic reduction of nitrate was carried out in the TiO₂ or Bi³⁺-TiO₂ suspension under UV irradiation. The reaction suspensions were prepared by adding 0.25 g of 143 144 catalyst into 250 ml of aqueous nitrate solution with an initial concentration of 2.25 mg l^{-1} of 145 NO₃-N. Prior to photoreaction, the suspension was magnetically stirred in the dark for 30 146 min to establish an adsorption/desorption equilibrium condition. The aqueous suspension 147 containing nitrate and photocatalyst was then irradiated by UV with constant stirring. At the 148 given time intervals, the analytical samples were taken from the suspension and immediately 149 centrifuged at 4000 rpm for 15 min, then filtered through a 0.45 µm Millipore filter to 150 remove particles. The filtrate was analyzed by spectrophotometer.

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152 2.6. Analytical methods

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The nitrate and nitrite concentrations were analysed by a HACH colorimeter (DR/820) 154 155 with HACH Nitraver 5 powder for nitrate and HACH Nitriver 3 powder for nitrite. Ammonia 156 concentrations was analysed by a HACH spectrophotometer (DR/2010) with HACH nesslers 157 reagent.

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- 159 3. Characterization of photocatalysts
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3.1. XRD analysis of TiO_2 and Bi^{3+} -TiO₂ photocatalysts 161

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The crystalline degree and crystal structure of TiO₂ and Bi³⁺-TiO₂ samples were 163 164 examined by XRD and the diffactograms are shown in Fig. 2. It has been reported by several groups (Linsebigler et al., 1995; Engweiler et al., 1996) that sol-gel samples of TiO₂ undergo 165 166 a phase transformation from anatase to rutile phase during sintering treatment. In this study all the samples were sintered at 500 °C for 4 h in a muffle furnace and the diffractograms in 167 Fig. 2 reveal that all the Bi³⁺-TiO₂ and pure TiO₂ samples possess an anatase phase. No 168 additional peaks are detected. 169

Based on the XRD results, the crystal sizes of the TiO_2 and Bi^{3+} - TiO_2 powders were calculated using the Scherrer equation (Lin et al., 1999) and were found to be between 16 and 22 nm. The lattice parameters "a" and "c" were measured as 0.38 nm and 0.95 nm in all samples. The doping of up to 2 wt% Bi^{3+} into the TiO_2 lattice therefore does not give significant changes in the diffractograms. Similar conclusions have previously been made by Xu et al. (2002) showing that XRD is not sensitive enough to detect such minor changes to the TiO_2 materials.

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3.2. ESEM, TEM and EDX analyses of TiO_2 and Bi^{3+} -TiO₂ photocatalysts

- 180 The texture and morphology of the pure TiO₂ sample in comparison with 1 wt%-doped 181 Bi³⁺-TiO₂ were also observed by electron microscopy. The typical ESEM micrographs shown 182 in Fig. 3 reveal that both the two samples were composed of particles with a similar size 183 184 about 15 nm. Since no obvious particle agglomeration occurred, the large surface area 185 conveys high adsorption abilities of the catalysts. Figure 4a shows the TEM bright-field 186 image of TiO₂ particles, with average diameter about 22 nm. The inserted image in this figure is their corresponding diffraction pattern. The first four rings correspond to the interplanar 187 distances (in nm) of 0.346, 0.227, 0.186 and 0.168. They are consistent with (101), (103), 188 (004/112) and (200) diffractions from anatase. Fig. 4b shows the bright-field image of Bi³⁺-189 190 TiO₂ particles. The average diameter of these particles is about 17 nm. Again, the inserted 191 figure is the corresponding diffraction pattern, which can be also indexed as anatase. 192 However, the calculated interplanar distances are slightly larger than that for pure TiO₂, as shown in the following for the corresponding first four diffractions (in nm): 0.357, 0.238, 193 0.192 and 0.173. The TiO₂ lattice is apparently expanded by Bi^{3+} doping. 194 195 EDX analysis was carried out for the pure and doped TiO₂ using SEM and TEM. Figure
- ¹⁹⁵ EDX analysis was carried out for the pute and doped $11O_2$ using SEM and TEM. Figure ¹⁹⁶ 5a shows results from SEM for TiO₂ where only Ti and O are detected. Figure 5b shows the ¹⁹⁷ SEM result for 1 wt% Bi³⁺-doped TiO₂ and the Bi L_a line is observed very weak, and more ¹⁹⁸ clearly shown in the inset from TEM-EDX, Fig. 5b. The analytical results from EDX are in ¹⁹⁹ reasonable agreement with the nominal amount of Bi³⁺ doped into TiO₂. EDX elemental ²⁰⁰ maps of samples for Ti, O and Bi show homogeneous elemental distributions and no ²⁰¹ clustering of Bi was detected in the 1 wt% Bi³⁺-TiO₂ sample.
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^{203 3.3.} XPS and the valence states of TiO_2 and Bi^{3+} - TiO_2 photocatalysts

The XPS spectrum shows that there are Ti, O and C on the surface of the pure TiO₂, and 205 Ti, O, C and Bi on the surface of Bi³⁺-doped TiO₂. The C resulted from the organic 206 207 precursors used in the sol-gel method and was not completely removed during the heat 208 treatment. According to the high resolution XPS spectra, the transitions involving the Ti 2p, O 1s, and Bi 4f orbitals are observed. For pure TiO₂ and 1 wt% Bi³⁺-TiO₂, the Ti 2p peaks are 209 narrow with slight asymmetry and have a binding energy of 458.70 eV (full width at half-210 maximum, FWHM 1.0 eV), showing the presence of Ti⁴⁺. There is no evidence for the 211 presence of Ti³⁺ in 1 wt% Bi³⁺-TiO₂. The O 1s wide peak structure for Bi³⁺-TiO₂ at 530.79 212 eV (FWHM 1.36 eV) is at a similar energy to the O 1s electron binding energy for TiO₂, 213 214 where the narrow peak has slight asymmetry with a binding energy of 529.81 eV (FWHM 1.15 eV). Finally, the Bi 4f peaks of Bi³⁺-TiO₂ consists of an individual peak at 162.12 eV 215 corresponding to Bi³⁺. 216

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3.4. Optical absorption properties of photocatalysts

220 The FTIR spectra of the photocatalysts diluted and pressed in KBr discs show a strong and broad feature between 470 and 690 cm⁻¹, due to Ti-O stretching vibration modes. Weak 221 features are observed at ~3430 and 1630 cm⁻¹, due to adsorbed water. These latter two bands 222 are also present in the KBr disc alone. The UV-visible absorption spectra of Bi^{3+} -TiO₂ 223 224 samples were measured in the wavelength range of 250-800 nm at room temperature and the 225 transmission spectra between 350-500 nm using DRS. The transmission spectrum of a KBr disc of 1 wt% Bi³⁺-TiO₂ exhibits an increasing absorption at wavelengths below 500 nm. A 226 227 clearer comparison of the doped and pure samples is given by DRS (Fig. 6) where it is evident that increasing the dosage of Bi³⁺ doped into the sample gives a rise to longer 228 wavelength absorption. Extending the absorption of TiO₂ further into the visible region is 229 230 expected to provide enhanced photocatalytic behaviour. A brief discussion is now given 231 concerning the reasons for the long wavelength tail in the doped photocatalysts.

According to theory (Serpone and Pelizzeti, 1989), semiconductors absorb light below a threshold wavelength λ_g (the fundamental absorption edge). The band gap energy value of anatase (TiO₂) is about 3.2 eV with the threshold wavelength $\lambda_g = 387.5$ nm. It is well known that intrinsic transitions give sharp increases in absorbance whereas impurity or defect state transitions give absorption tails in semiconductors. An impurity atom changes its local lattice environment, but since the 6s² configuration Bi³⁺ ion (ionic radius 103 pm) is unable to directly substitute the 4s⁰ Ti⁴⁺ ion (ionic radius 61 pm) using a "soft" chemical method of 239 preparation, a new phase is formed. An analogous case has been observed when the lanthanide ion Er^{3+} is doped into α -Al₂O₃ (Tanner et al., 2004) where the host ion size is also 240 241 much smaller, so that new compounds are formed, with ErAlO₃ being formed at lower dopant ion concentrations of Er^{3+} , rather than $Er_3Al_5O_{12}$. Several compounds have been well 242 characterized in the Bi³⁺-TiO₂ case: Bi₂Ti₂O₇ (Yao et al., 2004), Bi₄Ti₃O₁₂ (Yao et al., 2003a; 243 Pookmanee et al., 2004) and Bi₁₂TiO₂₀ (Yao et al., 2003b). The first of these comprises 244 disordered $(Bi_2O)^{4+}$ tetrahedral nets interpenetrating with corner-sharing $(Ti_2O_6)^{4-}$ octahedra 245 (Hector and Wiggin, 2004); the second consists of three $(Bi_2Ti_3O_{10})^{2-}$ layers sandwiched 246 between two $(Bi_2O_2)^{2+}$ layers (Xu et al., 2002); whereas the third comprises $(TiO_4)^{4-}$ 247 tetrahedra and a Bi-O polyhedral network (Yao et al., 2003b). All compounds exhibit two 248 249 characteristic features. First, the band gap is reduced from that of TiO₂, with the energy band assumed to be between the top of the (lone pair) Bi^{3+} 6s band and the bottom of the Ti^{4+} 3d 250 251 band (Yao et al., 2003b). Thus the absorption spectra extend to longer wavelengths so that lower energy photons can be absorbed for photoreaction. Second, the positively-charged Bi-252 O polyhedra can function as electron sinks, which has repercussions for the PL and 253 254 photocatalytic properties.

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256 3.5. PL spectra of photocatalysts

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258 The PL spectra are useful to disclose the efficiency of charge carrier trapping, migration 259 and transfer, and to understand the nature of electron-hole pairs in semiconductor particles 260 since PL emission results from the recombination of photo-excited free carriers. In this study, 261 the 325 nm excited PL spectra of all pressed-powder samples at room temperature were 262 examined in the range of 350-550 nm. The results (not shown here) indicated that the luminescence intensity of pure TiO₂ ($\lambda_{em}(max) \sim 388 \pm 10$ nm; FWHM ~ 75 nm) was 263 substantially guenched by the doping of Bi^{3+} . The relative intensity of the 0.3 wt% and 1 wt% 264 Bi^{3+} -doped samples was ~0.7 of that of undoped samples. No significant band shifts were 265 observed. Thus Bi³⁺ doping of TiO₂ hinders free carrier recombination under irradiation. The 266 emission spectra of pure TiO₂ and 1.0 wt% Bi³⁺-TiO₂ was also recorded at 10 K under 355 267 268 nm laser excitation and the results shown in Fig. 7 differ considerably from those at room temperature. First, the pure TiO_2 emission band is red-shifted to 542 nm (2.3 eV). 269 Furthermore, the quenching of emission by Bi³⁺ is more pronounced and the Bi³⁺-doped 270 sample emits at a slightly longer wavelength. The low energy emission band in the pure TiO_2 271 sample resembles the ~530 nm emission band reported for TiO_2 : Er^{3+} under 325 nm excitation 272

at 20 K. The latter has been assigned to the reduction of Ti^{4+} to Ti^{3+} after H₂O adsorption (Komuro et al., 2002). However, this hypothesis requires further confirmation since the emission could otherwise be due to self-trapped excitation states in TiO₂ (Kiisk et al., 2004). It is clear however that Bi³⁺ again acts as a trapping centre.

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278 **4.** Photocatalytic reduction of nitrate in aqueous solution

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280 4.1. Photocatalyst activity for nitrate reduction

282 To determine the photocatalytic activity of the prepared catalysts, two experiments were first carried out with HCOOH as a hole scavenger to reduce nitrate in aqueous solution with 283 an initial concentration of 2.25 mg l⁻¹ as NO₃-N at pH 3.19 using the pure TiO₂ and Bi³⁺-TiO₂ 284 catalysts, respectively. The concentrations of nitrate with reaction time are shown in Fig. 8. 285 286 The concentration of formic acid used in this study is based on a molar ratio of nitrate: formic 287 acid = 1:10, which is slightly more than theoretical demand of 1:8 as shown in later part of discussion. Compared to pure TiO₂, the Bi³⁺-TiO₂ catalyst exhibited a faster rate of nitrate 288 reduction significantly. To determine an optimum amount of bismuth deposited on the TiO₂ 289 surface, a set of experiments was then carried out to reduce nitrate in its solution using 290 different Bi³⁺-TiO₂ catalysts from 0.3 wt% to 2 wt% and the nitrate concentration was 291 292 quantified by the spectrophotometer. The experimental results shown in Fig. 8 demonstrated 293 that after 210 min reaction time, nitrate in all the suspensions were reduced by more than 45%. Among them, the 1.5 wt% Bi³⁺-TiO₂ catalyst achieved the highest efficiency of nitrate 294 reduction by 83%. A further more bismuth content on TiO2 seemed detrimental to the 295 296 efficiency of photocatalytic reduction of nitrate.

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298 *4.2. Effect of hole scavenger*

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In addition to the modification of catalysts, another way to promote photocatalytic performance is to add sacrificial electron donors (hole scavenger) to the reaction system. Distinct kinds of sacrificial reagents were commonly found to have different effects in various systems. Accordingly, choosing a suitable and effective sacrificial reagent becomes especially important for the improvement of catalytic performance. In this study, formic acid with a simple one-carbon molecular structure was chosen as a hole scavenger to investigate its effect on nitrate reduction. Hence, its oxidation to carbon dioxide is straightforward and involves minimal intermediate products (Aguado and Anderson, 1993; Sanuki et al., 1999).
Also, formic acid is capable of forming reducing radicals, which could help in the reduction
reaction (Kaise et al., 1994). In the presence of formic acid, nitrate reduction can be
expressed as follows:

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312	$NO_3^- + 2e^- + H_2O \rightarrow NO_2^- + 2OH^-$
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314	$NO_2^- + 6e^- + 7H^+ \rightarrow NH_3 + 2H_2O$
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316	$2NH_3 \rightarrow N_2 + 3H_2$
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One mol of nitrate requires 8 mol of electrons to be reduced to nitrogen, which needs equivalent 8 mol of HCOOH to scavenge the holes. Consequently CO_2 and $CO_2^{0^-}$ can be simple formed by these trapped photo generated holes:

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 $2\text{HCOO}^- + \text{h}^+ \rightarrow \text{CO}_2 + \text{CO}_2^{\circ} + \text{H}_2$

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It was reported that $CO_2^{0^-}$ species is much more active and has stronger reductive ability 324 325 than CO₂ (Li and Wasgestian, 1998). Thus it can reduce nitrate to nitrogen. Our experiments 326 confirmed that using a hole scavenger such as formic acid is an essential condition to proceed this photocatalytic reduction reaction, since no catalytic activity of either TiO₂ of Bi³⁺-TiO₂ 327 was observed in the nitrate solution without a hole scavenger. On the other hand, It was found 328 329 that the further increase of formic acid did not increase the catalytic activity significantly, 330 which may result from competition for adsorption between nitrate and formic anions. In the 331 same time, it was found that the pH increased from 3.19 to 5.83 due to the consumption of 332 formic acid as shown in Fig. 9.

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334 *4.3. Time dependence of photocatalytic reduction of nitrate ions*

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The time dependence of the photocatalytic nitrate reduction reaction over Bi³⁺-TiO₂ catalyst is shown in Fig. 9. At the beginning of reaction, the concentration of nitrate decreased rapidly, but only trace of nitrite and ammonia appeared in the solution. With the proceeding of the reaction, it had been found that the concentration of the nitrite and ammonia increased quickly, and the pH value of reaction solution also increased accordingly. Figure 9 describes that after certain reaction period, the concentration of ammonia was slowly 342 reduced. It can be seen from the reaction mechanism that the first two-step reactions from 343 nitrate to nitrite and then to ammonia are reduction reaction, but the later conversion of ammonia to nitrogen and hydrogen involves some oxidation reactions. Actually 344 photocatalysis is suitable for both oxidation and reduction reactions, since e^{-} and h^{+} are 345 346 generated simultaneously on TiO₂ under UV illumination. In our experiments, reduction 347 reaction was dominated in the initial stage due to the presence of formic acid as a hole 348 scavenger, but oxidation reaction might gradually increase due to much less formic acid left, 349 that is favorable to the conversion of ammonia to nitrogen gas. The pH rising might result 350 from two reasons of the reduction reaction from nitrite to ammonia and also loss of formic 351 acid. These results suggested that such a photocatalytic reduction reaction could affect pH in 352 the reaction solution significantly. Furthermore, such a heterogeneous reaction in aqueous 353 TiO₂ suspension is also dependent on its adsorption rate on the catalyst surface. Zhang et al. 354 (2005) have reported the acid-base effects for the photocatalytic reduction reaction of nitrite 355 ions, and found that nitrite could be adsorbed quickly onto the surface of TiO₂ in acidic medium, but at higher pH, the adsorbed nitrite could be desorbed completely. On the surface 356 of TiO₂, "Titanol" (Ti-OH) is present, which is amphoteric and occurs in an acid-base 357 358 equilibrium as indicated by the following equations.

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363 Therefore, the adsorption properties of catalysts can be greatly changed at different pH values. In an acidic environment, H⁺ ions are adsorbed onto the surface of TiO₂, which was 364 reported to have a large surface proton exchange capacity. The photogenerated electrons can 365 366 be captured by the adsorbed H^+ to form $H^{\circ}ads$, which is able to reduce nitrate (Zhang et al., 2005). The positively-charged titania makes nitrate and formic anions reach the stern layer 367 368 the surface of catalyst and adsorb to active sites easily. At high pH, the surface of catalyst has 369 a net negative charge due to a significant fraction of total surface sites present as TiO⁻. It has 370 been reported that metal-loaded catalysts (M-TiO₂) have been used in photocatalytic 371 reactions mainly because (i) they have a high electron affinity and hence increase the life 372 time of the excitations, thus slowing the recombination of the charge carriers (i.e., electrons 373 and holes) and (ii) they promote the dissociative adsorption of hydrogen as H_{ads} for metals 374 with low H₂ over potential (eg. Pt) or stabilize H_{ads} for metals with high H₂ over potential (e.g.

 $TiOH + H^+ \rightarrow TiOH_2^+ pH < 6.25$

 $TiOH \rightarrow TiO^- + H^+ \quad pH > 6.25$

Ru). Photocatalytic effectiveness was known to depend on how long the photo-generated
electrons are trapped on the metal centers and how efficiently they are used in sub-sequent
reduction reactions (Kominami et al., 2001). Moreover, the morphology and size of coated
metals are another crucial factors in determining catalytic activity (Ranjit and Viswanathan,
1997).

In this study, the Bi^{3+} doped on TiO_2 particles not only should prolong the life time of the photo-generated 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 reaction with e⁻ at the homogeneously-dispersed metal bismuth surface enhances the overall reaction as observed.

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386 *4.4. Discussion about photocatalytic nitrate reduction*

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As the mentioned above, metal-doped catalyst Bi3+-TiO2 showed higher photocatalytic 388 activity in nitrate reduction compared with pure TiO₂ catalyst. It has been generally believed 389 390 that the conversion of nitrate into nitrite is structure-sensitive and geometric effect of catalyst 391 plays an important role in catalytic hydrogenation of nitrate. Furthermore, metals have probably interacted with support. However in our study, XRD patterns (Fig. 2) of Bi³⁺-TiO₂ 392 catalysts only show all the main characteristic peaks of TiO₂ support, no characteristic 393 394 reflections for Bi or Bi containing phases are recorded, indicating that metal particles are well 395 dispersed or interact with TiO₂ support. Although the crystalline phase of Bi has not been detected, the effect of enhancement on nitrate reduction due to this metal doping was much 396 prominent. From the experimental results, it is clear that Bi³⁺-TiO₂ at intermediate doping 397 concentrations such as 1.5 wt% functions more effectively as a separation center. Presumably 398 399 the reduced efficiency at the highest doping concentration of 2 wt% might result from the formation of Bi³⁺ clusters. 400

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402 **5.** Conclusions

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In the present work, an enhancement of the photocatalytic activity of TiO_2 catalyst by doping with bismuth has been confirmed in the reaction of nitrate reduction in the presence of formic acid. It was found that with a suitable amount (1.5 wt%) of the Bi dopant effectively increases the photocatalytic activity of the TiO_2 . the Bi³⁺ doped on the TiO_2 surface behave as sites where electrons accumulate. Better separation of electrons and holes on the modified

409	TiO ₂ surface allows more efficient channeling of the charge carriers into useful reduction and
410	oxidation reactions rather than recombination reactions. The experiments demonstrated that
411	nitrate was effectively degraded in aqueous Bi^{3+} -TiO ₂ suspension by more than 83% within
412	150 min, while the pH of the solution increased from 3.19 to 5.83 due to the nitrate reduction
413	and consumption of formic acid. The reduction of nitrate occurs via nitrite and ammonia, and
414	eventually releases nitrogen gas.
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416	Acknowledgement
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508 List of Figure Captions

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511 Fig. 1. Schematic diagram of the photoreactor system: (1) gas; (2) water; (3) UV lamp; (4)
512 timer; (5) stirrer; and (6) quartz jacket.

514 **Fig. 2.** XRD diffractograms of (a) TiO_2 and (b-d) Bi^{3+} - TiO_2 . The structure corresponds to 515 anatase (A).

517 **Fig. 3.** ESEM micrographs of two photocatalysts: (A) TiO_2 and (B) 1 wt% Bi^{3+} - TiO_2 .

519 **Fig. 4.** TEM micrographs of (a) TiO_2 and (B) 1 wt% $Bi^{3+}-TiO_2$. The inserted figures are the diffraction patterns of the anatase phase.

522 **Fig. 5.** SEM-EDX of two photocatalysts: (A) TiO_2 and (B) 1 wt% $Bi^{3+}-TiO_2$. The inset in (B) 523 is the TEM-EDX result for (B) at higher sensitivity.

Fig. 6. Diffuse reflectance UV-vis spectra of pure and Bi³⁺-doped TiO₂ at room temperature.

527 **Fig. 7.** PL spectra of pure TiO_2 and 1 wt% Bi^{3+} -doped TiO_2 photocatalysts in the range of 528 440-740 nm at 10 K. The breaks in the curves are artifacts due non-overlap of the window 529 edges of the charge – coupled device detector. 530

531 **Fig. 8.** Reduction of nitrate by TiO_2 and Bi^{3+} - TiO_2 . (Initial concentration of NO_3^- -N = 2.25532 mg l⁻¹; pH 3.19; catalyst dosage = 1 g l⁻¹)

533 534 **Fig. 9.** pH change and variation of NO₃⁻-N, NO₂⁻-N and NH₃-N concentrations during 535 reaction (initial concentration of NO₃⁻-N = 2.25 mg l⁻¹ and catalyst dosage = 1 g l⁻¹).



- Fig. 1.







Fig. 3.





Fig. 5.











