Characterization of TiO₂ And An As-Prepared TiO₂/SiO₂ Composite And Their Photocatalytic Performance For The Reduction Of Low-Concentration N-NO₃⁻ In Water

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Characterization Of TiO$_2$ And An As-Prepared TiO$_2$/SiO$_2$ Composite And Their Photocatalytic Performance For The Reduction Of Low-Concentration N-NO$_3^-$ In Water

*Environmental Science and Pollution Research*

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Abstract: Excessive N-NO$_3^-$ water pollution has become a widespread and serious problem that threatens human and ecosystem health. Here, a TiO$_2$/SiO$_2$ composite photocatalyst was prepared via the sol-gel/hydrothermal method. TiO$_2$ and TiO$_2$/SiO$_2$ were characterized by X-ray diffraction (XRD), UV-Vis differential reflectance spectroscopy (DRS), Fourier infrared (FT-IR) spectroscopy, X-ray photoelectron spectroscopy (XPS), scanning electron microscopy (SEM), and energy-dispersive X-ray spectroscopy (EDS). Afterward, the photocatalytic performance of TiO$_2$ and TiO$_2$/SiO$_2$ to reduce low nitrate concentrations (30 mgN·L$^{-1}$) under UV light were evaluated and the effects of different factors on this process were investigated, after which the reaction conditions were optimized. Removal rates of up to 99.93% were achieved at a hole scavenger (formic acid) concentration of 0.6 mL·L$^{-1}$, a CO$_2$ flow rate of 0.1 m$^3$·h$^{-1}$, and a TiO$_2$ concentration of 0.9 g·L$^{-1}$. In contrast, TiO$_2$/SiO$_2$ at a 1.4 g·L$^{-1}$ concentration and a TiO$_2$ load rate of 40% achieved a removal rate of 83.48%. But with more than 98% of nitrogen generation rate, NO$_2^-$ and NH$_4^+$ were the minor products, whereas N$_2$ was the main product.

Keywords: low-concentration N-NO$_3$; TiO$_2$; TiO$_2$/SiO$_2$; Photocatalysis; Reduction reaction; Nitrogen conversion rate

1 Introduction

Water is a vital and often limiting resource for the development of human society. Urban sewage seepage, industrial wastewater infiltration, agricultural pesticides, and fertilizer application all contribute greatly to the exacerbation of N-NO$_3^-$ groundwater pollution, and this has become a serious environmental issue worldwide. In addition to being chemically stable, N-NO$_3^-$ is highly water-soluble and mobile, making it difficult to remove from water environments (Velu et al. 2021). This compound poses a serious risk to human and environmental health and has been linked to teratogenicity and carcinogenicity, in addition to the eutrophication of water bodies and land salinization (Ghafari et al. 2008, Tugaoen et al. 2017). Therefore, N-NO$_3^-$ is not only considered an indicator of conventional water quality but is also classified as a toxicological indicator. According to the World Health
Organization and the European Union, the concentration of N-NO$_3^-$ in drinking water should not exceed 10 and 11.3 mg/L, respectively.

Biological denitrification, a common water treatment method, requires the introduction of a carbon source, and the temperature and carbon to nitrogen ratio of this reaction must be carefully controlled (Yao et al. 2020). Further, the rapid aging of ion exchange membranes for physicochemical denitrification leads to high costs and, in addition to not fully removing nitrate, this method produces high concentrations of saline wastewater (Gao et al. 2019). Moreover, the reaction conditions of chemical reductive denitrification cannot be easily controlled and are prone to hydrogen and oxygen evolution and other side reactions, resulting in secondary environmental pollution (Garcia-Segura et al. 2018). In contrast, photocatalysis by semi-conductors is a novel and environmentally friendly method for N-NO$_3^-$ removal that is highly selective toward N$_2$, has fast reduction kinetics and a small footprint, and does not generate sludge.

Velu et al. (2021) reported N-NO$_3^-$ removal rates of up to 94% via photocatalysis using an Al$_2$O$_3$/MOGAC nano-composite. Li et al. (2021) degraded 50 mg L$^{-1}$ N-NO$_3^-$ with 1% Fe-LNO under UV light. After 120 min, the optimized nitrate removal rate reached 86.69% and the optimized N$_2$ selectivity was 85.71%. Bi et al. (2021) evaluated the degradation of nitrogen oxide catalyzed by TiO$_2$/0.25Nb$_2$O$_5$ under visible light and achieved a removal rate of 77.23%. Liu et al. (2021) reported that Ag$_3$Pd$_7$/g-C$_{1.95}$N$_4$ exhibited the highest photocatalytic activity and selectivity for the photocatalytic reduction of NO$_3^-$ and NO$_2^-$ under 25 $^\circ$C and 365 nm irradiation, and the removal rates of NO$_3^-$ and NO$_2^-$ were 87.4% and 61.8%, respectively. Hou et al. (2021) prepared 5 wt% Ag/SiO$_2@c$TiO$_2$ and reported that the nitrate removal rate and N$_2$ selectivity were respectively 95.8% ($C_0 = 2000$ mg/L) and 93.6% after 4 h. Wang et al. (2021) prepared 10 wt% SiW$_9$/TiO$_2$/Cu and reported that the N-NO$_3^-$ ($C_0 = 30$ mgN/L) removal rate and the N$_2$ selectivity were respectively 76.53% and 82.09% after UV radiation for 6 h.

TiO$_2$ has good photo-responsive performance with a band gap energy of 3.2 eV and can utilize radiation with wavelengths less than 390 nm. TiO$_2$ becomes excited when it is irradiated with light at wavelengths higher than its band gap energy, after which the excited electrons (e$^-$) in the valence band migrated to the conduction band. This process forms highly active negatively charged electrons and leaves positively charged holes (h$^+$) in the valence band, resulting in electron-hole pairs. The resulting
electrons and holes are strong oxidizing and reducing agents, which can degrade many pollutants when irradiated with light (Lv et al. 2019). In addition to its excellent optical properties, TiO$_2$ has become a popular catalyst for the photocatalytic reduction of N-NO$_3^-$ due to its non-toxicity, stability, and low cost (Li et al. 2019, Tsang et al. 2019, Yang et al. 2004).

For water treatment purposes, TiO$_2$ must be easily separated and recovered. Therefore, this compound is routinely modified by coating and is immobilized on a substrate to separate it from the treated water more effectively (Woottikrai et al. 2022). Typical coating modification methods mainly include electrochemical, hydrothermal, sol-gel, and chemical precipitation methods, among which the sol-gel method is the most common.

Therefore, this study assessed the photocatalytic treatment of low N-NO$_3^-$ concentrations in water using TiO$_2$. Further, to recycle the TiO$_2$, a sol-gel method was used to coat and immobilize it on SiO$_2$ to obtain a TiO$_2$/SiO$_2$ composite catalyst. Particularly, three aspects were systematically evaluated in this study: (a) the effects of different factors (catalyst dose, catalyst loading rate, hole scavenger dose, and type of shielding gas) on the photocatalytic degradation of N-NO$_3^-$, (b) catalyst stability, and (c) the mechanism of photocatalytic reduction of N-NO$_3^-$ by TiO$_2$ and the TiO$_2$/SiO$_2$ composite.

2 Materials and methods

In addition to TiO$_2$ nanoparticles, this study also evaluated a TiO$_2$/SiO$_2$ composite by loading different proportions of TiO$_2$ on the surface of SiO$_2$ particles. The photocatalytic reduction of N-NO$_3^-$ under UV light was simulated indoors.

2.1 Preparation of the TiO$_2$/SiO$_2$ composite catalyst

SiO$_2$ particles were immersed in a NaOH solution (pH = 10) and sonicated for 2 h to increase their surface roughness. Nanoparticle composites were generated using the sol-gel hydrothermal synthesis method (Jesus et al. 2021, Takari et al. 2021, Wang et al. 2017). Solution A was prepared by slowly adding 10 mL of butyl titanate to 20 mL of absolute ethanol, followed by 1.8 mL of glacial acetic acid while constantly stirring the mixture. Solution B was prepared by mixing 20 mL of absolute ethanol with 2 mL of distilled water. Solution B was then added drop by drop to A solution with rapid stirring and butyl titanate was slowly hydrolyzed with continued stirring until it formed a solvate. Different amounts of SiO$_2$ particles were added and sonicated to further hydrolyze the butyl titanate. Once SiO$_2$
was evenly dispersed, it was transferred to an autoclave with polytetrafluoroethylene (PTFE) at 200 °C for 2 h. The filtrate was then allowed to cool to room temperature and washed with water and ethanol until it became clear, after which it was dried at 60 °C to obtain a catalyst powder. Composite catalysts with different TiO$_2$ loads were then obtained (loading = mass of TiO$_2$/total mass of catalyst).

2.2 Sample characterization

TiO$_2$ nanoparticles, the TiO$_2$/SiO$_2$ composite catalyst, and the recovered (i.e., used in a reaction cycle) catalysts were characterized to study their morphology, structure, photochemical properties, and chemical stability.

2.2.1 Characterization by scanning electron microscopy (SEM)

Samples were characterized by SEM (20,000x, Hitachi S4800) and energy-dispersive X-ray spectroscopy (EDS) (HORIBA 7593-H) to examine their morphology and microstructure.

2.2.2 Characterization by X-ray diffraction (XRD)

An X-ray diffractometer (XRD, Ultima IV Advanced Diffractometer, CuKal) was used to analyze the crystal structure of the samples within a 10°–80° range at a 5°/min scanning speed. The samples were then evaluated based on their characteristic peaks.

2.2.3 Characterization by UV-Vis differential reflectance spectroscopy (DRS)

The photocatalysts were then examined via the UV-Vis diffuse reflectance test using a spectrophotometer (Lambda 750 S, 200–800 nm) and the results were used to evaluate the light absorption performance of the catalysts.

2.2.4 Characterization by Fourier infrared (FT-IR) spectroscopy

FT-IR tests were performed with a Bruker Vertex 70 FT-IR spectrophotometer within a 400–4000 nm wavelength range.

2.3 Photocatalytic reduction of N-NO$_3^-$

A commercial glass photoreactor was used for the photocatalytic reduction of N-NO$_3^-$, as shown in Fig. 3. The experimental light source was a 125 W high-pressure mercury lamp with a primary wavelength of 365 nm, and the device was equipped with an external water cooling system to ensure a
constant reaction temperature. For each experiment, 500 mL of KNO$_3$ ($C_0 = 30$ mgN/L) solution was added to the reactor, after which predetermined amounts of catalyst and hole scavenger (formic acid) were sequentially added with constant stirring. The reaction solution was continuously purged with shielding gas to eliminate the oxygen from the device. The UV lamp was turned on 30 min prior to the experiment, after which the reaction solution was collected with a syringe every hour and filtered through a 0.22 µm membrane. The concentrations of ammonia nitrogen, nitrate nitrogen, and nitrite nitrogen were then measured separately. Higher removal rates and superior catalytic performance were obtained at lower N-NO$_3^-$ residual concentrations. Further, higher N$_2$ production and selectivity were observed at lower ammonia nitrogen and nitrite nitrogen production levels.

![Photocatalytic reaction setup](image)

Fig. 1 Photocatalytic reaction setup: (1) UV light source; (2) water inlet; (3) water outlet; (4) air pump; (5) sampling port; (6) quartz cold trap; (7) reaction solution; (8) magnetic stirrer

### 2.4 Determination of indicators

#### 2.4.1 Measurement of indicators

N-NO$_3^-$ was determined via dual-wavelength UV spectrophotometry (HJ/T 346-2007), nitrite nitrogen was determined via N-(1-naiyl)-ethylenediamine spectrophotometry (GB 7493-87), and ammonia nitrogen was determined via Nessler's reagent spectrophotometry (HJ 535-2009).

#### 2.4.2 N$_2$ removal rate and conversion rate calculations

\[
\text{N-NO}_3^- \text{ removal rate} = \frac{(C_0 - C_1)}{C_0} \times 100\% \quad (2.4.2-1)
\]

\[
\text{N}_2 \text{ selectivity} = \frac{(C_0 - C_1) - (C_2 - C_3)}{C_0} \times 100 \% \quad (2.4.2-2)
\]

where $C_0$ refers to the initial N-NO$_3^-$ concentration in the solution; $C_1$, $C_2$, $C_3$ represent the
concentrations of N-NO$_3^-$, ammonia nitrogen, and nitrite nitrogen after the reaction, respectively.

3 Results and Discussion

3.1 Sample characterization

3.1.1 Crystal structure

The crystal structures of catalysts before and after the reactions were investigated by XRD and FT-IR. Figs. 2 and 3 illustrate the XRD and FT-IR spectra of the catalysts before and after the reactions, respectively. As shown in Fig. 2, the diffraction angle (2θ) of the sample in the 10°–80° range was consistent with the spectra of anatase TiO$_2$ (JCPDS No. 21-1272). Further, the 2θ diffraction peaks at 26.7°, 36.6°, 47.98°, 54.04°, and 62.86° (TiO$_2$/SiO$_2$ at 2θ = 25.44°, 38.1°, 48.16°, 54.72°, 55.16°, and 63.0°) correspond to the (101), (004), (200), (105), (211), (204) crystalline surfaces of anatase TiO$_2$, respectively, indicating that TiO$_2$ in the as-prepared composite maintained the anatase structure (Li et al. 2018, Yu et al. 2014). The peak shapes and peak positions of the XRD spectra of the catalysts before and after the reactions were largely equal, and the crystalline structure of anatase did not change, indicating that the structure of the catalysts prepared by this method did not change significantly before and after the reactions. However, some of the reactants adsorbed on the sample surface during the reaction process wakened the intensity of some characteristic peaks after the reaction.

As illustrated in Fig. 3, the catalysts exhibited IR absorption peaks at 3343, 1632, 1435, 1061, and 933 cm$^{-1}$ before and after the reactions. The absorption peak at 3343 cm$^{-1}$ corresponded to the O-H bond stretching vibrations caused by water and hydroxyl groups adsorbed on the TiO$_2$ surface, whereas the peaks at 1632, 1435, and 443 cm$^{-1}$ were characteristic of TiO$_2$. The very weak Ti-O-Si absorption peaks of SiO$_2$ at 1061 and 933 cm$^{-1}$ indicated that TiO$_2$ and SiO$_2$ were mainly physically bound (i.e., as opposed to chemically bound), which mainly changed the physical properties of the catalysts. However, the introduction of SiO$_2$ weakened the TiO$_2$ peak (Najafidoust et al. 2019, Yao et al. 2020). The grain size of the catalysts was calculated using the Debye-Scherrer Equation:

$$D = k\lambda/[\cos\theta(\beta + 180)] \times 3.14$$

(3.1.1-1)
where $k$ is the Scherrer constant (the cubic particle constant $k$ is 0.943), $\lambda$ is the Cu k$\alpha$1 incident wavelength ($\lambda = 0.15406$ nm), $\theta$ is the diffraction angle, and $\beta$ is the full half-maximum width. The full half-maximum width was calculated in radians and the strongest diffraction peak (101) of the catalysts was used to calculate the grain size. Table 3 summarizes the results of these calculations. Smaller catalyst grains possess a larger specific surface area and therefore have better photocatalytic performance and stronger redox ability (Lucchetti et al. 2017). Similarly, the electrons photogenerated by TiO$_2$ reach the catalyst surface more quickly when the catalyst grains are smaller, which reduces the electron-hole recombination rates and improves catalytic performance (Satayeva et al. 2018). Similarly, the solubility of the recovered catalysts increased due to the quantum size, and the catalytic performance was reduced by recrystallization in water during use, which led to an increase in crystal size.

Fig. 2 XRD spectra of ①TiO$_2$, ②recovered TiO$_2$, ③TiO$_2$/SiO$_2$, ④ recovered TiO$_2$/SiO$_2$, and TiO$_2$ compared to the XRD standard spectra of SiO$_2$

Fig. 3 FT-IR spectra of TiO$_2$, recovered TiO$_2$, TiO$_2$/SiO$_2$, and recovered TiO$_2$/SiO$_2$ at 400–4000 cm$^{-1}$
### Table 1 Catalyst grain sizes

| Photocatalyst          | β    | θ (°) | Size (nm) |
|-----------------------|------|-------|-----------|
| TiO$_2$               | 0.987| 12.612| 8.7       |
| recovered TiO$_2$     | 0.976| 12.675| 9.4       |
| TiO$_2$/SiO$_2$       | 1.048| 12.726| 7.8       |
| recovered TiO$_2$/SiO$_2$ | 0.947| 12.605| 8.6       |

3.1.2 Morphology and structure

The morphology and microstructure of the catalysts were investigated by SEM. Fig. 4(a) A-D shows representative SEM images (10000x) of TiO$_2$, recovered TiO$_2$, TiO$_2$/SiO$_2$, and recovered TiO$_2$/SiO$_2$, respectively. As illustrated in the figure, the catalysts exhibited spherical structures with heterogeneous sizes, and the recovered catalyst particles were slightly larger (Nguyen & Nguyen 2009). The elemental composition of the samples was determined via EDS mapping, and these results further confirmed whether the composite was successfully synthesized. As shown in Fig. 6 (b) and (c), Ti and O were uniformly distributed in TiO$_2$, whereas Ti, Si, and O were uniformly distributed in TiO$_2$/SiO$_2$.

The SEM images of samples demonstrated that the two catalysts were spherical in shape and similar in size both before and after the reactions. This was consistent with the results of XRD and the Debye-Scherrer Equation calculations, which further validated the stability of the samples.
Fig. 4 (a; A-D) Representative SEM images (10000x) of TiO$_2$, recovered TiO$_2$, TiO$_2$/SiO$_2$, and recovered TiO$_2$/SiO$_2$, respectively; (b) elemental mapping of the two samples; (c) EDS spectra of the two samples

3.1.3 Optical performance and band gap energy

The optical performance of a photocatalyst is a key feature that directly affects the photocatalytic activity of the materials. Fig. 5 (a) shows the UV-Vis DRS absorption spectra of TiO$_2$, recovered TiO$_2$, TiO$_2$/SiO$_2$, and recovered TiO$_2$/SiO$_2$ within a 200–800 nm range. Upon comparing the UV absorption curves of TiO$_2$ and TiO$_2$/SiO$_2$, we observed that the peak UV light absorption occurred at approximately 350 nm for both. However, TiO$_2$/SiO$_2$ had a stronger optical response to UV light, and the absorption band was shifted to the long-wave direction.

The band gap energy was calculated as described in previous studies (Liu et al. 2018, Sun et al. 2013, Zhou et al. 2011):

\[(\alpha h\nu)^n = B(h\nu - E_g)\]  

(3.1.3-1)
where $h\nu$ is the photon energy, $E_g$ is the optical band gap of the semiconductor, $\alpha$ is the absorption coefficient obtained from the scattering and reflection spectra according to Kubelka-Munk theory, $B$ is the proportionality constant, and the value of $n$ depends on the semiconductor, as well as the type of transition. Fig. 7(b) shows the band gap energy of TiO$_2$, recovered TiO$_2$, TiO$_2$/SiO$_2$, and recovered TiO$_2$/SiO$_2$. As illustrated in the figure, the band gap energy of TiO$_2$ was 3.17 eV, whereas the band gap energy of TiO$_2$/SiO$_2$ was approximately 2.88 eV, which was consistent with previous results. The band gap energy of TiO$_2$ and TiO$_2$/SiO$_2$ increased slightly after use, and the increase in band gap energy indicated that the energy required for the electron transition also increased. This weakened UV light absorption and light utilization ability, and ultimately decreased the catalytic ability of the catalysts, which was consistent with the theory of UV absorption (Zhou et al. 2017).

3.2 Effects of different factors on N-NO$_3^-$ removal rates

To investigate the influence of key factors on the removal rate of nitrates, two different gradients of each factor were selected for the orthogonal test, and the results are summarized in Table 2. The influencing factors exhibited the following order: N-NO$_3^-$ concentration $> \text{TiO}_2$ dose $> \text{formic acid dose}$. A gradient test was then conducted according to the degree of influence of each factor.
Table 2. Results of orthogonal tests of N-NO\textsubscript{3} degradation catalyzed by TiO\textsubscript{2}

| Sample No. | Nitrate nitrogen concentration (mg·L\textsuperscript{-1}) | Formic acid dose (mL·L\textsuperscript{-1}) | TiO\textsubscript{2} dose (g·L\textsuperscript{-1}) | Nitrate nitrogen removal rate (%) |
|------------|-------------------------------------------------------|---------------------------------------------|-----------------------------------------------|----------------------------------|
| 1          | 50                                                    | 0.5                                         | 0.5                                           | 91                               |
| 2          | 50                                                    | 1.0                                         | 1.0                                           | 93                               |
| 3          | 90                                                    | 0.5                                         | 1.0                                           | 73                               |
| 4          | 90                                                    | 1.0                                         | 0.5                                           | 53                               |
| Mean 1 (%) | 92                                                    | 82                                          | 72                                            |                                  |
| Mean 2 (%) | 63                                                    | 83                                          | 73                                            |                                  |
| Range      | 0.29                                                  | 0.09                                        | 0.11                                          |                                  |

3.2.1 Effects of TiO\textsubscript{2} dose on the removal of low-concentration N-NO\textsubscript{3}

Fig. 6 shows the effects of TiO\textsubscript{2} dose (0.6, 0.7, 0.8, 0.9, 1.0, and 1.1 g·L\textsuperscript{-1}) on the removal of 30 mg·L\textsuperscript{-1} N-NO\textsubscript{3} (formic acid dose = 0.6 mL·L\textsuperscript{-1}, CO\textsubscript{2} flow rate = 0.1 m\textsuperscript{3}·h\textsuperscript{-1}). As illustrated in Fig. 6, the removal rate of N-NO\textsubscript{3} exhibited an upward and then a downward trend with increasing TiO\textsubscript{2} doses. Further, the N-NO\textsubscript{3} removal rate and N\textsubscript{2} selectivity in the products reached the highest values (99.93% and 81.21%, respectively) when the TiO\textsubscript{2} dose was 0.9 g·L\textsuperscript{-1}. As shown in Fig. 8 (a), the reaction rate reached a maximum at a TiO\textsubscript{2} dose of 0.9 g·L\textsuperscript{-1}.

Theoretically, higher catalyst concentrations should increase the availability of electrons and free radicals and, in turn, N-NO\textsubscript{3} removal rates should continue to increase. However, catalytic performance decreased once the catalyst concentration reached a certain threshold, and similar results have been reported in several previous studies (Baniasadi et al. 2013, Sun et al. 2015). When the catalyst concentration was low, N-NO\textsubscript{3} molecules were not in full contact with it and the catalytic efficiency was low. In contrast, when the catalyst concentration exceeded a critical level, the light transmittance in the solution decreased as the concentration increased, resulting in sub-optimal light utilization and a decrease in catalytic efficiency (Peng et al. 2018, Sun et al. 2015).
3.2.2 Effects of formic acid dose on the removal rates of low-concentration N-NO$_3^-$

In this reaction, formic acid was used as the hole scavenger, and appropriate amounts of formic acid were added to improve the efficiency of the reaction. The N-NO$_3^-$ removal rate was only 11.9% in the experimental group without formic acid. Fig. 7 illustrates the effects of formic acid dose (0.3, 0.4, 0.5, 0.6, 0.7, and 0.8 mL·L$^{-1}$) on the removal rate of 30 mg·L$^{-1}$ N-NO$_3^-$ (TiO$_2$ dose = 0.9 g·L$^{-1}$, CO$_2$ flow rate = 0.1 m$^3$·h$^{-1}$). As shown in Fig. 7, the N-NO$_3^-$ removal rate first increased and then decreased with increasing formic acid concentration, and the N$_2$ selectivity in the products first increased and then stabilized. Further, both the N-NO$_3^-$ removal rate and N$_2$ selectivity in the products reached maximum levels (99.93% and 81.21%, respectively) when the formic acid dose was 0.6 mL·L$^{-1}$ [Fig. 7 (a)]. The reaction rate reached its maximum in the first 4 h and then slowed down as the reactant concentrations decreased.

The role of the hole scavenger in the photocatalytic reactions was to improve photocatalytic efficiency by irreversibly binding to the catalyst surface and preventing complexation with holes. Formic acid, a weak acid, had a weaker adsorption capacity with TiO$_2$ than nitrate ions. Formic acid and holes (h$^+$) reacted to produce ·CO$_2^-$, which in turn promoted further N$_2$ production (Chu & Anastasio 2003, Mack & Bolton 1999). Catalytic efficiency gradually increased with the addition of formic acid because the complexation of electrons and holes was prevented. However, excessive formic acid addition increased the number of formic acid molecules, and therefore these molecules were more likely to collide with the catalyst surface than the nitrate ions, thus decreasing catalytic efficiency.
Fig. 7 (a) Effects of formic acid dose on N-NO$_3^-$ photocatalytic reduction as a function of time; (b) effects of formic acid dose on N-NO$_3^-$ removal rate and N$_2$ selectivity in the products.

3.2.3 Effects of different types of shielding gas on low-concentration N-NO$_3^-$ removal rates

Fig. 8 shows the effects of different types of shielding gas (CO$_2$, N$_2$, air) on the removal rate of 30 mg·L$^{-1}$ N-NO$_3^-$ (formic acid dose = 0.6 mL·L$^{-1}$, TiO$_2$ dose = 0.9 g·L$^{-1}$, aeration rate = 0.1 m$^3$·h$^{-1}$). As indicated in the figure, the removal rates of N-NO$_3^-$ were 98.76% and 99.93% and N$_2$ selectivity in the products were 80.14% and 81.21% under protection by N$_2$ and CO$_2$, respectively, indicating that CO$_2$ was superior to N$_2$ in this case, although the difference was relatively subtle.

Nitrate removal is a reduction reaction, and shielding gas is introduced to remove dissolved oxygen from water and create a reduction environment in the closed reactor. Interestingly, the results of the air aeration experiment confirmed this notion. CO$_2$ is more effective than N$_2$ because the pH of the N$_2$-aerated solution is close to neutral under this reaction condition, whereas CO$_2$ dissolved in water can produce H$^+$. Photocatalytic reduction of nitrates requires the consumption of H$^+$, and therefore this reaction is more effective under weakly acidic conditions (Ren et al. 2015).
Fig. 8 (a) Effects of type of shielding gas on N-NO\textsubscript{3} photocatalytic reduction as a function of time; (b) effects of type of shielding gas on the N-NO\textsubscript{3} removal rate and N\textsubscript{2} selectivity in the products

3.2.4 Effects of TiO\textsubscript{2}/SiO\textsubscript{2} loading on N-NO\textsubscript{3} removal rates in low-concentration solutions

Fig. 9 shows the effects of different TiO\textsubscript{2}/SiO\textsubscript{2} loads (30\%, 35\%, 40\%, 45\%, 50\%) on the removal rate of 30 mg·L\textsuperscript{−1} N-NO\textsubscript{3} (formic acid dose = 0.6 mL·L\textsuperscript{−1}, TiO\textsubscript{2}/SiO\textsubscript{2} dose = 1.5 g·L\textsuperscript{−1}, CO\textsubscript{2} flow rate = 0.1 m\textsuperscript{3}·h\textsuperscript{−1}). As illustrated in Fig. 9, as the loading rate increased from 30\% to 50\%, the removal rate of N-NO\textsubscript{3} increased first and then decreased to a relatively stable level. The maximum N-NO\textsubscript{3} removal rate (78.89\%) was achieved with a TiO\textsubscript{2}/SiO\textsubscript{2} load of 40\%, and the N\textsubscript{2} conversion rate was 94.25\%.

At low loading rates, the amount of TiO\textsubscript{2} increased with higher loading rates, thus increasing the number of active sites of the catalyst, as well as the likelihood of contact between nitrate ions and the catalyst. Further, catalytic efficiency also increased at higher loading rates but then decreased with additional loading rate increases after reaching a peak. This was because too much TiO\textsubscript{2} accumulated on the SiO\textsubscript{2} surface, which was not conducive for dispersion. The specific surface area decreased and catalytic performance also decreased accordingly (Cai et al. 2018). Further, excessively high doping amounts resulted in decreases in the effective active sites in the center, as well as light energy utilization rates and catalytic efficiency.
3.2.5 Effects of TiO$_2$/SiO$_2$ dose on N-NO$_3^-$ removal rate in low-concentration solutions

The effect of different TiO$_2$/SiO$_2$ composite catalyst doses (1.1, 1.2, 1.3, 1.4, 1.5, and 1.6 g·L$^{-1}$) with 40% loading on the photocatalytic degradation of 30 mg·L$^{-1}$ N-NO$_3^-$ was investigated at a formic acid dose of 0.6 mL·L$^{-1}$ and a CO$_2$ flow rate of 0.1 m$^3$·h$^{-1}$. As shown in Fig. 10, the removal rate of N-NO$_3^-$ and conversion rate of ammonia nitrogen increased with higher TiO$_2$/SiO$_2$ doses and then decreased after reaching a peak. Both the N-NO$_3^-$ removal rate and conversion rate reached a maximum (83.48% and 98.80%, respectively) when the TiO$_2$/SiO$_2$ dose was 1.4 g·L$^{-1}$.

The N-NO$_3^-$ removal rate and N$_2$ selectivity in the products increased with higher doses due to increases in TiO$_2$ concentrations. Specifically, this increase in the concentration of effective catalysts could improve light utilization, resulting in an excellent removal effect. However, as these doses increased further, the N-NO$_3^-$ removal rate and N$_2$ selectivity in the products decreased due to the effect of gravity on SiO$_2$, which caused the deposition of the composite catalyst and reduced light utilization, and therefore catalytic efficiency was slightly decreased (Wang et al. 2021).
3.3 Sample stability

Catalyst stability is another important parameter to evaluate when assessing catalytic performance. To achieve this, the reacted catalyst was recovered and tested several times under the same conditions. After the reaction, the reaction system was allowed to stand and was then filtered. Our findings indicated that the recovery effect of TiO$_2$/SiO$_2$ was superior to that of TiO$_2$. The filtered catalyst was repeatedly washed with water and dried in an oven at 60 °C for reuse. Under optimal conditions (initial N-NO$_3^-$ concentration of 30 mg·L$^{-1}$, formic acid dose of 0.6 mL·L$^{-1}$, CO$_2$ flow rate of 0.1 m$^3$·h$^{-1}$, TiO$_2$ dose of 0.9 g·L$^{-1}$, 40 wt% TiO$_2$/SiO$_2$ dose of 1.4 g·L$^{-1}$) The experiments were repeated three times and the results are shown in Fig. 11. The catalytic efficiency of the two catalysts decreased after reapplication, indicating that the photocatalytic performance of the used catalysts was reduced. Further, the particle size of both catalysts increased after use, which affected light utilization and decreased catalytic efficiency. The difference in the catalytic efficiency of TiO$_2$ from 99.93% in the first use cycle to 72.38% in the second cycle was very significant, whereas the difference between the third and fourth cycles was not significant, both of which accounted for approximately 65% of the removal efficiency of the first cycle. This was because TiO$_2$ tended to agglomerate after use, which reduced its specific surface area and catalytic efficiency. The catalytic efficiency of TiO$_2$/SiO$_2$ decreased from 83.48% in the first cycle to 76.43% in the second cycle. Similar to TiO$_2$, the difference in the removal rate between the third and fourth cycles was not significant, both of which accounted for approximately 73% of the removal efficiency of the first cycle. Given that TiO$_2$ and SiO$_2$ were only physically bound, repeated washing would cause some of TiO$_2$ to fall off from SiO$_2$, thus decreasing the effective catalyst...
concentration and the overall catalytic efficiency.

Fig. 11 (a) Effect of the number of TiO$_2$ utilization cycles on N-NO$_3^-$ removal rates; (b) effect of the number of TiO$_2$/SiO$_2$ utilization cycles on N-NO$_3^-$ removal rates

3.4 Mechanism of N-NO$_3^-$ photocatalytic reduction

3.4.1 Kinetics of photocatalytic reduction of nitrates

In photocatalysis studies, the kinetics of photocatalytic reactions are commonly analyzed by the Langmuir-Hinshelwood kinetic equations:

\[ r = \frac{1}{V} \frac{dC}{dt} = \frac{kC}{1+(KC)^2} \]  

(3.4.1-1)

Given that the reaction kinetics of the photocatalytic reduction of nitrates follows the first-order reaction kinetic model, the Langmuir-Hinshelwood kinetic equation can be changed as follows:

\[ \ln \frac{C}{C_0} = -kt \]  

(3.4.1-2)

where $C_0$ refers to the initial concentration of ammonia nitrogen in the solution, $C$ refers to the concentration of ammonia nitrogen at any given moment, and $k$ refers to the kinetic constant.

As shown in Fig. 12, the concentration of nitrates was linearly related to the reaction time, and the correlation coefficients of TiO$_2$ and TiO$_2$/SiO$_2$ reached 0.95 and 0.99, respectively, indicating that the photocatalytic reduction of N-NO$_3^-$ was consistent with the first-order reaction. The kinetic constant of TiO$_2$ was 4.4 times higher than that of TiO$_2$/SiO$_2$. Therefore, TiO$_2$ was more effective than TiO$_2$/SiO$_2$ for the photocatalytic reduction of nitrates. Nevertheless, TiO$_2$/SiO$_2$ had a higher N$_2$ selectivity and
could be easily recycled.

Fig. 12 First-order kinetic model of the photocatalytic oxidation of ammonia nitrogen by TiO$_2$ and TiO$_2$/SiO$_2$

3.4.2 Mechanism of photocatalytic reduction of nitrates

Based on the results of this study and previous studies of photocatalysis by TiO$_2$, we proposed the potential mechanisms of photocatalytic reduction of N-NO$_3^-$ by TiO$_2$ (Fig. 13).

TiO$_2$ had a low-energy valence band and a high-energy conduction band, which were discontinuous and separated by a band gap. The electrons occupied the low-energy valence band and the high-energy conduction band was empty. When the incident light intensity was greater than or equal to the width of the band gap, the excited electrons in the valence band migrated to the conduction band, generating negatively charged electrons (e$^-$) in the conduction band and a hole (h$^+$) in the valence band (Pawar et al. 2018). The photogenerated electrons and holes were separated by an electric field and migrated to the catalyst surface, where the holes (h$^+$) combined with the formic acid on the catalyst surface to generate free radicals (·CO$_2^-$). The photogenerated electrons and ·CO$_2^-$ were highly reductive and contributed to the degradation of N-NO$_3^-$ and the further conversion of intermediates to N$_2$ (Chu & Anastasio 2003, Mack & Bolton 1999). NO$_3^-$ was reduced to N$_2$ and NO$_2^-$ (Eqs. 3.4.2-3-3.4.2-4) on the catalyst surface by the photogenerated electrons and ·CO$_2^-$, and NO$_2^-$ on the catalyst surface was reduced to N$_2$ (Eq 3.4.2-5) or NH$_4^+$ (Eq 3.4.2-6) in the presence of photogenerated electrons and ·CO$_2^-$ (Wang et al. 2021). The main product of the reaction was N$_2$, whereas NO$_2^-$ and NH$_4^+$ were produced in
trace amounts, which was consistent with previous studies (Doudrick et al. 2012, Ren et al. 2015).

\[ h\nu + TiO_2 \rightarrow e^- + h^+ \]  
(3.4.2-1)

\[ HCOO^- + h^+ \rightarrow \cdot CO_2^- + H^+ \]  
(3.4.2-2)

\[ NO_3^- + 2e^- + 2H^+ \rightarrow NO_2^- + H_2O \]  
(3.4.2-3)

\[ NO_3^- + 2 \cdot CO_2^- + 2H^+ \rightarrow NO_2^- + CO_2 + H_2O \]  
(3.4.2-4)

\[ 2NO_3^- + 10e^- + 12H^+ \rightarrow N_2 + 6H_2O \]  
(3.4.2-5)

\[ 2NO_3^- + 10 \cdot CO_2^- + 12H^+ \rightarrow N_2 + 10CO_2 + 6H_2O \]  
(3.4.2-6)

\[ NO_2^- + 6 \cdot CO_2^- + 8H^+ \rightarrow NH_4^+ + 6CO_2 + 4H_2O \]  
(3.4.2-7)

Fig. 13 Mechanism of photocatalytic reduction of N-NO\(_3^-\) by TiO\(_2\)

5 Conclusions

TiO\(_2\) exhibited an excellent effect on the photocatalytic reduction of N-NO\(_3^-\) in water. However, to enhance its recoverability and recyclability, a TiO\(_2\)/SiO\(_2\) composite catalyst was prepared by loading TiO\(_2\) on SiO\(_2\). The components in the TiO\(_2\)/SiO\(_2\) composite catalyst were evenly distributed, and the
two were mainly physically bound. This composite catalyst exhibited smaller TiO$_2$ particles on its
surface, which increased its specific surface area and improved light utilization. After the conjugation
of these two agents, their structure remained largely unchanged; however, the adsorption of the
reactants resulted in a larger crystal size, which reduced the catalytic performance. Further, the
recovery test demonstrated that the catalyst stability could still be further improved.

TiO$_2$ was more effective in treating low-concentration N-NO$_3^-$ wastewater, whereas TiO$_2$/SiO$_2$ was
more effective in treating medium-concentration N-NO$_3^-$ wastewater. Moreover, the selectivity of N$_2$ in
the products of TiO$_2$/SiO$_2$ was higher than that of TiO$_2$. In the photocatalytic reduction of N-NO$_3^-$, both
e$^-$ and ·CO$_2$ could reduce N-NO$_3^-$, and NO$_3^-$ could be reduced to N$_2$, NO$_2^-$, and NH$_4^+$; however, NO$_2^-$
and NH$_4^+$ occurred in trace amounts, and the final product was mostly N$_2$. 
Declarations

Ethics approval and consent to participate
Not applicable.

Consent for publication
Informed consent was obtained from all individual participants included in the study.

Availability of data and materials
All data generated or analysed during this study are included in this published article [and its supplementary information files].

Competing interests
The authors declare that they have no competing interests.

Authors’ contributions
Wanzhen Zhong: Conceptualization, Methodology, Writing - Original Draft.

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Shujuan Sun*: Writing - review & editing.

Lingsheng Wang: Investigation, Software, Resources.

Huaihao Liu: Validation, Formal analysis.

Junzhong Wang: Data Curation, Visualization.

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