



## Research paper

Visible active N-doped TiO<sub>2</sub>/reduced graphene oxide for the degradation of tetracycline hydrochloride

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## ABSTRACT

N-doped TiO<sub>2</sub> nanoparticles deposited on reduced graphene oxide sheets were successfully prepared by a photoreduction method. The synthesized N-TiO<sub>2</sub>/rGO composite was characterized by XRD, SERS, XPS, TEM, UV-vis DRS and PL, and its visible-light photocatalytic activity was evaluated by degradation of tetracycline hydrochloride (TC). The results showed that N-TiO<sub>2</sub>/rGO composites exhibited a more enhanced photodegradation activity compared to pure TiO<sub>2</sub> and N-doped TiO<sub>2</sub>. Trapping tests indicated that not ·OH and h<sup>+</sup> but ·O<sub>2</sub><sup>-</sup> was chiefly responsible for the photodegradation process. The reusable experiments showed that the prepared N-TiO<sub>2</sub>/rGO catalyst was stable during the photodegradation of TC.

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## 1. Introduction

As a broad-spectrum antibiotic produced by actinomycetes, tetracycline hydrochloride (TC) with its low price, wide antibacterial spectrum and less toxic side effect is widely used in the treatment of human and animal diseases [1–3]. However, TC is incompletely degraded due to containing benzene skeleton [4], its widespread overuse in animal husbandry and aquaculture production caused a series of residues, which have done serious harm to the ecological environment and human health [5,6]. Therefore, it is very significant for removal of TC residues from the environment.

Among a number of treatment methods for TC, a large number of studies confirmed that photocatalysis method has the advantage of environmental, handy and efficient [7–11]. TiO<sub>2</sub> as a photocatalyst has drawn great attention due to its non-toxic, low cost, good chemical stability and long reusability [12–14], but its photocatalytic activity is low due to limited optical utilization efficiency and recombination of photoinduced charge. In order to improve the optical absorption of TiO<sub>2</sub> and then to promote its photocatalytic activity, many methods have been developed such as the doping with transition metal ions and nonmetal elements [15–18]. Reports have shown that N-doped TiO<sub>2</sub> exhibits excellent

visible activity in wastewater treatment applications [19–21]. Another common method for enhancing the photocatalytic efficiency of TiO<sub>2</sub> is immobilization of TiO<sub>2</sub> nanoparticles on the surface of graphene [22–25]. Many studies have proved that graphene is ideal for electronic receivers or transfer bridges, which inhibits the recombination of photoinduced electron-hole pairs, expedites the electron transfer and thus promotes the photocatalytic activity [26–30]. Additionally, graphene can extend the optical absorption of TiO<sub>2</sub> into visible light region [26,31]. Thus, it is worth considering the hybridization of graphene with N-doped TiO<sub>2</sub> due to the cooperative effect of N doping and graphene. Actually, N-doped TiO<sub>2</sub>/graphene hybrids with high visible-light photocatalytic efficiency have been recently developed [32–34]. However, these studies always concentrate on the photocatalytic decomposition of dye and the photocatalytic hydrogen generation. As far as we know, there is no study on the visible-light photodegradation activity of antibiotic for N-doped TiO<sub>2</sub>/graphene hybrids.

In this work, N-doped TiO<sub>2</sub> (N-TiO<sub>2</sub>) nanoparticles were prepared using a sol-gel method and then were successfully deposited on reduced graphene oxide sheets by a photoreduction method. The photoactivity of the prepared N-TiO<sub>2</sub>/rGO composites was evaluated and its reusability was investigated by degrading TC solution. Interestingly, the N-TiO<sub>2</sub>/rGO composites exhibited higher photodegradation activity than pure TiO<sub>2</sub> and N-TiO<sub>2</sub>. Additionally, the N-TiO<sub>2</sub>/rGO composites showed excellent reusability. A mechanism for enhanced visible-light photodegradation activity of N-TiO<sub>2</sub>/rGO composite catalyst was also proposed.

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## 2. Experimental section

### 2.1. Synthesis of nitrogen-doped TiO<sub>2</sub>/reduced graphene oxide (N-TiO<sub>2</sub>/rGO)

Scheme of synthesis of N-TiO<sub>2</sub>/rGO composites was shown in Fig. S1.

N-TiO<sub>2</sub> samples were synthesized by a sol gel method. Firstly, 5 ml acetic acid and 12 ml tetrabutyl titanate were orderly added in 25 ml anhydrous ethanol during stirring condition (solution A). Secondly, 4.2 g urea was added in 20 ml anhydrous ethanol under agitating condition (solution B). Then, solution B was added into solution A with the drop speed of about 2 ml min<sup>-1</sup> under vigorous stirring. The obtained mixture was agitated for 2 h, and then aged for 24 h at room temperature in air to form homogeneous gel, which was dried at 70 °C for 12 h in an oven. Subsequently, the dried gel was milled into powders and calcined at 400 °C for 3 h in a furnace. Finally, the yellowish powder was obtained. For comparison, pure TiO<sub>2</sub> was also prepared without urea by the above experimental procedure.

Graphene oxide (GO) was synthesized from graphite powders by modified Hummer's method and as reported by Pei [34]. N-TiO<sub>2</sub>/rGO composites were prepared by a photoreduction method based on Kamat's work with minor modifications [35]. In a typical procedure, 0.025 g GO was dispersed in anhydrous ethanol by ultrasonic treatment for 30 min. Subsequently, 0.5 g N-TiO<sub>2</sub> was added in this dispersed GO solution, the mixture was stirred for another 30 min, and then irradiated by UV light for 2 h in nitrogen atmosphere. Finally, the resulting composite was obtained by filtration, rinsed with deionized water and anhydrous ethanol, and then dried at 80 °C for 24 h in a vacuum oven. Reduced graphene oxide (rGO) was also prepared without N-TiO<sub>2</sub> by the above experimental method.

### 2.2. Material characterization

X-ray diffraction (XRD) was performed by a XRD-6100 diffractometer with Cu K $\alpha$  radiation. Raman spectra were detected by a HR800 Raman spectrometer. X-ray photoelectron spectroscopy (XPS) spectra were implemented by ThermoFisher-VG Scientific instrument (ESCALAB 250Xi). Transmission electron microscopy (TEM) analysis was carried out using a TECNAI G2 F20 TEM system. UV-vis diffuse reflectance spectra (DRS) were collected by a UV-2700 spectrophotometer with a diffuse reflectance accessory. The photoluminescence (PL) emission spectra were recorded using HITACHI F-2500 fluorescence spectrophotometer.

### 2.3. Evaluation of photodegradation activity

The photocatalytic decompositions of TC aqueous solution (10 mg L<sup>-1</sup>) were carried out in a home-made 100 mL Pyrex glass vessel with a cooling jacket at ambient temperature controlled by recycled water. A 300 W Xe-arc lamp with a 400 nm cutoff filter was used as the radiation source. 50 mg photocatalysts were dispersed in 50 mL TC aqueous solution and stirred for 30 min to establish adsorption-desorption equilibrium in a dark room, and then the photocatalytic degradation reaction was started under visible light. 3 mL of TC solutions were withdrawn and centrifuged at intervals of 10 min during irradiation and then its concentration was measured by UV-vis spectrophotometer (UV-2700).

## 3. Results and discussion

### 3.1. Characterizations of as-prepared materials

The as-prepared samples were characterized by XRD. As seen from Fig. 1a, all samples exhibited similar XRD patterns. The peaks for all samples correspond to the anatase TiO<sub>2</sub> phase according to the JCPDS No. 21-1272. With the introduction of small nitrogen content and graphene, the intensity of the characteristic peak of TiO<sub>2</sub>, N-TiO<sub>2</sub> and N-TiO<sub>2</sub>/rGO is slightly decreased in sequence, which was attributed to the augment of lattice defects in TiO<sub>2</sub> crystals [34]. Especially, the doping of nitrogen causes the characteristic peaks of anatase TiO<sub>2</sub> shift to higher angles, which was ascribed to the compression strain caused by the difference of N and O binding characteristics (Fig. S2) [36]. Raman spectroscopy is widely used to obtain the global structural information of carbon materials. The Raman spectra of the as-prepared TiO<sub>2</sub>, N-TiO<sub>2</sub>, N-TiO<sub>2</sub>/rGO and rGO materials were shown in Fig. 1b, typical four peaks at ca. 143 (E<sub>g</sub>), 395 (B<sub>1g</sub>), 514 (A<sub>1g</sub>/B<sub>1g</sub>) and 639 (E<sub>g</sub>) cm<sup>-1</sup> are ascribed to anatase TiO<sub>2</sub> [34]. The Raman shifts at 1347 cm<sup>-1</sup> and 1595 cm<sup>-1</sup> are from D-band and G-band of rGO [37], which suggested the presence of rGO in N-TiO<sub>2</sub>/rGO. With the introduction of small nitrogen content and graphene, the intensity of the resolved Raman shift decreases. This point was consistent with the result of XRD (Fig. 1a).

The chemical states of elements in N-TiO<sub>2</sub>/rGO composites were obtained by XPS analysis. As shown in Fig. 2a, the survey spectrum of the N-TiO<sub>2</sub>/rGO composites confirms the existence of carbon, nitrogen, oxygen and titanium with the chemical binding energies of C 1s (284.8 eV), N 1s (401.3 eV), O 1s (531.2 eV), and Ti 2p<sub>3/2</sub> (458.9 eV), respectively. According to Fig. 2b, two peaks at 458.9 eV and 464.6 eV belong to the binding energies of the Ti2p<sub>3/2</sub> and

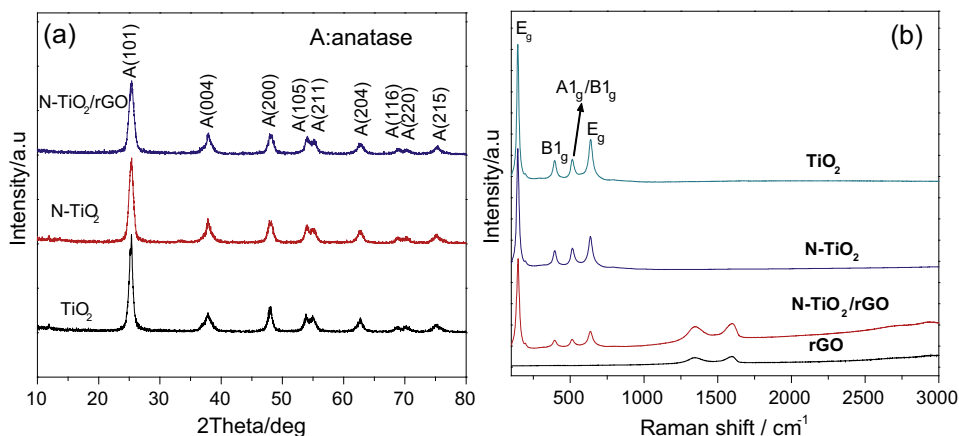


Fig. 1. (a) XRD patterns of TiO<sub>2</sub>, N-TiO<sub>2</sub> and N-TiO<sub>2</sub>/rGO, (b) Raman spectra of TiO<sub>2</sub>, N-TiO<sub>2</sub>, N-TiO<sub>2</sub>/rGO and rGO.

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