



Synthesis of magnetic graphene oxide–TiO₂ and their antibacterial properties under solar irradiation



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ABSTRACT

Titanium dioxide (TiO₂) has been intensively researched and increasingly used as antibacterial agent, but it suffers from separation inconvenience. Its effective removal from water after reaction while maintaining its high antibacterial activity becomes necessary. In this work, it was the first time the magnetic graphene oxide–TiO₂ (MGO–TiO₂) composites were prepared through a simple synthesis method. The results indicated that MGO–TiO₂ exhibited a good antibacterial activity against *Escherichia coli*. MGO–TiO₂ was found to almost completely inactivate the *E. coli* within 30 min under solar irradiation. The effect of inorganic ions present in *E. coli* suspension was also evaluated. Compared with other ions, HCO₃⁻ and HPO₄²⁻ had a greater influence on the antibacterial property.

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1. Introduction

The growing concerns about drinking water safety have put more stresses on the removal of pathogenic microorganisms [1]. Conventional disinfection methods such as chlorination and ozonation, are essential steps in centralized water-treatment. Despite their effectiveness in disinfection, these powerful oxidants may react with natural organic matter to form potentially mutagenic and carcinogenic disinfection by-products (DBPs) [2].

Photocatalytic inactivation is considered as a promising alternative for the removal of pathogens from water, as it can be potentially used without generating harmful by-products under solar irradiation. Titanium dioxide (TiO₂) is regarded as a suitable material because of its high catalytic activity, excellent chemical and thermal stability, low toxicity and cost [3,4]. Upon excitation by light, the photon energy generates electron–hole pairs on the TiO₂ surface, then the electrons and holes will react with oxygen and water molecules to form hydroxyl radicals (*OH), which are strong oxidants for disinfection of bacteria [5]. However, there are still many drawbacks. Firstly, a large bandgap (3.2 eV) of anatase TiO₂ restricts its use only to the narrow light-response range of ultraviolet (only

3–5% of total sunlight) [3]. Secondly, the low electron transfer rate and high electron recombination rate significantly limit the photo oxidation rate. Moreover, separation and reuse of the nano-TiO₂ pose another obstacle to practical application in drinking water [6].

Graphene oxide (GO) is chemically oxidized graphene, which attracts tremendous research interests due to its outstanding properties, including thermal and chemical stability, high mechanical strength, large specific surface area, good electron conductivity and water solubility [1]. The GO can effectively reduce the electron–hole recombination rate [3]. It has been reported that GO has excellent antibacterial performance, because GO generates reactive oxygen species and leads to DNA fragmentation [7].

In addition, a well-defined hybridized composites consisting of GO and TiO₂ was reported as an antimicrobial agent [1]. So far, all these studies on the antimicrobial properties of GO–TiO₂ were conducted in pure water under controlled laboratory conditions. Such studies ignored the interference of other substances in natural waters of nanometer materials. Therefore, more complex environments need to be investigated to determine the real effect of GO–TiO₂ on the bacteria.

With the rapid development of nanotechnology and increasing usage of nanoparticles, a new crisis has emerged (i.e. nanotoxicology). Chen et al. [8] observed that TiO₂ nanoparticles could induce DNA double strand breaks in bone marrow cells. Therefore, it is essential to remove the nanoparticles from aqueous solution, and

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a good choice to introduce magnetic nanoparticle into the nanometer antibacterial material.

The magnetic nanoparticles not only have the characteristics of nano-materials, but also have another important property- magnetism [9]. Iron-based magnetic nanoparticles have been used for an increasing number of environmental application [10]. It is worth mentioning that magnetic iron oxide nanoparticles also have the ability of bacterial inactivation. Auffan et al. [10] reported antimicrobial properties of Fe_3O_4 and $\gamma\text{-Fe}_2\text{O}_3$ nanoparticles toward the Gram-negative bacterium *Escherichia coli* and proved the release of Fe^{2+} from Fe_3O_4 and $\gamma\text{-Fe}_2\text{O}_3$ nanoparticles causing cytotoxicity. In our previous work, iron oxide loaded graphene nano-composites were prepared and its inactivation performance and mechanism of *E. coli* were reported [11].

This work reported a series of antibacterial nano-materials using a simple preparation method, by introducing TiO_2 and iron oxide magnetic (M) nanoparticles into GO nanosheets. Magnetic graphene oxide- TiO_2 (MGO- TiO_2) nanomaterials possessed the antimicrobial properties of three materials including TiO_2 , GO and magnetic nanoparticles and the separation convenience of magnetic nanoparticles. *E. coli* were used to evaluate the bactericidal property of the nano-composite under solar irradiation, because *E. coli* was often used for microbial indicators of drinking water monitoring. The optimal TiO_2 content in antibacterial nanomaterials was investigated. The nano-composites proposed in this work conquered the drawbacks of TiO_2 , integrated the advantages of each respective component and possessed more superior merits over previous TiO_2 -based antibacterial agent, including: (1) suppressing recombination of photo-generated electron-hole pairs through an effective charge transfer route from TiO_2 to GO, (2) providing additional antibacterial property with GO and iron oxide magnetic nanoparticles, and (3) easy separation from water owing to magnetic nanoparticles.

To our knowledge, no reports were found to synthesize multifunctional MGO- TiO_2 nanocomposites and used it for water disinfection under solar irradiation. In addition, the interferences from some common anions (i.e. HCO_3^- , Cl^- , SO_4^{2-} , NO_3^- and HPO_4^{2-}) and cations (i.e. K^+ and Na^+) in natural water were also investigated.

2. Experimental

2.1. Materials

Graphite powders were purchased from Jim-Shan-Ting New Chemical Factory (Shanghai, China). TiO_2 nanoparticles were used from Shanghai Aladdin Reagent Company (Shanghai, China). Sodium nitrate (NaNO_3), sulfuric acid (H_2SO_4 , 98%), potassium permanganate (KMnO_4), hydrogen peroxide (H_2O_2 , 30%), ferrous ammonium sulfate [$\text{NH}_4\text{Fe}(\text{SO}_4)_2 \cdot 12\text{H}_2\text{O}$], ammonium ferric sulfate [$(\text{NH}_4)_2\text{SO}_4 \cdot \text{FeSO}_4 \cdot 6\text{H}_2\text{O}$], ammonia solution (NH_3 , 25%) methanol (CH_3OH , 99.9%) and absolute ethanol ($\text{CH}_3\text{CH}_2\text{OH}$) were obtained from Sinopharm Chemical Reagent Company (Shanghai, China). Sodium hydrogen phosphate (Na_2HPO_4), sodium bicarbonate (NaHCO_3), sodium sulfate (Na_2SO_4), sodium chloride (NaCl), potassium sulfate (K_2SO_4) and potassium bicarbonate (KHCO_3) were supplied by Sinopharm Chemical Reagent Company (Beijing, China). All chemicals were analytical grade.

2.2. Preparation of GO

GO was prepared according to the Hummers' method [12–14]. Graphite powders (1 g) and NaNO_3 (0.5 g) were added to concentrated H_2SO_4 (23 mL) in a 1 L conical flask. Under ice bath condition, KMnO_4 (3 g) was added slowly with stirring, and the temperature of

the mixture was kept at below 10°C . Once the mixture was homogeneous, it was transferred to an oil bath maintained at 35°C and stirred for 30 min. Then the dispersion was diluted with 46 mL of warm ultrapure water (about 30°C) to form a brownish mixture, and the mixture was stirred for 30 min as the temperature was increased to 98°C , with subsequent addition of warm ultrapure water (140 mL), followed by slow addition of H_2O_2 (2.5 mL). The color of the suspension changed from brown to yellow. The suspension was filtered through a $0.1\ \mu\text{m}$ filter membrane, and washed with ultrapure water and absolute ethanol sequentially until the pH of the supernatant was 7. The GO samples were recovered finally and then dried in a vacuum desiccator.

2.3. Preparation of MGO

GO (1.0 g) described above was dispersed in ultrapure water (100 mL) using ultrasonic treatment for 30 min to obtain GO suspension. Under N_2 atmosphere, $(\text{NH}_4)_2\text{SO}_4 \cdot \text{FeSO}_4 \cdot 6\text{H}_2\text{O}$ (5.8 g) and $\text{NH}_4\text{Fe}(\text{SO}_4)_2 \cdot 12\text{H}_2\text{O}$ (10.7 g) were added to ultrapure water (100 mL) (molar ratio of 1.5:1 for Fe^{3+} and Fe^{2+}). Then mixed iron solution was quickly added with ammonia (10 mL), with subsequent addition of GO suspension with stirring in the water bath pot at 85°C for 45 min. Finally, the product was separated using the magnet and washed with ultrapure water and absolute ethanol until the pH was 7. The resulting MGO was dried in a vacuum oven at 60°C for 12 h.

2.4. Preparation of MGO- TiO_2

Firstly, various concentrations of TiO_2 dispersion were prepared by adding different amount of TiO_2 power (0.5, 1.0, and 1.5 g) in 100 mL ultrapure water and shaken for 30 min by ultra-sonication. The synthesis process of MGO- TiO_2 was similar to that of MGO, except that TiO_2 dispersion and iron salts were simultaneously added in the GO solution during the preparation of MGO- TiO_2 . According to the different amounts of TiO_2 , the final drying products were marked as MGO- TiO_2 -1, MGO- TiO_2 -2 and MGO- TiO_2 -3, respectively.

2.5. Characterization

Field emission scanning electron microscopy (FESEM) images were obtained using a JSM-6700FLV microscope. Transmission electron microscopy (TEM) was performed using a JEM-3010. Energy dispersive X-ray (EDS) measurement was conducted using the EDAX system attached to the same field emission scanning electron microscopy (JSM-6700FLV). The structure phases of the synthesized antibacterial materials were analyzed by X-ray diffraction (XRD) (D/max 2550 X-ray diffractometer, Rigaku, Japan). The analysis of elements and function groups on the surface of MGO- TiO_2 -2 was determined using X-ray photoelectron spectroscopy (XPS, Thermo Scientific Escalab 250Xi) with a Mg $\text{K}\alpha$ X-ray source (1254 eV of photons). The absorbance of the nanomaterials solutions during the tests was analyzed in a UV-Vis spectrophotometer (Shimadzu UV-2550). Lake shore 7410 vibrating sample magnetometer (VSM) was employed to record the magnetization curve.

2.6. Bacterial strain and growth culture media

The bacteria strain *E. coli* ATCC 25922 was purchased from the China Center for Type Culture Collection (Beijing, China). Before the experiment, all glasswares and solutions used in the experiments were autoclaved at 121°C for 15 min.

The bacterial strain was grown in Luria-Bertani (LB) medium (yeast extract 5 g, tryptone 10 g and NaCl 5 g in 1 L of deionized

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