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Fabrication of nitrogen doped graphene quantum dots-BiOI/$MnNb_2O_6$ p-n junction photocatalysts with enhanced visible light efficiency in photocatalytic degradation of antibiotics

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ABSTRACT

Novel p-n junction photocatalysts nitrogen doped graphene quantum dots (NGQDs)-BiOI/$MnNb_2O_6$ have been prepared via hydrothermal method for the environmental remediation. The photocatalytic activity of as-prepared photocatalysts was evaluated by the degradation of different antibiotics such as tetracycline (TC), oxytetracyline, ciprofloxacin and doxycycline. Compared with single $MnNb_2O_6$ and BiOI, the hybrid materials (NGQDs-BiOI/$MnNb_2O_6$) could significantly enhance photocatalytic activity. Meanwhile, both the BiOI/$MnNb_2O_6$ ratio (Bi/Mn ratio) and the amount of NGQDs displayed important influence on the antibiotics degradation. In addition, the 5%NGQDs-Bi/Mn sample performed the optimum photocatalytic degradation toward TC (87.2%) within 60 min. By further studies based on the electron spin resonance (ESR) and active species trapping experiments, this enhanced photocatalytic property could be ascribed to high charge carrier mobility of NGQDs and the p-n junction photocatalytic systems, which greatly promoted efficient separation of charge carriers.

1. Introduction

In the recent years, the elimination of antibiotics from aquatic ecosystem have aroused much interests due to their associated specific environmental risks and impact on environment issues and human health [1,2]. As the high production and usage of drugs in the world, antibiotics are widely applied in the treatment of bacterial infection, easily discharge into the aquatic ecosystem via the wastewater effluent, animal manure and soil erosion [3]. Recent researches have showed that the micropollutants of tetracycline antibiotics at the concentrations were about 4.58 mg kg^{-1}, 86–199 μg kg^{-1} and 0.13–0.51 μg L^{-1} in the animal dung samples, soils and surface waters in the environment, respectively [4,5]. Therefore, it is vital to find an effective method for eliminating the antibiotics from aqueous environments.

Semiconductor photocatalysis, which is considered as a green and sustainable technology, has aroused much interests because of its wide application in water purification and environmental protection by solar energy [6–9]. In order to effectively utilize visible light (48% of the incoming solar energy), lots of visible-light-driven photocatalysts have been prepared successfully, such as g-C_3N_4 [10], Ag_3VO_4 [11], $BiVO_4$ [12], Bi_2WO_6 [13] and other Bi-based photocatalysts [14,15]. Among these semiconductors, BiOI as a p-type bismuth oxyhalides semiconductor, exhibiting excellent photocatalytic activity under visible light irradiation because of its narrow band gap (Eg = 1.63–1.94 eV) [16,17]. However, the photocatalytic activity of single BiOI had been limited by some disadvantages, such as low efficiency of light absorption, slow rate of charge transfer and high recombination probability of the photogenerated electron-hole pairs. Therefore, it is necessary to further improve the photocatalytic activity for practical applications. Up to now, some strategies have been proposed to improve the photocatalytic activity of BiOI, such as modified by noble metals [18,19], constructed the heterojunctions [20,21], induced oxygen defect [22,23] and sensitizer [24]. Meanwhile, it has been proven that the heterostructures between a n-type semiconductor and a p-type semiconductor will greatly facilitate the separation and transfer of charge carriers because of the existence of an internal electric field built at the heterojunction interface, thus highly enhancing the photocatalytic activity.

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On the one hand, $MnNb_2O_6$, as a n-type transition metal niobate photocatalyst, had attracted much attention in photocatalytic applications due to its narrow band energy of 2.2 eV. Hu et al. had reported that the 3D flower-like nanostructure $MnNb_2O_6$ had excellent photocatalytic performance for photodegradation of methylene blue under visible light irradiation [25]. Therefore, it is believed that the p-n junction coupling of BiOI and $MnNb_2O_6$ will exhibit superior performance by efficiently utilizing visible light.

On the other hand, as a novel carbon materials with the size less than 10 nm, graphene quantum dots (GQDs) had been a new direction in current research due to their environmentally friendly, nontoxic degradable, and low-cost features [26–31]. Moreover, when the nitrogen atoms were introduced into the carbon lattice of quantum dots (NGQDs), it can modulate the electronic properties of quantum dots and induce the "activation region" on the GQDs surfaces [32–35]. This kind of activated region can participate in catalytic reactions directly, such as the oxygen reduction reaction [36,37]. Hence, we conceive of introducing the NGQDs into the p-n junction to act an ideal electron mediate and supporter, which extremely facilitate the charge migration and prolong the charge lifetimes by suppressing the recombination of photogenerated electrons and holes.

Based on the above consideration, we reported a novel p-n junction of NGQDs-BiOI/$MnNb_2O_6$ by a simple hydrothermal method. Antibiotics such as tetracycline (TC), oxytetracyline, ciprofloxacin and doxycycline were chosen as target pollutants to explore the photocatalytic performance. Results showed that both the Bi/Mn ratio and NGQDs amount displayed important influence on the photocatalyst activity. Furthermore, tentative mechanism of the enhanced photocatalytic activity was also discussed based on the active species trapping experiments and electron spin resonance (ESR) analysis.

2. Experiment section

2.1. Synthesis of NGQDs

The NGQDs was obtained by directly pyrolyzing $C_6H_5O_7(NH_4)_3$. 1 g $C_6H_5O_7(NH_4)_3$ and 20 mL of H_2O were put into a beaker and heated to 200 °C with an oil bath pan. Within 30 min, the color of the solution slowly became the light orange, implying the formation of NGQDs. Ultimately, a quantity of NaOH (10 mg/mL) solution were added to adjust the pH value of 7 [38].

2.2. Synthesis of $MnNb_2O_6$ nanostructures

Firstly, 0.5 g Nb_2O_5 and 3.37 g KOH were added in the 60 mL of distilled water and then transferred into a 100 mL Teflon-lined stainless steel autoclave at 200 °C for 3 days. After cooling naturally, the clear solution of $[Nb_6O_{19}]^{8-}$ was obtained. Then, the above solution (4 mL) was diluted with 10 mL distilled water. The pH of obtained aqueous solution was adjusted to 7.8 by the addition of HCL solution. After that, 0.035 g $MnCl_2{\cdot}4H_2O$ and 1 g K_2SO_4 were added under continuous stirring for 30 min. Finally, the obtained precursor was transferred into a 50 mL Teflon-lined stainless autoclave at 260 °C for 24 h. The product was filtered, washed with distilled water, and dried in a vacuum at 60 °C for 12 h.

2.3. Preparation of NGQDs-BiOI/$MnNb_2O_6$

Typically, 1 mmol of $Bi(NO_3)_3{\cdot}5H_2O$ was dissolved in 20 mL of ethylene glycol, and X (0.2, 0.33, 1, 3 and 5) mmol $MnNb_2O_6$ was added in above solution with continuous stirring for 30 min. Then, 1 mmol KI was dissolved in this solution and the color of solution became orange. Subsequently, 20 mL of distilled water was slowly dropped to the orange solution, red precipitate was generated gradually (abbreviated as 5Bi/Mn, 3Bi/Mn, Bi/Mn, Bi/3Mn, and Bi/5Mn). After that, different amount of the NGQDs was dissolved in above solution with continuous stirring for 60 min. The preparation of NGQDs-BiOI/$MnNb_2O_6$ with different starting mass ratios of NGQDs to BiOI/$MnNb_2O_6$ (0.01, 0.03, 0.05 0.07 and 0.1) were labeled as 1%NGQDs-BiOI/$MnNb_2O_6$, 3%NGQDs-BiOI/$MnNb_2O_6$, 5%NGQDs-BiOI/$MnNb_2O_6$, 7%NGQDs-BiOI/$MnNb_2O_6$ and 10%NGQDs-BiOI/$MnNb_2O_6$. Finally, the precursor was transferred into a 50 mL Teflon-lined stainless autoclave at 180 °C for 12 h. The obtained precipitate was collected by centrifugation, washed with the deionized water and absolute ethanol for several times, dried at 60 °C for 12 h. For comparison, pure BiOI was prepared with the same method without $MnNb_2O_6$ and NGQDs.

2.4. Characterization

X-ray diffraction (XRD) patterns measurements were undertaken using a D/MAX-2500 diffract meter (Rigaku, Japan) with a nickel-filtered Cu Kα radiation source (λ = 1.54056 Å). The X-ray photoelectron spectroscopy (XPS) was obtained by a Thermo ESCALAB 250X (America) electron spectrometer using 150WAl Ka X-ray sources. The scanning electron microscopy (SEM) was obtained by the Hitachi S-4800 field emission SEM (FESEM, Hitachi, Japan) to observe the morphology of the as-prepared samples. Transmission electron microscopy (TEM), high-resolution transmission electron microscopy (HRTEM) and High angle angular dark field-scanning transmission electron microscopy (HAADF-STEM) were gathered on an F20 S-TWIN electron microscope (Tecnai G2, FEI Co.), equipping with a 200 kV accelerating voltage. The photoluminescence (PL) spectra for solid samples were obtained on a F4500 (Hitachi, Japan) photoluminescence detector. UV–vis absorption spectra (DRS) was collected using a Shimadzu UV–vis 2550 spectrophotometer. Reflectance measurements were performed on powdered samples, $BaSO_4$ was used as a standard reference. The photocurrent and electrochemical impedance spectroscopy (EIS) measurements were conducted by use of a CHI852C electrochemical workstation and a CHI760E workstation, respectively. The ESR signals of radicals spin-trapped by spin-trapreagent 5,5-dimethyl-1-pyrroline N-oxide (DMPO) were examined on a Bruker EPR A 300-10/12 spectrometer.

2.5. Photocatalytic analysis

The photocatalytic activity of as-prepared samples were evaluated by the degradation of antibiotics (TC, oxytetracyline, ciprofloxacin and doxycycline) under visible light in a photochemical apparatus. A 250W xenon lamp with a cut-off filter was used to remove the wavelength less than 420 nm. In details, 50 mg of the sample power was dispersed into the 100 mL solution of antibiotics (10 mg/L), in order to the insure the adsorption equilibrium, the suspension solution was kept stirring for 30 min in darkness before irradiation. At the same irradiation intervals, 6 mL aqueous solution was sampled and separated from the suspended catalyst particles for analysis. The photocatalytic degradation ratio was tested via the intensity changes of the absorption peak at 357 nm, 275 nm, 277 nm and 271 nm to determine the concentration of TC, oxytetracyline, ciprofloxacin and doxycycline at different times by the same UV–vis spectrophotometer (UV-2550, Shimadzu, Japan).

2.6. Photoelectrochemical measurements

Photocurrent tests were carried out in a conventional three electrode system on the CHI852C electrochemical workstation by using 0.5 M Na_2SO_4 electrolyte, and the irradiation area was 1 cm^2 under 150 W xenon lamp. A Pt foil as the counter electrode and an Ag/AgCl