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Making of a metal-free graphitic carbon nitride composites based on biomass carbon for efficiency enhanced tetracycline degradation activity

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ABSTRACT

In this paper, a new metal-free photocatalyst (g-C_3N_4/C) coupled by graphitic carbon nitride (g-C_3N_4) and biomass carbon (waste paper used as carbon source) has been successfully synthesized. The g-C_3N_4/C exhibits obviously improved photocatalytic activity for degrading tetracycline, the degradation rate is more than 80%. It is more than four times than that of pure g-C_3N_4. Based on the structure and morphology characterization, the as-prepared g-C_3N_4/C represents a porous structure, which can provide a large surface area, increase the transmission route of photo-generated carriers and suppress the charge recombination. In addition, the capture experiments and ESR exploration show that both the h^+, ·OH and $\cdot O_2^-$ play the important roles in this metal-free photocatalytic reaction. More importantly, our work not only designs a better photocatalytic material, but also provides a new thinking for, waste recycling which coincides with the concept of sustainable development

1. Introduction

The environment pollution has been emerging in the company of the development of economy, hardly putting forward keeping human society [1–5]. For water pollution, especially antibiotic wastewater, the excessive use of antibiotics without effective regulation has brought many health problems [6–9]. Tetracycline (TC) a class of broad-spectrum antibiotics is always used as one of the most widely used antibiotics in the world. The misused of antibiotics will be a serious threat to the health of people and animals [10–12]. Accordingly, it is an urgent task to seek a suitable method to solve above problems.

At present, there are many ways to deal with the problem about wastewater in the environment. Adsorption and chemical coagulation are the two common techniques to treat such wastewater [13]. The most effective way is the photocatalytic technology [14]. Because it is an environment-friendly, green water pollution treatment method [15]. Semiconductor materials play an important role in photocatalytic technology. It is well known that semiconductor photocatalysts have received great attention because of its high performance and stability, potential applications to solar energy conversion [16], water splitting [17] and environmental purification [18,19]. To develop novel semiconductor photocatalysts with excellent and stable performance is still a challengeable task. As a semiconductor photocatalyst, TiO_2 has attracted extensive attention because of its superior performance [20]. However, there are still some disadvantages, such as the wide band gap (3.2 eV), which makes it only absorb ultraviolet (UV) light [21–23]. That the fast recombination rate of photo-generated electrons and holes results in unsatisfactory photocatalytic performance for the TiO_2 [24–27]. Therefore, much effort has been devoted to investigating and preparing highly efficient visible-light-driven photocatalysts. Graphitic carbon nitride (g-C_3N_4) as a new type of semiconductor photocatalyst is widely studied for expanding the energy utilization to the visible range of the solar spectrum [28]. Due to its potential application of solar energy conversion [29], toxic gas purification [30], water splitting [31], photocatalytic degradation organic contaminant under visible light irradiation received widespread concern by researchers [32]. Nevertheless, the photocatalytic efficiency of g-C_3N_4 is still limited by the high recombination rate of photo-induced carriers, which causes low photocatalytic efficiency [33]. Therefore, to solve the above problems, the increasing amount of carbon materials have stepped into researchers' attention on enhancing the photocatalytic performance of g-C_3N_4, such

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as graphene [34], carbon nanofibers [35], carbon nanotubes [36], carbon quantum dots [37], etc. Among these known carbon materials, biomass carbon, as a novel and eco-friendly carbon material, has aroused widespread concern in the field of photocatalysts owing to their biocompatibility, stable and good electrical conductivity ability.

Therefore, the construction of a novel biomass carbon modified g-C_3N_4 photocatalyst may be a good choice of improving the performance of g-C_3N_4. As well known, in the next few years, there is still a great demand for paper all over the world. However, waste paper resources cannot be effectively utilized. Therefore, it is important to solve the problem how to increase the recovery waste paper and make rational use of waste paper resources. Waste paper can be literally called "paper resources placed in the wrong place". Every year there will be a large amount of waste paper causing environmental pollution. This provides us with a sufficient source of raw materials to prepare biomass carbon and provides a good channel to the dispose waste resources, thereby improving resource utilization and realizing sustainable development goals.

In this work, the use of waste paper as raw material to synthesize biomass carbon, not only makes the source of raw materials wide range and lost cost, but also avoids waste of resources and reduces environmental pollution. Inspired by the above principles, we developed a novel composite photocatalyst of g-C_3N_4/C applied in removing of TC for the first time. In addition, the transmission electron microscope (TEM) has demonstrated that the g-C_3N_4/C composition of porous structure. The typical porous materials are beneficial to the good adsorption of the materials [38]. We have an insight into the influence of morphology, optical and electronic properties of g-C_3N_4/C photocatalyst by photoluminescence spectra (PL), transient fluorescence (FL), transient photocurrent and electrochemical impedance spectroscopy (EIS), etc. As expected, the as-prepared photocatalyst exhibits superior photocatalytic activity on degrading TC under the visible light. Moreover, the possible degradation intermediate product and mechanism of TC is investigated in detail by HPLC-MS, electron spin resonance (ESR) and radicals capture experiments. The unique feature material may provide a new insight to set photocatalyst model for environmental protection and sewage treatment.

2. Experimental

2.1. Materials

Urea (99%), isopropanol (IPA, AR), triethanolamine (TEOA, AR), ascorbic acid (AA), ethanol (C_2H_5OH, AR) and 5,5-dimethyl-1-pyrroline N-oxide (DMPO) are all purchased from Sinopharm Chemical Reagent Co., Ltd. Tetracycline (TC) is purchased from national institutes for food and drug control. All reagents are used as received from commercial suppliers without further purification, the deionized water is used throughout all experiments.

2.2. Materials synthesis

2.2.1. Synthesis of pure g-C_3N_4

The g-C_3N_4 was synthesized as follows: briefly, 5 g urea was dissolved in 10 ml deionized water and stirred by magnetic force for 0.5 h. Subsequently, the samples were placed in a vacuum drying oven at 60 °C for 24 h. Afterwards, put it into an open crucible in the muffle. Then, keep it at 500 °C for 2 h at the rate of 5 °C min^{-1} and ground the g-C_3N_4 into powders for further use.

2.2.2. Synthesis of pure c

To synthesize pure C: the waste paper scraps 1.0 g was put into an open crucible by annealing melamine in muffle. The remaining procedures were the same as those in synthesizing pure g-C_3N_4. After the alumina crucible cooling to room temperature, the samples were ground into powders for further use.

2.2.3. Synthesis of g-C_3N_4/C

To synthesize g-C_3N_4/C: the waste paper scraps (0.01, 0.02, 0.25, 0.5 and 1.0 g) were dipped into 5 g urea solution. To make it absorbed completely. The remaining procedures were the same as those in synthesizing pure g-C_3N_4. The obtained product was denoted as g-C_3N_4/C-0.01, g-C_3N_4/C-0.02, g-C_3N_4/C-0.25, g-C_3N_4/C-0.5, g-C_3N_4/C-1.0.

2.3. Characterization

The crystal structure properties of the prepared samples were evaluated by the X-ray diffraction (XRD) patterns on a D/max-RAX-ray diffractometer (Rigaku, Japan) using Cu Ka radiation source. FT-IR spectra were measured from KBr pellets as the sample matrix on a Nexus 870 FT-IR spectrometer. The transmission electron microscope (TEM) was performed by JEM-2100 transmission electron microscopy (JEOL, Japan). Scanning electron microscopy (SEM) was characterized by a Hitachi S-4800 with 5.0 kV scanning voltages (Hitachi, Japan). The nitrogen adsorption-desorption and Brunauer-Emmett-Teller (BET) was obtained on a surface area analyzer (NOVA 2200e, Quantachrome). Raman experiment was performed on a DXR spectrometer. The ultraviolet visible diffused reflectance spectra (UV–vis DRS) was carried out via an UV–vis spectrophotometer (Cary 300, USA). Photoluminescence (PL) and fluorescence decay spectra were measured on the Shimadz RF-5301 fluorescence spectrophotometer.

2.4. Photocatalytic experiments

The photocatalytic activities of the prepared samples were evaluated through decomposing TC under visible light irradiation (300 W Xe lamp with a 420 nm cut off filter), 0.1 g photocatalyst powders dispersed in aqueous solution of TC (100 mL, 10 mg L^{-1}). Before the light irradiation, the suspensions should go through ultrasonication and oscillation to get absorption-desorption equilibrium between TC and photocatalyst. Then, detect the concentration of TC by spectrophotometer (UV-2550) with the characteristic absorbance peak of 357 nm at room temperature.

2.5. Photoelectrochemical measurement

The measurements of photocurrent and electrochemical impedance were carried out on a workstation in a three-electrode model. The g-C_3N_4/C photocatalysts was used as the working electrode. The Pt electrode and Ag/AgCl electrode were used as the counter electrode and reference electrode. 0.05 g photocatalysts was dispersed in a certain amount of ethylene glycol with ultrasonication. Then, the photocatalysts were coated on 1×1 cm^2 fluorine-doped tin oxide glass electrode, and dried it in air for further use.

3. Results and discussion

3.1. XRD characterization

Fig. 1 is the XRD pattern of the synthesized C, g-C_3N_4 and the g-C_3N_4/C (we used that is the composite materials of g-C_3N_4/C-0.02, same as the next characterization), which provides more information on their specific crystal structures. For the XRD pattern of C, it could be seen that a conspicuous peak located in the range of 20–80°, which is the characteristic peak of pure carbon spectra [39]. The sharper peak at 27.4° belongs to the (002) diffraction peak of conjugated aromatic system [40,41] and the peak at 13.1°

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