Journal of Photochemistry and Photobiology A: Chemistry 358 (2018) 284–293

Contents lists available at ScienceDirect

Journal of Photochemistry and Photobiology A: Chemistry

journal homepage: www.elsevier.com/locate/jphotochem

Fabrication of the metal-free biochar-based graphitic carbon nitride for improved 2-Mercaptobenzothiazole degradation activity

Zhi Zhu[a,b], Wenqian Fan[c], Zhi Liu[c], Yang Yu[b], Hongjun Dong[b], Pengwei Huo[b,*], Yongsheng Yan[b,*]

[a] School of the Environment and Safety Engineering, Jiangsu University, Jiangsu, Zhenjiang 212013, China
[b] Institute of the Green Chemistry and Chemical Technology, School of Chemistry and Chemical Engineering, Jiangsu University, China
[c] School of the Environment and Safety Engineering, Liaoning Normal University, China

ARTICLE INFO

Article history:
Received 17 January 2018
Received in revised form 9 March 2018
Accepted 18 March 2018
Available online 22 March 2018

Keywords:
Metal-free
Biochar
2-Mercaptobenzothiazole
Magnolia precursor
Waste utilization

ABSTRACT

The present study describes a metal-free biochar-based photocatalyst of g-C_3N_4-C, in presence of an abundant fade magnolia as carbon precursor via facial in-situ together growth method. As a consequence, the g-C_3N_4-C shows a better degradation efficiency to 2-Mercaptobenzothiazole (90%) than pure g-C_3N_4 (49%) under the visible light. The improved photocatalytic performance of g-C_3N_4 is attributed to the biochar can significantly against the g-C_3N_4 reunion and stacking during high temperature treatment, because the biochar can act as the attachments that make the g-C_3N_4 flat and no accumulation, which will further increase the active sites. Additionally, photo-electrochemical measurements proved the separation efficiency of electron-holes of g-C_3N_4 is enhanced by introduced of biochar, due to its good electron transmission ability. Moreover, the ESR measurement and capture experiment further confirmed the active radicals on degradation of MBT are h^+ and $^{\bullet}O_2^-$. This work may provide a promising approach for wastewater treatment by waste utilization of solid biomass and increasing the photocatalytic performance of g-C_3N_4.

1. Introduction

Environmental pollution coexist in human society which are closely related to life [1]. Accordingly, it is urgently issue to seek a suitable method to address above problems in the 21st century [2–5]. For the past few years, a series of semiconductor photocatalysts, including metal oxides [6,7], oxynitrides [8,9], sulfides [10,11] and halides [12] have been explored, in particular, graphitic carbon nitride (g-C_3N_4) with narrow band gap, about ~2.7 eV, one of the most emphasized photocatalysts, has been widely applied in solar-initiated wastewater treatment [13,14]. However, the marginal absorption of visible light and low charge separation efficiency significantly limit the performance of bulk g-C_3N_4. Thus, various modification strategies have been developed to further improve the photocatalytic performance, including doped with foreign elements [15], surface decoration with noble metal [16,17], introducing co-catalysts [18] or constructed heterojunction with other energy-match semiconductor [19,20], etc.

Recently, coupling semiconductor with various carbonaceous materials like graphene, carbon nanofibers, carbon nanotubes have attracted great attention spans to improve the photocatalytic activity of bulk semiconductor [21–23]. For example, Xia et al. prepared carbon quantum dots modified BiOX photocatalyst by one-step hydrolysis method [24], Chen et al. designed a thin layer of amorphous carbon coating CdS photocatalyst [25], Gao et al. constructed carbon sheet modified Bi_2O_3 composite [26], the enhanced photocatalytic activity of the above photocatalysis confirmed that the introduced carbon material was an availably modified way for semiconductor photocatalyst. Therefore, designing and constructing of novel carbon modified g-C_3N_4 semiconductor using carbon source is a good choice to achieve high-performance photocatalysts.

Because of we are facing with serious problems of energy shortage, conversion of waste renewable resource to useful material is significant importance [27]. So that, utilizing the abundant and renewable biomass as carbon source, such as the waste of corn cobs, straw and withered flower for building carbon materials to modified g-C_3N_4 seems more meaningfull. Fortunately, the biochar shows outstanding conductivity, stability and often present special electronic and optical properties. Besides, the junctions of g-C_3N_4 with carbonaceous materials are favorable for

* Corresponding authors.
E-mail addresses: huopw@mail.ujs.edu.cn (P. Huo), yys@mail.ujs.edu.cn (Y. Yan).

https://doi.org/10.1016/j.jphotochem.2018.03.027
1010-6030/

the separation of electron-hole pairs and overall photo-conversion efficiency enhancement. Thus, applied the biochar in the field of photocatalysis, it can not only solve the environmental problems but also make the waste better used and achieve the goal of great deal.

In this work, using urea and magnolia blossoms powder as raw materials, the g-C_3N_4/biochar (g-C_3N_4-C) composites have been prepared through one-step thermal co-condensation method. And used the g-C_3N_4-C to degradation 2-Mercaptobenzothiazole (MBT) under visible light, for the MBT, it acts as a kind of mercaptan, has been widely used in the manufacturing of tires, rubber shoes, and other rubber products, it can also serve as a sensitive reagent for testing metal and an intermediate for synthesis of herbicides and cephalosporins. It is worth noting that MBT has a certain toxicity and is hard to remove, which will cause nausea and headaches if inhaled at low concentrations of MBT; higher concentrations will bring about fatal respiratory paralysis [28]. Therefore, removing and reducing MBT to limit damage to the environment and human health have aroused extensive attention. The in-situ together growth of biochar with g-C_3N_4 sheets and endows the intimate interaction between them, which can contribute more efficiency for charge carrier separation and the as-prepared composites displayed enhanced visible-light photoactivity towards degradation MBT than pure g-C_3N_4. The light absorption, surface area, morphology structure, optical and electronic properties of the prepared samples have been addressed in detail.

2. Experimental section

2.1. Materials

The withered magnolia blossoms are collected in large quantity from Zhenjiang city, Jiangsu province of China between March and April. Urea (AR) and 2-Mercaptobenzothiazole (MBT) are all supported by Aladdin Chemistry Co., Ltd. *p*-benzoquinone (BQ, AR), isopropanol (IPA, AR), triethanolamine (TEOA, AR) and 5, 5-dimethyl-L-pyrroline N-oxide (DMPO) are all purchased from Sinopharm Chemical Reagent Co., Ltd.

2.2. Synthesis

A certain amount of the withered magnolia blossoms were washed by deionized water for several times to remove adherent impurities and dried it at 80 °C for 10 h. Then, the dried magnolia blossoms are fully smashed by grinder and filtered with a 100 purpose sieve. Thereafter, different ratios of the filtered magnolia blossoms are added into 20 mL

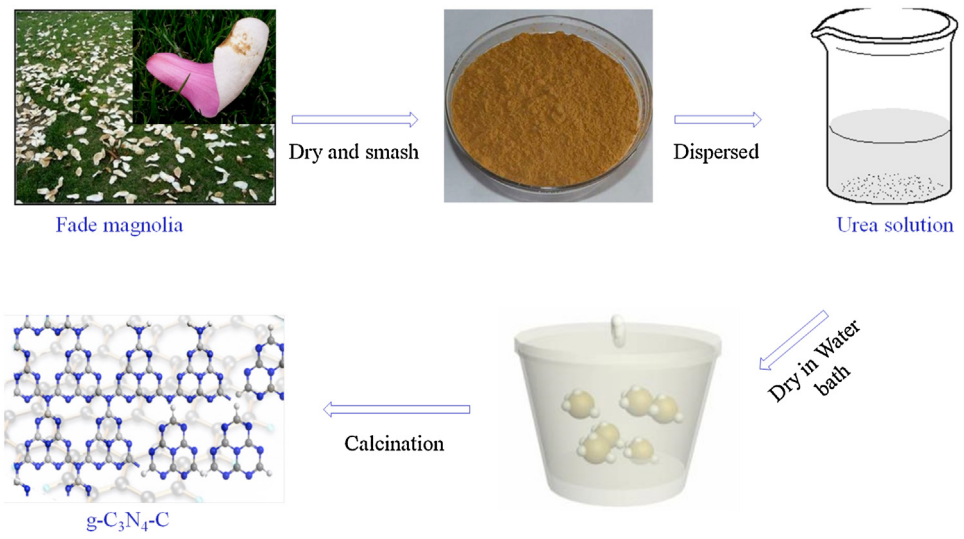
Urea solution ($V_{ethanol}/V_{water}$ = 1:3) within ultrasonic 5 h (5.0 g urea), then, heated and stirred in water bath for some time to get a well-dispersed mixture. After that, put the above mixture into an open crucible, heating 500 °C with the heating rate of 5 °C min^{-1} and keep for 2 h, the process are as illustrated in Scheme 1. The g-C_3N_4-C is ground it into powder for further using. The different content of withered magnolia blossoms (0.05 g, 0.1 g, 0.3 g 0.5 g, 1.0 g) to prepare g-C_3N_4-C is named as g-C_3N_4-$C_{0.05}$, g-C_3N_4-$C_{0.1}$, g-C_3N_4-$C_{0.3}$, g-C_3N_4-$C_{0.5}$, g-C_3N_4-$C_{1.0}$.

2.3. Characterization

The crystal properties of the as-prepared samples are characterized by powder X-ray diffractometer (XRD) with Ni-filtrated Cu K*a* radiation (40 kV, 200 mA) by a scan rate (2θ) of 0.05° S^{-1}. The morphological measurement is examined by transmission electron microscope (TEM). The Fourier transform infrared (FT-IR) spectra are collected on Nicolet Magna-IR 550 and used KBr as the reference sample. The specific surface areas are characterized by Brunauer-Emmett-Teller (BET) method and porosity analyzer (NDVA-2000e). The Ultraviolet visible diffused reflectance spectra (UV-vis DRS) are obtained via a UV–vis spectrophotometer (A Shimadzu UV-3600) using $BaSO_4$ as the reference. Transient photocurrent and electrochemical impedance spectroscopy (EIS) are investigated by an electrochemical workstation (CHI 852C, Germany). Electron spin resonance (ESR) signals of radicals spin-trapped by spin-trapped reagent 5, 5-dimethyl-L-pyrroline N-oxide (DMPO) is carried on a Bruker A300 ESR spectrometer at room temperature. The photoluminescence spectra (PL) and transient fluorescence (FL) are obtained on a F4500 photoluminescence detector (Hitachi, Japan). The obtained curves are fitted by using $f(t) = B + A_{1^*} \exp(-t/\tau_1) + A_{2^*} \exp(-t/\tau_2)$ and the average emission lifetime is calculated via $\tau_{ave} = [A_1\tau_1^2 + A_2\tau_2^2]/[A_1\tau_1 + A_2\tau_2]$.

2.4. Photocatalytic and trapping experiments

The photocatalytic activities of the as-prepared samples are measured by decomposition of MBT (100 mL, 10 mg L^{-1}) under visible-light (300 W Xenon lamp covered with a UV filter



Scheme 1. Schematic illustration of the preparation of g-C_3N_4-C via a in-situ together growth method.