



Hierarchical nanocomposites of polyaniline nanorods arrays on graphitic carbon nitride sheets with synergistic effect for photocatalysis



Shouwei Zhang^{a,b}, Lanping Zhao^c, Meiyi Zeng^a, Jiaying Li^b, Jinzhang Xu^{a,*},
Xiangke Wang^{b,*}

^a School of Materials Science and Engineering, Hefei University of Technology, Hefei 230031, China

^b Key Laboratory of Novel Thin Film Solar Cells, Institute of Plasma Physics, Chinese Academy of Sciences, PO Box 1126, 230031 Hefei, China

^c Education Training Center of Ningxia Electric Power Company, Yinchuan, Ningxia 750011, China

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ABSTRACT

Hierarchical nanocomposites of polyaniline (PANI) nanorod arrays on graphitic carbon nitride ($g\text{-C}_3\text{N}_4$) sheets (CN-PANI) were successfully synthesized by dilute polymerization under -20°C . The photocatalytic activities of the CN-PANI composites were evaluated using methylene blue (MB) and methyl orange (MO) as model pollutants. The CN-PANI composites displayed much higher photocatalytic activity than the pure $g\text{-C}_3\text{N}_4$ and PANI under visible light irradiation. Meanwhile, the degradation efficiency of MO was higher than that of MB under same irradiation conditions, which was mainly attributed to the difference of adsorption processes. The different adsorption behaviors of MB and MO on composites were due to the fact that they carry different charge, i.e., MO and CN-PANI composites have the opposite charge, leading to the enhanced MO adsorption due to the strong electrostatic forces between them. Conversely, MB had the same charge with PANI, thus resulting in a low adsorption capacity due to the electrostatic repulsion. By careful investigation of the influence parameters, a possible mechanism was proposed, i.e., the synergistic effect of $g\text{-C}_3\text{N}_4$ and PANI was responsible for the effective photogenerated charge separation, the large specific surface area and the energy band structure.

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Introduction

Organic pollution due to the indiscriminate disposal of wastewater is a worldwide environment concern and is harmful to human health. It is necessary to eliminate organic pollutants from wastewater before its release into the natural environment. For this reason, different methodologies, such as adsorption, oxidation, reduction, and electrochemical reactions, are proposed to remove these pollutants from aqueous solutions [1]. Among these methods, semiconductor photocatalysis as a high-profile method has been widely applied in degradation of organic pollutants [2].

As the most widely used photocatalyst, TiO_2 is a promising material for photocatalytic treatment of pollutants in water due to its peculiarities of chemical inertness, resistance to photocorrosion, low cost, and non-toxicity [3–5]. However, TiO_2 is a wide-band gap semiconductor (3.2 eV for anatase) and could only absorb about 3–5% of sunlight in the ultraviolet region, which greatly limits its

practical applications [6]. Therefore, the development of visible-light-driven photocatalysts has become a very important topic of research.

Recently, $g\text{-C}_3\text{N}_4$ has attracted much attention in the field of photocatalysis for its non-toxicity and abundance [7,8], which is only made up of carbon and nitrogen, could be used as a metal-free photocatalyst for solar energy conversion, hydrogen production and environmental pollution purification [9]. Moreover, unlike many photocatalysts of sulfide and oxynitride semiconductor, $g\text{-C}_3\text{N}_4$ is highly stable with respect to thermal, chemical, and photochemical attack owing to its tri-s-triazine ring structure and high degree of condensation [9]. All these superior properties imply that the $g\text{-C}_3\text{N}_4$ should be an ideal candidate material and holds promising potential in photocatalytic fields. However, there are many drawbacks of the $g\text{-C}_3\text{N}_4$ for photocatalysis, which include: (1) the high recombination rate of photogenerated charge, (2) an optical band gap of 2.7 eV, namely, the lack of absorption above 460 nm for solar spectra, and (3) the lower specific surface area [10].

To date, continuous attempts have been carried out to improve the photocatalysis efficiency of $g\text{-C}_3\text{N}_4$, for example, by chemical doping with metal or nonmetal elements [11–13], designing

* Corresponding authors. Tel.: +86 551 65592788; fax: +86 551 65591310.
E-mail addresses: xujz@zhu.edu.cn (J. Xu), xkwang@ipp.ac.cn (X. Wang).

nanoporous structures [14,15], and coupling with graphene [16,17], etc. The most promising solution is combining $g\text{-C}_3\text{N}_4$ with other semiconductors with suitable band gap to extend the absorption range of $g\text{-C}_3\text{N}_4$. Meanwhile, heterojunctions might be formed between the $g\text{-C}_3\text{N}_4$ and other semiconductors, which provides a potential driving force for the separation of photogenerated charge at the interfaces.

In the last decade, polyaniline (PANI) as photocatalyst has been the most extensively investigated in photocatalytic area, because it is one type of conducting polymer with good stability, corrosion protection, non-toxicity, facile and low cost synthesis [18]. Particularly, PANI has shown great potential due to its high absorption coefficient ($\sim 5 \times 10^4$) in the visible-light range and high mobility of charge carriers [19]. Furthermore, PANI is not only an electron donor but also an excellent hole acceptor after irradiation [20]. Therefore, PANI is usually adopted as an important additive to enhance the charge separation efficiency of the photocatalyst. Recently, more attentions have been focused on the combination of PANI with semiconductor photocatalysts. Zhang et al. [21] and Wang et al. [22] prepared PANI/TiO₂ composites via chemisorptions and in situ oxidative polymerization and then found the as-prepared samples had enhanced photocatalytic activity under natural light. Furthermore, PANI-CdS [23] and PANI-BiVO₄ [24] have also been developed and demonstrated efficient photocatalytic activity. Therefore, it is expected that the $g\text{-C}_3\text{N}_4$ -PANI photocatalyst from the combination of the PANI with $g\text{-C}_3\text{N}_4$ should have efficient photocatalytic activity under visible light irradiation.

Herein, we prepared hierarchical composites of PANI nanorods grown on the surface of $g\text{-C}_3\text{N}_4$ sheets used as the photocatalyst. The photocatalytic activities of the CN-PANI heterojunction composites were evaluated using methylene blue (MB) and methyl orange (MO) as model pollutants. The possible photocatalytic mechanism was discussed and proposed based on the experimental results.

Experiment section

Materials

Urea (99.3%, Alfa Aesar), aniline monomer ($\geq 99.5\%$, Sigma-Aldrich), perchloric acid (HClO₄), ammonium persulfate ((NH₄)₂S₂O₈, (APS)) and ethanol were analytical purity and were from Sinopharm Chemical Reagent Co., Ltd.

Synthesis of $g\text{-C}_3\text{N}_4$

$g\text{-C}_3\text{N}_4$ sheets were prepared according to a reported procedure [25]. In detail, 20 g urea (99.3%, Alfa Aesar) was put in a crucible with a cover and heated under static air in muffle furnace (Hefei Branch Crystal Materials Technology Co., Ltd., China) at 550 °C for 4 h with a ramping rate of 2.5 °C/min. The resultant light yellow powder was rinsed with deionized water and dried in a vacuum oven at 60 °C.

Synthesis of CN-PANI nanocomposites

CN-PANI nanocomposites were synthesized by dilute polymerization of $g\text{-C}_3\text{N}_4$ and aniline monomer [26]. In a typical procedure, 400 mg (or 200 mg, 600 mg) $g\text{-C}_3\text{N}_4$ was added into 160 mL of 1 M HClO₄ ethanol solution, and the mixtures were stirred until $g\text{-C}_3\text{N}_4$ was fully dispersed. Then 0.05 M aniline monomer ($\geq 99.5\%$, Sigma-Aldrich) was added into the above solution and stirred for 30 min at -20 °C to form uniform mixtures. The oxidant, (NH₄)₂S₂O₈ (APS) (the molar ratio of aniline/APS is 1.5) was dissolved in 40 mL of HClO₄ ethanol solution and cooled to -20 °C in refrigerator. The polymerization was performed after rapid addition of the pre-cooled APS solution, and the mixture was stirred for 24 h at -20 °C.

Finally, the black green precipitates were filtered and washed with water and ethanol. The samples were dried at 60 °C for 24 h under vacuum, and the 400CN-PANI (200CN-PANI, 600CN-PANI) composites were obtained.

Sample characterization

The crystal structures were analyzed by X-ray powder diffraction (XRD) patterns were recorded in reflection mode (CuK α radiation, $\lambda = 1.5418 \text{ \AA}$) on a Scintag XDS-2000 diffractometer. Fourier transforms infrared spectroscopy (FT-IR) was carried out on a Bruker EQUINOX55 spectrometer (Nexus) in KBr pellet at room temperature. The morphology and microstructures were observed using a field emission scanning electron microscope (FE-SEM, Sirion200, FEI Corp., Holland) and transmission electron microscopy (TEM, JEM-2011, JEOL, Japan). UV-Vis spectra were recorded on a Shimadzu UV-2550 spectrophotometer equipped with a Labsphere diffuse reflectance accessory. Thermogravimetric (TG) were measured by using a Shimadzu TGA-50 thermogravimetric analyzer from room temperature to 800 °C with heating rate of 10 °C/min and Ar flow rate of 50 mL/min. The N₂ adsorption-desorption isotherms at 77 K were measured using an adsorption instrument (TriStarII, Micromeritics Company, USA) to evaluate their pore structures and surface area. The electrochemical measurements were carried out on a CHI 660D electrochemical workstation (Shanghai Chen Hua Instrument Co., Ltd., China) by using three-electrode cells at room temperature.

Photocatalysis experiment

MB and MO were chosen as model pollutants for the photocatalytic degradation experiments. The photocatalytic activity of the various photocatalysts (25 mg) were examined by monitoring the degradation of an aqueous suspension of 100 mL of 10 mg/L MB/MO in a beaker under a constant stirring condition at 400 rpm/min at room temperature. The visible light source for the photo-irradiation was a 500 W Xe lamp (Beijing Zhongjiaojinyuan Technology Co., Ltd.) with a super cold filter, which provided the visible light region ranging from 400 nm to 700 nm. Prior to irradiation, the photocatalyst was suspended in the solutions with constant stirring under dark conditions for 2 h to ensure that the surface of the catalyst was saturated with MB/MO. During the photocatalysis processes, the samples (3 mL) were periodically withdrawn. The absorption spectra were recorded on a UV-Vis spectrophotometer (UV-2550, Shimadzu) at the maximal absorption wavelength of 663 nm (MB)/464 nm (MO).

Results and discussion

The XRD patterns of PANI, $g\text{-C}_3\text{N}_4$, 400CN-PANI composites are shown in Fig. 1. For pure $g\text{-C}_3\text{N}_4$, the strong peak located at 27.21 was the typical interplanar stacking peak of conjugated aromatic systems. The other peak at 12.81 belongs to an in-planar structural packing motif. Both peaks were the characteristic peaks commonly found in carbon nitride [27]. As compare to the pure $g\text{-C}_3\text{N}_4$, two new broad peaks at 20.12 and 25.26 were found in 400CN-PANI composite, which were the characteristic peaks of PANI [28]. The characteristic peaks of $g\text{-C}_3\text{N}_4$ sheets were less pronounced in 400CN-PANI, because the $g\text{-C}_3\text{N}_4$ was cover with PANI. The percentage of PANI in composite was measured by TG and the PANI contents in the 400CN/PANI composite were determined to be ~72%.

The FTIR spectra of $g\text{-C}_3\text{N}_4$ and 400CN-PANI composites were shown in Fig. 2. For $g\text{-C}_3\text{N}_4$, the bands at 1640.5 cm⁻¹, 1569.1 cm⁻¹, 1462.1 cm⁻¹ and 1412.2 cm⁻¹ were assigned to typical stretching vibration modes of heptazine-derived repeating

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