



Full Length Article

Synthesis of barbituric acid doped carbon nitride for efficient solar-driven photocatalytic degradation of aniline



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ABSTRACT

A series of barbituric acid doped carbon nitride (CN-BA) photocatalysts were successfully prepared by copolymerizing dicyandiamide with barbituric acid (BA). Under AM1.5 simulated sunlight, CN-BA photocatalysts exhibit enhanced photocatalytic activity compared to pure carbon nitride for the degradation of aniline. The highest activity is obtained with 2% doped CN-BA photocatalyst.

Results: on the photodegradation of aniline indicate that for the optimized CN-BA photocatalyst, the concentration of aniline solution was reduced gradually from 16 mg/L to 1.354 mg/L in 2 h. This corresponds to a 6 times higher photodegradation efficiency than pure carbon nitride samples. The enhanced photocatalytic activity of CN-BA relies on the enhanced surface area, the higher light absorption and the reduced recombination of the photo-generated electron-hole pairs. This interpretation results from multiple characterizations with EPR, BET, N₂ adsorption, Solid-state ¹³C NMR, UV-vis DRS, FESEM, and TEM. Under simulated sunlight irradiation, CN-BA is excited and generates electron-hole pairs. The photo-generated electrons in the CN-BA conduction band react with the molecular oxygen to form [•]O₂⁻. Part of the [•]O₂⁻ transforms into [•]OH, which further oxidizes aniline. Meanwhile, photo-generated holes in the valence band of CN-BA can benefit to the formation of [•]OH or directly oxidize aniline.

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1. Introduction

Aniline is an important precursor and intermediate compound which has been widely applied in the industrial production of polyurethanes, pharmaceuticals, pesticides and rubber additives [1,2]. However, aniline is a highly toxic and cancer-causing compound which is now considered as a major environmen-

tal pollutant. Nowadays, the major treatment processes for industrial aniline wastewater are based on bio-degradation and physical-adsorption methods [3]. But the aniline bio-degradation efficiency is quite low because of its high biological-toxicity. Physical-adsorption method is costly and unsuitable for degrading low-concentration industrial aniline wastewater. Therefore, it is critical to look for a low-cost, high-efficient and environmental friendly method for treating industrial aniline wastewater.

In recent years, semiconductor-based photocatalytic degradation has been regarded as a low cost, efficient and environmental friendly strategy to treat wastewater containing aniline [4–8]. TiO₂ have been widely used as a photocatalysts for the photocatalytic degradation of aniline in an aqueous solution under visible light irradiation. However, TiO₂ can only respond to UV irradiation, so there is a weak visible-light response when using TiO₂-based photocatalysts which strongly limits its practical applications under

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solar light. Therefore, developing novel high visible-light-response photocatalysts with high-efficiency and stability has become a hot topic in the field of the photocatalytic degradation of aniline.

Recently, a polymeric semiconductor photocatalyst, graphitic carbon nitride (CN), has attracted a great attention because of its relative narrow band gap, sufficiently negative conduction-band position and high chemical stability [9]. However, the photocatalytic activity of CN versus the degradation organic pollutants is quite low because of its relatively fast charge recombination and insufficient absorption in the visible-light spectral range. To improve the photocatalytic performance of CN, various modification methods have been applied through structure regulation [10–19], doping [20–27], surface hetero-junction and copolymerization [28–37]. Among those methods, copolymerization of CN has been regarded as an efficient route, not only for obtaining an enhance light-absorption, but also for creating surface hetero-structures which could reduce the recombination of photo-generated electron-holes.

In this study, barbituric acid doped graphitic carbon nitride (CN-BA) photocatalysts were synthesized by copolymerizing dicyandiamide (DCDA) with barbituric acid (BA) to improve the optical absorption, electronic and photoelectric properties of carbon nitride. Moreover, the catalytic activity of CN-BA versus the degradation of aniline in aqueous solution was investigated for the first time. All as-prepared CN-BA samples exhibited a higher photocatalytic degradation of aniline in aqueous solution respect to pure CN and the CN-BA-2.0 sample (see details in the experimental section) resulted in the highest photocatalytic activity. The concentration of aniline in aqueous solution degraded from 16 to 1.354 mg/L in the presence of CN-BA-2.0 under simulated sunlight irradiation for 2 h. The structure, surface area and optical properties of CN-BA samples were characterized by XRD, SEM, TEM, XPS, DRS and EPR spectra. The combined benefits of the BA doping in terms of optical, surface and texture properties lead to a significant improvement in the photocatalytic activity for degradation of aniline in aqueous solution under simulated sunlight irradiation. The mechanism leading to the photocatalytic degradation of aniline was also investigated systemically.

2. Experimental methods

2.1. Chemicals

All chemical reagents were of analytical grade. Dicyandiamide and barbituric acid (BA) were purchased from Sigma-Aldrich Química. Deionized water was used throughout in photocatalytic experiments.

2.2. Synthesis of CN and CN-BA

For the synthesis of CN samples, 2.0 g of dicyandiamide were sealed in a quartz boat and heated in air to 550 °C for 4 h with a heating-rate of 2.3 °C/min [38].

The BA doped CN samples were synthesized from dicyandiamide and BA by a thermal polymerization process. In a typical process, 2.0 g of dicyandiamide and different quality of BA were dispersed in 20 mL of deionized water. Water was successively removed by heating at 100 °C under stirring. The dried solid was grinded, transferred into a quartz boat and calcined in air at 550 °C for 4 h at the heating-rate of 2.3 °C/min. Resulting samples were denoted as CN-BA-X, where X (0.2, 0.5, 1.0, 2.0, 3.0) represents the mass fraction of BA.

2.3. Characterization

Crystallographic phases of powder were analyzed by X-ray diffraction (XRD) from X'Pert PRO. Fourier transformed infrared (FTIR) spectra were acquired with a Nicolet Magna-IR 170 spectrometer. The solid-state $[^{13}\text{C}]$ NMR spectra were recorded using a Bruker Advance III 500 spectrometer. X-ray photoelectron spectroscopy (XPS) measurements were performed on Thermo ESCALAB 250Xi instrument with a monochromatized Al K α line source (150 W). Electron paramagnetic resonance (EPR) measurements were performed on a Bruker ER200-SRC spectrometer. The UV–vis diffuse reflectance spectra (UV–vis DRS) were recorded on a U-41000, HITACHI spectrophotometer, Tokyo, Japan by using BaSO $_4$ as a reflecting sample. Surface morphology and structure were examined by ZEISS Ultra 55 field-emission scanning electron microscope (FESEM). Transmission electron microscopy (TEM) images were collected by using a JEM-2100HR field emission electron microscope. The Brunauer–Emmett–Teller (BET) surface area was determined with a Quantachrome Instruments Quadrasorb SI.

2.4. Photocatalytic test for degradation of aniline

The concentration of aniline in the aqueous solution was measured using a colorimetric method. In a typical experiment, the photocatalytic degradation of aniline was measured using a 300 W Xe lamp (AM 1.5, output light current is 15 A) as simulated sunlight. 100 mg of the as-prepared photocatalyst were added into 150 mL of an aqueous solution containing an aniline concentration of 16 mg/L. The suspension was stirred for 30 min with light irradiation to reach the absorption-desorption equilibrium. Then simulated sunlight irradiation was activated by shining the suspension with a 300 W Xe lamp (output light intensity is 1 sun, AM 1.5, 100 mW/cm 2). At time intervals of 30 min, the solution was sampled and centrifuged to remove the catalysts. The concentration of aniline within the centrifuged solution was determined by a colorimetric method. The detection limit method was estimated to be 1.6 mg/L.

2.5. The colorimetric method

The KHSO $_4$ (50 g/L), NaNO $_2$ (50 g/L), NH $_3$ SO $_3$ NH $_2$ (25 g/L) and N-(1-Naphthyl) ethylenediamine dihydrochloride (20 g/L) solutions were prepared in 50 mL conical flasks, respectively. 1 mL of the photodegraded (centrifuged) solution and 9 mL of deionized water were introduced into the 25 mL test tube with a glass stopper, then 1 mL of KHSO $_4$ solution was added to the solution. After that, a drop of NaNO $_2$ solution was introduced into the solution. Finally the NH $_3$ SO $_3$ NH $_2$ solution was used to wipe out the NaNO $_2$ excess by adding into the above mixture until a uniform solution was formed. After bubbles were entirely wiped out, 1 mL of N-(1-Naphthyl) ethylenediamine dihydrochloride chromogenic agent was added and the solution was diluted to 25 mL with deionized water. The absorbance of the aniline solution was then detected by 1 cm cell at 545 nm on a UV–vis spectroscopy after 30 min.

2.6. Photo-electrochemical experiments

To prepare the working electrodes, 300 mg of the sample and 20 mg 2-Naphthol

were grinded and dispersed in ethanol to form a slurry. Then the slurry was coated on FTO conductive glass sheet. After drying at 120 °C for 2 h in vacuum, the working electrodes were obtained. Photocurrent measurements were carried out in a conventional three-electrode electrochemical workstation (CHI 660E). Pt sheet and Ag/AgCl electrode were used as the counter and reference electrodes, respectively. A 0.5 M Na $_2$ SO $_4$ aqueous solution served as

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