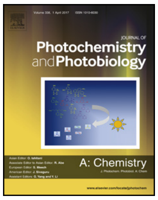
Journal of Photochemistry and Photobiology A: Chemistry 358 (2018) 61–69

Contents lists available at ScienceDirect

Journal of Photochemistry and Photobiology A: Chemistry

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



Facile synthesis of carbon-rich g-C_3N_4 by copolymerization of urea and tetracyanoethylene for photocatalytic degradation of Orange II

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ARTICLE INFO

Article history:
Received 4 December 2017
Received in revised form 4 February 2018
Accepted 27 February 2018
Available online xxx

Keywords:
g-C_3N_4
Copolymerization
Urea
TCNE
Photocatalytic

ABSTRACT

A novel graphitic carbon nitride (g-C_3N_4) photocatalyst was synthesized by a facile one-pot thermo-induced copolymerization method using urea and tetracyanoethylene (TCNE) for the first time. It was revealed that the as-prepared samples retained the original framework of g-C_3N_4, showed an increased surface area and enhanced visible-light harvesting, and promoted photoexcited charge carrier separation. The photocatalytic efficiency of the samples was investigated by degradation of Orange II solutions under visible-light irradiation ($\lambda > 420$ nm). The sample CN/TCNE-40 (40 mg TCNE in 30 g urea) achieved an Orange II degradation rate of about 91% in 60 min under visible-light irradiation, which is significantly higher than that of pristine g-C_3N_4 (51%). The pseudo-first-order rate constant for Orange II degradation on CN/TCNE-40 was 0.0317 min^{-1}, 4.88 times as large as that of pristine g-C_3N_4. The CN/TCNE-40 sample maintained its high photoactivity after five cycles under identical experimental conditions and could degrade Orange II at various pH conditions under visible-light irradiation, confirming the high durability of the photocatalyst. The mechanism of the enhanced photocatalytic performance was also discussed. The results suggested that the CN/TCNE samples are potential photocatalysts for environmental and energy applications.

1. Introduction

Energy shortage and environmental pollution are global crises and threats to the long-term development of modern human society [1,2]. Semiconductor-based photocatalysis has been considered to be one of the most attractive methods for environmental pollutant elimination and energy transformation, e.g., degradation of organic pollutants and splitting water to produce hydrogen [3,4]. Recently, Wang et al. reported that graphitic carbon nitride (g-C_3N_4) can be used as an attractive metal-free organic photocatalyst to promote water splitting for hydrogen generation under visible light [5]. Since then, g-C_3N_4, which possesses a suitable band gap (~2.7 eV), high thermal and chemical stability, and good electrical and optical properties, has attracted global attention and has become a new-generation polymeric semiconductor for water splitting, contaminant removal, selective oxidation, CO_2 reduction, solar cells, and sensing [6–12]. Nevertheless, the photocatalytic efficiency of bulk g-C_3N_4 is limited because of its low surface area, fast recombination rate of photogenerated electron–hole pairs, and lack of absorption in the visible-light region, which inevitably restricts its widespread application.

To take better advantage of g-C_3N_4, it is important to explore suitable strategies to improve the separation efficiency of photoinduced carriers and to optimize photoreactivity. Various methods have been implemented to improve the photocatalytic performance of bulk g-C_3N_4, such as mesoporous structure formation [13], doping [14,15], semiconductor coupling [16–20], immobilization [21], and copolymerization [22]. Among these, copolymerization with other organic compounds precursors is an effective route to fabricate modified g-C_3N_4 polymers with enhanced photocatalytic activity; this method has attracted increased attention because it retains the metal-free nature of g-C_3N_4 [23–25], which has an important merit over metal-

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https://doi.org/10.1016/j.jphotochem.2018.02.036
1010-6030/

containing g-C_3N_4 in that metal-free g-C_3N_4 prevents potential toxic metal leaching that usually causes secondary contamination during water purification. However, the effect of copolymerization on the photocatalytic performance of g-C_3N_4 is affected by the synthesis method and the selected precursor [26,27]. Therefore, seeking appropriate comonomers with a diverse chemical composition and structure to modify the band structure and optoelectronic properties of carbon nitride is a relevant and important task.

It has been reported that carbon-rich g-C_3N_4exhibits a large surface area, retarded photogenerated electron–hole recombination, increased visible-light absorbance, and enhanced photoreduction activities[28,29]. In this study, tetracyanoethylene(TCNE), a carbon-rich material containing only C and N (similar to g-C_3N_4) and four cyano groups that can directly integrate into the carbon nitride polymers, was investigated to improve the photocatalytic activity of g-C_3N_4. A facile one-pot thermally induced copolymerization method was developed to synthesize TCNE-modified g-C_3N_4 polymers (CN/TCNE) using urea as the g-C_3N_4 precursor and TCNE as the modifier. The photocatalytic efficiency was investigated by the photodegradation of Orange II in aqueous solutions under visible-light irradiation. One interesting finding was that the as-fabricated CN/TCNE-40 samples exhibited remarkably enhanced visible-light-induced degradation performance and high stability, which demonstrated their versatile application as a photocatalyst.

2. Experimental section

2.1. Materials and chemicals

Urea were purchased from Kermel (99%, Tianjin, China), and TCNE (98%) and Orange II (99.9%) were provided by Acros Organics (New Jersey, USA). The other reagents were of analytical grade and used without further purification. Double distilled water was used throughout this study.

2.2. Synthesis of g-C_3N_4

Graphitic carbon nitride was prepared by a thermally induced copolymerization method using urea as the precursor. In a typical run, 30 g urea was taken in a crucible with a loose cover and then heated at 550 °C for 4 h in a muffle furnace at a heating rate of 20 °C/min. When the temperature was cooled down to room temperature, solid pristine g-C_3N_4 was obtained, which was ground to a powder for further use.

2.3. Synthesis of CN/TCNE

TCNE-copolymerized g-C_3N_4 (CN/TCNE) was also synthesized via the facile one-pot thermally induced copolymerization method mentioned above. In detail, 30 g urea and a certain amount of TCNE were mixed and ground evenly and collected in a crucible, and the same method as that used for the synthesis of pristine g-C_3N_4 was followed. The as-obtained materials were denoted as CN/TCNE-x, where x represents the amount of TCNE added (x = 10 mg, 20 mg, 40 mg, 60 mg, 120 mg, 240 mg).

2.4. Characterization of samples

The crystal structure of the as-prepared samples was analysed by X-ray diffraction (XRD, Rigaku Ultima IV, Japan). The morphology and size were detected by scanning electron microscopy(SEM, JSM-7500F, JEOL, Japan) and transmission electron microscopy (TEM, JEOL2100, Japan), and Fourier transform infrared (FTIR) spectra were recorded on a Varian 640 FT-IR spectrophotometer (Varian Inc., Palo Alto, CA, USA) using KBr pellets dispersed with sample powders. The steady and time-resolved fluorescence of samples were studied by photoluminescence (PL, FLS980, UK) spectra. The specific surface area and pore size distributions were measured using liquid nitrogen at 77 K using a Micromeritics ASAP 2020 instrument via the Brunauer-Emmett-Teller (BET) method (Quantachrome, USA). X-ray photoelectron spectroscopy (XPS, Escalab 250Xi, Thermo Fisher Co., USA) was performed to investigate the chemical compositions and states of the materials. A UV–visible (UV–vis) spectrophotometer was used to record the UV–visible diffuse spectra of these samples (UV-2700, Shimadzu Japan). The amperometric photocurrent–time (i–t) responses were carried out by an IM6e electrochemical workstation (ZAHNER, Germany). All nuclear magnetic resonance (NMR) spectroscopy experiments were performed on an Agilent 600 MHz NMR spectrometer DD2 (Agilent Technologies, USA).

2.5. Photodegradation of Orange II

Photocatalytic efficiencies of the CN/TCNE samples were evaluated for the degradation of Orange II (10 mg/L) under visible-light irradiation derived from a Xe source (500 W) with a cut-off filter (420 nm). In a typical experiment, 100 mL Orange II aqueous solution was added with 50 mg photocatalyst (0.5 g/L) into a double-jacket reactor with cycling water pumped from a water bath at 20 °C. A magnetic stirrer was used to ensure that the photocatalyst dispersed homogeneously during the reaction. The

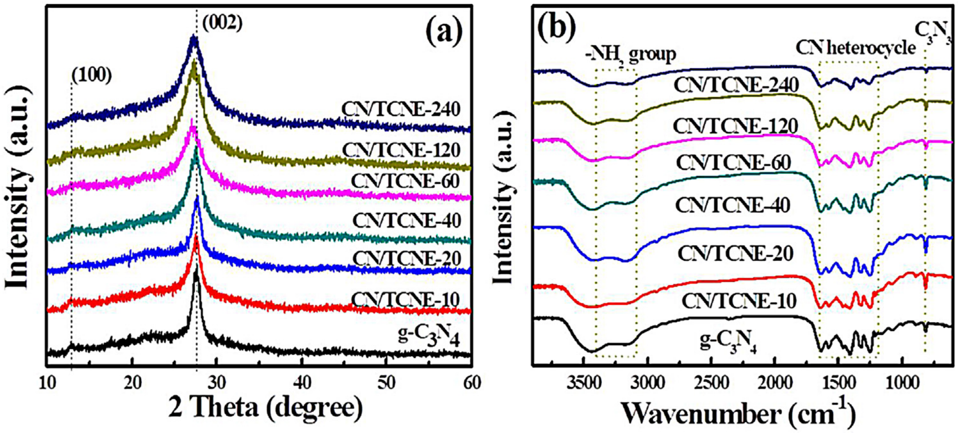

Fig. 1. (a) XRD patterns and (b) FT-IR spectra of g-C_3N_4 and CN/TCNE samples.