



“Dyed” graphitic carbon nitride with greatly extended visible-light-responsive range for hydrogen evolution



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ARTICLE INFO

Article history:

Received 30 December 2015

Revised 17 March 2016

Accepted 19 March 2016

Available online 26 April 2016

Keywords:

Graphitic carbon nitride

Dye

Methyl orange

Broad spectral responsive range

Hydrogen evolution

ABSTRACT

The precursor of carbon nitride pretreated with dye sensitization (methyl orange) before condensation would possess a spectral response of the resultant product extended even to the near-infrared range. The color of the products, in this case, can be delicately controlled by the amount and kind of dyes, so the process is termed “dyeing.” Their corresponding absorption edge would reach 560 and 675 nm after introduction of 0.05 and 0.15 g dye, respectively. It is assumed that the chromophores and auxochromes that impart color to the molecules are introduced into the π -conjugated system and also extend delocalization. The highest hydrogen evolution rate of the dyed carbon nitride reached 470 $\mu\text{mol/g h}$, compared with an increase by a factor of 1.7 for bulk carbon nitride. This new concept of dyeing will inspire further investigation on developing broad spectral light-responsive photocatalysts for hydrogen production.

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1. Introduction

Since the pioneer work by Fujishima and Honda on photoelectrochemical water splitting, great interest has been stimulated in semiconductor photocatalysts to address global energy and environmental issues during the past three decades [1–4]. Semiconductor photocatalysts, especially those with functional nanostructures, can be used to harvest visible light, excite charge couples, and split water into hydrogen and oxygen molecules. Extensive efforts have been devoted to exploring and modifying new semiconductors as active, efficient photocatalysts. However, great challenges still remain: the utilization efficiency of solar light is comparatively low, especially in the visible/near-infrared range [5–11]. Meanwhile, as environmental and economic issues place more emphasis on sustainability, environmental benignness, and scalability, the search for energy-rich chemicals is being redirected to abundant photosensitizers with band gaps in the range of visible light [12].

Recently, graphitic carbon nitride ($g\text{-C}_3\text{N}_4$), a metal-free polymeric semiconductor, has attracted considerable attention due to its unique electronic properties and chemical and physical stability

[1,11,13,14]. In particular, it has been regarded as a catalytic material whose π -conjugated system based on the sp^2 hybridization of C–N atoms serves as an ideal prospective site for photocatalysis [15,16]. Nevertheless, the catalytic performance is generally restricted by rapid recombination of photoinduced carriers and low surface areas due to highly stacked layers [17]. In addition to traditional methodologies adopted with conventional semiconductors, such as doping, dye-sensitization, heterostructure formation, and morphology construction [13,18–21], newly emerging methods such as exfoliation and copolymerization with other monomers have also been exploited to extend the visible light response and increase the efficiency of photocatalytic hydrogen evolution [3,16,22–24]. Among the various routes to better visible-light responsive capability, dye sensitization, as a straightforward strategy to enable energy conversion of visible light over a wider range of wavelengths, is a promising way to improve photocatalytic hydrogen evolution [25,26]. The dyes generally employed for hydrogen evolution improvement can be cataloged into metal complexes and organic dyes [27]. Metal complexes can further be divided into Ru-complexes and other transition metal complexes, such as metal porphyrins/phthalocyanines and analog. Organic dyes consist of xanthenes, cation organic dyes, D- π -A organic dyes, and analog. However, there also exist critical problems in dye-sensitized systems that greatly limit the applications of dye-sensitized H_2 production system. High cost of dyes, poisonousness, and long-term instability in harsh environments are the key issues

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[28,29]. In this regard, new strategies should be developed, most importantly, to extend visible light response for commercial, efficient, and stable and even panchromatic light-responsive solar-to-hydrogen conversion.

We present here a facile and straightforward route to synthesize graphitic carbon nitride with highly extended visible light response, and demonstrate its great potential in solar-to-hydrogen energy conversion. Instead of conventional dye sensitization with graphitic carbon nitride, in this case, its precursor is presensitized with methyl orange before the condensation process. The color of the resultant carbon nitride varies gradually as the added amount of methyl orange piles up. The dyed carbon nitride shows greatly enhanced visible light absorption, and its absorption even extends to the near-infrared range. As a consequence, the electronic structure is delicately controlled. As expected, the hydrogen evolution rate is greatly enhanced, reaching 1.7 times higher than that of pristine carbon nitride, despite the fact that the pre sensitization can be further optimized. The mechanism involved has also been delicately investigated and presented.

2. Experimental

2.1. Materials

N,N-Dimethylformamide (C_3H_7NO), dicyandiamide ($C_2H_4N_4$), chloroplatinic acid ($H_2PtCl_6 \cdot 6H_2O$), and triethanolamine ($C_6H_{15}NO_3$) were purchased from Sinopharm Chemical Reagent Co., Ltd. (Shanghai, China). All reagents were analytically pure and used as purchased without further purification.

2.2. Catalysis synthesis

In this work, DMF-soluble dicyandiamide and methyl orange were chosen as $g-C_3N_4$ precursor and dye sensitizer, respectively. In a typical presensitization procedure, 6.20 g of dicyandiamide was dispersed into 20 mL of DMF, to which x g ($x = 0, 0.05, 0.10, 0.15, 0.20, 0.25, \text{ and } 0.40$) of dye sensitizer (methyl orange) was added. The mixtures were magnetically stirred for 12 h at ambient temperature to form homogeneous solutions. After that, they were transferred to an oven and got dried at $100^\circ C$ overnight. The synthesis of graphitic carbon nitride was according to a typical and straightforward procedure as reported in the literature [12]. The dye-sensitized precursor was put into a crucible with a cover and heated to $550^\circ C$ for 4 h at a heating rate of $2.3^\circ C/min$ in static air. The resultant sample was cooled naturally and ground into fine powder.

2.3. Materials characterization

X-ray diffraction patterns of the samples were recorded with a $Cu K\alpha$ diffractor (XRD; X'pert, Philips, Eindhoven, The Netherlands) from 5° to 60° with a step size of $0.0167^\circ 2\theta s^{-1}$. The surface morphologies and structure of the dyed graphitic carbon nitride were examined using a field emission scanning electron microscope (FE-SEM; JSM-6701F, JEOL, Tokyo, Japan) and a high-resolution transmission electron microscope (HRTEM; JEM-3010, JEOL, Tokyo, Japan). Fourier transform infrared (FT-IR) spectra of the resultants were recorded in a matrix of KBr with an infrared spectrometer (SENSOR27, Bruker, Billerica, MA, USA). Diffuse reflectance spectra (DRS) were characterized using a UV-vis spectrometer (U-3900H, Hitachi, Tokyo, Japan) with a Labsphere diffuse reflectance accessory. Texture characteristics were calculated according to the Brunauer-Emmett-Teller (BET) method with nitrogen adsorption-desorption isotherm measurements (V-Sorb 2800 P, Gold APP Corp., Beijing, China). The sample was degassed with Nyquist plots of the condensation products of dye-sensitized precursors

obtained using an electrochemical impedance spectrometer (CHI660E, Chenhua, Shanghai, China). It was performed in a conventional three-electrode cell: Pt plate as the counter electrode, sample film-deposited fluoride-tin oxide (FTO) as the working electrode, and saturated calomel electrode (SCE) as the reference electrode. The method of preparation of the sample film on deposited FTO was according to our previous work [30]. Elemental analysis was performed by an element analyzer (Vario Macro cube CHNS, Elementar, Hanau, Germany) to probe the content of carbon and nitrogen. X-ray photoelectron spectroscopy (XPS; VG ESCALAB 220i-XL, Thermo Scientific, Waltham, MA, USA) with an Al $K\alpha$ source ($E = 1486.6$ eV) was used to characterize the delicate chemical composition and valence band spectra of each sample. Electron paramagnetic resonance (EPR) spectra of the pristine and dyed carbon nitride-derived radicals were obtained using a digital X-band spectrometer (EMX-220, Bruker, Billerica, MA, USA). The experimental setup was as follows: power 5.05 mW, microwave frequency 9.79 GHz, and center field of 3510.00 G. A time-resolved PL decay spectrum with a time resolution of 10 ps was measured. Time-resolved fluorescence measurements were carried out with a single-photon counting setup (PML, Becker & Hickl, Edinburgh, UK) and the excitation pulse was 380 nm.

2.4. Hydrogen evolution rate tests

Photocatalytic H_2 production on pristine and dyed carbon nitride was evaluated under visible light irradiation ($\lambda > 420$ nm). Reactions were performed in a lateral irradiation reaction vessel connected with a closed gas circulation system. A quantity 80 mg of sample was dispersed in 100 mL of a mixed solution containing triethanolamine (10 vol.%) as a sacrificial electron donor and $H_2PtCl_6 \cdot 6H_2O$ (3 wt.%) as precursor of Pt. The system was evacuated several times, followed by irradiation with a 300 W Xeon lamp (MAX-302, Asahi Spectra, Torrance, CA, USA). Different UV bandpass filters were applied at the light source to select light with defined wavelengths. The reactant solution was maintained at $5^\circ C$ with external water-cooling circulation. The evolved hydrogen was detected and calculated in situ using a gas chromatography device (GC98908, Lighthouse, Shanghai, China) and argon as the carrier gas.

3. Results and discussion

SEM images of CN, CN-0.10, and CN-0.4 are shown in Fig. 1a, b, and d, respectively, while images of other samples are collected in Fig. S1 (Supporting Information). There were no distinctive discrepancies in the microscale morphologies of carbon nitride with/without presensitization. High-resolution typical TEM images of CN-0.10 in Fig. 1e and f show that the sample contained smooth and flat layers, with edges being backfolded and buckled. Interestingly, as shown in Fig. 1c, a gradient change was detected in the resultant color of the presensitized carbon nitride from typically yellow to dark brown. To further explore the relationship between the product color and the kind of dye employed, the same experiments were conducted replacing methyl orange with the same amount of Rhodamine B and methylene blue (structure depicted in Fig. S2). The color of the resultant products, illustrated in Fig. S3 (Supporting Information), was black and gray for the precursors presensitized with Rhodamine B and methylene blue, respectively. This implied that different kinds of dyes introduced into the pretreatment would result into carbon nitride of different colors. As pristine carbon nitride is typically yellow [18,30], the pretreatment process in this study was termed “dyeing” and the resultants are called “dyed” carbon nitride.

Fig. 2 shows XRD patterns of pristine and dyed graphitic carbon nitride. The in-planar arrangement of the periodic unit represented

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