



Facile synthesis of carbon- and oxygen-rich graphitic carbon nitride with enhanced visible-light photocatalytic activity

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ABSTRACT

A facile method has been developed for the preparation of g-C₃N₄ with increased specific surface area and visible light absorption. Carbon- and oxygen- rich graphitic carbon nitride (C,O-g-C₃N₄) were fabricated by heating thiourea with a small quantity of citric acid. The products were then exfoliated by thermal oxidation of C,O-g-C₃N₄ in air. Both specific surface area and optical absorption increased with the incorporation of carbon and oxygen. Exfoliated C,O-g-C₃N₄ exhibited significantly enhanced photocurrent and excellent photocatalytic performance in hydrogen evolution reaction under visible-light irradiation.

1. Introduction

Semiconductors-mediated photocatalytic water splitting is a promising technique as it generates hydrogen fuels from water using energy from sunlight [1–3]. In a hydrogen evolution process, a photocatalyst with an appropriate conduction band potential is necessary for the transfer of photogenerated electrons to water molecules [4,5]. It is also favorable if the band gap of the photocatalyst is narrow enough so it can be excited by a wide range of solar spectrum. Previous studies were focused mainly on metal oxides and sulphides [6–10]. For highly UV-active semiconductors, band gap narrowing by foreign-atom doping is a common strategy to achieve broad spectral response [11–14]. Narrow band gap metal sulphides showed remarkably high rates of hydrogen evolution under visible-light irradiation. However, some metal sulphides are not suitable for practical applications as they are unstable and toxic [15,16].

Metal-free graphitic carbon nitride (g-C₃N₄) is an emerging material for various applications [17–21]. The chemically stable g-C₃N₄ possesses conduction band edge suitable for hydrogen evolution reaction together with optical absorption in the visible-light region. It also has a great potential in large-scale production because it can be synthesized from commonly available precursors [22]. To improve the activity of g-C₃N₄, methods including foreign-atom doping [23–27], self-doping [28–30], copolymerization [31–34] and morphology control [35–38] have been applied. Efficient composite photocatalysts [39–43] were also fabricated, but they usually involved complicated synthetic procedures and scarce elements.

Niu et al. [44] reported a simple thermal oxidation approach to

exfoliate bulk g-C₃N₄ into nanosheets with improved hydrogen evolution performance. However, the nanosheets lost part of their visible-light response in exchange for their increased specific surface area and charge transport ability. It would be advantageous to simultaneously exfoliate g-C₃N₄ and retain its ability to harvest energy from the visible-light spectrum.

In this chapter, a photocatalyst of carbon- and oxygen-rich graphitic carbon nitride (C,O-g-C₃N₄) was fabricated by a facile thermal condensation of thiourea with a small quantity of citric acid. Thermal oxidation was then carried out to obtain exfoliated C,O-g-C₃N₄. The experimental data revealed that C,O-g-C₃N₄ not only possesses a further increased specific surface area, but also increased visible-light absorption over pristine g-C₃N₄. Furthermore, exfoliated C,O-g-C₃N₄ exhibited excellent photocatalytic performance in hydrogen evolution reaction under visible-light irradiation.

2. Experimental

2.1. Synthesis of exfoliated C,O-g-C₃N₄

In a typical synthesis procedure, a grinded mixture of 10 g of thiourea and 20 mg (ie. 0.2 wt%) of citric acid was placed in a covered crucible and heated at 550 °C for 2.5 h with a ramp rate of 10 °C/min. The as-prepared product (bulk C,O-g-C₃N₄) was then grinded and placed in an open crucible, followed by heating at 500 °C for 2 h with a ramp rate of 2 °C/min to obtain exfoliated C,O-g-C₃N₄. For comparison, pristine g-C₃N₄ was synthesized by repeating the above procedures without adding citric acid. The final yields of exfoliated C,O-g-

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C₃N₄ and exfoliated g-C₃N₄ were about 4 wt% and 6 wt% respectively.

2.2. Characterization

The morphologies of the products were characterized by transmission electron microscopy (TEM, Tecnai, FEI) and field-emission scanning electron microscopy (FESEM, Quanta 400 FEG, FEI). AFM images were obtained using a tapping mode with an atomic force microscope (Dimension Icon, Bruker). Brunauer-Emmett-Teller approach was used to determine the specific surface area. Measurements were carried out at 77 K in a Surface Area and Pore Size Analyzer (Quadrasorb-SI, Quantachrome). X-ray diffraction (XRD) patterns were recorded using a diffractometer (SmartLab, Rigaku) with Cu K α 1 irradiation ($\lambda = 1.5406 \text{ \AA}$). The chemical structures of the products were characterized using a Fourier-transform infrared spectrometer (Nicolet iS10, ThermoFisher). X-ray photoelectron spectroscopy (XPS, Leybold Heraeus SKL-12) was applied to study the surface chemical structures. UV–vis spectra were recorded on a UV–vis spectrometer (Cary 100, Agilent). Photoluminescence measurements were performed using a fluorescence spectrometer (F-4500, Hitachi).

2.3. Photoelectrochemical measurements

The photoelectrochemical measurements were performed in a three-electrode electrochemical cell by using an electrochemical workstation (660D, CHI). 2.5 mg of photocatalyst powders were dispersed in a Nafion solution (1 mL, 0.05 wt% in ethanol) and sonicated for 10 min to form a homogeneous suspension. 0.1 mL of the suspension was deposited onto of an ITO conductive glass (1.0 cm \times 1.0 cm) to form the working electrode. Pt foil (1.0 cm \times 1.0 cm) and Ag/AgCl were the counter and reference electrodes. The electrolyte was a 0.1 M Na₂SO₄ aqueous solution. A 300 W xenon arc lamp was used as the irradiation source and the average light intensity was about 100 mW/cm². The photocurrent responses under illumination of visible light were analyzed. Mott-Schottky plots were recorded at 500 Hz, 1000 Hz and 1500 Hz.

2.4. Photocatalytic hydrogen evolution

The photocatalytic H₂ evolution experiments were carried out in a Pyrex reaction cell connected to a closed gas circulation and evacuation system. 25 mg of photocatalyst powders were dispersed in 50 mL of aqueous solution containing 10 vol% triethanolamine as a sacrificial agent. 0.75 wt% Pt was loaded onto the samples by photoreduction of H₂PtCl₆ [45]. The solution was irradiated by a 300 W xenon arc lamp equipped with a 400 nm cut-off filter. The quantity of hydrogen gas generated from photocatalytic water splitting was measured by a Techcomp GC7900 gas chromatograph equipped with a thermal conductivity detector and two molecular sieve columns (TDX-01) in parallel. Ultra-high purity argon was used as a carrier gas.

3. Results and discussion

3.1. Morphologies and structures

The morphologies of the products were investigated using SEM and TEM. Bulk C,O-g-C₃N₄ was in the form of solid agglomerates composing of micron-sized individual units (Fig. 1a). After thermal exfoliation, the samples loosened and became softer agglomerates as shown in SEM images (Fig. 1b). A similar trend could be observed in bare g-C₃N₄ (Fig. S1). The change in morphology of the individual units can be observed in the TEM images (Fig. 1c and d). The TEM images of exfoliated C,O-g-C₃N₄ provides evidence that the agglomerates were formed by the stacking of some sheet-like structures, which are corresponding to layers of polymeric C₃N₄ formed by melon units. The successful exfoliation was further supported by the significantly increased specific

surface area (Table S1) and reduced thickness (Fig. S2) of the photocatalyst.

The crystal structures of the products were investigated by using XRD (Fig. 2). The consistency of the two peaks suggests that the crystal structures are the same, and the patterns matched well with the typical g-C₃N₄ nanostructures [19]. A small peak corresponding to in-planar repeating tri-s-triazine units retained at 13.1°, while the shift of the graphitic peak from 27.6° to 27.8° can be attributed to a denser packing of some basic sheets in the structures during thermal exfoliation [44]. The IR spectra in Fig. S3 match the typical g-C₃N₄ nanostructures reported by the others [24,25,37] and suggest that neither thermal exfoliation nor citric acid addition made a significant change in the core bonding environment.

It is possible that the FT-IR signals corresponding to the change in surface chemical structures were masked by the strong signals from the polymeric melon units, which are the major composition of g-C₃N₄ photocatalysts. To specifically study the surface chemical states of the exfoliated photocatalysts, high resolution XPS spectra were obtained (Fig. S4). No significant binding energy shift can be observed in C 1s, N 1s, O 1s and S 2p spectra. There are three peaks corresponding to C–C (284.6 eV), C–N–C and C–O (286.2 eV), C=N and C=O (288.0 eV) in the C 1s spectra [29]. For C,O-g-C₃N₄, the peaks at 284.6 eV and 286.2 eV became larger than those of g-C₃N₄, suggesting that with the addition of carbon- and oxygen-rich citric acid, more C–C and C–O bonds could be formed on the surface.

The three feature peaks in the N 1s spectra represent the typical C–N=C (398.4 eV), C₃N (398.9 eV) and C–N–H (400.8 eV) in the polymeric melon units [25]. The broad peak at the O 1s spectra could be attributed to some surface oxygen groups (–OH and O–C). More surface oxygen groups in C,O-g-C₃N₄ could possibly weaken the inter-planar interaction between layers of g-C₃N₄ and hence promote the exfoliation process, resulting in a further increased surface area (Table S1). A similar phenomenon was observed in the exfoliation of graphene oxide [46]. The lower XRD peak intensities for C,O-g-C₃N₄ (Fig. 2) also indicate the disruption of stacking between layers due to extra surface oxygen groups. Results from FT-IR, XPS and XRD suggest that extra carbon and oxygen were introduced into g-C₃N₄ in the form of surface functional groups, which could possibly be originated from the copolymerization with citric acid. Previous studies also achieved the incorporation of functional groups into g-C₃N₄ through copolymerization [31,32].

Weak signals can be found in the S 2p spectra, and the sulphur atoms should be originated from thiourea, the major precursor in the synthetic process. However, trace quantities of sulphur were detected that the effect of sulphur to the photocatalysts should be insignificant. The surface atomic ratios of N:C:O for g-C₃N₄ and C,O-g-C₃N₄ were determined to be 1.00:0.91:0.29 and 1.00:1.02:0.38. The above results further support the successful loading of extra carbon and oxygen through copolymerization with citric acid.

3.2. Optical properties

Fig. 3a and b are the UV–vis absorption spectra of the products. For both bulk and exfoliated products, higher overall absorption intensity could be observed for C,O-g-C₃N₄, suggesting that C,O-g-C₃N₄ is able to harvest a wider range of visible light to generate more electron-hole pairs for further reactions. Tauc plots corresponding to the absorption spectra were applied to estimate the bandgap of the products (Fig. 3c and d). The blue shift of bandgap after exfoliation could be explained by quantum confinement effect which would shift the conduction band and valence band edges to opposite directions [47]. For both bulk and exfoliated products, red shift could be observed after incorporation of carbon and oxygen. It was reported that self-doping [28–30] could narrow the bandgap of g-C₃N₄ photocatalysts. The higher absorption shoulder at about 500 nm indicate the presence of more defect states [48] in C,O-g-C₃N₄. The above results suggest that incorporation of

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