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Enhancement of photocatalytic hydrogen evolution activity of g-C_3N_4 induced by structural distortion via post-fluorination treatment

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ABSTRACT

Graphic carbon nitride (g-C_3N_4) has recently attracted a great deal of attention for its application in solar energy conversion. The photocatalytic activities, however, suffer from fast electron-hole recombination and insufficient solar absorption of g-C_3N_4. Here, a modified g-C_3N_4 (CNF) photocatalyst, which was prepared by a simple hydrothermal treatment with dilute hydrofluoric acid (0.1 M HF), has achieved a 2.4-fold enhanced photocatalytic activity for hydrogen production under visible light irradiation compared to pristine g-C_3N_4. It is demonstrated that a structural distortion is introduced in the CNF sheets without the formation of C—F bonds after the hydrothermal treatment, which can effectively separate photogenerated electron-hole pairs. Interestingly, the g-C_3N_4 treated by oil bath reflux reaction with dilute hydrofluoric acid (CNFO) under the same reaction condition (concentration, temperature and duration) has no sign of structural distortion, and shows a decline in the photocatalytic H_2 evolution activity. This may be attributed to the enhanced localization mobility of π electrons induced by the formation of C—F bonds after the oil bath treatment. These findings provide a better understanding on the effect of different fluorination treatments on the surface states and photocatalytic activities of g-C_3N_4-based materials. Additionally, this work presents a promising strategy to improve the photocatalytic H_2 evolution activity of g-C_3N_4 or related polymer semiconductors via microstructure engineering.

1. Introduction

As fossil energy reserves decrease ceaselessly, many efforts have been made to find new substitutes. Hydrogen is one of the ideal alternative candidates that can be used in fuel cells to generate electricity with water as an only product and no carbon emission. Moreover, hydrogen can be generated from water which is abundant on the earth. Therefore, the most challenging yet promising process for hydrogen evolution is water splitting by catalysis, including electrochemical catalysis and photocatalysis using solar energy [1–5]. It is believed that the exploitation and development of highly efficient photocatalysts for hydrogen production may solve the energy crisis and mitigate the global warming.

Graphitic carbon nitride (g-C_3N_4) has been widely used in water splitting for hydrogen generation, environmental remediation and energy storage [6–8] due to its excellent physicochemical property, including suitable band structure, chemical stability, cheap and easy preparation since Wang et al. firstly introduced it to the photocatalytic field [9]. Especially, the appropriate conduction band position endows g-C_3N_4 excellent photocatalytic ability for hydrogen generation. However, low utilization of solar energy and severe recombination of electron-hole pairs still restrain the hydrogen production efficiency of g-C_3N_4. In recent years, a series of strategies have been developed to improve its photocatalytic activity, such as nanostructure design [10], exfoliation [11], elemental doping [12], copolymerization [13] and heterojunction construction [14]. Doping of heteroatoms has been regarded as an effective method to expand semiconductor's absorption range of solar spectrum since visible light active nitrogen-doped TiO_2 was developed by Asahi et al. [15]. For g-C_3N_4, nonmetal elements including boron [16–18], oxygen [19], fluorine [20], phosphorus [21], sulfur [22,23], bromine [24] and iodine [12] doped g-C_3N_4 have been successfully synthesized and exhibit significantly improved photocatalytic activity. Moreover, the enhancement of photocatalytic activity in the nonmetal element doped g-C_3N_4 is mainly ascribed to the red-

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shift of absorption edge and up-shift of conduction band, but it is rarely reported that the enhancement arises from the acceleration of charge separation in the doped g-C_3N_4. Hence, it is necessary to find out an efficient approach to improve the charge separation for boosting photocatalytic activity of g-C_3N_4.

In the early research of g-C_3N_4, fluorine-containing inorganic salts were used as starting materials in the preparation of fluorine doped g-C_3N_4, and fluorine atom was used to expand the optical absorption range of g-C_3N_4 by replacing nitrogen atom [16,25]. It was found that fluorine dopant gave much less promotional effect on the optical absorption of g-C_3N_4 compared with other halogen dopants, even blue-shift of absorption edge occurred in fluorine modified g-C_3N_4. It was attributed to the high electronegativity of valence electrons in fluorine atoms, which can decrease the electron cloud density of π-electrons, and the mobility of electrons in π-system become more localized. Wang et al. [20] synthesized F-doped g-C_3N_4 with excellent photocatalytic activity by co-heating dicyanamide and NH_4F. Unfortunately, the transport property of charge carriers was not reported. Recently, it was reported that the charge separation can be improved in TiO_2 and g-C_3N_4 by microstructure engineering after fluorine doping. Yang et al. [26] successfully activated the inert rutile TiO_2 for high-performance photocatalytic hydrogen evolution by engineering a crystalline Ti^{3+} core/amorphous Ti^{4+} structure after hydrogenation and fluorination. This smart design can regulate the transport behavior of electrons and holes from the bulk of a particle to the surface by suppressing the transport of electrons in conduction band and facilitating the transport of holes in valence band. Wang et al. [27] theoretically studied F-doped g-C_3N_4 as well as pristine g-C_3N_4 and proposed structural distortion to explain the reason for the enhanced photocatalytic activity of F-doped g-C_3N_4 for the first time. The structural distortion induced by fluorine doping and heat treatment significantly improves the photocatalytic activity of g-C_3N_4. The enhancement of photocatalytic activity can be attributed to the narrowed bandgap and the effective separation of photogenerated electron-hole pairs, which originate from the synergetic effect between fluorine doping and heat treatment. These results inspire us to consider which way of fluorination can improve the charge separation of g-C_3N_4 and the relationship between chemical state of fluorine atom and photocatalytic activity of g-C_3N_4.

In this paper, two kinds of modified g-C_3N_4 samples were synthesized by static hydrothermal reaction with dilute hydrofluoric acid (CNF) and by oil bath reflux reaction with the hydrofluoric acid (CNFO), respectively. To our surprise, C−F bonds only formed in CNFO sample, which showed a decline in photocatalytic activity for hydrogen evolution. However, CNF sample with no formation of C−F bonds exhibited an obvious improved photocatalytic activity. Characterization results demonstrated that a structural distortion is introduced in CNF sample and plays an important role in accelerating charge separation. On the other hand, the strong electronegativity of fluorine from C−F bonds enhances localized mobility of π-electrons in CNFO, which restrains the migration of charge carriers. These findings can deepen our understanding about the effect of electronegativity of doping atoms on the photocatalytic activity of g-C_3N_4 and provide a simple method that can effectively separate photogenerated electron-hole pairs via microstructure engineering.

2. Experimental section

2.1. Synthesis of photocatalysts

The typical synthesis of g-C_3N_4 involves the calcination of melamine as follows. In detail, 5 g of melamine was added to a crucible with a cover and calcined at 550 °C for 3 h at a heating rate of 5 °C/min in a muffle furnace, then the grinded powder was annealed at 500 °C for 2 h. The obtained sample (g-C_3N_4) was denoted as CN. For the post-fluorination, 0.15 g the obtained CN and 25 mL 0.1 M HF were added to a 50 mL Teflon lined autoclave and reacted at 160 °C for 10 h under static condition, the obtained sample was washed with deionized water several times (denoted as CNF). For comparison, 0.15 g CN and 25 mL 0.1 M HF were added to a 50-mL flask to carry out oil bath reflux reaction at 160 °C for 10 h under ambient pressure, and the obtained sample was denoted as CNFO. In addition, 0.15 g CN and 25 mL deionized water were hydrothermally reacted at 160 °C for 10 h under static condition without HF, the obtained sample was denoted as CNH.

2.2. Characterization

X-ray diffraction (XRD) was conducted on a Rigaku smartlab system at 45 kV and 200 mA with Cu Kα radiation ($L_{K\alpha 1}$ = 1.540593 Å, $L_{K\alpha 2}$ = 1.544414 Å), at a scan rate of 5° min^{-1} and a step size of 0.020° in 2θ. Fourier transform infrared (FT-IR) measurements were recorded on KBr pellets using Bruker VERTEX 70 spectrophotometers. Transmission electron microscopy (TEM) was carried out on a FEI Tecnai F30 microscope at 300 kV. Atomic force microscopy (AFM) was performed using a Keysight Technologies (5500AFM/STM) scanning probe in tapping mode. The surface area analysis was performed from the nitrogen adsorption-desorption isotherms at 77 K with a Micromeritics Model ASAP 2020 instrument. The average pore diameter and pore volume of samples were calculated based on the Barrett − Joyner − Halenda (BJH) method. XPS with Al K X-rays radiation operated at 300 W (XPS: Kratos XSAM800 spectrometer, USA) was used to analyze the surface properties. The shift of binding energy due to relative surface charging was corrected using the C 1 s level at 284.8 eV as an internal standard. The spectra were fitted using a nonlinear least square fitting program (XPSPEAK) with a linear background and to the 80% Gaussian/20% Lorentzian peak shape. The EPR spectra were registered at room temperature in dark and under UV-light illumination respectively, using a Bruker EMXPlus-10/12-3.8k spectrometer at a microwave frequency of 9.8 GHz. The UV–vis absorbance spectra were obtained for the dry-pressed disk samples using a Scan UV–vis spectrophotometer (PerkinElmer, Lambda 950) equipped with an integrating sphere assembly. The spectra were recorded at room temperature in air within the range 200–800 nm. The steady-state photoluminescence spectra were gained by using a LabRAM HR spectrometer (HORIBA Jobin Yvon, France) with a laser excitation of 325 nm. The time-resolved spectroscopy was detected by a fluorescence spectrometer (F950) with an excitation wavelength of 365 nm and the signals were collected at excitation wavelength of 500 nm.

2.3. Electrochemical test

Electrochemical impedance spectroscopy (EIS), Mott-Schottky plot and transient photocurrent response were measured on electrochemical station (CHI660B, Shanghai Chenhua Limited, China) under ambient condition. All tests were performed on a conventional three-electrode cell in 0.5 M Na_2SO_4 solution. In detail, the carbon nitride electrode was prepared by dropping 10 μL aqueous slurry that consists of 5 mg of the prepared sample and 1 mL absolute ethanol containing 100 μL 0.05 wt % Nafion solution, on a glassy carbon electrode as the working electrode. A Pt wire and a standard Ag/AgCl electrode were used as the counter electrode and the reference electrode, respectively. The EIS was carried out in the frequency range of 0.01 Hz to 10^6 Hz with an AC voltage amplitude of 5 mV. Mott-Schottky tests were performed with the potentials ranging from 0 V to 1 V (vs. Ag/AgCl) at 1.7 kHz. The light source for transient photocurrent response measurement was a 10W LED lamp (wavelength range: 420–430 nm).

2.4. Photocatalytic hydrogen evolution test

The photocatalytic hydrogen evolution test was carried out in an online photocatalytic hydrogen production system (CEL-SPH2N, CEAULIGHT, Beijing). In detail, 50 mg of photocatalyst was added to an aqueous solution (40 mL 3 wt.% $H_2PtCl_6{\cdot}6H_2O$ solution and 10 mL hole

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