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Making co-condensed amorphous carbon/g-C_3N_4 composites with improved visible-light photocatalytic H_2-production performance using Pt as cocatalyst

Quanlong Xu [a], Bei Cheng [a], Jiaguo Yu [a, b, *], Gang Liu [c, **]

[a] State Key Laboratory of Advanced Technology for Materials Synthesis and Processing, Wuhan University of Technology, Wuhan, 430070, PR China
[b] Department of Physics, Faculty of Science, King Abdulaziz University, Jeddah, 21589, Saudi Arabia
[c] CAS Key Laboratory of Standardization and Measurement for Nanotechnology, CAS Center for Excellence in Nanoscience, National Center for Nanoscience and Technology, Beijing, 100190, PR China

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ABSTRACT

Novel composites comprising amorphous carbon and graphitic carbon nitride (g-C_3N_4) were fabricated via facial one-step thermal condensation of glucose and urea precursors. The as-prepared composites were systematically characterized. The photocatalytic activity towards H_2 production under visible light was examined. By fine-tuning the weight ratio of precursors, the composites exhibited enhanced photocatalytic activity. The photocatalytic H_2 evolution rate of optimal composite was 212.8 μmol $h^{-1}g^{-1}$, about 10-fold larger than that of pure g-C_3N_4. The intimate interface between the amorphous carbon and g-C_3N_4 plays the key role for prolonging the charge carrier lifetime and accelerating the charge transfer kinetics, which benefit the photocatalytic performance. Besides, the enhanced photocatalytic performance is also attributed to the improved visible-light absorption and enlarged surface area. Apart from H_2 production, the high-performance g–C_3N_4–based photocatalysts are potentially applicable for CO_2 reduction, organic synthesis and environmental remediation.

1. Introduction

Driven by the increasing environmental and energy concerns, visible responsive heterogeneous photocatalysis has attracted great attention over last decades [1–5]. To date, a series of semiconductor photocatalysts [6], including metal oxides [7–10], oxynitrides [11], sulfides [12,13] and halides [14], have been explored. In general, an ideal photocatalyst should possess a proper bandgap, band potential with either sufficient reduction or oxidation power, and photostability [3]. However, poor visible light harvesting and low charge separation efficiency significantly limit the performance of semiconductor photocatalysts. Thus, developing efficient, abundant and sustainable photocatalysts represents a major in heterogeneous catalysis.

Recently, two-dimensional (2D) polymeric g-C_3N_4 photocatalyst has attracted great attention owing to the photostability and proper band potentials for water splitting under visible light [15–19]. In particular, g-C_3N_4 can form π-conjugated graphitic planes with tri-*s*-triazine ring units assembled by sp^2 hybridization of carbon and nitrogen. The tri-*s*-triazine ring unit with high condensation degree enables g-C_3N_4 to process desirable stability as well as electronic structure [20–22]. Nevertheless, the adjacent conjugated planes of bulk g-C_3N_4 are stacked by the weak van der Waals interaction with weak electron coupling, which is unfavorable for the electron transfer and photoactivity [23,24]. Moreover, the efficiency of bulk g-C_3N_4 under visible-light illumination is limited by the marginal absorption of visible light and high charge recombination rate [25,26]. Various approaches were introduced to enhance the photocatalytic activity, such as morphology control [27,28], copolymerization [29,30], doping metal [23] or non-metal [31,32] elements into the matrix and forming heterojunctions [33–36]. To this end, combining carbonaceous materials with g-C_3N_4 is promising to enhance the photocatalytic performance since two π-conjugated systems potentially stabilize the hybrids and induce

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* Corresponding author. State Key Laboratory of Advanced Technology for Materials Synthesis and Processing, Wuhan University of Technology, Wuhan, 430070, PR China.

** Corresponding author. CAS Key Laboratory of Standardization and Measurement for Nanotechnology, CAS Center for Excellence in Nanoscience, National Center for Nanoscience and Technology, Beijing, 100190, PR China.

E-mail addresses: jiaguoyu@yahoo.com (J. Yu), liug@nanoctr.cn (G. Liu).

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photocatalytic synergy [37,38]. Indeed, coupling g-C_3N_4 with various carbonaceous materials like ordered mesoporous carbon (OMC) [39], carbon nanotube (CNT) [40], fullerene [41], graphene [25,42,43] and carbon nanodots [44–46], has been shown to improve the photocatalytic activity. It is reported that g-C_3N_4 photocatalysts modified by N-doped graphitic carbon significantly extended and delocalized the aromatic π-conjugated system, thereby promoting the separation and transfer of charge carriers [47]. The ternary heterostructure composed of GR/C_3N_4/CDots was also constructed [48]. The GR and CDots not only provided increased specific surface area, but also enhanced visible light absorption as well as the π-π interactions among the carbon materials, which were indeed favorable for the efficient separation of photo-generated charge carriers. Keeping in mind the inherent difference in energy levels of the two components should enable effective charge separation and the interface contact should facilitate charge transfer [49–51]. Fortunately, carbonaceous materials often present low work function to modify the electronic and optical properties of hybrids [37]. Besides, the junctions with a combination of g-C_3N_4 with carbonaceous materials are favorable for the separation of electron-hole pairs and overall photo-conversion efficiency enhancement.

In this work, using urea and glucose as starting materials, amorphous carbon/g-C_3N_4 composites have been prepared through one-step thermal co-condensation method. The in-situ growth of carbon in the interlayer of g-C_3N_4 endows the intimate interaction between carbon and g-C_3N_4, which can contribute more efficiency for charge carrier separation. The as-prepared composites displayed enhanced visible-light photoactivity towards H_2 evolution. The light absorption, surface area and photocatalytic efficiency as a function of amorphous carbon weight percentage in the composites have been addressed in detail.

2. Experimental section

2.1. Samples preparation

All reagents used in the synthetic processes were used as purchased without further purification treatment. Pure g-C_3N_4 was synthesized by heating 10.0 g urea in a covered crucible at 500 °C for 2 h with a temperature raise rate of 5 °C/min. Upon cooling down, light yellow powders were obtained and then grounded into fine powders. Herein, a crucible covered with a lid was employed to drive the intermediates generated in the pyrolysis process to polymerize into g-C_3N_4. Amorphous carbon/g-C_3N_4 composites were prepared via the one-step thermal co-condensation approach. Typically, 10 g urea was mixed with different amounts of glucose. Subsequently, the homogenous mixture of urea and glucose was put into a crucible with a cover and annealed at 500 °C for 2 h at ramp rate of 5 °C/min. By this approach, the bulk condensation of urea and glucose occurs in a muffle furnace. Then, the as-obtained products were grounded into fine powders. The mass ratio of glucose to urea was changed from 0.05% to 0.5%, and the obtained photocatalysts were denoted as CNCx. x represents the weight ratio in preparation, which are CNC0.05, CNC0.1, CNC0.25 and CNC0.5. Amorphous carbon was prepared by heating glucose under identical conditions as those of amorphous carbon/g-C_3N_4 nanocomposites.

2.2. Characterization

The structures of the as-prepared photocatalysts were recorded on a D/MAX-RB X-ray diffractometer (Rigaku, Japan) using Cu Kα radiation source at room temperature. Scanning electron microscopy (SEM) was characterized by JSM-7500F (JEOL, Japan). Transmission electron microscopy (TEM) images were obtained by JEM-2100F electron microscopy (JEOL, Japan) with an accelerating voltage of 200 kV. The specific surface area data were collected by nitrogen adsorption isotherms using a Micromeritics ASAP 2020 apparatus. All samples were conducted at −196 °C after degassing at 150 °C for 4 h. Fourier transform infrared (FT-IR) spectra were conducted using KBr pellets with IRAffinity-1 spectrometer (Shimadzu, Japan). To estimate the chemical composition and valence states of as-prepared samples, X-ray photoelectron spectroscopy (XPS) were adopted by using ESCALab 250 Xi electron spectrometer (Thermo Scientific Corporation, USA) with Al Kα radiation as the source. The diffuse reflectance spectra (DRS) were employed to investigate the optical properties of the synthesized samples by using UV–visible spectrometer (UV 2550, Shimadzu, Japan). The reagent of $BaSO_4$ was used as the reference. Photoluminescence (PL) spectra were recorded on a Fluorescence Spectrophotometer (F-7000, Hitachi, Japan) with the excitation wavelength of 365 nm. The time-resolved fluorescence measurements were recorded on an Edinburgh FLS920 at an excitation wavelength of 345 nm. The obtained curves were fitted by using the following equation:

$$f(t) = B + A_1 \times \exp(-t/\tau_1) + A_2 \times \exp(-t/\tau_2) \qquad (1)$$

The average emission lifetime was calculated via the following equation:

$$\tau_{ave} = \left[A_1\tau_1^2 + A_2\tau_2^2\right] \Big/ [A_1\tau_1 + A_2\tau_2] \qquad (2)$$

2.3. Photocatalytic H_2 evolution

The photocatalytic activity of the prepared samples was evaluated by the water splitting reaction under visible light irradiation. The photocatalytic H_2 evolution reactions were performed using a side-irradiated gas-closed system. In each experiment, 50 mg of photocatalysts was dispersed into 80 mL of aqueous solution, which comprised of 15 vol % triethanolamine (TEOA) as the sacrificial reagent. Before the light irradiation, the sealed reaction system was purged with high-purity N_2 gas for 0.5 h to remove the dissolved air in the aqueous solution. 1.0 wt% Pt was loaded onto the as-prepared photocatalysts as a co-catalyst from H_2PtCl_6 aqueous solution via *in situ* photodeposition. To ensure the uniform irradiation of the suspension, the suspension was agitated during the photocatalytic process. A 350 W xenon arc lamp was used as the light source with a cutoff filter ($\lambda \geq 420$ nm). The evolved H_2 was measured by gas chromatograph. Typically, 0.4 mL of gas was collected from the top space of the sealed reactor by syringe and analyzed by gas chromatograph (Shimadzu, Japan) equipped with a thermal conductivity detector (TCD). The apparent quantum efficiency (AQE) was detected using four 3 W LEDs at centered wavelength of 420 nm and calculated based on the following equation:

$$AQE(\%) = 2N_{H2}/N_p \qquad (3)$$

where N_{H2} is the number of generated H_2 molecules and Np is the number of emitted photons.

2.4. Photoelectrode fabrication and electrochemical measurement

Photoelectrochemical properties of the samples were performed in a conventional three electrode system. The electrodes were fabricated as following. 30 mg of photocatalysts was added into 5 mL of anhydrous ethanol and then grounded to form