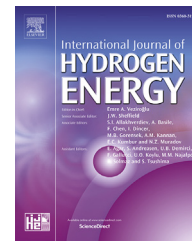




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In situ fabrication of CDs/g-C₃N₄ hybrids with enhanced interface connection via calcination of the precursors for photocatalytic H₂ evolution

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ABSTRACT

Novel carbon dots (CDs)/graphitic carbon nitride (g-C₃N₄) hybrids were fabricated via an in situ thermal polymerization of the precursors, urea and glucose. This heterojunction catalyst exhibited enhanced photocatalytic H₂ evolution activity under visible-light ($\lambda > 420$). A sample of CDs/g-C₃N₄ hybrids, CN/G0.5, which was prepared from 0.5 mg of glucose in 6.0 g of urea (8.3×10^{-3} wt% glucose), exhibited the best photocatalytic performance for hydrogen production from water under visible light irradiation, which is about 4.55 times of that of the bulk g-C₃N₄ (BCN). The improvement of photocatalytic activity was mainly attributed to the construction of built-in electric field at the interface of CDs and g-C₃N₄, which could improve the separation of photogenerated electron-hole pair. Moreover, the tight connection of CDs with g-C₃N₄ would serve as a well electron transport channel, which could promote the photocatalytic H₂ evolution ability.

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Introduction

Focusing on the energy shortage and environmental pollution, hydrogen produced by water splitting under solar irradiation is becoming an attractive pathway as a clean and renewable energy resource [1–3]. An *n*-type TiO₂ single-crystal electrode for photocatalytic water splitting into H₂ and O₂ under ultraviolet (UV) light irradiation was firstly reported by Fujishima and Honda in 1972 [4]. Since that, various metallic compounds-based semiconductors, such as ZnO [5], perovskite [6] and CdS [7], have been proved as promising

photocatalysts for water splitting. However, their widespread application is greatly restricted by their high cost, poor stability and toxicity.

In recent years, graphitic carbon nitride (g-C₃N₄), a metal-free polymeric semiconductor with a typical two-dimensional structure, has received much attention for applications in photocatalytic water splitting [8–11], CO₂ reduction [12,13] and pollutant degradation [14,15], due to its high thermal and chemical stabilities and an appropriate band gap (2.7 eV). However, the photocatalytic activity of g-C₃N₄ is greatly hindered by the rapid recombination of photogenerated charge carriers and the inefficient utilization for

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visible-light [16]. Various strategies have been proposed to improve the photocatalytic activity of g-C₃N₄, such as doping [17–19], exfoliation [20], morphology control [21], preparation [22] and effective construction of surface heterojunctions [23–25]. It has been proved that an appropriate band structure could be constructed by the effective construction of surface heterojunctions, e.g. g-C₃N₄/TiO₂ [23,26], g-C₃N₄/ZnO [27] and g-C₃N₄/BiOI [28,29], through which the light absorption could be enhanced and the separation of electron-hole pairs could be promoted.

Carbon dots (CDs), a new family member of carbon-based nanomaterials, have drawn a great attention because of their unique electronic properties [30,31]. Very recently, Kang et al. reported carbon quantum dots (CQDs)/g-C₃N₄ composites prepared by calcinating urea and ammoniated CQDs at 550 °C for overall water splitting under visible light irradiation [32]. Tang et al. also reported that the CQDs/g-C₃N₄ composites fabricated by using g-C₃N₄ nanosheets and CQDs with a hydrothermal method could respond to near-infrared light to produce hydrogen from water [33]. As far as we know, these are the two typical strategies for the fabrication of CDs/g-C₃N₄ composites, i.e. the direct blending of the as-prepared CDs and g-C₃N₄ by a hydrothermal method [34–37] and the calcination of the as-prepared CDs with a g-C₃N₄ precursor [12,32,38,39]. It is noted that the formation of effective heterojunctions is highly depended on the interfacial contacts of the two components.

Herein, we report for the first time the in situ fabrication of CDs/g-C₃N₄ hybrids by calcinating their precursors, urea and glucose, at 550 °C. The two precursors were mixed in a homogeneous aqueous solution, thus the hydrogen bonding between the hydroxyl groups of glucose and the amino groups of urea, could make a uniform distribution of glucose in the urea matrix. Hence, in the following steps, the recrystallization and calcination of glucose mixed urea, could yield CDs/g-C₃N₄ hybrids with enhanced interfacial connections and finally an even distribution of CDs in the g-C₃N₄ matrix. The obtained hybrids would have enhanced interfacial connections between g-C₃N₄ and CDs, prohibited agglomeration and burning of CDs during calcination. Thus, the charge transfer would be promoted and the recombination of electrons and holes would be prevented. As expected, such prepared CDs/g-C₃N₄ hybrids exhibited greatly improved photocatalytic activity as well as stability for hydrogen evolution from water as compared with the bulk g-C₃N₄ (BCN).

Experimental section

Materials

All the chemicals were of analytical purity and were used as received.

Catalysts synthesis

Synthesis of BCN

BCN was prepared by thermal polymerization of urea in a semi-closed system according to literature procedures [40, 41]. Typically, 6 g of urea was put into a 50 mL crucible. And then

the crucible was wrapped with two layers of aluminum foil, heated to 550 °C at a rate of 5 °C min⁻¹ in a tube furnace. Kept at this temperature for 2 h, and then cooled to room temperature. The sample was milled into powders in an agate mortar. This resultant bulk g-C₃N₄ was marked as BCN.

Synthesis of CN/Gx (x = 0, 0.25, 0.5, 1.0 and 5.0)

CN/Gx hybrids were constructed by similar procedures as those of BCN, and the flow chart is shown in Fig. S1†. In a typical case, 6 g of urea and different contents of glucose (0, 0.25 mg (4.7 × 10⁻³ wt%), 0.5 mg (8.3 × 10⁻³ wt%), 1.0 mg (1.7 × 10⁻² wt%) and 5.0 mg (8.3 × 10⁻² wt%)) were dissolved in 10 mL of deionized water in a 50 mL crucible, then transferred to a drying oven and kept at 80 °C until most of the water was evaporated. Then the crucible was taken out of the oven and was allowed to be gradually cooled down to room temperature, stacked needle-like urea containing glucose crystals were obtained. Succeeding thermal polymerization yielded CDs/g-C₃N₄ hybrids with different CDs contents, which were marked as CN/Gx (x = 0, 0.25, 0.5, 1.0 and 5.0), x represents the milligrams of glucose charged in 6 g of urea.

Synthesis of CDs and CN/C0.5

For comparison, a sample of CDs/g-C₃N₄ hybrids, CN/C0.5, in which the chemical composition is same as that of CN/G0.5, was prepared. The only difference is that the CDs were firstly prepared and then mixed with the urea aqueous solution. Succeeding procedures were the same as those of CN/Gx preparation. Firstly, 40 mg of glucose was dissolved in 40 mL of deionized water, and then transferred into a 50 mL Teflon-lined autoclave and heated at 180 °C for 6 h [42]. After cooling to room temperature, CDs were obtained as a brown solution and was collected into a beaker. Then, 0.5 mL of the as-prepared CDs solution was directly mixed with 6 g of urea in 10 mL of deionized water in a 50 mL crucible to prepare the precursor of CN/C0.5 and then calcinated as those of CN/Gx preparation.

Characterization

X-ray diffraction (XRD) patterns were collected on Rigaku Ultima IV using Cu irradiation from 5° to 80°. Morphologies of the hybrids were examined by using a Tecnai G2 20 200 kV transmission electron microscopy (TEM). Fourier transform infrared spectra (FTIR) were obtained using a Bruker tensor II spectrometer in the range of 4000–400 cm⁻¹. X-ray photoelectron spectroscopy (XPS) was performed on a Thermo Fisher ESCALAB 250 Xi XPS instrument using Al K α (1486.6 eV) radiation as the X-ray source. UV–Vis diffuse reflectance spectra (DRS) were recorded on an Agilent Cary 5000. Photoluminescence spectra (PL) were detected with a PTI QuantaMaster 40 phosphorescence/fluorescence spectrofluorometer excited by incident light of 380 nm.

Photoelectrochemical and linear sweep voltammetry (LSV) measurements

Photoelectrochemical measurements were performed on a RST5000 electrochemical workstation (Suzhou Risetest Instrument Co., Ltd, China) using a conventional three-electrode

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