Effective light scattering and charge separation in nanodiamond@g-C$_3$N$_4$ for enhanced visible-light hydrogen evolution

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ABSTRACT

Development of heterostructured photocatalysts that promotes charge separation of semiconductor materials is crucial towards efficient photocatalytic hydrogen evolution. Here nanodiamond (ND) @graphitic carbon nitride (g-C$_3$N$_4$) nanosheet heterostructures were synthesized via a facile one-step pyrolysis approach. The ND@g-C$_3$N$_4$ heterostructures exhibit enhanced photocatalytic activity for hydrogen evolution from water splitting as compared with pristine g-C$_3$N$_4$. The optimal heterostructures with 10 wt% ND loading content show the best performance in photocatalytic H$_2$ evolution under visible light irradiation, which is more than 5.6 times higher than that of the pristine g-C$_3$N$_4$. The increased light-trapping induced by the scattering of the NDs promotes more localized charge carriers generation, which is clarified by the combined experimental results and finite difference time domain simulations. Meanwhile, the effective charge separation at the ND@g-C$_3$N$_4$ interface due to the energy level matching can synergistically induce the enhanced photocatalytic activity of g-C$_3$N$_4$.

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1. Introduction

To mitigate the increasing global energy and environmental issues, the conversion of solar energy into hydrogen energy is regarded as a green and sustainable strategy at present. Highly efficient photocatalyst for H$_2$ evolution from water splitting over semiconductor has been widely considered to be a promising route to this end [1—3]. Despite the fact that conversion of water and solar energy into clean hydrogen (H$_2$) energy since the pioneering discovery of photocatalytic water splitting in 1972, a photocatalyst with high photocatalytic performance under sunlight to cater for the demand of practical applications is still urgently demanded [4]. Graphitic carbon nitride (g-C$_3$N$_4$), as a metal-free semiconductor, has emerged as an attractive visible-light photocatalyst for H$_2$ evolution from water splitting owing to its unique characteristics like mild band gap (2.7 eV), abundance, suitable band potentials,

high physicochemical stability, nontoxic, low-cost, etc. However, the photocatalytic performance solely using g-C$_3$N$_4$ as photocatalyst is still very poor because of the fast recombination of photoinduced electron-hole pairs and limited photon absorption [5—8]. To solve this problem, g-C$_3$N$_4$ coupling with an appropriate semiconductor to form a heterostructure is one of the most efficient approaches, which can form a coupling hybridization. The band bending generated at the interface of the two semiconductors can induce a built-in field, suggesting the dissociation of excitons through transferring the photogenerated electrons and holes in opposite direction. As a result, the photogenerated electron-hole pairs are effectively separated at the interfaces of the two semiconductors, and the recombination of electron-hole pairs is finally restrained [7—14]. For the heterostructure photocatalysts, the sufficient interfacial contact between the two components is critical for improving charge separation efficiency [15]. Besides, the establishment of tight junctions between the two semiconductors also depends on their physicochemical properties, such as energy level matching and the change of active sites [7,16].

Prior research has demonstrated that coupling g-C$_3$N$_4$ with the zero dimensional semiconductors, such as Ag$_3$PO$_4$ [17], TiO$_2$

nanoparticles [18,19], carbon nanodots [20], and graphene quantum dots [21], could effectively achieve sufficient contact interface to promote charge transfer and separation [22,23]. However, the photocatalytic activities for hydrogen evolution over the most of g-C_3N_4-based heterostructure composites are still low due to the influence of several factors, such as the crystal structure, band structure of the counterpart component, and the photophysical properties in the interface of the heterostructure, etc. Therefore, the development of more effective g-C_3N_4-based heterostructure photocatalysts is highly desirable [24].

Among various carbon nanomaterials, nanodiamond (ND) has been considered a promising photocatalyst owing to its relatively negative conduction band edge position (−0.9 eV vs. NHE) relative to TiO_2 (−0.5 eV vs. NHE), high carrier mobility, large specific surface area, small Bohr radius and large exciton banding energy, which may facilitate the transfer of photogenerated carriers to the photocatalyst surface, subsequently promote carrier separation [25]. Meanwhile, the low toxicity of ND endows it with great potential in practical applications [26]. Recent studies have indicated that ND indeed improves photocatalystic efficiency of the photocatalysts, such as Cu_2O [27], TiO_2 [9,28], due to its large specific area and enhanced tight junctions for promoting carrier separation. Besides, because there exists large difference in the refractive index between the diamond (2.42) [29] and g-C_3N_4 (<1.5) [30], the light-scatting will be very strong in the ND-g-C_3N_4 interface, resulting in the multiple interfacial reflection and the increase in the optical paths when the incident light is propagating between the optically denser medium to the thinner one. As a result, the utilization ratio of the incident light can be effectively enhanced for outstanding photocatalystic performance.

Considering the above facts, we believe that ND can overcome the above-mentioned disadvantages of g-C_3N_4. In this contribution, we reported that ND@g-C_3N_4 heterostructure exhibited high photocatalytic H_2 evolution performance and photostability. The efficient light scattering of NDs can enhance the visible light response of the ND@g-C_3N_4 heterostructure. Meanwhile, the NDs promote the transfer and separation of the photogenerated carriers by forming a type-II heterostructure. Because of the above synergistic effect, ND@g-C_3N_4 heterostructure exhibits high carrier generation and separation ability and low charge transfer resistance in the process of the H_2 evolution experiment. This work may provide a new insight for the smart design and synthesis of novel g-C_3N_4 based heterostructure photocatalysts for efficient H_2 evolution.

2. Experimental section

2.1. Materials

NDs with an average size of 5 nm were purchased from Zhengzhou Sino-Crystal Diamond. Chloroplatinic acid ($H_2PtCl_6 \cdot 6H_2O$, 37.5% Pt basis) were purchased from Sigma Aldrich Corp. Anhydrous ethanol, triethanolamine (TEOA) and melamine were purchased from Macklin Corp. All reagents were used without further purification.

2.2. Synthesis of ND@g-C_3N_4 heterostructure

The ND@g-C_3N_4 heterostructure was synthesized by an in-situ self-assembly process. In brief, 10 g of melamine were poured into a mortar, then different amount of NDs were added to the melamine, then the mixture were fully grind for 2 h. Finally, the gray mixture was transferred into a silicon dioxide crucible covered with a lid. The reaction chamber was heated up to 580 °C with a step of 10 °C min^{-1} in air and the reaction time was maintained for 120 min. The ND@g-C_3N_4 heterostructures with various ND content were obtained and subsequently washed with distilled water to remove impurities. For comparison, pure g-C_3N_4 was also synthesized using a similar procedure without the addition of ND.

2.3. Characterization

The morphologies of g-C_3N_4 and ND@g-C_3N_4 were observed by a field emission scanning electron microscopy (FESEM, JSM 6700F) at an acceleration voltage of 15 kV. The XRD pattern of the g-C_3N_4 and ND@g-C_3N_4 were obtained by an X-ray diffractometer (Panalytical X′ Pert Pro) using Cu k$_\alpha$ as the irradiation source (λ = 1.5046 Å). Transmission electron microscopy (TEM), high resolution transmission electron microscopy (HRTEM) and scanning transmission electron microscope (STEM) images were recorded in a JEOL JEM-2100F field emission microscope. X-ray photoelectron spectroscopy (XPS) data were acquired using a Kratos AXIS HIS 165 spectrometer with a monochromatized Al KR X-ray source (1486.71 eV). UV−vis diffusive reflectance spectra (UV−vis DRS) were performed by a Hitachi UH4150 UV−Visible/NIR spectrophotometer equipped with an integrating sphere. N_2 adsorption-desorption isotherms and pore-size distributions were obtained on a Micromeritics Tri-Star II 3020 surface area analyzer at 77 K. Photoluminescence (PL) spectra of the samples were recorded in a Hitachi F-7000 spectrofluorometer with an excitation wavelength of 385 nm. The time-resolved PL spectra of the g-C_3N_4 and ND@g-C_3N_4 were measured by a Horiba FL-322 spectrometer using a 370 nm NanoLED monitoring the emission at 437 nm.

2.4. Photoelectrochemical measurements

Electrochemical measurements were performed on a CHI660E electrochemical instrument with a standard three-electrode system. The calomel electrode (saturated KCl) and Pt foil were used as the reference electrode and counter electrode, respectively. The working electrode was fabricated as follows: 10 mg of the as-prepared photocatalyst was suspended in a mixed solution of ethanol (1 mL) and 0.1 wt% Nafion solution (20 μL) and then dip-coated onto an indium tinoxide (ITO) glass electrode. The coated area on the ITO glass was controlled to be 1 cm^2. The film was dried in air and subsequently calcined at 80 °C for 6 h. The photocurrent response was obtained using a 150 W Xe lamp with an AM 1.5 filter as the light source and potassium ferricyanide and potassium ferrocyanide aqueous solution (0.5 mmol L^{-1}) as the electrolyte. Electrochemical impedance spectroscopy (EIS) measurements were determined at an AC voltage magnitude of 5 mV over the frequency range of 0.1−10 kHz.

2.5. Photocatalytic activity test

Photocatalytic H_2 evolution was carried out in an online CEL-SPH2N photocatalysis reaction system (CEAULIGHT, Science and Technology Ltd, Beijing, China) with a 250 mL quartz photoreactor connected to a closed gas circulation and evacuation system, using a 300 W Xe lamp, equipped with an optical 420 nm cut-off filter. In a typical experiment, 50 mg of the photocatalyst powder was suspended in a 100 mL of aqueous solution containing TEOA (10%) as a sacrificial electron donor. The loading of Pt was conducted by an in situ photodeposition method using H_2PtCl_6 as Pt precursor. The reactant solution was thoroughly degassed under flowing high-purity N_2 for 30 min prior to H_2 evolution experiment. The reaction solution was magnetically stirred and the temperature of the reaction solution was carefully maintained below 5 °C during the entire experiment. The evolved H_2 was analyzed automatically every 1 h through a gas chromatographer (GC-7920) equipped with a thermal conductivity detector with high-purity N_2 as a carrier gas.