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Red Phosphor/g-C₃N₄ Heterojunction with Enhanced Photocatalytic Activities for Solar Fuels Production

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Abstract:

We report a composite photocatalyst by coupling red phosphor (r-P) and graphitic carbon nitride (g-C₃N₄). The introduction of g-C₃N₄ onto r-P surface led to considerable improvement on the photocatalytic activity for H₂ production and CO₂ conversion into valuable hydrocarbon fuel (CH₄) in the presence of water vapor. The enhancement could be attributed to the effective separation of photogenerated electrons and holes across the r-P/g-C₃N₄ heterojunction. Owing to the advantages of non-toxicity, low cost and abundance in nature, this active heterostructural r-P/g-C₃N₄ photocatalyst would have great potential for efficient solar fuels production.

Keywords: photocatalysis, H₂ production, CO₂ conversion, heterostructure, carbon nitride

1. Introduction

Solar fuels have been considered as one of the most important renewable clean energy resources in the future. In the past decade, it has attracted tremendous efforts on developing various photocatalysts to generate chemical fuels through solar water splitting or CO₂ reduction [1-5]. Researchers have recognized that a single-component semiconductor photocatalyst is hardly competent for efficient solar fuels generation due to the problems of limited visible-light harvesting, rapid charge recombination, and poor stabilities [1-3]. Therefore, recently more and more attentions have focused on multi-component photocatalysts consisting of different semiconductor nanostructures, such as CdS/TiO₂ and p-CaFe₂O₄/n-PbBi₂Nb_{0.9}W_{0.1}O₉ photocatalytic nanodiode [6-8], in which the created heterojunctions can significantly improve the photogenerated charge separation and thereby promote the photocatalytic efficiency. Nevertheless, these hybrid photocatalysts involve at least one metal-containing semiconductor as a major component that would raise economic cost concern in terms of large-scale production.

Herein, we report a new hybrid photocatalyst made by coupling red phosphor (r-P) with graphitic carbon nitride (g-C₃N₄), referred as PCN-x (x is the mass percentage of g-C₃N₄ in the hybrid). Both components in this hybrid photocatalyst are composed by inexpensive earth-abundant elements, and exhibit wide absorption range in the visible light [9-13]. Although their conduction band edges are capable of reducing water for H₂ evolution according to literatures, the individual use of either material showed limited photocatalytic efficiency because of the high recombination rate of photogenerated electrons and holes [11-17]. Significantly, we found that the prepared PCN-x hybrids exhibit remarkably enhanced H₂ evolution yield in visible-light-driven water reduction. Even more, such a combination leads to a surprising enhancement on the

CH₄ production yield in photocatalytic CO₂ conversion. This discovery demonstrates the potential of using economic materials for efficient solar fuels production.

2. EXPERIMENTS

2.1. Preparation of PCN-x hybrids

All of the reagents were used without further treatment. The g-C₃N₄ used in this study was prepared by heating urea ($\geq 97.0\%$, Sigma-Aldrich) to 550 °C for 4 h in Ar atmosphere. Red phosphor/g-C₃N₄ hybrids (PCN-x) were prepared by annealing the mixture of red phosphor and g-C₃N₄ in inert atmosphere. In a typical process, an appropriate amount of g-C₃N₄ was mixed with r-P ($\geq 97.0\%$, Sigma-Aldrich). The mixture was ground for 30 min in a mortar and transferred into an alumina crucible that was sealed with aluminium silicate. The crucible was calcined at 380 °C for 2 h in Ar atmosphere, and then cooled down to room temperature in Ar atmosphere. Pure red phosphor sample without mixing g-C₃N₄ was also treated under the identical condition for comparison purpose.

2.2. Characterizations

X-ray powder diffraction (XRD) data were collected on a Shimadzu XRD-6000 X-ray diffractometer using Cu K α 1 radiation at a scan rate of 1°/min. The acceleration voltage and the applied current were 40 kV and 40 mA, respectively. Morphologies and structure of PCN-x hybrids were observed by field emission scanning electron microscopy (SEM: JEOL JSM-7600F) and transmission electron microscopy (TEM: JEOL JEM-2100F). TEM was operated at an accelerating voltage of 200 kV. UV–vis diffuse reflectance spectra (DRS) were recorded over the spectral range 320–800 nm on a Lambda 750 UV/Vis/NIR spectrophotometer (Perkin Elmer, USA). BaSO₄ was used as a reflectance standard. The photoluminescence (PL) spectra were obtained on a Shimadzu RF-5310PC fluorometer at an excitation wavelength of 350 nm. X-ray

photoelectron spectra (XPS) of the as-prepared photocatalysts were recorded on a Thermo Scientific Theta Probe XPS using Al K α radiation (1486.6 eV) and the binding energy values were calibrated with respect to C (1s) peak (284.6 eV). Fourier transform infrared spectra (FTIR) of the samples were recorded between 400 and 4000 cm⁻¹ on an IRAffinity-1 FTIR spectrometer.

2.3. Photocatalytic hydrogen evolution

Photocatalytic H₂ production reactions were carried out in a 50-mL closed quartz flask reactor, which was sealed with Suba Seal rubber septa (Sigma-Aldrich). Typically, 10 mg of the prepared PCN-x hybrids were suspended in 10 mL aqueous solution of L-ascorbic acid (0.1 M, pH=4.0). A small amount of H₂PtCl₆ solution (61 μ L, 0.08 wt%) was injected into the reactor to load 0.5 wt % Pt as co-catalyst on PCN-x surfaces through photodeposition. The reactor was purged with argon to drive away the residual air. The photocatalytic hydrogen evolution was initiated by irradiating the suspension with a 300-W xenon lamp (MAX-302, Asahi Spectra, USA) coupled with a UV cut-off filter ($\lambda > 420$ nm). The gas product were analyzed periodically through a gas chromatograph (GC-7890A, Agilent) with a TCD detector.

2.4. Photocatalytic conversion of CO₂ into CH₄

The photocatalytic CO₂ reduction was performed in a 100 mL gastight reactor with a quartz window and two side-sampling ports. In a typical process, 0.5 wt% Pt loaded PCN-x hybrids (20 mg) were dispersed on a 4-cm² glass substrate. The glass with powder photocatalysts was then put into the reactor. Prior to the irradiation, the reaction system was purged with high purity CO₂ for 30 min to remove the residual air and 0.2 ml ultrapure water was injected into the reaction system. A 500-W xenon arc lamp was used as the light source for the photocatalytic reaction. During the reaction, the gas product was analyzed periodically through a gas chromatograph (GC-7890A, Agilent) with a TCD detector.

3. RESULTS AND DISCUSSION

3.1. Sample characterizations

The PCN-x photocatalysts were prepared by annealing the mixture of red phosphor and g-C₃N₄ with different mass ratio in Ar atmosphere, as illustrated in Fig. 1A. PCN-5 and PCN-30 were used as representative samples for the studies. X-ray diffraction (XRD) patterns (Fig. 2) show no phase changes of both r-P and g-C₃N₄, and no sign of new product formation during the annealing process. The characteristic peak at 27.4° as the signature of interlayer aromatic packing indicates that the crystal structure of C₃N₄ was retained after the thermal treatment [11]. The FT-IR analyses (Fig. S1) further confirm that the original graphitic C-N backbones keep unchanged after hybridization with r-P, and show no vibrational peak of P-related groups in the PCN-x hybrids, indicating that the annealing process unlikely initiates new chemical bonding between r-P and g-C₃N₄. The UV-vis spectra (Fig. 3) of the PCN-x hybrids exhibit mixed absorption features of r-P and g-C₃N₄ [9, 11]. As expected, r-P and g-C₃N₄ show their fundamental absorption edge at 700 nm and 460 nm, respectively. The absorption edge of g-C₃N₄ becomes more evident with the increase of g-C₃N₄ content in PCN-x hybrids.

Scanning electron microscopy (SEM) analyses (Fig. 1) reveal that in the PCN-5 hybrid, large g-C₃N₄ nanosheets with thickness of several tens nanometers are coating on the surface of r-P particles, while pure r-P particles show quite smooth and clean surfaces. The g-C₃N₄ layer was confirmed by energy-dispersive X-ray spectroscopy (EDS) as shown in Fig. S2. Increasing the g-C₃N₄ ratio leads to heavier g-C₃N₄ coverage over the r-P surfaces (Fig. 1D). Notably, g-C₃N₄ preferably coats on the uneven r-P surface area as evidenced by the less g-C₃N₄ coating on the very smooth area of r-P surfaces (Fig. S3, indicated by arrow 1) with some free g-C₃N₄ particles inevitably existing (Fig. S3, indicated by arrow 2).

This heavy g-C₃N₄ coating was hardly visualized in transmission electron microscopy (TEM), nevertheless, we still can observe g-C₃N₄ nanosheets adhering on the r-P edges as shown in Fig. 4. However, high-resolution TEM images of the samples are not attainable because these g-C₃N₄ nanosheet structures seem too thin and tend to transform into spherical structures under high energy focusing electron beam (Fig. S4). Note that upon thermal treatment (380 °C for 2 h), the pure g-C₃N₄ appears as velvet-like sheets with rolling edges (Fig. S5). Such flexible structures allow g-C₃N₄ anchoring on the r-P surfaces and in particular wrapping on the r-P edges, which creates heterojunctions between r-P and g-C₃N₄ for charge transfer [18].

3.2. Photocatalytic H₂ evolution

In order to identify the contribution of these heterojunctions, we have compared these samples for visible-light-driven ($\lambda > 420$ nm) photocatalytic H₂ generation from water reduction. Ascorbic acid (0.1 M) was used as sacrificial reagent, and Pt (0.5 wt%) were loaded as co-catalyst on the samples via in-situ photodeposition [19]. Control experiments confirm no H₂ evolution without photocatalysts or light illumination. As illustrated in Fig. 5A, the pure r-P sample showed very weak activity for H₂ production (22 $\mu\text{mol}\cdot\text{h}^{-1}\cdot\text{g}^{-1}$). However, upon loading of 5 wt% g-C₃N₄ (as PCN-5) onto r-P surfaces, the H₂ evolution rate (310 $\mu\text{mol}\cdot\text{h}^{-1}\cdot\text{g}^{-1}$) was enhanced more than ten times and even comparable to that of pure g-C₃N₄ (340 $\mu\text{mol}\cdot\text{h}^{-1}\cdot\text{g}^{-1}$). In comparison, a simple mixture of r-P with 5 wt% g-C₃N₄ only showed a H₂ evolution rate of 70 $\mu\text{mol}\cdot\text{h}^{-1}\cdot\text{g}^{-1}$. These results demonstrate that thermal annealing facilitates the formation of r-P/g-C₃N₄ heterojunctions for effective charge separation in PCN-5, thereby leading to this enhanced H₂ evolution rate (more than 4 times enhancement by annealing). The photocatalytic activity can be further enhanced (up to 1000 $\mu\text{mol}\cdot\text{h}^{-1}\cdot\text{g}^{-1}$ for H₂ evolution) by increasing g-C₃N₄ content to 30 wt% (PCN-30). The above results clearly demonstrate that the r-P/g-C₃N₄ interface plays an essential

role on enhancing photocatalytic H₂ evolution. Higher g-C₃N₄ loading on r-P leads to larger interfaces and thereby effective separation of photogenerated electrons and holes towards enhanced photocatalytic activities [20-22].

3.3. Photocatalytic CO₂ conversion

Furthermore, since the reduction potential from CO₂ to CH₄ ($\text{CO}_2 + 8\text{H}^+ + 8\text{e}^- \rightarrow \text{CH}_4 + 2\text{H}_2\text{O}$) is around -0.24 V, the high conduction band (CB) edge of r-P (-0.25 V vs. NHE) and g-C₃N₄ (-1.2 V vs. NHE) allows us to use the PCN hybrids for photocatalytic conversion of CO₂ into hydrocarbon fuels [9, 11, 23-25]. As shown in Fig. 5B, the PCN-30 exhibited a CH₄ production yield of 295 $\mu\text{mol}\cdot\text{h}^{-1}\cdot\text{g}^{-1}$, which is twice higher than pure r-P (145 $\mu\text{mol}\cdot\text{h}^{-1}\cdot\text{g}^{-1}$) and nearly three times higher than pure g-C₃N₄ (107 $\mu\text{mol}\cdot\text{h}^{-1}\cdot\text{g}^{-1}$). This comparison results further demonstrate that the coupling between r-P and g-C₃N₄ effectively promote the overall photocatalytic activity for CO₂ reduction.

3.4. Mechanism of enhanced photocatalytic activity

The enhanced photocatalytic activity could be attributed to the effective interfacial charge transfer between r-P and g-C₃N₄ across the heterojunction as illustrated in Fig. 6. Since the CB edge of g-C₃N₄ (-1.2 V vs. NHE) is more negative than that of r-P (-0.25 V vs. NHE), the photoexcited electrons on g-C₃N₄ surface could transfer to r-P through the interfaces created by annealing. Similarly, the photoinduced holes on the r-P surface move towards g-C₃N₄ due to the difference in valence band (VB) edge potentials. The accumulated electrons on r-P surfaces reduce the H⁺ or CO₂ into valuable fuels, while the holes on g-C₃N₄ surfaces oxidize the electron donor (ascorbic acid for H₂ production and OH⁻ for CO₂ reduction, respectively). The effective separation of photogenerated electrons and holes thus enhances the photocatalytic activities [21,

22]. In addition, the network structure of g-C₃N₄ can act as an excellent electron transport platform to facilitate the charge transfer process [17, 18].

The interfacial charge transfer could be also evidenced by the decreased photoluminescence (PL) intensity in the PCN-5 hybrid (Fig. 7) as compared to pure g-C₃N₄. This result further confirms photoinduced electron flowing direction from g-C₃N₄ to r-P, causing PL quenching of g-C₃N₄ in PCN-5. Meanwhile, the interfacial charge transfer could be further supported by the enhanced TAOH fluorescence intensity on PCN-5 as compared to that on pure g-C₃N₄ (Fig. S6, see supporting information for details). This observation also indicated that the r-P/g-C₃N₄ heterojunctions allow the photocatalyst to supply more photogenerated holes to generate more ·OH radicals and thus higher TAOH concentration with stronger fluorescence signal.

In addition, X-ray photoelectron spectroscopy (XPS) analyses reveal that the annealing process neither creates new species such as P₃N₅ nor leads to P-doping into the g-C₃N₄ lattice (P₃N₅ is a very stable species) [26]. As shown in Fig. S7, the P 2p signal can be deconvoluted into ~129.3 eV and ~130.1 eV for P 2p_{3/2} and P 2p_{1/2}, respectively, which are the typical signatures for 2p binding energy of red phosphorus. No binding energy shift is observed for PCN-30 as compared to pure r-P, indicating no P-N bonding formation.

4. Conclusions

In summary, hybrid structures of r-P and g-C₃N₄ are prepared through solid state annealing method. We found that small amount introduction of g-C₃N₄ onto r-P surface led to considerable improvement on the photocatalytic activity for H₂ production and CO₂ conversion into CH₄. The enhancement could be attributed to the effective separation of photogenerated electrons and holes across the r-P/g-C₃N₄ heterojunction. This work provides a new insight on developing

active metal-free heterostructural photocatalysts and demonstrates the great potential of using economic materials for efficient solar fuels production.

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Electronic Supplementary Information

Supplementary data associated with this article can be found, in the online version, at doi:XXXX

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Figure Captions

Fig. 1. (A) schematic illustration of hybridizing g-C₃N₄ on r-P surfaces via annealing. Increasing the g-C₃N₄ mass ratio leads to higher surface coverage of g-C₃N₄ on r-P surfaces. (B)-(D) SEM images of r-P, PCN-5, and PCN-30. The right column shows the magnified images of r-P, PCN-5, and PCN-30, respectively. Scale bar: 10 μ m.

Fig. 2. XRD patterns of PCN-x hybrids. The XRD patterns of pure g-C₃N₄ and r-P that were treated at 380 °C for 2 h were also provided for comparison.

Fig. 3. UV-vis absorption spectra of PCN-5, PCN-30, g-C₃N₄ and r-P sample.

Fig. 4. TEM image of PCN-30. The covered g-C₃N₄ layer on r-P surfaces, and linked g-C₃N₄ particle were labeled.

Fig. 5. Photocatalytic (A) H₂ and (B) CH₄ production rate of r-P, PCN-5, PCN-30, and g-C₃N₄ photocatalysts.

Fig. 6. Energy band diagram of p-n junction for PCN-x under zero bias and schematic illustration of electron-hole separation process after excitation.

Fig. 7. Photoluminescence spectra of r-P, PCN-5 and g-C₃N₄ at an excitation wavelength of 350 nm.