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Article (Special Issue on Photocatalytic H₂ Production and CO₂ Reduction)

The embedded CuInS₂ into hollow-concave carbon nitride for photocatalytic H₂O splitting into H₂ with S-scheme principle

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ARTICLE INFO

Article history:

Received 1 July 2019

Accepted 24 July 2019

Published 5 January 2020

Keywords:

Hollow carbon nitride

Hydrogen evolution

Solar light absorption

Directional charge transfer

Apparent potential difference

ABSTRACT

It is still a great challenge to effectively optimize the electronic structure of photocatalysts for the sustainable and efficient conversion of solar energy to H₂ energy. To resolve this issue, we report on the optimization of the electronic structure of hollow-concave carbon nitride (C₃N₄) by deviating the *sp*²-hybridized structure of its tri-s-triazine component from the two-dimensional plane. The embedded CuInS₂ into C₃N₄ (CuInS₂@C₃N₄) demonstrates an increased light-capturing capability and the promoted directional transfer of the charge carrier. Research results reveal that the hollow structure with an apparent potential difference between the concave and convex C₃N₄ drives the directional transfer of the photoinduced electrons from the Cu 2*p* orbital of CuInS₂ to the N 1*s* orbital of C₃N₄ with the S-scheme principle. The H₂ evolution efficiency over CuInS₂@C₃N₄ is up to 373 μmol·h⁻¹ g⁻¹ under visible irradiation, which is 1.57 and 1.35 times higher than those over the bulk *g*-C₃N₄ with 1 wt% Pt (238 μmol·h⁻¹ g⁻¹) and *g*-C₃N₄ with 3 wt% Pd (276 μmol·h⁻¹ g⁻¹), respectively. This suggests that the apparent potential difference of the hollow C₃N₄ results in an efficient reaction between the photogenerated electrons and H₂O. This work supplies a new strategy for enhancing the sustainable solar conversion performance of carbon nitride, which can also be suitable for other semiconductors.

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1. Introduction

Photocatalytic H₂ production from H₂O splitting is suggested to be a promising strategy for solar-photon energy conversion owing to its green and renewable characteristics [1–3]. In a general artificial photocatalytic procedure, the photocatalytic process involves four procedures, i.e., photon absorption, generation of e⁻/h⁺, charge transfer from provider to active sites, and reduction of absorbed H₂O or H₃O⁺ to H₂ [3,4]. Achieving enhanced photon capture and efficient utilization of solar en-

ergy is still challenging [5]. As a result, photon energy needs to exceed the transition energy of photogenerated e⁻ in the bandgap; the directional charge-transfer and its designated interaction with the absorbed H₂O are required. The former requires significant photon energy to excite photogenerated charges; however, this requirement cannot be met. The second factor dynamically reflects a competition in the utilization of the photogenerated charge, and e⁻ transfers to H₂O slowly (~μs); however, e⁻ recombines with h⁺ rapidly (~ps) [6,7]. Although there are many strategies to be attempted [8,9], such as

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Study was supported by the National Natural Science Foundation of China (21871155), the K. C. Wong Magna Fund in Ningbo University, Fan 3315 Plan, and Yongjiang Scholar Plan.

DOI: S1872-2067(19)63490-X | http://www.sciencedirect.com/science/journal/18722067 | Chin. J. Catal., Vol. 41, No. 1, January 2020

the heteroatom doping, heterojunction construction, and plasmonic noble metal loading, it is still difficult to integrate the electricity and optics of semiconductors to simultaneously satisfy the thermodynamic and dynamic requirements of photo-generated carriers.

Taking 2D π -conjugated carbon nitride as a representative, g -C₃N₄ is a typical visible-excitation semiconductor (~ 2.7 eV), and its CB potential is -1.23 V (vs. NHE at pH = 7) [10,11]. Generally, g -C₃N₄ has been used as a photocatalyst for reductive photocatalytic reactions, e.g., splitting H₂O into H₂ [12–18], CO₂ [19–23], O₂ [24–26], and/or heavy metal reduction [27–30]. It is known that g -C₃N₄ is usually in the form of the layered bulk agglomeration in thermal polymerization, which results in a small surface area, low-photon absorption, and serious charge–carrier recombination [31]. Thus, noble metal (Pt) is often used as a support for g -C₃N₄ to enhance its photo-induced electron migration and utilization in H₂O splitting into H₂. However, its H₂ evolution efficiency does not match the photocatalyst cost requirements [32,33]. Essentially, it is necessary to understand that the migration and action mechanism of photogenerated electrons from the atomic orbital structures of g -C₃N₄ and its electronic structure can be consequently adjusted to optimize the utilization of photo-induced electrons and H₂ production performance over g -C₃N₄. It is revealed that g -C₃N₄ is composed of sp^2 -hybridized C–N bonds with lone electrons on the p_z orbitals, which form π -conjugated structures [34–36]. When the sp^2 -hybridized structure of g -C₃N₄ deviates from the two-dimensional plane, the π -electron density shifts from the concave to the convex sp^2 -hybridized structure along with the hybridization intermediate between sp^2 and sp^3 in the g -C₃N₄ layers [36–38]. This causes the electron to directly trend from concave to convex. Moreover, the curved-hollow g -C₃N₄ can increase its surface density, and the undulating surface increases its absorbance and improves the photosensitivity of its intrinsic or composite materials [39]. In view of this, we synthesized hollow-concave carbon nitride (C₃N₄), and CuInS₂, as the typical narrow-bandgap sample, was embedded and grown in the cavity of C₃N₄ by hydrothermal method. Research results confirm that the constructed CuInS₂@C₃N₄ photocatalysts demonstrated increased light-absorption intensity from normal 455 to 480 nm due to the light scattering effect caused by the hollow structure. The good directional migration capability of the charge carriers from CuInS₂ to C₃N₄ has been achieved under the action of the apparent potential difference between the concave to the convex of the sp^2 -hybridized structure of C₃N₄, which thus promotes the effective spatial separation, and enhances the utilization of photogenerated carriers with the direct S-scheme mechanism. As a result, CuInS₂@C₃N₄ photocatalysts exhibit higher efficiency toward H₂ evolution compared with the bulked g -C₃N₄ supported 1 wt% Pt and g -C₃N₄ loaded 3 wt% Pd.

2. Experimental

2.1. Photocatalysts preparation

2.1.1. Synthesis of hollow-concave C₃N₄

SiO₂ nanospheres with an average size in the range of 300–350 nm were prepared according to a previous report [40]. C₃N₄ was synthesized by direct heat treatment using SiO₂ nanospheres as a template. Specifically, 2.0 g of melamine powder was evenly mixed with 1.0 g of SiO₂ nanospheres. Finally, the mixture was placed in a crucible (20 mL). The crucible, including precursors and templates, was firstly heated in a muffle furnace at 320 °C for 2 h at a linear ramp rate of 10 °C min^{−1}, and then heated at 550 °C for 4 h at the same ramp rate. After the temperature was decreased to room temperature, the sample was impregnated into an NH₄HF₂ solution (4 mol·L^{−1}) for 6 h, and then washed with deionized water. Ultimately, a yellow powder of C₃N₄ was obtained.

2.1.2. Synthesis of CuInS₂@C₃N₄ composites

In a typical synthesis of CuInS₂@C₃N₄ composites, C₃N₄ (0.49 g), InCl₃·4H₂O (1 mmol), CuCl (1 mmol), and thiourea (3 mmol) were successively added into 50 mL of ethylene glycol, and stirred for 1 h at room temperature; subsequently, the mixture was transferred to a Teflon-lined stainless steel autoclave (100 mL) and heated at 200 °C for 12 h. After cooling to room temperature naturally, the product was collected, washed, and dried at 60 °C for 4 h to afford CuInS₂@C₃N₄. Besides, the bulk carbon nitride (g -C₃N₄) was prepared by heating 2.0 g of melamine at 550 °C for 2 h. Meanwhile, pristine CuInS₂ nanoparticles and CuInS₂/ g -C₃N₄ were prepared by the same method as that for CuInS₂@C₃N₄.

2.2. Characterization

The data of the composition, crystal type, and chemical valence of the photocatalytic materials were obtained by XRD-6000 and XPS (XSAM800), and the binding energy for all samples was referred according to C 1s at 284.6 eV in the XPS characterization. The morphology was determined by FESEM (Hitachi, SU-70). The optical property was examined using a UV2600 (Shimadzu) and RF6000 (Shimadzu), and the excitation wavelength of the fluorescence was 325 nm at room temperature. The specific surface area and pore radius distribution were tested on a Micromeritics ASAP 3020. The Mott–Schottky analysis, electrochemical impedance spectroscopy, transient photocurrent response, and linear sweep voltammetry were performed on an electrochemical workstation (CHI 660C Chenhua Instruments) in a Na₂SO₄ solution. Time-resolved photo-luminescence spectra were recorded on an FLS920 fluorescence lifetime spectrophotometer (Edinburgh, Instruments, UK).

2.3. Photocatalytic H₂O splitting test

Fifty milligrams of the prepared photocatalyst was dispersed into 100 mL of an aqueous solution containing 10 vol% triethanolamine along with Na₂S (0.25 mol L^{−1}) and Na₂SO₃ (0.2 mol L^{−1}) solutions. Prior to light exposure, the oxygen in the photocatalytic system was removed by bubbling with N₂. Under irradiation by a 350 W Xe lamp equipped with optical filter ($\lambda \geq 420$ nm), a continuous magnetic stirrer was applied at the bot-

tom of the reactor to contain the photocatalyst particles in suspension throughout the experiment. A portion (0.4 mL) of the product was sampled intermittently with septum (1 mL), and the gas was analyzed using a GC-2014 instrument equipped with a 5 Å molecular sieve column (Shimadzu).

3. Results and discussion

3.1. Crystal composite and morphology

The size of the pristine CuInS_2 is about 100–120 nm (Fig. 1(A)), and C_3N_4 demonstrates the uniform hollow-concave structure with a diameter of 300–350 nm (Fig. 1(B)). Using these hollow concave as nucleation sites, the grown CuInS_2 has a larger size of 250–300 nm than that of the pristine CuInS_2 , and finally covers the surface of C_3N_4 (Fig. 1(C)). Element mappings confirm the uniform distributions of C, N, Cu, In, and S for the $\text{CuInS}_2@\text{C}_3\text{N}_4$ sample in Fig. 1(D). The XRD spectra of the as-prepared $g\text{-C}_3\text{N}_4$, C_3N_4 , CuInS_2 , $\text{CuInS}_2@\text{C}_3\text{N}_4$ samples are shown in Fig. 2. Both $g\text{-C}_3\text{N}_4$ and C_3N_4 demonstrate two characteristic diffraction peaks at 13.1° and 27.4° , which reflect the (100) plane originating from the in-planar packing structure of conjugated tri-s-triazine, and the (002) plane corresponding to the interlayer stacking of the conjugated aromatic structure [23,24], respectively. However, the intensity of diffraction peak over C_3N_4 is weaker in comparison with that of $g\text{-C}_3\text{N}_4$, which is because the electroneutrality of the delocalized tri-s-triazine structure is broken by the apparent potential difference between the concave and convex surfaces in the process of deviating from the plane [41,42]. In combination with CuInS_2 , there are diffraction peaks at 27.9° , 46.4° , and 54.9° over the $\text{CuInS}_2@\text{C}_3\text{N}_4$ sample corresponding to the (112), (204), and (116) crystal planes of the chalcopyrite-type CuInS_2 (JCPDS 85-1575), respectively. It is noticed that the half peak widths of these peaks are decreased compared with those of the CuInS_2 sample, suggesting that the hollow-concave as nucleation sites

Fig. 2. XRD spectra for $g\text{-C}_3\text{N}_4$, C_3N_4 , CuInS_2 and $\text{CuInS}_2@\text{C}_3\text{N}_4$.

was beneficial to the CuInS_2 growth. It is observed that the strong diffraction peak of (002) in C_3N_4 is almost the same with that of (112) in CuInS_2 , and the former is overlapped by the latter, while the peak of (100) for C_3N_4 is extremely weak, and does not indicate the presence of C_3N_4 in the composite. Thus, there appear to be no diffraction peaks for C_3N_4 in the XRD pattern of $\text{CuInS}_2@\text{C}_3\text{N}_4$. The composite and chemical valence states of the photocatalysts were tested by XPS, and the corresponding spectra are shown in Fig. 3. The binding energies in the tests are referred to according to C 1s at 284.6 eV. In Fig. 3(A), there are two Cu 2p signals of the pristine CuInS_2 at 931.7 and 951.5 eV corresponding to the Cu $2p_{3/2}$ and Cu $2p_{1/2}$ of Cu^+ [43,44]. However, for the Cu^+ signal of the $\text{CuInS}_2@\text{C}_3\text{N}_4$ sample, the binding-energy data are increased to 931.9 and 951.7 eV, respectively. The N 1s spectra of the C_3N_4 sample in Fig. 3(B) are fitted into the signals at 398.2, 399.7, and 401.2 eV, corresponding to sp^2 -hybridized N ($\text{C}=\text{N}-\text{C}$), bridging N ($(\text{C})_3-\text{N}$), and N-H in the delocalized tri-s-triazine structures [45,46], respectively. In combination with CuInS_2 , the N 1s binding-energy data of the sp^2 -hybridized N is slightly decreased to 398.0 eV. This phenomenon may indicate the strong interaction between the composites attributed to the transportation of electrons from CuInS_2 to C_3N_4 and attainment of thermodynamic balance. Moreover, the C 1s, S 2p, and In 3d spectra of $\text{CuInS}_2@\text{C}_3\text{N}_4$ are shown in Fig. S1, and these binding energies were not been changed before and after combination between C_3N_4 and CuInS_2 . The BET area data were calculated to be 3.2, 30, and $120 \text{ m}^2\text{g}^{-1}$ for CuInS_2 , $\text{CuInS}_2@\text{C}_3\text{N}_4$, and C_3N_4 , respectively; the corresponding pore-size distributions using the BJH method are 8.8, 9.0, and 6.3 nm. The elaborate data of BET areas and pore sizes, as well as adsorption-desorption isotherms and pore size distributions are listed in Table S1 and Fig. S2. Therefore, evidently, the two physical properties of $\text{CuInS}_2@\text{C}_3\text{N}_4$ have been enhanced by the addition of C_3N_4 .

3.2. Optical and electrical properties

Fig. 1. SEM images for CuInS_2 (A), C_3N_4 (B), $\text{CuInS}_2@\text{C}_3\text{N}_4$ (C), and element distribution overlapping map for C, N, S, In and Cu in $\text{CuInS}_2@\text{C}_3\text{N}_4$ (D).

Fig. 3. High resolution XPS spectra of Cu 2p (A) and N 1s (B).

According to the above characterizations of crystal composition and morphology, the hollow-concave structure of the C₃N₄ obtained by deviating the delocalized tri-s-triazine from the plane will strengthen the photon absorption capabilities and electron transfer performances of its composite. In Fig. 4, it can be observed that the photon absorption edge of *g*-C₃N₄ is 455 nm; however, its absorption boundary of C₃N₄ shows an obvious red shift to 480 nm along with enhanced photon absorption intensity due to the light scattering effect caused by the hollow structure [47,48]. Moreover, it is clear that pristine CuInS₂ displays a wide light absorption owing to its intrinsic narrow bandgap. Taking advantage of the hollow structure of C₃N₄ and the narrow bandgap of CuInS₂, the constructed CuInS₂@C₃N₄ shows enhanced absorption from UV to near NIR, suggesting that the formed structure is beneficial for photon absorption and utilization [48]. According to the Kubelka-Munk function vs. light energy in Fig. 4(B), the band-gap energies of C₃N₄ and CuInS₂ are calculated to be 2.50 and 1.20 eV, respectively. In a subsequent test of photoluminescence emission spectrum (Fig. 5(A)), *g*-C₃N₄ displays the strongest fluorescence intensity in the wavelength range of 450–1000 nm, revealing the serious recombination of photogenerated e⁻ and h⁺ over *g*-C₃N₄. For the C₃N₄ sample, it is seen that its fluorescence intensity is much lower, suggesting the good separation and transfer efficiency of the photogenerated charge carriers over

C₃N₄ under the effect of the apparent potential difference between its inner and outer hollow surfaces. Furthermore, the CuInS₂@C₃N₄ sample shows a lower signal intensity compared to that of C₃N₄, confirming that the photogenerated charge carriers can be spatially transferred over the CuInS₂@C₃N₄ sample. In combination with the XPS results in Fig. 3, we can preliminarily prove the electron transfer from Cu⁺ of CuInS₂ to N of C₃N₄, which, therefore, is bound to improve the conductivity and charge utilization efficiency of CuInS₂@C₃N₄. In Fig. 5(B), EIS-Nyquist characterization confirms that improved conductivity of CuInS₂@C₃N₄ has been obtained. It is seen that the semicircle plots originate from the charge transportation from CuInS₂@C₃N₄ to the electrolyte. As a result, the CuInS₂@C₃N₄ sample demonstrates smaller electric-resistance in comparison to those of C₃N₄ and *g*-C₃N₄. Under visible-light illumination, photogenerated charge carriers over samples migrate into their back contact and interact with the electrolyte to yield photocurrent reflected as the *i*-*t* spectra (Fig. 5(C)) [49]. Clearly, CuInS₂@C₃N₄ presents the highest anodic photocurrent intensity. Linear sweep voltammetry was used to investigate the interaction barrier between the electron and H₂O [50–52]. In Fig. 5(D), polarization plots of *g*-C₃N₄, C₃N₄, and CuInS₂@C₃N₄ were obtained at a scan rate of 10 mV/s. The initial potentials at 0.5 mA/cm² are -0.42, -0.36, and 0.016 V for the *g*-C₃N₄, C₃N₄, and CuInS₂@C₃N₄ samples, respectively. The overpoten-

Fig. 4. (A) Optical absorption spectra of for *g*-C₃N₄, C₃N₄, CuInS₂ and CuInS₂@C₃N₄ samples; (B) Plots of (αhv)^{1/2} vs. photon energy (hν) for C₃N₄ and CuInS₂.

Fig. 5. Photoluminescence emission spectrum (A), electrochemical impedance spectra (B), transient photocurrent response (C), and linear sweep voltammetry (D) for $g\text{-C}_3\text{N}_4$, C_3N_4 , CuInS_2 and $\text{CuInS}_2@\text{C}_3\text{N}_4$ samples.

tial at -10 mA/cm^2 for C_3N_4 is much lower than that for $g\text{-C}_3\text{N}_4$, suggesting that the apparent potential difference of the hollow-concave C_3N_4 can lower the interaction barrier between the electron and H_2O . Under the effect of the apparent potential difference, $\text{CuInS}_2@\text{C}_3\text{N}_4$ presents the lowest overpotential (-0.52 V), which is favorable for H_2 production in photocatalytic H_2O splitting [52,53].

3.3. Photocatalytic activity

Accordingly, the photocatalytic activities have been tested by H_2 yield efficiency using a Xe lamp equipped with an optical filter ($\lambda > 420 \text{ nm}$), as shown in Fig. 6(A). The H_2 evolution efficiencies of pristine $g\text{-C}_3\text{N}_4$ and CuInS_2 are 67 and $12 \mu\text{mol}\cdot\text{h}^{-1}\text{g}^{-1}$. When C_3N_4 was used as the photocatalyst in H_2O splitting, its H_2 evolution efficiency was $107 \mu\text{mol}\cdot\text{h}^{-1}\text{g}^{-1}$. Moreover, the H_2 evolution efficiencies are 135 and $373 \mu\text{mol}\cdot\text{h}^{-1}\text{g}^{-1}$ over $\text{CuInS}_2/g\text{-C}_3\text{N}_4$ and $\text{CuInS}_2@\text{C}_3\text{N}_4$, respectively. The effects of irradiation time on the H_2 production efficiency over the $g\text{-C}_3\text{N}_4$, C_3N_4 , $\text{CuInS}_2/g\text{-C}_3\text{N}_4$, and $\text{CuInS}_2@\text{C}_3\text{N}_4$ photocatalysts are displayed in Fig. 6(B), and the durative H_2 evolution is achieved with no declining trend. However, the H_2 efficiency trend plots vs. irradiation time are clearly distinct. Under visible-light irradiation, the H_2 production efficiency over $g\text{-C}_3\text{N}_4$ increases tardily, while high H_2 evolution efficiencies over C_3N_4 ,

$\text{CuInS}_2/g\text{-C}_3\text{N}_4$, and $\text{CuInS}_2@\text{C}_3\text{N}_4$ can be obtained. In particular, $\text{CuInS}_2@\text{C}_3\text{N}_4$ exhibits an excellent evolution rate. Meanwhile, the apparent quantum yield of $\text{CuInS}_2@\text{C}_3\text{N}_4$ is 4.32% at a wavelength of 420 nm, which is 1.63 times higher than that of $\text{CuInS}_2/g\text{-C}_3\text{N}_4$ (2.65%). Moreover, we also compared the H_2 evolution efficiency of $\text{CuInS}_2@\text{C}_3\text{N}_4$ with that of $g\text{-C}_3\text{N}_4$ with 1% Pt and 3% Pd prepared according to literature [45,54]. In Fig. 6(C), it is presented that $\text{CuInS}_2@\text{C}_3\text{N}_4$ shows higher activity than the 1 wt% Pt/ $g\text{-C}_3\text{N}_4$ ($238 \mu\text{mol}\cdot\text{h}^{-1}\text{g}^{-1}$) and 3 wt% Pd/ $g\text{-C}_3\text{N}_4$ ($276 \mu\text{mol}\cdot\text{h}^{-1}\text{g}^{-1}$). Thus, the hollow concave structure of C_3N_4 promotes the transmission and utilization efficiency of photogenerated electrons under the action of apparent potential difference, which has great advantages in replacing noble-metal co-catalysts and accelerating the photogenerated electron transmission. The stability test of $\text{CuInS}_2@\text{C}_3\text{N}_4$ was performed as shown in Figure 6D. After three recycles, $\text{CuInS}_2@\text{C}_3\text{N}_4$ presented efficient H_2 evolution performance under visible-light irradiation. However, its H_2 -evolution efficiency was decreased from 373 to $355 \mu\text{mol}\cdot\text{h}^{-1}\text{g}^{-1}$ in the fourth recycle. When sacrificial agents were added into the reaction system again, the performance over $\text{CuInS}_2@\text{C}_3\text{N}_4$ increased to $375 \mu\text{mol}\cdot\text{h}^{-1}\text{g}^{-1}$. Thus, the decline in performance was due to the consumption of sacrificial agents. Therefore, $\text{CuInS}_2@\text{C}_3\text{N}_4$ demonstrates high stability. In combination with the series of characterizations, the strengthened light absorption from visi-

Fig. 6. H₂ evolution efficiency (A, C), H₂ amount change with prolonging the irradiation time (B) for samples, and photocatalytic stability for CuInS₂@C₃N₄ (D).

ble to the near-infrared region, effective charge-transfer capability, and the lowered H₂ overpotential over CuInS₂@C₃N₄ ensure a highly efficient H₂ production, which is attributed to the hollow concave structure of C₃N₄ and its structure-induced apparent potential difference.

3.4. Photocatalytic mechanism

Kinetically, time-resolved fluorescence spectrum was recorded to probe the separation, transfer, and utilization of photo-induced carriers [55]. In Fig. 7, The decay spectra of CuInS₂, C₃N₄, and CuInS₂@C₃N₄ have been fitted into three different lifetime processes: τ_1 , τ_2 , and τ_3 , to demonstrate the radioactive process, non-radioactive step, and energy transfer [56,57]. The radioactive step arises from the recombination of e⁻ and h⁺. The τ_1 values for CuInS₂ (0.0023 ns) and C₃N₄ (3.2 ns) are lower than that for CuInS₂@C₃N₄ (6.2 ns), and the percent of charge carriers decrease from 95% and 49.2% over CuInS₂ and C₃N₄, respectively, to 32.6% over CuInS₂@C₃N₄, revealing that the photogenerated charge carriers have been spatially transferred from CuInS₂ to C₃N₄ over the CuInS₂@C₃N₄ sample. In the subsequent process, the relaxation effect of the partial photo-induced carriers results in the non-radioactive step and energy transfer, which is critical for the utilization of photogenerated electrons and photocatalytic H₂O splitting. It is seen that τ_2

and τ_3 for CuInS₂@C₃N₄ (35 and 12 ns) are longer than those of CuInS₂ (0.0013 and 1.6 ns), and C₃N₄ (20 and 5.7 ns), and the corresponding proportions of photo-induced carriers over CuInS₂@C₃N₄ (67.4%) are clearly higher than those of CuInS₂ (5%) and C₃N₄ (50.8%), suggesting that more photo-induced

Fig. 7. Time-resolved fluorescence spectra for C₃N₄, CuInS₂ and CuInS₂@C₃N₄.

carriers participate in the photocatalytic H_2O splitting. According to the Kubelka-Munk function vs. light energy in Fig. 4(B) [58], the band-gap energies of C_3N_4 and CuInS_2 are calculated to be 2.50 and 1.20 eV, respectively. In Fig. S3, the Mott-Schottky plots demonstrate that C_3N_4 possesses the n-typical semiconductor feature, and its CB potential is -1.60 V at $\text{pH} = 7$. Thus, the corresponding VB is calculated to be 0.90 V. In Fig. S3(A), the CB and VB potentials of CuInS_2 have been calculated to be -0.20 and 1.00 V, respectively. Based on these results, we propose a suitable photocatalytic mechanism for photocatalytically yielding H_2 over $\text{CuInS}_2@\text{C}_3\text{N}_4$, as displayed in Scheme 1. Since C_3N_4 and CuInS_2 possess small band gaps, e^- and h^+ can favorably generate and migrate from the VB to CB of both semiconductors under visible-light irradiation. The XPS results in Fig. 3 reveal the electron transfers from Cu^+ of CuInS_2 to N of C_3N_4 over $\text{CuInS}_2@\text{C}_3\text{N}_4$. For the traditional Type-II photocatalytic mechanism in accordance with the research of Yu et al. [59], electrons migrate from a higher CB to a lower CB, and the holes migrate from a lower VB to a higher VB. Noticeably, the XPS results reveal that the electron transfer principle does not conform to the Type-II photocatalytic mechanism; however, $\text{CuInS}_2@\text{C}_3\text{N}_4$ follows the S-scheme mechanism of the photocatalytic H_2O splitting into H_2 [60]. The photogenerated e^- tentatively migrates from the CB of CuInS_2 to the VB of C_3N_4 through the interaction between N and Cu^+ under the action of the apparent potential difference between the concave and convex of the hollow C_3N_4 . Furthermore, the photogenerated h^+ remains on the CuInS_2 surface, which efficiently completes the spatial separation and directional migration of the photogenerated carriers. Meanwhile, the H_2O dissociative adsorption is advantageously performed on the convex surface of C_3N_4 . As a result, e^- smoothly reduces the H_2O molecule to produce H_2 on the convex surface of C_3N_4 , while h^+ oxidizes the sacrificial agent on the surface of CuInS_2 .

4. Conclusions

In summary, utilizing the advantage of the apparent potential difference of hollow-concave carbon nitride, CuInS_2 nanoparticles have been impregnated within C_3N_4 for the photo-

catalytic H_2O splitting into H_2 . The constructed $\text{CuInS}_2@\text{C}_3\text{N}_4$ exhibits higher photocatalytic performance than the bulk $g\text{-C}_3\text{N}_4$ with 1% Pt and $g\text{-C}_3\text{N}_4$ with 3% Pd in a visible-light hydrolysis system. Experimental analyses confirm that the high efficiency of the H_2 evolution over $\text{CuInS}_2@\text{C}_3\text{N}_4$ mainly arises from (1) the increased light-capturing capability owing to the incident light within the hollow C_3N_4 by multiple light scattering, and (2) the directional migration of the charge carrier due to the apparent potential difference of the hollow-concave C_3N_4 caused by deviating the sp^2 -hybridized structure of its tri-s-triazine component from the two-dimensional plane. The research develops an effective strategy for promoting successive solar energy conversions over carbon nitride, which can also be suitable for other semiconductors.

Acknowledgments

Study was supported by the National Natural Science Foundation of China (21871155), the K. C. Wong Magna Fund in Ningbo University, Fan 3315 Plan, and Yongjiang Scholar Plan.

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Scheme 1. S-scheme principle for water splitting into H_2 over $\text{CuInS}_2@\text{C}_3\text{N}_4$ with directional charge transfer.

Graphical Abstract

Chin. J. Catal., 2020, 41: 122–130 doi: S1872-2067(19)63490-X

The embedded CuInS₂ into hollow-concave carbon nitride for photocatalytic H₂O splitting into H₂ with S-scheme principle

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S-scheme principle for water splitting into H₂ over CuInS₂@C₃N₄ with directional charge-transfer under the effect of an apparent potential difference of the hollow-concave C₃N₄ caused by deviating the sp²-hybridized structure of its tri-s-triazine component from the two-dimensional plane.

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基于S-型光催化机制CuInS₂内嵌中空凹面氮化碳光催化分解H₂O制H₂

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摘要: 光催化分解H₂O合成H₂是绿色可再生的太阳能光子能量转换策略之一。目前, 增强光催化材料对太阳能光子的捕获并将之有效利用仍然是一个具有挑战性的课题。光催化分解H₂O反应包括三个过程: 太阳能光子能量促使光生电子在半导体材料带隙中的跃迁; 光生电子定向传输; 光生电子与吸附在半导体材料表面的H₂O分子发生反应。第一过程需要强的太阳光子捕获能力以产生足够的光生载流子; 第二、三过程在动力学上反映了光生载流子在各个竞争过程中能否有效利用的问题, 如光生电子迁移与H₂O作用的速度很慢(~μs), 而电子与空穴的复合速度快(~ps)。目前研究者很难协调半导体材料的电学和光学特性以满足光生载流子在热力学和动力学两方面的要求。g-C₃N₄是由C、N原子通过sp²杂化组成的二维π共轭体系。当g-C₃N₄结构偏离二维平面时, 共轭体系的π电子由凹面迁移到凸面, 促使凹、凸面形成表观电势差, 有利于电子的定向传输。本文通过卷曲sp²杂化离域均三嗪体系偏离二维平面, 得到空心凹面g-C₃N₄结构, 便捷地优化了半导体的电子结构。将CuInS₂嵌入生长于空心g-C₃N₄的凹面, 所构成的半导体光催化材料CuInS₂@C₃N₄展现了增强的光捕获能力, 以及电子定向传输转移能力。结合XPS、光电流测试、电化学阻抗谱、稳态及瞬态荧光等表征手段揭示空心g-C₃N₄凹、凸面表观电势差驱动光生电子以S-型光催化作用机制从CuInS₂的Cu 2p向g-C₃N₄的N 1s的路径转移。因而, 所构建的CuInS₂@C₃N₄在可见光激发下产氢效率提高到373 μmol·h⁻¹·g⁻¹, 其产氢效率分别是二维平面g-C₃N₄负载1 wt%Pt和3 wt%Pd效率的1.57倍和1.35倍, 表明空心g-C₃N₄凹、凸面电势差可以显著地促进光生电子分离和利用率, 从而提高光催化分解水制氢效率。本文可增强g-C₃N₄的可持续太阳能转换性能, 也适用于其他半导体材料以替代贵金属光催化体系, 降低光催化产氢技术成本, 促进光催化技术的应用。

关键词: 空心氮化碳; 产氢; 太阳光吸收; 电子定向传输; 表观电势差

收稿日期: 2019-07-01. 接受日期: 2019-07-24. 出版日期: 2020-01-05.

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基金来源: 国家自然科学基金(21871155); 宁波大学王宽城教育基金; 宁波市泛3315计划.

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