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Article

Rational design of ternary NiS/CQDs/ZnIn₂S₄ nanocomposites as efficient noble-metal-free photocatalyst for hydrogen evolution under visible light

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ABSTRACT

The NiS/CQDs nanocomposite (CQDs represents carbon quantum dots), with a mass ratio of NiS/CQDs to be 1.19:1 based on the ICP result, was obtained via a facile hydrothermal method from a mixture of CQDs, Ni(OAc)₂ and Na₂S. The self-assembly of ZnIn₂S₄ microspheres on the surface of NiS/CQDs was realized under microwave conditions to obtain a ternary NiS/CQDs/ZnIn₂S₄ nanocomposite. The as-obtained NiS/CQDs/ZnIn₂S₄ nanocomposite was fully characterized, and its photocatalytic hydrogen evolution under visible light irradiation was investigated. The ternary NiS/CQDs/ZnIn₂S₄ nanocomposite showed superior photocatalytic activity for hydrogen evolution than ternary CQDs/NiS/ZnIn₂S₄, which was obtained by deposition of NiS in the preformed CQDs/ZnIn₂S₄. The superior photocatalytic performance of ternary NiS/CQDs/ZnIn₂S₄ is ascribed to the introduction of CQDs, which act as a bridge to promote the vectorial transfer of photo-generated electrons from ZnIn₂S₄ to NiS. This result suggests that the rational design and fabrication of ternary CQDs-based systems are important for the efficient photocatalytic hydrogen evolution. This study provides a strategy for developing highly efficient noble-metal-free photocatalysts for hydrogen evolution using CQDs as a bridge to promote the charge transfer in the nanocomposite.

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1. Introduction

Semiconductor-based photocatalytic hydrogen evolution can convert and store solar energy in the form of clean hydrogen and is believed to be one of the most promising strategies to tackle the global energy shortage and environmental pollution [1,2]. Ever since the pioneer work by Fujishima and Honda [3] on a TiO₂-based photoelectrochemical cell for hydrogen evolution, great efforts have been devoted to the development of semiconductors for photocatalytic hydrogen evolution. A variety of semiconductor-based photocatalysts have been de-

veloped for hydrogen evolution under visible light during the past two decades [4–9]. Among them, metal sulfides are promising photocatalysts due to their lower band gaps, which fall in the visible light region [2,10–12]. As a ternary chalcogenide, hexagonal ZnIn₂S₄ has attracted extensive interest in photocatalysis owing to its suitable band gap of ca. 2.4 eV and considerable stability [13–17]. However, the photocatalytic activity for hydrogen evolution over bare ZnIn₂S₄ is low because of the poor separation efficiency and low migration ability of the photoexcited charge carriers.

For semiconductor-based photocatalytic hydrogen evolu-

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tion systems, cocatalysts are usually required because cocatalysts can provide catalytic active sites by lowering the overpotential for hydrogen evolution over the semiconductor photocatalysts [11,18]. Although noble metals are usually used as cocatalysts for hydrogen evolution, their high price and scarcity restrict their practical applications [19]. Recently, using of inexpensive layered transition metal chalcogenides, like MoS₂ [20], WS₂ [21] and CoS [22], as noble-metal-free cocatalysts to promote the semiconductor-based photocatalytic hydrogen evolution has been extensively studied. As a p-type semiconductor, NiS is well known to be a good electrocatalyst for cathodic hydrogen evolution in water electrolysis [23]. The application of NiS as a cocatalyst to enhance the photocatalytic hydrogen evolution over CdS has been reported [24]. Our previous studies also revealed that NiS can be an appropriate cocatalyst for ZnIn₂S₄, and the hydrothermally prepared NiS/ZnIn₂S₄ shows superior photocatalytic activity for hydrogen evolution under visible light [25].

A fast electron transfer from the photo-excited semiconductor to the cocatalyst is important for the efficient photocatalytic hydrogen evolution, which depends not only on the relative band positions of the semiconductor and the cocatalyst, but also on their interface as well as the electronic conductivity of the nanocomposite [26,27]. It is therefore anticipated that the introduction of a component with high electronic conductivity to promote the charge transfer in the semiconductor-cocatalyst system should enhance its photocatalytic activity for hydrogen evolution. Carbon quantum dots (CQDs), a novel class of nanocarbons, has shown many potentials in a variety of fields, ascribing to their fascinating properties [28–32]. Due to their good electronic conductivity, CQDs have been used in photocatalysis to fabricate binary semiconductor/CQDs nanocomposites to promote the charge separation in semiconductor-based photocatalysts [33–35]. It is therefore anticipated that the introduction of CQDs as a bridge into the binary NiS/ZnIn₂S₄ system would promote the charge transfer from ZnIn₂S₄ to NiS, which could result in a further improvement of its performance for photocatalytic hydrogen evolution.

Herein, we reported the rational design and fabrication of the ternary NiS/CQDs/ZnIn₂S₄ nanocomposite as a superior noble-metal-free photocatalyst for hydrogen evolution under visible light. The self-assembly of ZnIn₂S₄ microspheres in the presence of preformed NiS/CQDs resulted in the efficient ternary NiS/CQDs/ZnIn₂S₄ nanocomposite for hydrogen evolution (Scheme 1), in which CQDs act as a bridge to promote the electron transfer from photo-excited ZnIn₂S₄ to NiS. The photocatalytic performance over ternary NiS/CQDs/ZnIn₂S₄ is much higher than ternary CQDs/NiS/ZnIn₂S₄, which was obtained via deposition of NiS on the preformed CQDs/ZnIn₂S₄. This study provides a strategy to promote the photocatalytic hydrogen evolution over semiconductor-based photocatalysts by incorporating CQDs.

2. Experimental

2.1. Catalyst preparation

All the reagents were commercially available and used without further purification. The CQDs was prepared by heating citric acid according to the literature [36]. For the preparation of NiS/CQDs nanocomposite, a mixture of CQDs (29 mg) and Ni(OAc)₂ (56 mg, 0.32 mmol) was dispersed in a degassed *N,N*-dimethylformamide (DMF) (16 mL). Then 1.6 mL Na₂S (0.2 mol/L) aqueous solution was added. Afterwards, the resultant solution was stirred at 90 °C in an oil bath for 4 h. To synthesize NiS/CQDs/ZnIn₂S₄ nanocomposites, different amounts of the as-obtained NiS/CQDs were dispersed in water (60 mL) and ultrasonicated for 10 min. Then ZnCl₂·6H₂O (0.136 g, 1.0 mmol) and InCl₃·4H₂O (0.586 g, 2.0 mmol) were added to the above suspension containing NiS/CQDs nanocomposite under vigorous stirring. Thioacetamide (TAA, 0.3 g, 4.0 mmol) was added and the resultant suspension was sealed in a Teflon-lined double-walled digestion vessel and reacted at 120 °C for 60 min using a microwave system (Ethos A, Milestone, Italy). After reaction, the resultant product was collected by centrifugation, washed with deionized water and absolute ethanol, and dried at 60 °C. The NiS/CQDs/ZnIn₂S₄ nanocomposites with different amounts of NiS/CQDs were denoted as *x* wt% NiS/CQDs/ZnIn₂S₄, in which *x* = 0.5, 1.0, 1.5, 2.0 based on the ratio in the feed materials.

Bare ZnIn₂S₄ was synthesized from ZnCl₂·6H₂O, InCl₃·4H₂O and TAA under microwave heating at 120 °C for 60 min. NiS/ZnIn₂S₄ and CQDs/ZnIn₂S₄ were prepared from ZnCl₂·6H₂O, InCl₃·4H₂O and TAA in the presence of preformed NiS and CQDs, respectively, under microwave heating at 120 °C. The ternary CQDs/NiS/ZnIn₂S₄ nanocomposite was prepared by deposition of NiS in the presence of preformed CQDs/ZnIn₂S₄ under microwave treatment.

2.2. Catalyst characterization

X-ray diffraction (XRD) of the as-obtained products was carried out on a D8 Advance X-ray diffractometer (Bruker, Germany) using Cu K_α (λ = 1.5406 Å) radiation at a voltage of 40 kV and 40 mA. XRD patterns were scanned over the angular range of 10°–70° (2 θ) with a step size of 0.02°. IR analyses were carried out on a Nicolet IS50 FT-IR spectrometer. X-ray photoelectron spectroscopy (XPS) measurements were performed on a PHI Quantum 2000 XPS system (PHI, USA) with a monochromatic Al K_α source and a charge neutralizer. All the binding energies were referenced to the C 1s peak at 284.6 eV of the surface adventitious carbon. The morphology of the

Scheme 1. Illustration of the formation of the NiS/CQDs/ZnIn₂S₄ nanocomposite.

samples was obtained by a field emission scanning electron microscopy (SEM, JSM-6700F). Transmission electron microscopy (TEM) and high-resolution transmission electron microscopy (HRTEM) images were obtained in a JEOL model JEM 2010 EX instrument at an accelerating voltage of 200 kV. The powder particles were supported on a carbon film coated on a 3 mm diameter fine-mesh copper grid. The sample suspension in ethanol was sonicated and a drop was dripped on the support film. UV-visible diffuse reflectance spectra (UV-DRS) of the powders were obtained with BaSO₄ used as a reflectance standard in the UV-visible diffuse reflectance experiment. Electrochemical impedance spectroscopy (EIS) was measured on an electrochemical analyzer (Zahner, Germany) in a standard three-electrode system using the prepared samples as the working electrodes with an active area of ca. 0.25 cm², a Pt wire as the counter electrode, and Ag/AgCl (saturated KCl) as a reference electrode. The electrolyte was a mixed aqueous solution containing K₃[Fe(CN)₆] (1 mmol/L), K₄[Fe(CN)₆] (1 mmol/L) and KCl (0.1 mol/L). Impedance data were fitted with ZSimpWin software (Princeton Applied Research). Inductively coupled optical emission spectrometry (ICP-OES) was performed on Optima 8000 (PerkinElmer). Before the ICP-OES experiment, the solid sample was digested in a mixture of HNO₃ and Milli-Q water.

2.3. Photocatalytic hydrogen evolution

Photocatalytic experiments for hydrogen evolution were carried out in a closed gas circulation and evacuation system fitted with a top Pyrex window. 50 mg of photocatalyst was dispersed in 100 mL of aqueous solution containing 10 mL triethanolamine (TEOA) as sacrificial reagent. The suspension was irradiated with a 300 W Xe lamp equipped with a 420 nm cut-off filter to provide the visible light irradiation. The reactant solution was maintained at room temperature by a flow of cooling water during the photocatalytic reaction. The amount of hydrogen evolved was determined with an on-line gas chromatograph equipped with a TCD detector.

3. Results and discussion

The NiS/CQDs nanocomposite was obtained by a hydrothermal treatment in a mixture of CQDs, Ni(OAc)₂ and Na₂S. The XRD of the as-obtained product shows characteristic peaks at 30.1°, 34.7°, 46.0° and 53.5° assignable to (100), (101), (102) and (110) crystallographic planes of hexagonal NiS (JCPDS No. 75-0613), indicating the formation of NiS nanoparticles during the hydrothermal treatment (Fig. 1(a)) [37]. The FT-IR spectrum shows two peaks at 1393 and 1583 cm⁻¹, corresponding to symmetric and asymmetric stretches of the carboxylate groups of CQDs. As compared with those observed over bare CQDs (1388 and 1576 cm⁻¹), these peaks shift slightly to longer wavelength, suggesting the existence of interaction between NiS and CQDs (Fig. 2(a) and (b)) [38]. It is believed that the rich hydroxyl and carboxylate groups on the CQDs surface can act as the adsorption sites for Ni²⁺. The reaction of these surface adsorbed Ni²⁺ with S²⁻ to form NiS

Fig. 1. XRD patterns of (a) NiS/CQDs, (b) bare ZnIn₂S₄ and (c) 1.0 wt% NiS/CQDs/ZnIn₂S₄ nanocomposite.

Fig. 2. FT-IR spectra of (a) CQDs, (b) NiS/CQDs and (c) 1.0 wt% NiS/CQDs/ZnIn₂S₄ nanocomposite.

nuclei, which further grow up to form the resultant NiS nanoparticles on the surface of CQDs. The mass ratio of NiS to CQDs in the as-obtained NiS/CQDs was determined to be 1.19:1 by ICP-OES.

The as-obtained NiS/CQDs nanocomposite was further used to fabricate ternary NiS/CQDs/ZnIn₂S₄ nanocomposites with different amounts of NiS/CQDs. The rich functional groups on the surface of CQDs act as adsorption sites for cationic Zn²⁺ and In³⁺ ions, which react with S²⁻ anions provided by the decomposition of TAA under microwave conditions to form ZnIn₂S₄ nuclei deposited on CQDs surface. The ZnIn₂S₄ nuclei grow up to form ternary the NiS/CQDs/ZnIn₂S₄ nanocomposite [39]. The mass ratio of NiS:CQDs:ZnIn₂S₄ in the as-obtained 1.0 wt% NiS/CQDs/ZnIn₂S₄ nanocomposite was determined to be ca. 1.19:1:200 based on ICP-OES measurements. The XRD pattern of the as-obtained ternary NiS/CQDs/ZnIn₂S₄ nanocomposite (take 1.0 wt% NiS/CQDs/ZnIn₂S₄ for example) shows characteristic peaks of hexagonal ZnIn₂S₄ (JCPDS No. 65-2023) at 2θ values of 21.5°, 27.6°, 30.4°, 39.8°, 47.2°, 52.4° and 55.6°, indicating that hexagonal ZnIn₂S₄ has been successfully obtained (Fig. 1(b) and 1(c)) [40,41]. Although no characteristic peaks assignable to either NiS or CQDs are observed in the XRD patterns of the resultant product due to their low amount in the nanocomposite, the presence of CQDs is evidenced from the FT-IR spectrum of 1.0 wt%

NiS/CQDs/ZnIn₂S₄ nanocomposite, by showing peaks at 1393 and 1586 cm⁻¹, corresponding to symmetric and asymmetric stretches of the carboxylate groups (Fig. 2(c)) [38]. In addition, the XPS spectrum of the 1.0 wt% NiS/CQDs/ZnIn₂S₄ nanocomposite in the C 1s region shows three peaks at 284.6, 286.5 and 288.3 eV, ascribable to the *sp*² hybridized carbon (C–C), epoxy/hydroxyl carbon (C–O) and carboxy carbon (O–C=O), respectively, further confirming the presence of CQDs in the NiS/CQDs/ZnIn₂S₄ nanocomposite (Fig. 3(a)) [42]. The XPS spectrum in the Ni 2p region shows two sets of peaks. The two peaks at 855.2 and 872.5 eV can be assigned to Ni²⁺ 2p_{3/2} and Ni²⁺ 2p_{1/2} in NiS, while the other two small peaks at 856.8 and 874.2 eV can be assigned to Ni²⁺ 2p_{3/2} and Ni²⁺ 2p_{1/2} coordinated with O, suggesting the interaction between NiS and CQDs (Fig. 3(b)) [43]. The XPS spectrum of NiS/CQDs/ZnIn₂S₄ in the S 2p region shows a broad peak, which can be deconvoluted to two sets of S²⁻, with the peaks at 162.3 and 163.5 eV assigned to S²⁻ in NiS, while those at 161.8 and 163.0 eV to S²⁻ in ZnIn₂S₄, by comparison with bare ZnIn₂S₄ (Fig. 3(c)) [44,45]. The XPS in the O 1s region can also be deconvoluted to three peaks, with the peak at 530.7 eV ascribed to O²⁻ in Ni–O bonds, in consistent with the XPS spectrum in the Ni 2p region, while the peaks at 531.2 and 532.1 eV assigned to the C–O and O–H bonds, respectively, further confirming the presence of the NiS/CQDs [42]. Peaks in Zn²⁺ 2p (1022.4 eV and 1045.8 eV) and In³⁺ 3d (445.1 and 452.5 eV) regions are also observed. However, as compared with bare ZnIn₂S₄, all the peaks shift to higher binding energy, indicating the existence of strong interaction between hexagonal ZnIn₂S₄ and NiS/CQDs (Fig. 3(c), (e) and (f)) [46].

The SEM image of 1.0 wt% NiS/CQDs/ZnIn₂S₄ nanocomposite shows that it consists of flower-like microspheres with an average size of 3.0 μm, assembled by a

large number of interwoven ultrathin nanosheets (Fig. 4(a)), similar to the morphology of bare ZnIn₂S₄ (Supporting Information Fig. S1). The mechanism for the formation of hexagonal ZnIn₂S₄ flower-like microspheres has been well elucidated previously and is believed to be driven by the anisotropy growth tendency of hexagonal ZnIn₂S₄, whose nuclei are prone to form nanosheets and a further self-assembly resulting in the flower-like microspheres [47]. The TEM image shows that nanoparticles of NiS/CQDs with a dimension of ca. 30 nm are deposited on ZnIn₂S₄ nanosheets (Fig. 4(b)). In addition to lattice fringes of 0.32 nm, which corresponds to (102) crystallographic planes of hexagonal ZnIn₂S₄, clear lattice fringes of 0.29 nm and 0.22 nm, which can be assigned to the (100) plane of NiS and (100) plane of graphite CQDs, respectively, can also be observed in the HRTEM image of the 1.0 wt% NiS/CQDs/ZnIn₂S₄ nanocomposite (Fig. 4(c)) [48,49]. The HRTEM image of ternary NiS/CQDs/ZnIn₂S₄ nanocomposite clearly shows CQDs contact with both ZnIn₂S₄ and NiS, indicating that CQDs act as a bridge to connect hexagonal ZnIn₂S₄ and NiS (Fig. 4(c)). On the contrary, even though CQDs and NiS are also deposited on the surface of ZnIn₂S₄ in the CQDs/NiS/ZnIn₂S₄ nanocomposite obtained via the deposition of NiS on the preformed CQDs/ZnIn₂S₄, no contact between CQDs and NiS is observed (Supporting Information Fig. S2). It is anticipated that the transfer of the photo-generated electrons from ZnIn₂S₄ to NiS is more facilitated over the NiS/CQDs/ZnIn₂S₄ nanocomposite as compared with that over CQDs/NiS/ZnIn₂S₄ nanocomposite due to the existence of a bridge of CQDs with excellent electronic conducting properties.

The UV-vis DRS of NiS/CQDs/ZnIn₂S₄ nanocomposite is shown in Fig. 5. As compared with bare ZnIn₂S₄, the incorporation of NiS/CQDs nanocomposite enhances the light

Fig. 3. XPS spectra of 1.0 wt% NiS/CQDs/ZnIn₂S₄ and ZnIn₂S₄ nanocomposite in (a) C 1s, (b) Ni 2p, (c) S 2p, (d) O 1s, (e) Zn 2p and (f) In 3d regions.

Fig. 4. (a) SEM, (b) TEM and (c) HRTEM images of 1.0 wt% NiS/CQDs/ZnIn₂S₄ nanocomposite.

absorption of ZnIn₂S₄ in 500–800 nm regions, in agreement with the color change from yellow for bare ZnIn₂S₄ to light green for NiS/CQDs/ZnIn₂S₄ nanocomposite [50].

The photocatalytic performance of the NiS/CQDs/ZnIn₂S₄ nanocomposite was investigated under visible light irradiation using TEOA as the sacrificial agent and was compared with that over NiS/CQDs, bare ZnIn₂S₄, CQDs/ZnIn₂S₄ and NiS/ZnIn₂S₄ (Fig. 6). Hydrogen evolved over irradiated NiS/CQDs was almost negligible, even though previous studies have revealed that CQDs can act as a photocatalyst for hydrogen evolution in the presence of EDTA as a sacrificial agent [38]. However, in our case, the photocatalytic activity of NiS/CQDs is much lower as compared with semiconductor-based photocatalysts like ZnIn₂S₄ (Fig. 6(a)). Bare ZnIn₂S₄ shows low activity for photocatalytic hydrogen evolution under visible light irradiation, with 26 μ mol of hydrogen evolved in 5 h (Fig. 6(b)). The introduction of 1.0 wt% CQDs into ZnIn₂S₄ resulted in an improvement of the photocatalytic activity, with 61 μ mol of hydrogen evolved in 5 h over 1.0 wt% CQDs/ZnIn₂S₄ (Fig. 6(c)). As previous studies indicated, NiS can be a suitable cocatalyst for ZnIn₂S₄, and improved photocatalytic activity for hydrogen evolution was observed over 1.0 wt% NiS/ZnIn₂S₄, with 88 μ mol of hydrogen evolved in 5 h (Fig. 6(d)) [25]. A significantly enhanced photocatalytic activity was observed over the 1.0 wt% NiS/CQDs/ZnIn₂S₄ nanocomposite, with 142 μ mol of hydrogen evolved after irradiated for 5 h, 1.6 and 2.3 times that over 1.0 wt% NiS/ZnIn₂S₄ and 1.0 wt% CQDs/ZnIn₂S₄, respectively (Fig. 6(e)). The amount of hydrogen evolved over the ternary 1.0 wt% NiS/CQDs/ZnIn₂S₄ nanocomposite

increased linearly with the irradiation time, indicating its stability during the photocatalytic hydrogen evolution. In addition, no obvious loss of the activity was observed after three cycling tests, and the catalyst after three runs showed similar XRD patterns as that of fresh NiS/CQDs/ZnIn₂S₄ nanocomposite (Fig. 7).

The amount of NiS/CQDs in the ternary NiS/CQDs/ZnIn₂S₄ nanocomposite also influenced its photocatalytic activity. It was found that the photocatalytic activity was first improved with the increase amount of NiS/CQDs, with the optimum performance observed over the 1.5 wt% NiS/CQDs/ZnIn₂S₄ nanocomposite, by showing 201 μ mol of hydrogen evolved in 5 h (Fig. 8). However, a further increase of the amount of NiS/CQDs in the ternary NiS/CQDs/ZnIn₂S₄ nanocomposite led to a decrease of its performance.

The controlled experiment revealed that a mechanical mixture of 1.0 wt% NiS/CQDs and ZnIn₂S₄ showed an inferior performance for hydrogen evolution, with only 64 μ mol of hydrogen generated in 5 h, as compared with 142 μ mol of hydrogen evolved over ternary 1.0 wt% NiS/CQDs/ZnIn₂S₄ nanocomposite, indicating that the effectiveness of the electron transfer from ZnIn₂S₄ to NiS via CQDs is influenced by the interaction between the three components. In addition, to our expectation, ternary 1.0 wt% CQDs/NiS/ZnIn₂S₄ obtained via the deposition of NiS on the preformed CQDs/ZnIn₂S₄ also showed a lower photocatalytic activity for hydrogen evolution, with only 105 μ mol of hydrogen evolved in 5 h (Fig. 9). This

Fig. 5. UV-vis spectra of bare ZnIn₂S₄, 1.0 wt% CQDs/ZnIn₂S₄ and 1.0 wt% NiS/CQDs/ZnIn₂S₄ nanocomposite.

Fig. 6. Time-dependent hydrogen evolution over (a) NiS/CQDs, (b) bare ZnIn₂S₄, (c) 1.0 wt% CQDs/ZnIn₂S₄, (d) 1.0 wt% NiS/ZnIn₂S₄ and (e) 1.0 wt% NiS/CQDs/ZnIn₂S₄ nanocomposite. Reaction conditions: catalyst, 0.05 g; 100 mL aqueous solutions containing 10 mL TEOA.

Fig. 7. (a) Cycling tests of photocatalytic hydrogen evolution over 1.0 wt% NiS/CQDs/ZnIn₂S₄ nanocomposite; (b) XRD patterns of 1.0 wt% NiS/CQDs/ZnIn₂S₄ nanocomposite before and after photocatalytic reaction.

result confirms that the transfer of photo-generated electrons from ZnIn₂S₄ to NiS is more facilitated over the NiS/CQDs/ZnIn₂S₄ nanocomposite than over the CQDs/NiS/ZnIn₂S₄ nanocomposite. Unlike that in NiS/CQDs/ZnIn₂S₄, most of CQDs in CQDs/NiS/ZnIn₂S₄ do not directly contact with NiS, which makes it not as efficient as that in NiS/CQDs/ZnIn₂S₄ to promote the electron transfer from ZnIn₂S₄ to NiS. The superior charge transfer in the NiS/CQDs/ZnIn₂S₄ nanocomposite was evidenced from the electrochemical impedance spectra (EIS) analysis by showing a smaller semicircle as compared with that of bare ZnIn₂S₄, NiS/ZnIn₂S₄ and CQDs/NiS/ZnIn₂S₄ nanocomposite (Fig. 10) [51]. These results indicate that the rational design of the ternary CQDs-based system to enable CQDs to act as a bridge to promote the vectorial transfer of the photo-generated electrons from the semiconductor to the cocatalyst is important for realization of efficient photocatalytic hydrogen evolution. Therefore, the mechanism for the superior photocatalytic hydrogen evolution over the ternary NiS/CQDs/ZnIn₂S₄ nanocomposite under visible light irradiation is shown in Scheme 2. In the ternary NiS/CQDs/ZnIn₂S₄ nanocomposite, electrons and holes are generated when ZnIn₂S₄ is irradiated with visible light. A directional transfer of the photo-generated

electrons from ZnIn₂S₄ to NiS, the cocatalyst for hydrogen evolution, can be promoted by CQDs acting as an electron mediator, ascribed to their excellent electronic conductivity [52,53].

Fig. 9. The amount of hydrogen evolved over (a) 1.0 wt% NiS/CQDs/ZnIn₂S₄, (b) 1.0 wt% NiS/CQDs+ZnIn₂S₄ and (c) 1.0 wt% CQDs/NiS/ZnIn₂S₄ nanocomposite in 5 h. Reaction conditions: catalyst, 0.05 g; 100 mL aqueous solutions containing 10 mL TEOA.

Fig. 8. Photocatalytic hydrogen evolution rate over NiS/CQDs/ZnIn₂S₄ nanocomposites with different amounts of NiS/CQDs. Reaction conditions: catalyst, 0.05 g; 100 mL aqueous solutions containing 10 mL TEOA.

Fig. 10. Nyquist plots of experimental impedance data for ZnIn₂S₄, 1.0 wt% NiS/ZnIn₂S₄, 1.0 wt% CQDs/NiS/ZnIn₂S₄ and 1.0 wt% NiS/CQDs/ZnIn₂S₄ nanocomposite.

Scheme 2. Proposed mechanism for photocatalytic hydrogen generation over NiS/CQDs/ZnIn₂S₄ nanocomposite under visible light irradiation.

4. Conclusions

In summary, ternary NiS/CQDs/ZnIn₂S₄ nanocomposites which show superior photocatalytic hydrogen under visible light were obtained via self-assembly of ZnIn₂S₄ in the presence of preformed NiS/CQDs. The superior photocatalytic performance observed over ternary NiS/CQDs/ZnIn₂S₄ nanocomposite can be ascribed to the presence of CQDs acting as a bridge to promote the vectorial transfer of the photo-generated electrons from ZnIn₂S₄ to NiS. This study highlights the great potential of using CQDs for fabricating highly efficient ternary nanocomposites for photocatalytic hydrogen evolution.

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Graphical Abstract

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Rational design of ternary NiS/CQDs/ZnIn₂S₄ nanocomposites as efficient noble-metal-free photocatalyst for hydrogen evolution under visible light

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CQDs act as a bridge to promote the charge transfer from ZnIn₂S₄ to NiS in the ternary NiS/CQDs/ZnIn₂S₄ nanocomposite.

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三元NiS/CQDs/ZnIn₂S₄光催化体系的合理设计及其产氢性能

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摘要: 氢气是一种清洁能源, 利用半导体光催化技术将水转化成氢气是解决全球能源危机和环境污染问题的有效途径之一。开发高效的光催化体系以实现水分解产氢是目前能源领域中的一个研究热点。六方相的ZnIn₂S₄是一种三元金属硫化物, 因其具有能够吸收可见光的窄带隙(约2.4 eV)和良好的化学稳定性, 在光催化产氢方面得到了较好应用。在半导体光催化产氢体系中, 往往需要加入助催化剂来提供产氢活性位并降低产氢反应的过电位, 这种半导体/助催化剂体系中光催化产氢效率不仅取决于助催化剂的组成和结构, 还受二者界面之间光生电子传输效率的影响。我们课题组前期研究发现, NiS作为一种廉价的非贵金属助催化剂能够提高ZnIn₂S₄在可见光下的光催化产氢活性。考虑到碳量子点(CQDs)是一种具有良好导电能力的纳米材料, 并已被负载于半导体光催化剂上来促进半导体表面光生电子的传输, 本文将CQDs作为光生电子传输的“桥梁”引入到NiS/ZnIn₂S₄体系中, 用来促进光生电子从ZnIn₂S₄到NiS的定向传输, 从而提高其光催化产氢效率。

实验首先合成NiS/CQDs复合材料, 然后在其存在下进行ZnIn₂S₄的自组装制得NiS/CQDs/ZnIn₂S₄。利用X射线粉末衍射、扫描电镜、透射电镜、傅立叶红外光谱、X射线光电子能谱和紫外-可见漫反射光谱对催化剂的组成、结构及光学性质进行了详细表征, 考察了其在可见光下以三乙醇胺(TEOA)为牺牲剂时的光催化分解水产氢性能。结果表明, 含有CQDs的NiS/CQDs/ZnIn₂S₄光催化剂在光照5 h后的产氢总量达到142 μmol, 分别为相同条件下ZnIn₂S₄和NiS/ZnIn₂S₄产氢总量的5.5和1.6倍。相比于通过将NiS沉积在预先合成的CQDs/ZnIn₂S₄上所获得的CQDs/NiS/ZnIn₂S₄光催化剂, NiS/CQDs/ZnIn₂S₄显示出更优越的光催化产氢活性。TEM观测发现, 在NiS/CQDs/ZnIn₂S₄中CQDs与ZnIn₂S₄和NiS均有明显的接触, 表明CQDs作为“桥梁”连接了ZnIn₂S₄和NiS, 这种结构有利于光生电子由ZnIn₂S₄至NiS定向传输。而CQDs/NiS/ZnIn₂S₄光催化剂中的CQDs和NiS没有直接接触。电化学交流阻抗实验发现, NiS/CQDs/ZnIn₂S₄中电子的传导能力比CQDs/NiS/ZnIn₂S₄中的强, 说明相比于CQDs/NiS/ZnIn₂S₄, 在NiS/CQDs/ZnIn₂S₄中的CQDs更有效地促进了光生电子由ZnIn₂S₄至NiS定向传输。该研究提供了一种以CQDs作为促进光生电子定向传输的“桥梁”来构筑高效产氢光催化体系的方法。

关键词: 光催化; 制氢; 硫化镍; 碳量子点; ZnIn₂S₄

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