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MoS₂-coated microspheres of self-sensitized carbon nitride for efficient photocatalytic hydrogen generation under visible light irradiation

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Abstract: We have successfully coated the self-sensitized carbon nitride (SSCN) microspheres with a layer of MoS₂ through a facile one-pot hydrothermal method by using (NH₄)₂MoS₄ as the precursor. The resulted MoS₂-coated SSCN photocatalyst appears as a core-shell structure and exhibits enhanced visible-light activities for photocatalytic H₂ generation as compared to the un-coated SSCN and the standard g-C₃N₄ reference with MoS₂ coating. The photocatalytic test results suggest that the oligomeric s-triazine dyes on the SSCN surface can provide additional light-harvesting capability and photogenerated charge carriers, and the coated MoS₂ layer can serve as active sites for proton reduction towards H₂ evolution. This synergistic effect of surface triazine dyes and MoS₂ coating greatly promote the activity of carbon nitride microspheres for visible-light-driven H₂ generation. This work provides a new way of future development of low-cost noble-metal-free photocatalysts for efficient solar-driven hydrogen production.

Keywords: Graphitic carbon nitride; Molybdenum disulfide; Photocatalysis; hydrogen generation; dye sensitization

1. Introduction

The main challenges of current society in terms of energy and environment are production of renewable and clean energy with reduced emission of carbon dioxide. An attractive approach for producing hydrogen gas is water splitting by using photocatalysts under solar light irradiation [1-8]. Although scientists have made tremendous efforts on photocatalyst development over the past 40 years, it is still challenging to obtain suitable materials that can be commercialized for solar water splitting due to the following critical issues: (1) weak visible light response; (2) low quantum efficiency; (3) poor stability in photocatalytic reactions; (4) high cost. Recently, metal-free graphitic carbon nitride (g-C₃N₄) based materials are known as very promising photocatalysts because of strong visible-light absorption, tailorable electronic structures, low cost, and high stability [9-20].

The processes for solar hydrogen generation over a photocatalyst include absorption of visible light, separation and transport of photogenerated electrons and holes, and proton reduction into H₂ by the photogenerated electrons on the photocatalyst surface. In our previous studies, in order to promote visible-light activities of g-C₃N₄-based photocatalysts, we have developed a “self-sensitized” surface by oligomeric s-triazine-based dyes that extend light absorption range and provide additional photo-electrons for proton reduction[21, 22]. At this point, a catalyst for hydrogen evolution reaction (HER) is needed on the “self-sensitized” carbon nitride surface to for effective H₂ generation. MoS₂ is a well-known catalyst for hydrogen evolution reaction (HER) and water splitting [23-30]. However, in most previous reports, the deposition of MoS₂ catalysts was commonly achieved at high temperature (>210 °C) [25-27, 31]. There are very few reports on growth of MoS₂ catalysts on metal-free surfaces at mild conditions.

Herein, we reported a low-temperature hydrothermal approach to coat MoS₂ catalysts on the surface of self-sensitized carbon nitride (SSCN) microspheres to form SSCN@MoS₂ core-shell structures (Scheme 1).

The cooperation of the surface triazine-based oligomer (TBO) dyes with MoS₂ catalyst on the microsphere surface provides additional light-harvesting capability with adjacent active sites for H₂ evolution, which leads to promoted visible-light activities for photocatalytic H₂ generation comparing to the un-coated SSCN and the standard g-C₃N₄@MoS₂ reference. As such, this work provides a new way for the development of noble-metal-free photocatalysts for efficient solar-driven hydrogen production.

2. Experimental

2.1 Photocatalyst preparation

The self-sensitized carbon nitride (SSCN) microspheres were prepared via a solvothermal approach by using 1,3,5-triazine based precursors (cyanuric chloride and cyanuric acid with a molar ratio of 1.8) according to our previous work [21, 22]. Typically, the triazine precursors (150 mg) were added into 15 ml acetonitrile. The solution was subsequently transferred to a Teflon-lined autoclave (20 ml), which was sealed and kept at 200 °C for 20 hours. After reaction, the powder products were collected via centrifugation, washed with water and ethanol, and dried. For the preparation of control sample, the as-prepared SSCN powder was treated with the base Piranha solution (volume ratio of NH₃: H₂O₂: H₂O = 1:1:5) at 60 °C for 3 hours to remove the surface TBO dyes, and the obtained sample is denoted as SSCN-P.

The MoS₂ coated SSCN sample (SSCN@MoS₂) was prepared through a one-pot hydrothermal method by using (NH₄)₂MoS₄ as sulfur and molybdenum source. In a typical MoS₂ coating procedure, 30 mg of the SSCN sample was added into 10 mL water containing (NH₄)₂MoS₄ with stirring, followed by ultrasonication for 5 min. In this solution, a desired amount of (NH₄)₂MoS₄ (0.08, 0.393, 0.786, 1.56, 3.12, 7.8, 11.7 mg) was used to prepare samples with different MoS₂ contents (MoS₂ wt% = 0.2%, 1%, 2%, 4%, 8%, 20%, 30%, respectively). Thereafter, the solution was transferred to a Teflon-lined autoclave (20 ml), which was sealed and kept at 160 °C for 10 h. During this process, (NH₄)₂MoS₄ was decomposed into MoS₂ on the SSCN

surface. The final product powder was washed by water, and collected upon centrifugation followed by drying. The same MoS₂-coating method was used for treating the SSCN-P sample to obtain g-C₃N₄@MoS₂ with 4 wt% MoS₂. For comparison purpose, we prepared a reference sample (g-C₃N₄@MoS₂) by using standard g-C₃N₄ which was prepared by heating melamine at 500 °C for 6 hours. The same MoS₂-coating method was used for treating g-C₃N₄ to obtain g-C₃N₄@MoS₂ with 4 wt% MoS₂.

2.2 Characterizations

The XRD-6000 X-ray diffractometer (Cu K α source) was used to measure the XRD patterns at a scan rate of 2° min⁻¹. The JEOL JSM-7600F scanning electron microscope (SEM) was used for SEM imaging at an acceleration voltage of 5 kV. TEM images and elemental mapping were obtained by a JEOL JEM 2100 EX equipment at an accelerating voltage of 200 kV. The Fourier Transform Infrared (FTIR) spectra were obtained from the Perkin Elmer FTIR Spectrometer GX. The UV-Vis spectra were measured on a UV/vis/NIR spectrophotometer (Lambda 750, Perkin-Elmer, USA). The X-ray Photoelectron Spectroscopy (XPS) was performed on a VG ESCALAB 250 XPS system with a monochromatized Al K α X-ray source (15 kV, 200 W). The photoelectrochemical tests were carried out by using the conventional three-electrode electrochemical cell with a working electrode, a platinum wire counter electrode and a saturated calomel electrode (SCE) as reference electrode. In the photoelectrochemical test, the working electrode was immersed in the Na₂SO₄ solution (0.5 M) and irradiated by visible light ($\lambda > 420$ nm).

2.3 Photocatalytic H₂ generation

The photocatalytic H₂ generation test was performed by using a quartz reactor. Typically, the sample powder (10 mg) was suspended in an aqueous solution (10 mL) of triethanolamine (TEOA, 15 vol %). Prior to irradiation, the suspension was bubbled with nitrogen gas for 20 min to remove O₂ in the reactor. The visible light source was provided by using a MAX-302 xenon lamp (Asahi Spectra) with a UV cut-off filter

($\lambda > 420$ nm). The produced hydrogen amount was analyzed at one-hour interval by the gas chromatograph (Agilent 7890A) equipped with TCD detector.

3. Results and discussion

Fig. 1A shows the XRD patterns of the prepared samples. The SSCN sample shows a peak at 27.2° , which can be attributed to the stacking of conjugated hexatomic heterocycles [32-36]. No characteristic peak at $\sim 13^\circ$ was observed, suggesting that the in-planar repeat packing of heptazine units is imperfect and disordered in the SSCN sample [33, 34]. The structure of the unmodified SSCN sample has been clearly characterized in our previous work with detailed discussion on the identification of surface TBO dyes [21]. For the SSCN@MoS₂ sample, a new peak at 14.3° appears corresponding to (002) facet of orthorhombic phase MoS₂ [27, 29, 37, 38], and its intensity rises with increasing MoS₂ amount (Fig. 2A). This result indicates successful coating of MoS₂ on the SSCN surface. Nevertheless, the characteristic FTIR bands belonging to MoS₂ cannot be clearly distinguished in the FTIR spectra of SSCN@MoS₂ (Fig. 1B and 2B) due to the overlapping of signature FTIR peaks of SSCN and MoS₂. Fig. 1C compares the UV-visible absorption spectra of SSCN and SSCN@MoS₂. The pure SSCN sample appearing red exhibits a longer absorption threshold at 670 nm due to the self-sensitization [21, 22]. After MoS₂ coating, the SSCN@MoS₂ shows the enhanced tail absorption from 600 to 800 nm due to the absorption by MoS₂ (Fig. 2C).

Further, we have characterized the as-prepared SSCN@MoS₂ sample by SEM and TEM with elemental mapping. The SEM image of SSCN@MoS₂ (Fig. 3A and B) reveals a thin layer coating on the well-defined SSCN microspheres (0.8-1.6 μm in diameter). The TEM images (Fig. 3C and D) indicate that the thickness of coated layer is about 10-20 nm. The HRTEM image (Fig. 3E) shows a lattice fringe of 0.62 nm, corresponding to the (002) spacing of hexagonal MoS₂ [26, 27, 29, 37, 39-41]. The EDS pattern, line scan and elemental mapping (Fig. 3F-N) show the presence of carbon, nitrogen, oxygen and chlorine in the SSCN

microsphere as well as the sulfur and molybdenum elements corresponding to the MoS₂ coating. In particular, Mo and S are distributed on the surface of SSCN, as shown in Fig. 3K, L and N, indicating the formation of SSCN@MoS₂ core-shell structure.

X-ray photoelectron spectroscopy (XPS) was used to determine the composition of SSCN@MoS₂ and chemical state of different elements. The C 1s, N 1s, O 1s and Cl 2p XPS results (Fig.4) indicate that the composition and structure of the carbon nitride core and surface TBO dyes did not change upon MoS₂ coating [21, 22]. The high-resolution Mo 3d XPS spectrum (Fig. 5A) shows the binding energies of Mo 3d_{5/2} and Mo 3d_{3/2} peaks at 229.0 and 232.4 eV, respectively, which are typical values for Mo⁴⁺ in MoS₂ [30, 42-44]. The S 2p XPS spectrum (Fig. 5B) reveals the presence of both monosulfide S²⁻ (S 2p_{3/2} and S 2p_{1/2} at 161.7 and 162.8 eV) and disulfide S₂²⁻ (S 2p_{3/2} and S 2p_{1/2} at 163.2 and 164.2 eV), which are consistent with previous reports on MoS₂ [30, 42-46]. Moreover, the atomic ratio of Mo/S is estimated as ~1:2 according to the XPS result (Fig. 5), in good agreement with the nominal atomic composition of MoS₂. In short summary, the above characterization results prove that the MoS₂ layer has been successfully coated on the SSCN microsphere, which will be beneficial to photocatalytic H₂ evolution.

The photocatalytic activity of SSCN@MoS₂ for H₂ generation was tested in the TEOA solution (15 vol%) under visible light irradiation. Firstly, the effect of MoS₂ amount was evaluated. The obtained results (Fig. 6A) indicate that the MoS₂ coating can significantly enhance the photocatalytic H₂ generation rate of SSCN samples (almost no H₂ evolution over pure SSCN), and the photocatalytic activity of SSCN@MoS₂ depends on the quantity of MoS₂ coating with an optimal amount of 4.0 wt.%. The activity of the optimal sample is much higher than that of reference sample of g-C₃N₄@MoS₂ with the same MoS₂ coating amount (4.0 wt.%) as shown in Fig. 6B. When the MoS₂ loading is low, the photocatalytic H₂ generation rate was promoted with increasing amount of MoS₂ as active sites for HER. However, the excess MoS₂ coating would obstruct

the light absorption of the SSCN core, and consequently decrease the overall photocatalytic activity. As such, all of the MoS₂-coated samples were prepared with the MoS₂ coating amount of 4.0 wt.%.

In order to gain better understanding on the role of MoS₂ coating for enhanced photocatalytic H₂ evolution, we have applied a similar protocol to coat MoS₂ onto the SSCN-P sample which was obtained by treating SSCN with the base Piranha solution to remove the surface TBO dyes. The resulted sample is denoted as SSCN-P@MoS₂, and the characterizations results are shown in Fig. 7. The SSCN-P@MoS₂ sample exhibits significantly lower photocatalytic H₂ generation rate (0.24 $\mu\text{mol h}^{-1}$) as compared to SSCN@MoS₂ (0.91 $\mu\text{mol h}^{-1}$) as shown in Fig. 8A. Nevertheless, this activity is still much higher than that of pure SSCN (almost no H₂ evolution).

In addition, we have carried out photoelectrochemical tests in Na₂SO₄ solution (0.5 M). The photocurrent responses (Fig. 8B) of different samples, SSCN, SSCN-P, SSCN@MoS₂ and SSCN-P@MoS₂, follow the same trend as their photocatalytic H₂ generation rates. The stability of SSCN@MoS₂ under visible light irradiation was tested by the re-cycling test. As shown in Fig. 8C, the H₂ generation rate did not decrease after three cycles over three days, and the sample after recycling test showed no change in the XRD, FTIR and SEM analyses (Fig. 9), suggesting excellent stability of the SSCN@MoS₂ photocatalyst in the photocatalytic reaction.

All above test results imply that the surface TBO dyes can effectively harvest visible light and supply additional photogenerated electrons [21, 22], and meanwhile, the coated MoS₂ layer on the SSCN surface serves as active sites for proton reduction. Accordingly, we propose the synergistic effect of the MoS₂ coating and surface TBO dyes, resulting in promoted activities for photocatalytic H₂ generation over the SSCN@MoS₂ sample. The principle is depicted in Fig. 10. Upon excitation of SSCN@MoS₂ with visible light, the excited electrons of surface TBO dyes jump to the conduction band (CB) of carbon nitride

microsphere core, and then transport to the nearby coated MoS₂ for H⁺ reduction. Meanwhile, TEOA in the solution would consume the photogenerated holes and recover TBO dyes. In addition, the carbon nitride core can also be excited to supply active electrons which could transfer to the coated MoS₂ for H₂ generation. Thus both the carbon nitride core and surface TBO dyes of SSCN microspheres contribute to the visible-light-driven photocatalytic activity.

4. Conclusion

The MoS₂ coated self-sensitized carbon nitride (SSCN@MoS₂) microspheres with core-shell structures were prepared through a one-pot hydrothermal method by using (NH₄)₂MoS₄ as the precursor. The SSCN@MoS₂ photocatalyst exhibits promoted activities for visible-light-driven H₂ generation comparing to the pure SSCN, the SSCN-P@MoS₂ (without self-sensitization), and the standard g-C₃N₄@MoS₂ reference. The self-sensitization by surface TBO dyes can effectively harvests visible light and supply extra photogenerated charge carriers, and meanwhile, the coated MoS₂ layer on SSCN can serve as active sites for proton reduction towards H₂ evolution. This synergistic effect of surface TBO dyes and MoS₂ coating on the carbon nitride microspheres leads to the greatly enhanced activity for visible-light-driven H₂ generation.

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Figure captions

Scheme 1 Schematic illustration of the preparation procedure of MoS₂-coated SSCN (SSCN@MoS₂).

Fig. 1 (A) XRD patterns, (B) FTIR spectra, and (C) UV-visible adsorption spectra of MoS₂, SSCN and SSCN@MoS₂.

Fig. 2 (A) XRD patterns, (B) FTIR spectra, and (C) UV-visible absorption spectra of SSCN@MoS₂ with different MoS₂ content.

Fig. 3 (A and B) SEM images, (C and D) TEM and (E) HRTEM images, (F-M) element mapping and (N) line scan profile of SSCN@MoS₂.

Fig. 4 The high-resolution XPS spectra of C 1s (A), N 1s (B), O 1s (C), and Cl 2p (D) for SSCN@MoS₂.

Fig. 5 The high-resolution XPS spectra of Mo 3d (A) and S 2p (B) for SSCN@MoS₂.

Fig. 6 (A) Photocatalytic hydrogen evolution over SSCN@MoS₂ with different MoS₂ content under visible light irradiation ($\lambda > 420$ nm, 10 mg catalyst). (B) Photocatalytic hydrogen evolution over g-C₃N₄@MoS₂ and SSCN@MoS₂ under visible light irradiation ($\lambda > 420$ nm, 10 mg catalyst).

Fig. 7 (A) XRD patterns, (B) FTIR spectra, and (C) UV-visible absorption spectra of SSCN-P and SSCN-P@ MoS₂.

Fig. 8 (A) Photocatalytic hydrogen evolution over SSCN, SSCN@MoS₂, and SSCN-P@MoS₂ samples under visible light irradiation (10 mg sample, $\lambda > 420$ nm). (B) Photocurrent under irradiation ($\lambda > 420$ nm) in Na₂SO₄ solution (pH 7.0) of SSCN, SSCN-P, SSCN@MoS₂ and SSCN-P@MoS₂. (C) Cycling test of SSCN@MoS₂ for photocatalytic H₂ generation under visible light irradiation (60 mg sample, $\lambda > 420$ nm).

Fig. 9 (A) XRD patterns, (B) FTIR spectra, (C) SEM images of SSCN@MoS₂ sample before and after photocatalytic H₂ evolution.

Fig. 10 Schematic illustration of the proposed principle of photocatalytic H₂ evolution over SSCN@MoS₂ under visible light irradiation.

<Scheme 1>

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