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Significant Enhancement in Photocatalytic Hydrogen Evolution from Water by MoS₂ Nanosheet-coated ZnO Heterostructure Photocatalyst

Yong-Jun Yuan,*^a Fang Wang,^b Bin Hu,^b Hong-Wei Lu,*^a Zhen-Tao Yu,^b Zhi-Gang Zou^b

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Novel MoS_2 nanosheet-coated ZnO heterostructure photocatalyst was successfully synthesized via a simple hydrothermal method. The two-dimensional MoS_2 nanosheets were intimately deposited on ZnO surface to form an intimate function, which favors the charge-transfer and suppresses the recombination of the photogenerated electron-hole pairs between MoS_2 and ZnO, resulting in significantly enhanced

- ¹⁰ photocatalytic activity for hydrogen evolution. The photocatalytic activities of MoS_2 -ZnO composite photocatalysts with different MoS_2 contents for hydrogen production were systematically evaluated. The 1.00 wt% MoS_2 -ZnO photocatalyst shows the highest H₂ production rate of 768 µmol h⁻¹ g⁻¹ in presence of Na₂S and Na₂SO₃ as the sacrificial reagents, which is 14.8 times higher than that of pure ZnO. The photocatalytic activity of MoS_2 as a cocatalyst for H₂ evolution reaction is much higher than many noble
- ¹⁵ metals such as Pt, Rh, Ru and Au, suggesting that MoS₂ could act as a potential substitute for noble metals in photocatalytic H₂ production systems. This work presents a noble-metal-free, highly-efficient, and stable MoS₂ cocatalyst to suppress the recombination of electron-hole pairs of ZnO, resulting in enhanced photocatalytic hydrogen production activity.

Introduction

- ²⁰ The conversion of solar energy to hydrogen via photocatalytic water-splitting represents a promising solution for addressing both energy crisis and climate problem.¹⁻³ One of the key challenges for the application of such technology is the development of efficient photocatalysts. Over the past several ²⁵ decades, much effort has been undertaken to construct photocatalytic systems that based on semiconductor materials, such as metal oxides,⁴⁻⁶ sulfides,⁷⁻⁹ oxynitrides,^{10,11} phosphates,^{12,13} and organic polymers.¹⁴⁻¹⁸ Among those photocatalysts, nanostructured zinc oxide (ZnO) is a potential ³⁰ candidate because of its abundance, low-cost, nontoxicity, excellent stability and availability. However, the pure ZnO shows
- poor photocatalytic activity for hydrogen evolution and organic dye degradation, which could be assigned to the quick recombination of photogenerated electron-hole pairs before ³⁵ migrating to the surface for reactions.¹⁹⁻²¹ Loading of noble metal
- on ZnO surface to form ZnO-metal heterostructure is an effective method to suppress the recombination of electron-hole pairs and then raise the photocatalytic efficiency of ZnO. Numerous successful systems to evolve H₂ have been constructed utilizing Z_{PO} in combination with different aches reaches and Δr^{22}
- ⁴⁰ ZnO in combination with different noble metals, such as Ag, Pt,²³ and Au.²⁴ Due to the high cost of noble metals, it is highly

^a College of Materials and Enviromental Engineering, Hangzhou Dianzi University, Hangzhou, Zhejiang 310018, P.R. China. Email:yjyuan@hdu.edu.cn or luhongwei@hdu.edu.cn required to explore cocatalysts composed of earth-abundant elements for developing highly-efficient ZnO-based 50 photocatalysts.

The graphene-like MoS_2 is an excellent catalyst for both photochemical and electrochemical hydrogen evolution reaction, $^{25-28}$ which exhibits potentially wide application toward different semiconductors, such as TiO₂, 29 CdS, 30 ZnIn₂S₄, 31 CdSe, 32 and 55 C₃N₄.³³ Both computational and experimental results confirmed that the active sites of MoS₂ for hydrogen production reaction stemmed from the unsaturated sulfur atoms at the Mo $(10\overline{1}0)$ edge.34,35 Many studies have shown that the two-dimensional layered-structured MoS₂ with high exposure of the edges exhibits 60 much higher activity than those commonly used noble metals, such as Pt, Pd, Au, and Rh. 33,36 The layered MoS₂ not only serves as electron sink to suppress the recombination of electron-hole pairs, but also provides effective proton reduction sites, dramatically facilitates hydrogen evolution reaction. Therefore, 65 the two-dimensional MoS₂ was considered to be a promising alternative to noble metals as an efficient cocatalyst for photocatalytic H₂ production reaction because of its highefficiency, low-cost, nontoxicity, and excellent photostablility. It is expected that the hybridization of ZnO with layered MoS₂ 70 would reduce the recombination of electron-hole pairs, and increase the photocatalytic activity of ZnO. The MoS₂ modified ZnO composite photocatalyst has shown excellent activity for the photodegradation of organic dyes.^{37,38} However, to the best of our knowledge, no previous study regarding application of MoS₂-75 ZnO composite photocatalyst with layered MoS₂ nanosheets as the cocatalyst for hydrogen evolution has been reported to date.

In this study, for the first time, we report the synthesis of layered MoS_2 nanosheet-coated ZnO hydrid photocatalysts via a hydrothermal method for photocatalytic hydrogen production in

⁴⁵ ^b Ecomaterials and Renewable Energy Research Center (ERERC), College of Engineering and Applied Science, Nanjing University, Nanjing, Jiangsu 210093, P.R.China.

the presence of Na₂S and Na₂SO₃ as the sacrificial reagents. The photocatalytic hydrogen evolution activity over ZnO can be significantly enhanced by loading the layered MoS₂ as a cocatalyst, and the hydrogen evolution rate of MoS₂-ZnO hybrid ⁵ photocatalyst is higher than that of ZnO-based photocatalysts

- s photocatalyst is higher than that of ZhO-based photocatalysts loaded with Rh, Ru, Pt or Au as the cocatalyst. Moreover, the MoS₂-ZnO composites show excellent stability during the photocatalytic hydrogen evolution reaction. This study may provide a high potential of the developing of noble-metal-free,
- ¹⁰ highly-efficient, and stable ZnO-based photocatalysts for hydrogen production.

Experimental

Equipment

The nanoscale images of ZnO, MoS₂, and MoS₂-ZnO composites ¹⁵ were obtained by using field emission scanning electron microscope (FE-SEM) (NOVA NANOSEM230, USA) or transmission electron microscopy (TEM) (JEOL JEM-200CX, Japan). The Brunauer-Emmett-Teller (BET) surface areas of the samples were obtained by nitrogen absorption using a

- ²⁰ Micromeritics TriStar 300 absorption apparatus (USA). All samples were degassed at 200 °C for 10 h then measured at 77 K, and the BET surface areas were determined by a multipoint BET method used absorption data. The UV-visible (UV-vis) diffuse reflectance spectra of solid samples were measured with a UV-vis
- ²⁵ spectrophotometer (UV-2550, Shimadzu) at room temperature and transformed to the absorption spectra according to the Kubelka-Munk relationship. The X-ray Diffraction (XRD) spectroscopy were recorded on a D/MAX-2500 automatic powder diffractometer equipped with the graphite ³⁰ monochromatized Cu K α radiation ($\lambda = 0.1542$ nm) flux with
- ³⁰ monochromatized Cu K α radiation ($\lambda = 0.1542$ nm) flux with scan rate of 10° min⁻¹ and in the 2 θ range of 10-80° at 40 kV and 40 mA. The X-ray photoelectron spectroscopy (XPS) spectra were recorded on an ESCALAB 250 apparatus using monochromated Al $K\alpha$ radiation at 150 W in the pass energy ³⁵ model (PE = 50 eV).

Preparation of ZnO nanoparticles

All solvents were reagent grade quality, obtained commercially and used without further purification except as noted. ZnO nanoparticles were prepared by a modified hydrothermal route,⁴³ 40 where 1.14 g zinc acetate dehydrate and 1.40 g

- hexamethylenetetramine (HTMA) was dissolved into 40 mL deionized water, then the mixed solution was transferred into a 50 mL Teflon-lined sealed stainless steel autoclave and maintained at 120 °C for 12 h under autogenous pressure. After the reaction
- ⁴⁵ solution was cooled to room temperature, the resulting white solid product was isolated from the solution by centrifugation and washed with deionized water for three times.

Preparation of MoS2-ZnO composite photocatalysts

MoS₂-ZnO composite photocatalysts were synthesized through a ⁵⁰ simple hydrothermal method. The formation processes of 1.00 wt% MoS₂-ZnO (1.00 wt% of MoS₂) were described. Typically,

1.5 mg sodium molybdate dehydrate and 3.0 mg thiourea was dissolved together in 30 mL deionized water to form a transparent solution. Then 100 mg ZnO nanoparticles were added into the ⁵⁵ above reaction solution and stirred to form a suspension. The mixed solution was stirred and then transferred into a 50 mL autoclave, heated at 210 °C for 24 h, and then air-cooled to room temperature. The pale grey product was isolated from solution by centrifugation and subsequently washed with deionized water for ⁶⁰ three times, and the resulting product was dispersed in water by sonication and fully dried by lyophilization. Finally, the resulting powder was collected and heated in air at 350 °C for 4 h. The pure MoS₂ was obtained by the similar synthetic processes using sodium molybdate and thiourea as reactants.

65 Photocatalytic hydrogen production

The photocatalytic experiments were carried out in a Pyrex vessel, which was attached a closed gas-circulation and evacuation system. Photoreduction of H₂O to H₂ was performed by dispersing 100 mg of MoS₂-ZnO photocatalyst in a 100 mL ⁷⁰ aqueous solution containing 0.1 M Na₂S and 0.1 M Na₂SO₃ as the sacrificial reagents. The photocatalytic system was thoroughly degassed and irradiated by a 300 W Xe lamp. The temperature of the reaction solution was maintained at 25 °C by a flow of cooling water during the reaction. The evolved H₂ was in situ ⁷⁵ monitored periodically by an online gas chromatograph with a thermal conductivity detector (Shimadzu GC-8A, argon as a carrier gas and MS-5A column). The different noble metals, including Pt, Ru, Rh and Au, were loaded on ZnO in-situ by photoreduction method using H₂PtCl₄, RuCl₃, RhCl₃ and HAuCl₄ ⁸⁰ aqueous solutions, respectively.

Results and discussion



Fig.1 SEM (a) and TEM (b) images of ZnO nanoparticles, SEM image of 2.00 wt% MoS₂-ZnO composite photocatalyst (c), and ss SEM image of MoS₂ nanosheets (d).

The morphology of pure ZnO nanoparticles obtained by the hydrothermal synthesis was characterized by FE-SEM and TEM. As shown in Fig. 1(a) and 1(b), the SEM and TEM images of ZnO clearly illustrate the typical morphology of ZnO

- ⁵ nanoparticles with an average agglomerate size of 30~50 nm. The ZnO nanoparticles have homogeneous distribution and only a fraction of them existed in agglomeration. After loading MoS₂ on ZnO surface, the morphology of MoS₂-ZnO composite shown in Fig. 1(c) was similar to that of pure ZnO nanoparticles. The MoS₂
- ¹⁰ nanosheets were not observed in MoS_2 -ZnO composite, which could be assigned to the small amount of MoS_2 on the surface of ZnO. The pure MoS_2 prepared by the hydrothermal method was also characterized by SEM, Fig. 1(d) reveals the typical twodimensional structure of MoS_2 nanosheets.
- ¹⁵ The XRD patterns of the pure ZnO and MoS₂-ZnO composites with various MoS₂ loading amounts were displayed in Fig. 2. The diffraction peaks of as-prepared composites are well defined, indicating the crystalline character of the synthesized composites. The pure ZnO displays seven main diffraction peaks
- ²⁰ at $2\theta = 31.74^{\circ}$, 34.40° , 36.29° , 47.50° , 56.55° , 62.91° and 67.97° , which can be attributed to the (100), (002), (101), (102), (110), (103), and (112) lattice plane of the hexagonal ZnO (JCPDS card No. 36-1451), respectively.⁴⁰ However, no characteristic diffraction peaks of MoS₂ were observed in the XRD patterns of
- ²⁵ MoS₂-ZnO composites, which could be attributed to the low content of MoS₂ existed in MoS₂-ZnO composites. The presence of MoS₂ in MoS₂-ZnO composites can be checked by TEM and



Fig. 2 X-ray diffraction patterns for pure ZnO and MoS₂-ZnO ³⁰ composites loading with various amounts of MoS₂.



Fig.3 (a) TEM image of 2.00 wt% MoS_2 -ZnO composite photocatalyst and magnified TEM image of the selected frame from image (a).



Fig. 4 XPS spectra of MoS_2 -ZnO (a) Mo 3d; (b) S 2p; (c) Zn 2p and (d) O 1s.

XPS analysis. As shown in Fig. 3(a), the TEM image of 2.00 wt% MoS₂-ZnO shows a typical layered structure of MoS₂ deposited 40 on the surface of ZnO nanoparticles. The magnified TEM image of MoS₂-ZnO composite in Fig. 3(b) shows that the layered MoS₂ was coated on ZnO surface to form intimate interfaces. From the TEM image, the lattice fringes of ZnO with a d-spacing of 0.26 nm can be assigned to the (001) lattice plane of hexagonal ZnO.⁴⁰ $_{45}$ The (002) plane of hexagonal MoS₂ with a lattice spacing of 0.61 nm was also observed in 2.00 wt% MoS₂-ZnO composite,³⁴ which comprises only 3~5 layers of MoS₂ nanosheets. The chemical composition of the MoS₂-ZnO composites was also confirmed by XPS analysis. As shown in Fig. 4, the 2.00 wt% 50 MoS₂-ZnO sample shows the binding energy at 232.2, 228.8, 226.2, 162.8 and 161.8 eV, which can be assigned to Mo $3d_{3/2}$, Mo $3d_{5/2}$, S 2s, S $2p_{1/2}$ and S $2p_{3/2}$, respectively.²⁹ On the other hand, the binding energy of Zn 2p1/2, Zn 2p3/2 and O 1s were also observed at 1044.8, 1021.6 and 530.0 eV, respectively.^{41,42} The 55 above TEM and XPS observations indicate that the layered MoS₂ was successfully grown on the surface of ZnO.

The surface areas of as-prepared products were investigated by the nitrogen absorption measurement. The nitrogen absorption-desorption isotherms of pure ZnO, MoS₂, and 2.00 wt% 60 MoS₂-ZnO composite were shown in Fig. 5. The BET surface areas of as-prepared ZnO nanoparticles and MoS2 nanosheets were measured to be 27.75 and 52.45 m² g⁻¹, respectively. The specific surface area of 2.00 wt% MoS2-ZnO composite is determined to be 32.45 m² g⁻¹. These results indicating that the 65 BET surface area of MoS₂-ZnO composite is higher than that of pure ZnO, but it is lower than that of pure MoS₂. The UV-vis diffuse reflectance spectra of pure ZnO and MoS2-ZnO composite photocatalysts were investigated. In Fig. 6, the pure ZnO shows a strong absorption in the ultraviolet region with a band gap of 70~3.37 eV. After introducing layered MoS2, the MoS2-ZnO composites show the similar absorption in the ultraviolet region and slightly enhanced light harvesting in the visible region as comparison to pure ZnO sample. The ability of MoS2-ZnO composites to absorb visible light strengthened with the 75 increasing MoS₂ contents, which agrees with the color of MoS₂-ZnO composites that vary from white to grey.



Fig. 5 Nitrogen absorption-desorption isotherms of pure ZnO, MoS₂, and 2.00 wt% MoS₂-ZnO composite.



5 Fig. 6 UV-vis diffuse reflectance spectra of pure ZnO and MoS₂-ZnO composites.



Fig. 7 Dependence of steady rate of H₂ production by MoS₂-ZnO on loading amounts of MoS₂. Measurement conditions: 0.1 g ¹⁰ sample, 100 mL aqueous solution of 0.1 M Na₂S and 0.1 M Na₂SO₃, and light source of 300 W Xe lamp.

The photocatalytic H₂ production activities of pure ZnO and MoS_2 -ZnO composites were conducted in an aqueous solution containing 0.1 M Na₂S and 0.1 M Na₂SO₃ as the sacrificial ¹⁵ reagents under the full spectra irradiation by a 300W Xe lamp. As shown in Fig. 7, the pure ZnO sample exhibits a very low photocatalytic activity with a H₂ evolution rate of 52 µmol h⁻¹ g⁻¹, although it has strong absorption in the ultraviolet region. The

poor activity of pure ZnO nanoparticles could be attributed to the 20 fast recombination of photogenerated electron hole pairs. After loading the layered MoS₂ on ZnO surface, which resulted in significantly increased H₂ production rate. A plot of the variation in activities of MoS2-ZnO photocatalysts loaded with different amounts of MoS2 was also shown in Fig. 7. The 0.25 wt% MoS2-25 ZnO composite photocatalyst shows a hydrogen evolution rate of 261 μ mol h⁻¹ g⁻¹, which is about 5 times higher than that of pure ZnO nanoparticles. When the loading amounts of MoS2 were further increased to 0.50 and 1.00 wt%, the H₂ evolution rates were enhanced to be 460 and 768 μ mol h⁻¹ g⁻¹, which is 8.8 and 30 14.8 times higher that of pure ZnO sample, respectively. The enhancement of activities with the loading amounts of MoS₂ could be attributed to an increase in the density of active sites for hydrogen production reaction. However, a further increase in the loading amounts of MoS₂ to1.50 and 2.00 wt%, resulted in a $_{35}$ decreasing hydrogen production rate of 498, and 275 μ mol h⁻¹ g⁻¹, respectively. The decreased hydrogen evolution activities of photocatalysts loaded with relatively larger amounts of MoS₂ could be assigned to the shading effect of MoS₂, which blocks light absorption of ZnO component. Similar observations have 40 been encountered in previous studies that using MoS₂ as a cocatalyst.^{33,44}. However, when the 1.00 wt% MoS₂-ZnO

composite was used as the photocatalyst in aqueous solution of 0.1 M Na₂S and 0.1 M Na₂SO₃, no appreciable H₂ production was produced in photocatalytic system under visible light irradiation. ⁴⁵ The result rules out the possibility of the photosensitization of ZnO with photoexcited MoS₂ for hydrogen evolution reaction. A similar phenomenon has also been observed in other MoS₂-based photocatalytic hydrogen production system.⁴³

A tentative mechanism proposed for the enhanced H₂ ⁵⁰ production activities for MoS₂-ZnO composite photocatalysts is illustrated in Scheme 1. Under ultraviolet illumination, the conduction band (CB) electrons of ZnO are excited to the valence band (VB), creasing holes in the VB. The CB position of MoS₂ below the CB of ZnO permits the transfer of electrons from the ⁵⁵ CB of ZnO to the CB of MoS₂, where not only serves as an electron sink, but also provides effective proton reduction sites, hence dramatically facilitates hydrogen production reaction. Moreover, the TEM result (Fig. 3(b)) shows the formation of intimate interface between ZnO and MoS₂ in MoS₂-ZnO ⁶⁰ composites, and the intimate junction facilitates the electron



Scheme 1. Schematic diagram of the photocatalytic H_2 generation over the MoS₂-ZnO photocatalyst.



Fig. 8 The rate of H₂ evolution on ZnO loaded with 1.00 wt % of different cocatalysts. Measurement conditions: 0.1 g sample, 100 mL aqueous solution of 0.1 M Na₂S and 0.1 M Na₂SO₃, and light s source of 300 W Xe lamp.



Fig. 9 Cycling runs for the photocatalytic hydrogen production in presence of 1.00 wt% MoS₂-ZnO photocatalyst. Measurement conditions: 0.1 g sample, 100 mL aqueous solution of 0.1 M Na₂S ¹⁰ and 0.1 M Na₂SO₃, and light source of 300 W Xe lamp.



Fig. 10X-ray diffraction patterns for 1.00 wt\% MoS_2 -ZnO photocatalyst before and after photocatalytic reaction.

transfer from the ZnO to MoS_2 , leading to the enhancement of ¹⁵ photocatalytic H₂ production activity.^{33,34}

Noble metals such as Pt, Rh, Ru and Au are the most effective cocatalysts for photocatalytic hydrogen production reaction.⁴⁵⁻⁴⁸ For comparison purposed, 1.00 wt% of those noble metals was, respectively, introduced on the surface of ZnO by in-situ

20 photodeposition from the corresponding complexes of metals as the precursors. Fig. 8 shows the rates of H₂ production on ZnO loaded with 1.00 wt% of those noble metals. Among those noble metals, Rh was demonstrated to be the best cocatalyst for hydrogen production reaction, the 1.00 wt% Rh-ZnO sample $_{25}$ shows the highest H₂ evolution rate of 153 µmol h⁻¹ g⁻¹, which is approximately one-fifth of the 1.00 wt% MoS₂-ZnO composite photocatalyst. Those results suggest that the layered MoS₂ can act as a more efficient cocatalyst for ZnO semiconductor. The excellent H₂ activation property of MoS₂ and the intimate 30 junction between MoS₂ and ZnO increase the active sites and suppress the recombination of the electron-hole pairs, remarkable enhancement respectively. leading to of photocatalytic H₂ evolution activity.

To estimate the photocatalytic stability of the MoS₂-ZnO ³⁵ composite photocatalysts, the time courses of photocatalytic H₂ evolution over 1.00 wt% MoS₂-ZnO photocatalyst were conducted for three consecutive operations. In Fig. 9, no noticeable degradation of H₂ production was observed with the prolonged light irradiation time, indicating that MoS₂-ZnO ⁴⁰ composite has good photocatalytic stability. After 12 h of photocatalytic reaction, the H₂ production rate during the third circle can keep ca. 94% that of the first circle, and the MoS₂-ZnO composite photocatalyst was collected and characterized by XRD. As shown in Fig. 10, the MoS₂-ZnO photocatalyst does not ⁴⁵ present any difference in XRD spectra, suggesting that the MoS₂loaded ZnO composite photocatalyst has sufficient stability for photocatalytic H₂ evolution reaction.

Conclusions

In conclusion, we have synthesized layered MoS2 nanosheets on 50 ZnO nanoparticles via a hydrothermal approach. The photocatalytic hydrogen evolution activity of ZnO was significantly enhanced by loading MoS₂ nanosheets as a cocatalyst in presence of Na2S and Na2SO3 as the sacrificial reagents. The 1.00 wt% MoS2-ZnO heterostructure photocatalyst ss shows the highest H₂ production rate of 768 μ mol h⁻¹ g⁻¹, which is about 14.8 times higher than that of pure ZnO. The photocatalytic activity of MoS₂ as the cocatalyst is much higher than noble metals such as Pt, Rh, Ru and Au on the surface of ZnO, indicating that MoS₂ can act as a more efficient cocatalyst for 60 hydrogen evolution reaction. The excellent H₂ activation property of layered MoS₂ and the intimate interface between ZnO and MoS_2 are supposed to responsible for the enhanced H_2 evolution activities of MoS₂-ZnO photocatalysts. This work demonstrates that the two-dimensional MoS2 nanosheets will be a new 65 promising cocatalyst for developing highly-efficient, noblemetal-free, and stable ZnO-based photocatalysts with potential application in solar-to-H₂ conversion.

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