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MoSe₂/ZnO/ZnSe hybrids for efficient Cr(VI) reduction under visible light irradiation

Zhenxing Ren ^a, Xinjuan Liu ^{b,*}, Zhihao Zhuge ^b, Yinyan Gong ^b, Chang Q. Sun ^{c,#}^a Institute of Applied Chemistry, Shanxi University, Taiyuan 030006, Shanxi, China^b Institute of Optoelectronic Materials and Devices, College of Optical and Electronic Technology, China Jiliang University, Hangzhou 310018, Zhejiang, China^c School of Electrical and Electronic Engineering, Nanyang Technological University, Singapore 639798, Singapore

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ABSTRACT

Photocatalysis activated by visible light remains highly challenging. Here, we report novel MoSe₂/ZnO/ZnSe (ZM) hybrids fabricated via a simple hydrothermal method for photocatalytic reduction of Cr(VI) under visible light irradiation. ZM hybrids show improved photocatalytic reduction ability under visible light irradiation compared to pure ZnO owing to good visible light absorption and rapid electron transfer and separation. The ZM hybrid shows the highest Cr(VI) reduction rate of 100%. Moreover, the photocatalytic Cr(VI) reduction process is mainly controlled by photoinduced electrons.

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1. Introduction

Due to global warming and uncontrolled use of resources, environmental contamination and energy shortage have become very serious issues in the world [1–5]. Photocatalytic reduction of Cr(VI) to Cr(III) using semiconductor photocatalysts is regarded as a green measure to solve serious environmental and energy problems [6–9]. Typical photocatalysts such as ZnO and TiO₂ exhibit excellent catalytic activity toward the reduction of heavy metal ions and CO₂, degradation of organic pollutants, and water splitting due to their outstanding physical and chemical properties [10–20]. Notably, the main factors that affect the photocatalytic activity are quick charge carrier recombination and narrow solar energy absorption range [21–23]. Therefore, for industrial applications, it is important

to develop high-efficiency photocatalysts that respond to visible light [24–31].

It is reported that the introduction of a narrow band semiconductor into a wide band semiconductor, yielding hybrids, is an effective way to solve this problem [32–36]. To date, various narrow band semiconductors with suitable band positions such as transition metal sulfides (MoS₂, NiS, and WS₂) and transition metal phosphides (Ni₂P, CoP, and Fe_xP) have been used to expand the light absorption range and accelerate charge transfer, thereby improving the visible light catalytic activity of pure wide band semiconductors [37–39]. Recently, much research has been performed on transition metal dichalcogenides (TMDs) owing to their unique two-dimensional structures and good physical and chemical properties for wide applications in lubricants, batteries, supercapacitors, and photocatalysis

* Corresponding author. Tel/Fax: +86-571-86872475; E-mail: lxj669635@126.com

Corresponding author. E-mail: ecqsun@ntu.edu.sg

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[40–42]. MoS₂ has been widely used as a highly efficient non-noble metal cocatalyst for H₂ evolution because of its unique chemical and photoelectronic properties. Compared to MoS₂, MoSe₂ (a typical 2D TMD with a similar layered structure) is more metallic, making it an ideal support matrix for semiconductors [43]. It has been demonstrated that the introduction of MoSe₂ is beneficial for charge separation and transfer, enhancing the catalytic hydrogen production activity of g-C₃N₄ and ZnIn₂S₄. However, reports on MoSe₂-based hybrids for enhanced photocatalytic reduction of Cr(VI) on ZnO are rare.

In this work, a series of MoSe₂/ZnO/ZnSe (ZM) hybrids were synthesized by a simple hydrothermal method for Cr(VI) reduction under visible light irradiation. The ZM hybrids obtained by the introduction of ZnSe and MoSe₂ into ZnO were expected to exhibit enhanced visible light photocatalytic Cr(VI) reduction activity compared to pure ZnO, which has not been reported so far. The photocatalytic mechanism was studied by trapping experiments and characterization methods.

2. Experimental

See supporting information section.

3. Results and discussion

3.1. Formation mechanism

The possible formation mechanism for MoSe₂/ZnO/ZnSe hybrids is illustrated in Scheme 1. ZnO nanoparticles were fabricated by a solvothermal reaction. After ZnO nanoparticles are dissolved in a solution containing Na₂SeSO₃, Na₂MoO₄, and NaBH₄, MoO₄²⁻ ions are reduced to Mo⁴⁺ by NaBH₄, and then, Mo⁴⁺ cations combine with Se²⁻ anions, forming MoSe₂ nuclei, as per Reaction (1). In our previous studies, MoSe₂, MoSe₂/TiO₂, and MoSe₂/CQD composites were fabricated by a similar solvothermal reaction [32,43,44]. In this study, ZnO nanoparticles have been used as a template to obtain ZnSe by an anion exchange reaction with a Se²⁻ source. The ZnO nanoparticles react with water to form Zn(OH)₂ during the hydrothermal reaction at 180 °C, as per Reaction (2) [45]. Then, Se²⁻ anions react with Zn(OH)₂ to form ZnSe nuclei by heterogeneous nucleation and growth, as per Reaction (3) [46]. The difference in the solubility product constant (*K*_{sp}) values of ZnO (6.8 × 10⁻¹⁷) and ZnSe (3.6 × 10⁻²⁶) is the main driving force for the formation of ZnO/ZnSe hybrids [47]. Subsequently, the long reaction time and high temperature in the sealed autoclave promote crystal growth

Scheme 1. Schematic illustration of the possible formation mechanism for MoSe₂/ZnO/ZnSe hybrids.

Fig. 1. XRD patterns of ZnO and ZM-1.

from MoSe₂ sheets and ZnSe nanoparticles, resulting in the formation of MoSe₂/ZnO/ZnSe hybrids.

3.2. Characterization

The X-ray diffraction (XRD) patterns of ZnO and ZM-1 are shown in Fig. 1. The diffraction peaks in the ZnO pattern are assigned to wurtzite-structured ZnO (JPCDS 36-1451). New peaks at 27.5°, 45.6°, and 54° corresponding to the (111), (220), and (311) planes of cubic ZnSe, respectively, are observed in the XRD pattern of ZM-1, demonstrating the formation of ZnSe (JPCDS 80-0021) [48]. The peaks at 27.6°, 31.7°, 36.5°, 45.6°, and 56.9° correspond to the (006), (101), (104), (107), (0012) planes of hexagonal MoSe₂ (JPCDS 72-1420), respectively, which coincide with the diffraction peaks of ZnO and ZnSe. The XRD pattern of ZM-1 hybrid is similar to that of ZnO, confirming that the introduction of ZnSe and MoSe₂ into ZnO does not change the crystal structure of ZnO.

The field-emission scanning electron microscopy (FESEM) images of ZnO, ZM-0.5, ZM-1, and ZM-2 are shown in Fig. 2. The SEM image of ZnO displays nanoparticles with diameters of about 100 nm. After ZnO nanoparticles are dissolved into the solution containing Na₂SeSO₃ and Na₂MoO₄, MoSe₂ sheets and

Fig. 2. FESEM images of various samples. (a) ZnO; (b) ZM-0.5; (c) ZM-1; (d) ZM-2.

Fig. 3. TEM (a) and high-resolution TEM (b) images of ZM-1 sample.

ZnSe nanoparticles are formed, finally resulting in the formation of ZM hybrids (Fig. 1(c) and (d)). The thickness of MoSe₂ sheets is not quite uniform, and it ranges from about 20 nm to 50 nm.

The transmission electron microscopy (TEM) image of ZM-1 are shown in Fig. 3(a). ZnO and ZnSe nanoparticles are embedded into MoSe₂ sheets, forming a compact interface, which is beneficial for charge carrier separation, thus improving the photocatalytic activity. The lattice spacing is calculated as 0.65 nm, which is assigned to the (003) crystal planes of hexagonal 2H-MoSe₂ (JPCDS 72-1420). In addition, the lattice spacing for (100) crystal planes of ZnO (JPCDS 36-1451) and (200) crystal planes of ZnSe (JPCDS 80-0021) is determined to be 0.28 nm.

To further verify the presence of MoSe₂, ZnO, and ZnSe, elemental distribution mapping was performed using the energy-dispersive X-ray spectroscopy (EDS) detectors connected to

FESEM and HRTEM instruments, as shown in Figs. S1 and S2. In Fig. S1, the distributions of Zn, O, Mo, and Se elements are clearly observed, demonstrating the existence of ZnO, ZnSe, and MoSe₂. In addition, the presence of Zn, O, and Se elements is revealed by HRTEM-EDS, as shown in Fig. S2, further proving the formation of ZnSe and ZnO. No impurity element is detected, proving the high purity of ZM hybrids.

Fig. 4(a) shows the Fourier-transform infrared (FTIR) spectra of ZnO, ZM-0.5, ZM-1, and ZM-2. All samples display two absorption bands at around 3425 and 1632 cm⁻¹ corresponding to the hydroxyl groups of surface-absorbed water molecules [49]. For ZnO, the absorption band at 450 cm⁻¹ corresponds to the stretching mode of Zn–O [50]. The FTIR spectra of ZM hybrids are similar to that of MoSe₂ previously reported [51]. Moreover, with increasing MoSe₂ content, the intensity of the Zn–O stretching peak decreases, because ZnO nanoparticles are possibly covered by MoSe₂ sheets and ZnSe nanoparticles. Fig. 4(b) shows the Raman spectra of ZnO, ZM-0.5, ZM-1, and ZM-2. For ZnO, four characteristic peaks corresponding to low E₂, A₁, high E₂, and A₁ modes are observed at 99, 333, 438, and 1158 cm⁻¹, respectively [52,53]. Compared to the Raman spectrum of pure ZnO, those of ZM hybrids exhibit a new peak at 242 cm⁻¹ corresponding to the A_{1g} mode of MoSe₂ [51], further confirming the existence of ZnO and MoSe₂ in the hybrids.

The high-resolution X-ray photoelectron spectroscopy (XPS) Zn 2p, O 1s, Mo 3d, and Se 3d profiles for ZM-1 are shown in

Fig. 4. FTIR (a) and Raman (b) spectra of ZnO, ZM-0.5, ZM-1, and ZM-2.

Fig. 5. High-resolution XPS Zn 2p (a), O 1s (b), Mo 3d (c), Se 3d (d) profiles for ZM-1.

Fig. 6. UV-Vis diffuse absorption spectra of ZnO, ZM-0.5, ZM-1, and ZM-2.

Fig. 5. As observed in Fig. 5(a), the high-resolution Zn 2p spectrum shows characteristic Zn $2p_{1/2}$ and $2p_{3/2}$ peaks at 1045.5 and 1022.5 eV, respectively, which are assigned to Zn^{2+} existing in the form of ZnO and ZnSe. The O 1s peak (Fig. 5(b)) is deconvoluted into two peaks at 530 and 531.7 eV, corresponding to the lattice oxygens of ZnO and surface hydroxides, respectively. In Fig. 5(c), two peaks are observed at 228.7 and 232.4 eV, which are assigned to Mo $3d_{5/2}$ and Mo $3d_{3/2}$, respectively. The Se $3d_{5/2}$ and $3d_{3/2}$ peaks (Fig. 5(d)) centered at 54.4 eV and 55.3 eV, respectively, are ascribed to Se^{2-} of ZnSe and MoSe₂, demonstrating the formation of ZnSe and MoSe₂. Fig. S3 shows the high-resolution XPS Zn 2p, O 1s, Mo 3d, and Se 3d profiles for pure ZnO and MoSe₂. Compared to the O 1s, Mo 3d, and Se 3d XPS peaks of pure ZnO and MoSe₂, those of ZM hybrids (ZM-1) are slightly shifted due to the interaction between them. All results confirm the successful synthesis of ZM hybrids by the hydrothermal process.

Fig. 6 shows the UV-Vis diffuse absorption spectra of ZnO, ZM-0.5, ZM-1, and ZM-2. ZnO shows good UV light absorption. On the other hand, ZM hybrids display enhanced light absorption ability in the visible light range due to absorption contribution from ZnSe₂ and MoSe₂. Therefore, ZM hybrids can be employed as promising visible light photocatalysts.

3.3. Photocatalytic activity

The visible light photocatalytic Cr(VI) reduction activities of ZnO and ZM hybrids were investigated (Fig. 7). As observed in Fig. 7(a), with increasing irradiation time, Cr(VI) absorption reduces, confirming the decrease in Cr(VI) concentration. Fig. 7(b) shows the time-resolved Cr(VI) reduction rates for ZnO and ZM hybrids. The Cr(VI) reduction rate for ZnO is only 7% owing to the narrow light absorption and charge recombination. After hybridization, the photocatalytic Cr(VI) reduction rate clearly increases and depends on the Na₂MoO₄ amount. The Cr(VI) reduction rates are 12%, 100%, and 53% after 180 min of visible light irradiation. With increasing Na₂MoO₄ amount, the Cr(VI) reduction rate first increases and then decreases. The values of rate constant (k) for ZnO, ZM-0.5, ZM-1, and ZM-2 are 0.0005, 0.0007, 0.0074, and 0.0043, respectively (Fig. S4). ZM-1 shows the best catalytic visible light activity and the highest Cr(VI) reduction rate.

The photostability of photocatalysts is very important in practical application. The long-term stability of ZM-1 toward the photocatalytic reduction of Cr(VI) under visible light irradiation was investigated, as shown in Fig. S5. No obvious decrease in the Cr(VI) reduction rate is observed after three cycles. The crystal structure of ZM-1 after the catalytic reaction was characterized by XRD. As shown in Fig. S6, no significant difference is observed before and after the catalytic reaction, indicating the good stability of ZM hybrid photocatalysts.

Fig. 7. (a) Variation in UV-Vis absorbance of Cr(VI) with time using ZM-1; (b) photocatalytic reduction of Cr(VI) by ZnO, ZM-0.5, ZM-1, and ZM-2 under visible light irradiation; (c) photocatalytic reduction of Cr(VI) using ZM-1 in the presence of AgNO₃; and (d) proposed photocatalytic mechanism for ZM hybrids.

3.4. Possible photocatalytic mechanism

In the photocatalytic Cr(VI) reduction process using ZM hybrids (Fig. 7(d)), the valence band (VB) electrons of MoSe₂ are aroused under visible light irradiation, resulting in electron–hole pairs. Subsequently, the charge carriers migrate to the photocatalyst surface to participate in redox reactions. The conduction band (CB) and VB potentials for ZnO are –0.4 and –2.8 V (vs. NHE), respectively [46], while the values for ZnSe are –0.64 and –2.16 V (vs. NHE) [46], respectively, and those for MoSe₂ are –0.92 and –1.12 V (vs. NHE) [54], respectively. According to the definition of a heterojunction [55], the MoSe₂/ZnO/ZnSe hybrid is a type-II heterojunction photocatalyst. The Cr(VI)/Cr(III) potential is 0.51 V vs. NHE [56]; thus, Cr(VI) can be reduced to Cr(III) by electrons. The XPS Cr 2p profile (Fig. S7) confirms the existence of Cr(III). The spectrum shows peaks at 577.3 and 586.9 eV corresponding to Cr 2p_{1/2} and Cr 2p_{3/2} orbitals, respectively, which are attributed to Cr(VI) and Cr(III). This result confirms that Cr(VI) reduces to Cr(III) in the photocatalytic process. Several studies have shown that the Cr(III) species precipitate on the surface of the photocatalyst as Cr₂O₃ or Cr(OH)₃ during the photocatalytic process. To prove the role of photogenerated electrons, a controlled trapping experiment was performed using an electron scavenger (AgNO₃), as shown in Fig. 7(c). It is found that the photocatalytic Cr(VI) reduction rate obviously decreases with the addition of AgNO₃, confirming that the photogenerated electrons control the Cr(VI) reduction process [57,58]. Meanwhile, the gas chromatography measurement results from our previous work demonstrate that holes oxidize H₂O, yielding O₂ [32,44]. The catalytic reaction processes are summarized as follows:

In photocatalysis, the adsorption of Cr(VI), light absorption, as well as charge transportation and separation are crucial factors [59,60]. Charge carrier transfer and separation play a decisive role in the catalytic reaction, which was investigated by electrochemical impedance spectroscopy (EIS). Fig. 8(a) shows the Nyquist plots of ZnO, ZM-0.5, ZM-1, and ZM-2. It is

found that with increasing Na₂MoO₄ amount, the charge transfer resistance first decreases and then increases, confirming that the appropriate MoSe₂ content can facilitate the transfer and prolong the charge carrier lifetime, thereby enhancing the catalytic activity. Excessive MoSe₂ recombination centers in the ZM hybrids facilitate charge recombination, thus leading to decreased photocatalytic activity [61–63]. Moreover, the charge separation and transfer behaviors of the as-prepared samples were investigated by photoluminescence (PL) and photoelectrochemical measurements. Fig. S8(a) and (b) show the transient photocurrent responses and PL spectra recorded at an excitation wavelength of 300 nm for ZnO and ZM-2. As observed, ZM-2 shows a higher photocurrent and a lower PL intensity due to the stepwise structure of band edge levels of the ZM hybrids. All results are in agreement with the EIS results. Because the CB potentials of MoSe₂ and ZnSe are more negative than those of ZnO, electrons are transferred from the CB of MoSe₂ and ZnSe to ZnO, thereby hindering the charge carrier recombination and prolonging the lifetimes of the photoinduced electron–hole pairs. According to the stepwise structure of band edge levels of the ZM hybrids, the introduction of MoSe₂ and ZnSe can facilitate the separation of photoinduced electron–hole pairs, which is beneficial to the photocatalytic process.

Besides the recombination of photoinduced charge carriers, the specific surface area plays a decisive role in the catalytic reaction, as shown in Fig. 8(b). All samples show type-IV isotherms with H₃ hysteresis loops, confirming the mesoporous structures of the samples. The specific surface areas, pore volumes, and average pore sizes of ZnO, ZM-0.5, ZM-1, and ZM-2 are listed in Table S1. As shown, the specific surface area and pore volume first increase and then decrease with increasing MoSe₂ content, which is in accordance with the catalytic activity [64].

On the basis of the above results, a mechanism for the enhanced photocatalytic activity of the ZM hybrids is proposed. The introduction of MoSe₂ and ZnSe increases light absorption in the visible light region and the specific surface area. EIS, PL, and photocurrent measurements show that the recombination of photoinduced electron–hole pairs is effectively inhibited owing to the stepwise structure of energy levels in the ZM hy-

Fig. 8. (a) Nyquist plots and (b) nitrogen adsorption-desorption isotherms of ZnO, ZM-0.5, ZM-1, and ZM-2.

brid photocatalysts. The enhanced photocatalytic activity is ascribed to the increased visible light absorption, more active sites, and reduced charge carrier recombination. Moreover, photoinduced electrons control the Cr(VI) reduction process.

4. Conclusions

ZM hybrids are successfully prepared via a facile solvothermal method. ZM hybrids exhibit enhanced visible light Cr(VI) reduction activity compared to pure ZnO. The introduction of MoSe₂ and ZnSe increases the BET surface area and light absorption and inhibits charge carrier recombination due to the matched energy levels and good interfacial contact between them, enhancing the photocatalytic reaction. Moreover, the photoinduced electrons control the photocatalytic Cr(VI) reduction process. The current work can provide valuable guidance to designing novel hybrid photocatalysts for environmental purification.

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Graphical Abstract

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Zhenxing Ren, Xinjuan Liu *, Zhihao Zhuge, Yinyan Gong, Chang Q. Sun *
Shanxi University, China;
China Jiliang University, China;
Nanyang Technological University, Singapore

MoSe₂/ZnO/ZnSe hybrids display excellent photocatalytic activity for Cr(VI) reduction under visible light irradiation.

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MoSe₂/ZnO/ZnSe复合物用于高效可见光催化还原Cr(VI)

任振兴^a, 刘心娟^{b,*}, 诸葛志豪^b, 官银燕^b, 孙长庆^{c,#}

^a山西大学应用化学学院, 山西太原030006, 中国

^b中国计量大学光与电子技术学院, 光电材料与器件研究院, 浙江杭州310018, 中国

^c新加坡南洋理工大学电气与电子工程学院, 新加坡639798, 新加坡

摘要: 半导体光催化还原Cr(VI)为Cr(III)被认为是一种能够解决环境和能源问题的绿色技术。典型光催化剂ZnO和TiO₂在还原重金属离子和二氧化碳, 降解有机污染物, 分解水等领域均已被证明是一种有潜力的光催化剂。但是, 它们窄的太阳吸收范围和快的光生载流子复合限制了其实际应用。因此, 探索能够响应可见光的高效光催化剂是非常急切的课题。

研究表明, 引入窄带半导体构筑异质结复合光催化剂是一种提高ZnO和TiO₂可见光催化活性的有效途径。随着二维石墨烯研究的热潮, 具有类石墨烯结构的材料, 如过渡金属硫化物MX₂(M=Mo, W, Nb, Ta, Zr; X=S, Se)以其独特的“三明治夹心”层状结构受到了研究者的高度重视。在这些MX₂材料中, MoS₂是间接带隙半导体, 能带为1.2 eV, 并且随着层数的减小, 能带增加到1.8 eV, 因此, 它对可见光具有很好的吸收能力。MoS₂具有比表面积大、吸附能力强、反应活性高等优异的物理和化学性能, 被广泛应用于光催化、制氢反应、太阳能电池及锂离子电池等领域。类似于MoS₂, MoSe₂也应该是一种具有潜力的窄带光催化剂。不幸的是, 对于MoSe₂在光催化还原Cr(VI)中的应用, 还鲜有报道。本文基于ZnO, ZnSe和MoSe₂构筑复合光催化剂, 由于它们存在阶梯型的能级结构, 使得此复合物能够展现优异的可见光催化性能, 这是一种提高ZnO可见光催化活性的有效方法。

扫描电子和高分辨透射电子显微镜结果显示, ZnO和ZnSe纳米颗粒分散在二维MoSe₂片周围, 形成很好的界面接触, 有利于光生电子-空穴对的快速转移和分离, 促进光催化反应的进行. 紫外可见吸收光谱结果表明, MoSe₂/ZnO/ZnSe (ZM) 复合物在可见光区域展现了很好的吸收. 电化学阻抗谱和光电流响应曲线结果表明, ZM复合物中光生载流子复合被有效抑制, 延长了其寿命. 光催化还原Cr(VI)的实验结果发现, 与纯ZnO相比, ZM复合物展现了优异的光催化活性. 在可见光照射180 min后, ZM复合物对Cr(VI)的还原率达到100%. 优异的光催化活性归因于其优异的可见光吸收、阶梯型能级结构和光生载流子的有效转移. 光催化重复性实验和X射线衍射图结果表明, 在光催化反应之后ZM复合物的结构没有发生变化, 具有良好的稳定性. 本工作可为进一步设计具有理想功能的二维复合光催化剂提供有价值的信息.

关键词: 过渡金属硫化物; MoSe₂; ZnO; ZnSe; Cr(VI)

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*通讯联系人. 电话/传真: (0571)86872475; 电子信箱: lxj669635@126.com

#通讯联系人. 电子信箱: ecqsun@ntu.edu.sg

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