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Article

One-pot hydrothermal synthesis of willow branch-shaped MoS₂/CdS heterojunctions for photocatalytic H₂ production under visible light irradiation

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ABSTRACT

Willow branch-shaped MoS₂/CdS heterojunctions are successfully synthesized for the first time by a facile one-pot hydrothermal method. The as-prepared samples were characterized by X-ray diffraction, X-ray photoelectron spectroscopy, scanning electron microscopy, transmission electron microscopy, nitrogen adsorption-desorption measurements, diffuse reflectance spectroscopy, and photoelectrochemical and photoluminescence spectroscopy tests. The photocatalytic hydrogen evolution activities of the samples were evaluated under visible light irradiation. The resulting MoS₂/CdS heterojunctions exhibit a much improved photocatalytic hydrogen evolution activity than that obtained with CdS and MoS₂. In particular, the optimized MC-5 (5 at.% MoS₂/CdS) photocatalyst achieved the highest hydrogen production rate of 250.8 μmol h⁻¹, which is 28 times higher than that of pristine CdS. The apparent quantum efficiency (AQE) at 420 nm was 3.66%. Further detailed characterizations revealed that the enhanced photocatalytic activity of the MoS₂/CdS heterojunctions could be attributed to the efficient transfer and separation of photogenerated charge carriers resulting from the core-shell structure and the close contact between MoS₂ nanosheets and CdS single-crystal nanorods, as well as to increased visible light absorption. A tentative mechanism for photocatalytic H₂ evolution by MoS₂/CdS heterojunctions was proposed. This work will open up new opportunities for developing more efficient photocatalysts for water splitting.

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1. Introduction

Since photoelectrochemical water splitting was first reported by Fujishima and Honda in 1972, photocatalytic water splitting into hydrogen using semiconductor photocatalysts and solar energy has been considered as one of the most promising approaches to cope with the global energy crisis and environmental pollution issues. Various semiconductor materials

have been developed for photocatalytic hydrogen evolution applications [1]. However, their practical use in water splitting is still limited by several intrinsic disadvantages such as poor visible light harvesting, low activity, and high cost. Therefore, the identification of more efficient photocatalysts for hydrogen production is still a task of great importance. Considerable efforts have been devoted to exploring new visible-light-driven photocatalysts or to promoting the separation of photogenerated

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ated charge carriers by modifying the photocatalysts [2,3].

CdS, a semiconductor with appropriate band gap (~ 2.4 eV) for effective visible light absorption and suitable photoredox potentials for H^+ reduction, has emerged as the most promising visible light photocatalysts for hydrogen generation [4–7]. However, the application of pristine CdS photocatalysts is severely limited by rapid recombination of electrons and holes [8–10]. In addition, the photocorrosion of CdS caused by the oxidation of photogenerated holes results in poor stability in aqueous solutions [11–13]. Therefore, various modification strategies have been developed to enhance the performance of CdS photocatalysts [14], including loading co-catalysts [15–17], forming heterojunctions [18–20], introducing surface modifications [21], and doping with metal [22] or nonmetal [23] elements. Among these strategies, coupling with co-catalysts has been proved to be an effective approach for improving the photocatalytic performance [24–26]. In general, noble metals such as Pt, Au, and Ag have been used as efficient co-catalysts to enhance the photocatalytic H_2 evolution rate. However, the practical application of these metals is severely hampered by their limited availability and high cost. Therefore, developing inexpensive, earth-abundant, and efficient co-catalysts, especially non-precious metal-based ones, is a highly desirable goal.

MoS_2 , a two-dimensional transition metal dichalcogenide (TMD) with unique layered structure and special properties, has attracted considerable scientific interest in various applications such as electrocatalysts [27], photocatalysts [24,28,29], sensors [30], supercapacitors [31], batteries [32], and adsorbents [33–35]. Recently, several reports have indicated that MoS_2 could act as an effective co-catalyst for photocatalytic hydrogen production and organic pollutant degradation under visible light irradiation [36–41]. For example, Yang et al. [24] fabricated a multilayered MoS_2 -coated $CdS@MoS_2$ core-shell structure, which presented remarkable hydrogen production activity and high durability under visible light irradiation. Zhao et al. [42] synthesized an $n-BiVO_4@p-MoS_2$ heterojunction photocatalyst with excellent performance in the photocatalytic reduction of Cr^{6+} and oxidation of crystal violet (CV) under visible light irradiation. Zhang et al. [25] reported the preparation of $CdS@MoS_2$ irregular nanospheres for efficient photocatalytic hydrogen evolution. Qin et al. used an electrospinning-mediated photodeposition method to fabricate $MoS_2/CdS-TiO_2$ nanofibers, which showed good performance in photocatalytic hydrogen evolution. Exciting advances have been made in the synthesis of MoS_2/CdS nanostructures with fascinating morphologies, including nanowires [24,43], nanorods [44], and nanospheres [25]. However, the development of novel MoS_2/CdS nanostructures with unique morphology is still a task of great importance. In addition, most of the reported synthesis procedures include two or more complicated steps, which limit large-scale production of photocatalysts. Therefore, developing a facile, mild, and cost-effective approach for the synthesis of MoS_2/CdS nanostructures with unique morphology is a highly desirable goal.

Herein, we designed and fabricated a new willow branch-shaped MoS_2/CdS photocatalyst through a facile one-pot hydrothermal method. We tested the photocatalytic

hydrogen evolution activity under visible light irradiation of MoS_2/CdS heterojunctions with different molar ratios of MoS_2 and CdS. The as-prepared MoS_2/CdS heterojunctions exhibited a remarkably improved photocatalytic activity under visible light irradiation. The optimized 1 at% MoS_2/CdS sample showed the highest H_2 production rate, $250.8 \mu mol h^{-1}$, which is about 28 times higher than that of pristine CdS. Detailed experiments showed that the extended and intimate interfacial contact between MoS_2 and CdS can promote the transfer and reduce the recombination of photogenerated charge carriers. This work provides a simple method for the facile synthesis of novel MoS_2/CdS materials.

2. Experimental

2.1. Sample preparation

Willow branch-shaped MoS_2/CdS heterojunctions were prepared by a facile one-pot hydrothermal method. In a typical procedure, 5 mmol of $Cd(NO_3)_2 \cdot 4H_2O$, a given amount of $Na_2MoO_4 \cdot 2H_2O$, and 15 mmol of CH_4N_2S were added into 35 mL of deionized water under stirring at room temperature. Then, the mixture was transferred into a 50 mL Teflon-lined stainless steel autoclave and heated at $220^\circ C$ for 24 h. After the reaction, the precipitates were collected and washed several times with ultrapure water and absolute ethanol. After drying in a vacuum oven at $60^\circ C$, willow branch-shaped MoS_2/CdS samples were obtained. The MoS_2 loading could be easily adjusted by changing the amount of $Na_2MoO_4 \cdot 2H_2O$. A series of MoS_2/CdS heterojunctions with different Mo:Cd molar ratios (0, 0.01, 0.02, 0.05, 0.1, and 0.2) were prepared and labeled MC-0, MC-1, MC-2, MC-5, MC-10, and MC-20, respectively. Pure MoS_2 was also synthesized using the same procedure, except that no CdS was added. In addition, an MC-m sample was obtained by physical mixing of MoS_2 and CdS to illustrate the advantages of the one-pot hydrothermal method.

2.2. Characterization

The crystal structures of the as-prepared products were investigated by powder X-ray diffraction (XRD) measurements performed on a Rigaku D/max-2200/PC instrument using $Cu K_\alpha$ radiation (40 kV). X-ray photoelectron spectroscopy (XPS) experiments were conducted on an ESCALAB 250 X-ray photoelectron spectrometer in an ion-pumped chamber. The morphologies of the samples were characterized by field-emission scanning electron microscopy (FESEM) using a JEOL JSM7500F instrument. Transmission electron microscopy (TEM) measurements were conducted on a Tecnai G2 F20 S-TWIN instrument with a field emission gun at 20 kV. The Brunauer-Emmett-Teller (BET) specific surface areas were measured at $-196^\circ C$ on a Gold APP V-sorb 2800 system. The Barrett-Joyner-Halenda (BJH) method was adopted to calculate the pore size distribution from the desorption branch of the isotherms. UV-vis diffuse reflection spectroscopy (DRS) measurements were performed using a Shimadzu UV-vis 2550 (Japan) spectrophotometer. Photoluminescence (PL) spectra were

Fig. 1. XRD patterns of all samples, together with standard diffraction patterns of CdS and MoS₂/CdS composites.

measured at room temperature using an LS55 (Perkin-Elmer, USA) fluorescence spectrometer. Transient photocurrent, electrochemical impedance spectroscopy (EIS), and Mott-Schottky (M-S) measurements were performed on an electrochemical workstation (CHI 660e) under UV-visible light irradiation using a standard three-electrode system. A 300 W Xe lamp and a 0.5 mol/L Na₂SO₄ solution were used as the light source and electrolyte, respectively.

2.3. Photocatalytic activity measurements

Photocatalytic hydrogen evolution activities of all samples were evaluated under visible light irradiation in a 250 mL top-irradiation quartz reactor at room temperature. A 300 W xenon lamp with a 420 nm cut-off filter was chosen as the visible light source. In the photocatalytic hydrogen evolution tests, 80 mg of photocatalyst was dispersed in 80 mL of mixed aqueous solution containing 8 mL lactic acid, serving as the sacrificial agent. A continuous magnetic stirrer was applied to keep the photocatalyst in suspended form during the complete experiment. Before irradiation, the reaction system was pumped to vacuum to ensure that it was held under anaerobic conditions. The evolved hydrogen was analyzed using a gas chromatograph equipped with a thermal conductivity detector (TCD, GC-9700, China; molecular sieve 5 Å column, N₂ carrier). The apparent quantum efficiency (AQE) of 80 mg of catalyst for H₂ evolution was measured with the same experimental setup. A 300 W Xe lamp equipped with a band-pass filter (420 nm) was used as the light source. The average intensity of the irradiation was determined by an irradiometer (FZ-A, Beijing Normal University Optical Instrument). The AQE was calculated according to the following equation:

$$\text{Quantum yield} = \frac{\text{number of reacted electrons}}{\text{number of incident photons}} \times 100\%$$

$$= \frac{2 \times \text{number of evolved H}_2 \text{ molecules}}{\text{number of incident photons}} \times 100\%$$

3. Results and discussion

Powder XRD analysis was carried out to investigate the

Fig. 2. SEM images of (a) MC-0, (b) MC-1, (c) MC-2, (d) MC-5, (e) MC-10, and (f) MC-20.

crystal structures and phase composition of the obtained CdS and MoS₂/CdS composites, as shown in Fig. 1. All samples possess similar XRD patterns. The main diffraction peaks at 24.8°, 26.5°, 28.2°, 43.7°, 47.8°, and 51.8° can be readily indexed to the hexagonal phase of CdS (JCPDF No. 41-1049) [18,45]. No obvious diffraction peaks of MoS₂ are observed for the MoS₂/CdS samples, probably because of the ultrathin structure, low content, and low crystallinity of MoS₂ [46–51].

The morphology and structure of pure CdS and MoS₂/CdS composites were investigated by FESEM and TEM experiments, respectively. The SEM images in Fig. 2 show that all samples exhibit similar willow branch morphologies. This shows that the introduction of the Mo source has no effect on the morphology of CdS, so that uniform MoS₂/CdS composites with different molar ratios can be produced by the strategy proposed in this work. The TEM image of the MC-5 sample in Fig. 3a reveals that the willow branch-shaped MoS₂/CdS composite consists of rod-like subunits. The high-resolution TEM (HRTEM) images (Fig. 3c and 3d) reveal that ultrathin MoS₂ nanosheets are coated on the CdS nanorods. The one-pot hydrothermal method adopted in this work contributes to create

Fig. 3. (a) TEM images of MC-5; (b) Photograph of willow branch; (c, d) HRTEM images of MC-5; (e) TEM image and corresponding elemental mappings of (f) Cd, (g) Mo, and (h) S.

an intimate contact between MoS₂ and CdS, which facilitates the electron transfer. The measured interlayer lattice spacing of 0.68 nm can be assigned to the (002) crystal planes of MoS₂. This few-layer and partially covered MoS₂ structure may allow taking full advantage of the favorable features of both MoS₂ and CdS components and can facilitate the photocatalytic H₂ evolution. The diffraction spots in the inset of Fig. 3c reveal the single-crystalline nature of CdS, which may contribute to the electron transport and reduce the bulk recombination. The corresponding energy-dispersive X-ray spectroscopy (EDX) elemental mappings of Cd, Mo, and S in Fig. 3e–3h confirm the homogeneous dispersion of Cd, Mo, and S, denoting a uniform coating of MoS₂ nanosheets over CdS single crystals.

The chemical composition and valence states of the elements present in the MC-5 sample were investigated by XPS. The XPS survey spectrum of the MC-5 sample in Fig. 4a clearly shows the existence of Cd, Mo, S, and O, along with trace amounts of C. The high-resolution XPS spectrum of Cd in Fig. 4b shows two peaks at 411.5 and 404.7 eV, which can be assigned to the characteristic binding energies of Cd 3d_{3/2} and Cd 3d_{5/2}, respectively, in CdS [44]. The XPS spectrum of Mo 3d in Fig. 4c, with two peaks at 231.2 and 227.9 eV, is consistent with the binding energies of 3d_{3/2} and 3d_{5/2} of Mo⁴⁺ in MoS₂, respectively [35]. In addition, the two peaks centered at about 235.1 and 232.0 eV can be attributed to the +6 oxidation state of Mo [52], which is likely formed by the partial oxidation of MoS₂ or

through the incorporation of O elements [46]. The observed peak at 225.9 eV matches well with the binding energy of S 2s in sulfides. The two peaks at 162.5 and 161.2 eV in the S 2p spectrum can be assigned to the S 2p_{1/2} and S 2p_{3/2} levels of S²⁻, respectively (Fig. 4d) [53]. The XPS results thus further confirm the presence of MoS₂ in the obtained MoS₂/CdS sample.

Moreover, the BET surface area and pore structure of MC-0, MC-5, and MC-20 were determined by N₂ adsorption-desorption isotherms at −196 °C, and are shown in Fig. 5. The three samples exhibited similar type V isotherms with H3 hysteresis loops, denoting a mesoporous structure. The BET surface area of MC-5 was calculated to be 8.3 m² g^{−1}, which is higher than that of MC-0 (6.2 m² g^{−1}) and MC-20 (4.6 m² g^{−1}). The increase in the BET surface area of MC-5 can be attributed to the ultrathin MoS₂ nanosheets on the surface of CdS [54,55]. However, as more MoS₂ was introduced in the sample (MC-20), the agglomeration of ultrathin nanosheets reduced the surface area of the heterojunction. The pore size distribution curves in Fig. 5b indicate that the CdS and MoS₂/CdS heterojunctions are rich in pores with sizes between 2 and 100 nm, showing the presence of well-developed mesoporous and macroporous structures in the samples. The MC-5 nanostructure with core-shell morphology shows a dramatically increased pore volume, which may facilitate the diffusion of reactants and improve the photocatalytic H₂ evolution activity.

The special core-shell structure is beneficial for improving

Fig. 4. (a) XPS survey spectrum of MC-5 sample; (b) Cd 3d, (c) Mo 3d, and (d) S 2p high-resolution XPS spectra of MC-5.

Fig. 5. Nitrogen adsorption-desorption isotherms (a) and corresponding pore size distributions (b) of the MC-0, MC-5, and MC-20 samples.

the optical performance [24]. Fig. 6a shows the UV-vis-near-infrared (NIR) DRS spectra of the as-prepared MC-0, MC-5, MC-20, and pure MoS₂ samples. A significant band gap absorption at wavelengths shorter than 520 nm was observed for the pure CdS (MC-0) sample. Coating with MoS₂ resulted in an apparent enhancement of the visible light absorption from 520 to 800 nm. The band gap of pristine CdS and MoS₂ can be calculated from the UV-vis DRS curves according to the formula:

$$(\alpha h\nu)^n = A(h\nu - E_g)$$

where α is the absorption coefficient, h is the Planck's constant, ν is the frequency of the incident light, A is a constant, E_g is the band gap energy, and $n = 1/2$ or 2 for indirect or direct band gap semiconductors, respectively. The corresponding Kubelka-Munk-transformed reflectance spectra are shown in Fig. 6b. The obtained E_g values for CdS and MoS₂ are 2.30 and 1.31 eV, respectively. Obviously, the narrow band gap of MoS₂ improves the visible and near-infrared absorption of MoS₂/CdS heterojunctions. The enhanced light absorption of MoS₂/CdS heterojunctions is expected to favor the formation of a higher number of photogenerated electrons available for the photocatalytic H₂

evolution reaction.

Photocatalytic H₂ generation activities of all samples without noble metal co-catalysts were evaluated under visible light illumination ($\lambda \geq 420$ nm), using lactic acid (10 vol%) as scavenger. Fig. 7 compares the average photocatalytic H₂ evolution rate of MoS₂/CdS core-shell heterojunctions with different molar ratios of MoS₂ and CdS. No H₂ was detected when only MoS₂ was used as catalyst, suggesting that MoS₂ is inactive for photocatalytic H₂ evolution. Bare CdS exhibits very low catalytic activity, owing to the fast recombination of photogenerated electron-hole pairs. However, all MoS₂/CdS heterojunctions exhibit a much higher photocatalytic H₂ generation rate, with the MC-5 sample reaching the maximum value of 250.8 $\mu\text{mol h}^{-1}$, which is about 28 times higher than that of bare CdS (9.1 $\mu\text{mol h}^{-1}$). The calculated AQE is $\sim 3.66\%$ at 420 nm. Further increasing the MoS₂ amount results in a decreased H₂ evolution rate. For example, when the molar ratio of MoS₂ reaches 20 at% (MC-20), the average H₂ evolution rate decreases to 107.6 $\mu\text{mol h}^{-1}$. This may be due to the "shielding effect", i.e., excessive MoS₂ may block the light absorption of CdS and prevent the effective contact between active sites and reactants [54,56,57].

Fig. 6. (a) UV-vis-NIR spectra of the as-prepared samples; (b) Estimation of band gap values of (a) MC-0 and (b) MoS₂ from the $(\alpha h\nu)^{1/n}$ vs. $h\nu$ plots.

Fig. 7. Comparison of photocatalytic H₂ evolution activity of willow branch-shaped MoS₂/CdS heterojunctions and physically mixed MoS₂/CdS composite under visible light irradiation.

The core-shell structure formed by MoS₂ and CdS may promote the separation and transfer of photogenerated charge carriers, resulting in an enhancement of the photocatalytic H₂ evolution activity. Moreover, the physically mixed MoS₂/CdS composite (MC-m) shows a much lower photocatalytic H₂ evolution activity, further illustrating the advantages of the unique core-shell structure developed in this work.

To further investigate the improvement in the photocatalytic activity of MoS₂/CdS heterojunctions, their charge separation and transfer behavior were investigated by photoelectrochemical tests. Fig. 8a presents the PL spectra of all samples. It is generally accepted that the PL emission results from the recombination of free charge carriers [43]. In the case of the MC-0 sample, the strongest emission band at 533 nm is attributed to the near-band-edge emission of CdS. The strong intensity is due to the fast recombination of photogenerated charge carriers. The obvious decrease in the PL intensities of MoS₂/CdS heterojunctions reflects their efficient transfer and separation of photoinduced electron-hole pairs [58]. MC-5 shows the lowest emission intensity among all samples, denoting its highest charge transfer efficiency and lowest electron-hole recombination rate. The efficient separation of photogenerated electrons and holes was further evidenced by transient photocurrent response analysis. As shown in Fig. 8b, MC-0 (pure CdS) exhibits a much lower photocurrent density because of its high electron-hole recombination rate. The MC-5 photocatalyst exhibits

a higher photocurrent density than CdS and MC-20, suggesting a more efficient separation of photoexcited electron-hole pairs [25,59]. The efficient migration and separation of charge carriers is further supported by the EIS measurements. The EIS Nyquist plots of pure CdS, MC-5, and MC-20 in Fig. 8c reveal that the arc radius corresponding to the three electrodes decreases in the order MC-5 < MC-20 < MC-0 under visible light illumination. Generally, a smaller arc diameter in the EIS spectrum indicates a lower electron-transfer resistance and a more efficient transfer and separation of photogenerated charge carriers. Hence, the MC-5 sample is the most effective at promoting the transfer and separation of photogenerated charges [60]. The more efficient separation of photogenerated charge carriers in MC-5, associated with the intimate contact between MoS₂ and CdS, results in its superior performance in the photocatalytic H₂ evolution.

In addition, the Mott-Schottky analysis was employed to determine the conduction and flat band potentials of CdS and MoS₂. It is well known that the type of semiconductor can be determined from the slope of the Mott-Schottky plot [61]. The positive slopes of the Mott-Schottky plots shown in Fig. 9a and 9b indicate that both the CdS and MoS₂ materials investigated in this work are n-type semiconductors. The flat band potentials (vs. saturated calomel electrode, SCE) of CdS and MoS₂, obtained from the Mott-Schottky plots, are approximately equal to -1.35 and -0.64 V, respectively. The conduction band (CB) potential (E_{VB}) of an n-type semiconductor is known to be approximately equal to the flat-band potential [62]. Thus, the estimated conduction band potentials (vs. normal hydrogen electrode, NHE) of CdS and MoS₂ are -1.11 and -0.4 V, respectively. Moreover, the valence band potential (E_{VB}) can be estimated by the following equation:

$$E_{VB} = E_{CB} + E_g$$

Taking into account the DRS results, the E_{VB} values of CdS and MoS₂ were calculated to be 1.19 and 0.91 V, respectively. The overall energy band structure of the MoS₂/CdS heterojunctions is displayed in Fig. 9c.

Based on the analyses discussed above, we can propose a tentative mechanism for the enhanced photocatalytic H₂ production of willow branch-shaped MoS₂/CdS heterojunctions. Under visible light irradiation, most of the photogenerated electrons and holes will recombine in pure CdS, and only a small fraction will participate in the photocatalytic reaction, leading to a lower H₂ evolution activity. After the formation of

Fig. 8. (a) Room-temperature PL spectra of all as-prepared samples ($\lambda_{\text{ex}} = 434$ nm); (b) transient photocurrent response and (c) electrochemical impedance spectra of MC-0, MC-5, and MC-20.

Fig. 9. (a, b) Mott-Schottky plots of MC-0 and MoS₂, used for determining the flat-band potentials; (c) Schematic illustration of proposed mechanism for the enhanced photocatalytic H₂ evolution.

MoS₂/CdS heterojunctions, electrons generated in CdS will transfer from the CB of CdS to MoS₂, owing to their matching energy band potentials, and will then be captured by H⁺ to form H₂. Moreover, the intimate junction formed between MoS₂ and CdS through the one-step method can effectively assist the transfer of electrons. As a consequence, charge recombination will be substantially reduced, enhancing the photocatalytic activity. In addition, the increased visible light absorption will promote the production of photogenerated electrons and holes, as evidenced by the transient photocurrent response and PL spectra; this is also an essential factor promoting the photocatalytic activity. Therefore, these effects considerably enhance the photocatalytic H₂ evolution activity of MoS₂/CdS heterojunctions under visible light irradiation.

4. Conclusions

Novel willow branch-shaped MoS₂/CdS heterojunctions were prepared through a facile one-pot hydrothermal method for the first time. The MC-5 sample showed the highest photocatalytic H₂ generation efficiency under visible light irradiation

(250.8 $\mu\text{mol h}^{-1}$), which is about 28 times higher than that of pure CdS. The higher hydrogen generation efficiency of MC-5 can be attributed to its increased visible light absorption, accelerated charge transport, and suppressed charge recombination. This work thus introduces a potentially effective photocatalyst for solar energy conversion.

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Graphical Abstract

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One-pot hydrothermal synthesis of willow branch-shaped MoS₂/CdS heterojunctions for photocatalytic H₂ production under visible light irradiation

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Novel willow branch-shaped MoS₂/CdS heterojunctions synthesized via a one-pot hydrothermal method show excellent photocatalytic H₂ evolution activity.

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一锅水热法制备柳枝状MoS₂/CdS异质结材料及其可见光催化产氢性能

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摘要: 自从1972年Fujishima和Honda发现TiO₂光电催化分解水产氢以来, 半导体光催化分解水产氢技术被认为是解决能源危机和环境污染问题最有效的策略之一. 然而, 由于TiO₂的可见光吸收能力差、活性低、价格高等问题限制了其实际应用, 因此寻求和发展高效的可见光催化剂具有重要意义. CdS半导体材料具有合适的带隙及导带位置, 可以有效吸收可见光产生电子并将H⁺还原生成H₂, 是目前公认的较好的可见光催化产氢材料之一. 然而光催化过程中CdS材料较快的电子-空穴复合速度极大降低了其效率, 如何促进光催化过程中电子-空穴对的分离成为研究重点. 研究表明, 采用负载助催化剂、构筑异质结、表面修饰、金属/非金属元素掺杂等技术可明显提高CdS的光催化产氢性能, 其中发展非贵金属助催化剂引起了广泛兴趣.

近年有文献报道过渡金属硫化物MoS₂用于光催化助催化剂, 可以明显提高光催化性能. 目前已制备出具有不同形貌的MoS₂/CdS异质材料如纳米球、纳米棒、纳米纤维等, 但多数MoS₂/CdS异质材料的制备采用两步法或多步法, 制备工艺复杂, 易引入杂质, 阻碍了其实际应用. 因此, 发展简单温和的一步法制备具有新颖形貌的MoS₂/CdS异质材料具有重要意义.

本文采用简单的一步水热法制备了一种新颖的柳枝状MoS₂/CdS异质材料. 采用X射线衍射、场发射扫描电子显微镜、透射电子显微镜、X射线光电子能谱、紫外-可见漫反射吸收光谱和氮气吸附-脱附测试对所得样品进行了表征. 结果表明, 制备的柳枝状MoS₂/CdS异质材料具有核壳结构, 两者之间形成紧密的异质结. 光催化性能测试表明, 制备的MoS₂/CdS异质材料相比纯相CdS产氢性能明显提高, 优化后的MoS₂/CdS异质材料(MoS₂/CdS摩尔比为5:100)的产氢性能是纯CdS的28倍. 通过紫外-可见漫反射光谱、荧光光谱分析、光电流、EIS阻抗谱及莫特肖特基曲线测试发现, CdS与MoS₂之间致密的异质核壳结构有助于光生载流子的迁移与分离, 从而明显提高光催化活性.

关键词: 硫化镉; 硫化钼; 光催化; 水分解; 产氢; 异质结; 核壳结构; 可见光

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