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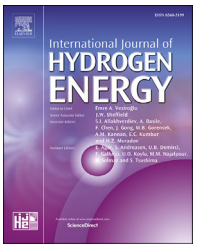

Reduced graphene oxide as an efficient support for CdS-MoS_2 heterostructures for enhanced photocatalytic H_2 evolution

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ABSTRACT

Cadmium sulphide nanorods-reduced graphene oxide-molybdenum sulphide(CdS-rGO-MoS_2) composites were successfully synthesized using hydrothermal process for enhancing the interfacial contact between CdS nanorods and MoS_2 layer. The good contact between CdS and MoS_2 is important for improving the photocatalytic hydrogen (H_2) evolution. The morphological and structural studies showed the production of highly pure CdS phase with nanorod-like structure dispersed on rGO-MoS_2 layer. X-ray photoelectron spectroscopy (XPS) and Raman results confirmed the reduction of graphene oxide (GO) into reduced graphene oxide (rGO). The higher photocurrent density of CdS-rGO-MoS_2 composites compared to CdS/MoS_2 and the fluorescence quenching observed for this composite provided some evidence for an inhibition of electron-hole recombination, which leads to a longer life time of the photogenerated carriers. Fast electron transfer can occur from CdS nanorods by the bidimensionnel rGO area to MoS_2 layer due to the intimate interfacial contact. Composite CdS-rGO-MoS_2 with 20 wt% rGO was found to be the most effective photocatalyst for H_2 evolution (7.1 mmol $h^{-1}g^{-1}$). The good photocatalytic performance arose from the positive synergistic effect between CdS, rGO and MoS_2 elements.

Introduction

Photocatalytic H_2 production using non noble metals and earth-abundant elements (metal oxides, sulfides …) has received much attention as a green, economical, and promising way to convert solar energy into preservable H_2 [1–3]. Thus, the development of efficient visible-light-driven photocatalysts is of great importance, because of their useful absorption of the solar spectrum. CdS as *n*-type semiconductor with a narrow band gap (2.4 eV) has been applied for visible light H_2 evolution due to its suitable conduction band gap edge for H_2 evolution reaction [4,5]. However, for practical applications, CdS is still limited by the high photogenerated carriers recombination, poor stability, and its photocorrosion [6]. Alternatively, finding novel, environmental-friendly electrocatalysts with CdS-based substrate has proven to be successful way that could hinder the charge carrier recombination, which greatly improves the catalyst activity [7–9]. TiO_2/CdS has been reported as a promising candidate

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for efficient H_2 evolution [10,11]. Similarly, it has been demonstrated that hybridization of CdS with carbon spheres [12], $BiVO_4$ nanowires [13,14], MoS_2 [15–22], and MoS_2/TiO_2 nanofibers [23] allowed to enhance the visible light H_2 evolution and reduce the recombination of photogenerated carriers. Loading CdS on reduced graphene oxide (rGO) has been regarded as an effective and feasible way for improving the photocatalytic activity [24–26]. In this line, Hong et al. [26] have demonstrated the good performance of rGO loading on CdS for photocatalytic H_2 evolution.

For instance, the photocatalytic H_2 evolution using CdS-rGO-MoS_2 composites has been described only in a few reports [27–30]. For example, MoS_2 photodeposited onto rGO/CdS was evaluated for synergistic photocatalytic hydrogen generation [29]. It was found that under synergistic condition, the photocatalytic hydrogen evolution rate was 4.3 times higher than that under antisynergistic condition. Similarly, Chang et al. [31] showed the highest photocatalytic activity of MoS_2/graphene-CdS.Yang et al. [27] reported on the influence of MoS_2 cocatalyst on the photocorrosion and photoactivity of CdS combined with graphene. It was found that the photocatalytic activity of tiny $MoS_2$was better than stacked layer structure of MoS_2 [27]. This result was attributed to the ability of tiny MoS_2 to reduce the photocorrosion and increase the active sites of CdS on the graphene surface.

Although the above results clearly emphasized that the good contact between CdS and $MoS_2$was necessary for improving the photocatalytic H_2 evolution, a number of researchers have focused on the design of CdS-rGO in one step and then adding MoS_2 using different approaches (photodeposition or hydrothermal …) to prepare CdS-rGO-MoS_2 nanohybrid. Little attention has been paid to reduce GO on CdS nanorods and layer of MoS_2 in one step.

Herein, to improve the photocatalytic performance of CdS/MoS_2 heterostructures, we report a one pot facile *hydrothermal method* to prepare CdS nanorods/rGO/MoS_2 *nanocomposites with different GO contents*. The application of CdS/rGO/MoS_2 nanohybrids for photocatalytic H_2 evolution in water *via* visible-light-treatment showed enhanced photocatalytic performance compared to the CdS/MoS_2 solely.

Experimental

Reagents

Cadmium acetate dihydrate ($Cd(Ac)_2{\cdot}2H_2O$), thiourea (NH_2CSNH_2), molybdate dihydrate ($Na_2MoO_4{\cdot}2H_2O$), hydrochloric acid (HCl), and graphite powder (<20 μm)were of analytical grade. All reagents and products used for cleaning, synthesis and analyses were purchased from Sigma-Aldrich and utilized as-received. Graphene oxide (GO) used in this work was prepared using a modified Hummers' method [32].

Synthesis of MoS_2

Typically, 0.36 g of sodium molybdate dihydrate ($Na_2MoO_4{\cdot}2H_2O$) was dissolved in 30 cm^3 of ultrapure water. Secondly, 0.47 g of aqueous thiourea (NH_2CSNH_2) soultion was added to the above soultion, mixed together and sonicated for 30 min. Then, the pH of the solution was adjusted to 4 by addition of HCl (0.1 M). The solution turned from colorless into yellow, and then transferred into a 120 cm^3Teflon-lined stainless steel autoclave which was heated at 200 °C for 24 h. The resultant powder was cleaned using ultrapure water and dehydrated overnight at 80 °C.

Synthesis of CdS-rGO-MoS_2

1 mmol of $Cd(Ac)_2{\cdot}2H_2O$ was dissolved in 30 cm^3ultrapure water. Under continuous stirring, freshly prepared NH_2CSNH_2 solution (1 mmol) was added dropwise to $Cd(Ac)_2{\cdot}2H_2O$ at room temperature to form a transparent solution. Then, sonicated MoS_2 sheets/graphene oxide(MoS_2/GO) aqueous solution with 1:2 wt% ratio was added to the above mixture and stirred for 30 min. The resulting solution was placed into 120 cm^3Teflon-lined stainless steel autoclave and heated at 200 °C for 24 h. The formed material was cleaned with ultrapure water 5 times and dried overnight at 80 °C. CdS-MoS_2 was synthesized by a similar method without adding GO in the solution.

Physicochemical analyses

X-ray diffraction patterns were recorded using an X'pert Pro X-ray diffractometer (Rigaku D/max-2500). Transmission electron microscopy (TEM, Hitachi H-7600-FE-TEM) imaging was obtained by utilising a Gatan SS CCD camera, the bright-field images were acquired by a Digital Micrograph software. Scanning electron microscopy (SEM, Hitachi S-4300-FE-SEM, secondary electron (SE) mode) was used to analyze the morphology of the nanostructures. Micro-Raman spectroscopy was performed using a visible Labram HR spectrometer (Horiba Jobin-Yvon Raman spectrometer)under the excitation of 532 nm. Absorption spectra were obtained using a UV–vis, Varian CARY 5G spectrophotometer. Fluorescence measurements were acquired in the spectral range of 500–600 nm under the excitation wavelength of 325 nm. Transient photocurrent measurements were carried out in 0.1 M aqueous Na_2SO_4 solution placed into 120 mL reactor and under irradiation of 300 W Xe lamp (100 mW/cm^2); the lamp was connected to a UV and IR filter.

Electrochemical impedance spectroscopy (EIS) experiments were performed at an applied potential of 0.2 V. For this, a 50 μL aliquot of a (0.1 M KCl + 5 mM $[Fe(CN)_6]^{4/3-}$) solution was casted on the electrode surface then the frequency was swept from 100 MHz to 0.1 Hz. All the EIS data are presented as Nyquist plots (i.e., the reciprocal of the real component of the impedance plotted against the imaginary one).

Catalytic activity measurements

The photocatalytic activity of CdS-rGO-MoS_2 composites for hydrogen evolution was performed in water solution. The photocatalysis experiments were carried out in a 120 mL pyrex-glass reactor molded with a quartz disc. A 300 W Xe lamp(100 mW/cm^2) attached to a UV and IR filters was used for the irradiation.

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