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Exploring co-catalytic graphene frameworks for improving photocatalytic activity of Tin disulfide nanoplates

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ABSTRACT

The exploration of high efficient photocatalysts for water-splitting is a challenge as well as an opportunity for future applications in renewable sustainable energy. In this paper, a two dimensional photocatalytic Tin disulfide/graphene hybrid nanosheets (SnS_2/rGO HNs) with identically 2D structural configurations have been prepared via a facile hydrothermal route. The as-prepared SnS_2/rGO HNs photoanode demonstrates improved photoelectrochemical (PEC) performance when compared to bare SnS_2 electrodes. X-ray diffraction pattern and Raman spectra are carried out and confirm that the as-prepared SnS_2/rGO HNs are pure and well crystalized. Additional morphological and microstructural tests verify a high yield of SnS_2/rGO HNs with good quality, indicating the relatively stability of graphene platform with high specific surface area. Further PEC measurements demonstrate the photocurrent density of SnS_2/rGO HNs attain maximum under 100 mW/cm^2 when the applied potential is 0 V and varies from 321 nA/cm^2 to 244 nA/cm^2 while the applied potential increase from 0 V to 1.0 V. Besides that, the duration test exhibits no detectable distinction after processing 25 cycles. The PEC improvement is proposed to derive from the positive synergetic effect between SnS_2 and co-catalytic graphene framework. We hope this work can provide fundamental illustration about the PEC performance of two-dimensional SnS_2/rGO HNs, offering extendable availabilities for its potential application into high-performance PEC and photovoltaic devices.

1. Introduction

The efficient hydrogen production from photoelectrochemical (PEC) water-splitting is fundamental important for catering to the need of sustainable energy source. (Han et al., 2014a; Hisatomi et al., 2014; Ismail and Bahnemann, 2014; Luo et al., 2017; Qiu et al., 2014; Swierk et al., 2015; Zahedi et al., 2015; Zhang and Pan, 2011) Exploring of photocatalysts that exploit potential advantages of sunlight to oxidize and reduce water into renewable and environment-friendly energy has attracted substantial attentions. (Li et al., 2016; Zhang et al., 2016b) In the past few decades, titanium dioxide (TiO_2) shows promising activities toward water splitting since the first report by Fujishima and Honda. (Chen and Mao, 2007; Fujishima and Honda, 1972; Ren et al., 2012; Zhang et al., 2016c) Whereas, two main disadvantages of TiO_2: (i) low photogenerated electron-hole separation rate and (ii) inferior absorption coefficient, has impeded its further application. Although numerous approaches are contributed to improve the PEC performance of TiO_2, the up-to-date PEC performance of TiO_2 seems to reach their intrinsic limitations. (Bai et al., 2014; Borges et al., 2016; Linsebigler et al., 1995; Ren et al., 2016; Zhang et al., 2011a) In this regards, further exploration of well-qualified photocatalytic alternatives with broadband absorption properties is of great interest in meeting the requirement of practical applications.

During recent years, two-dimensional (2D) layered semiconductors are emerging to be fundamentally interesting and technologically attractive. (Chen et al., 2017; Li et al., 2014; Ponraj et al., 2016; Ren et al., 2017b; Zhang et al., 2016a) Benefiting from the excellent optoelectronic properties and controllable bandgap structure, 2D layered materials have been widely applied in the photo-electrical field. Most recently, Tin disulfide (SnS_2) with identically 2D structural configuration has attracted great interests. (Zhang et al., 2015, 2011b) Both theoretic calculations and experimental studies reveal the band gap of SnS_2 ranges from 2.18 eV to 2.44 eV, (Chang et al., 2005; Hu et al., 2013; Su et al., 2014) which means SnS_2 possess preferable solar absorption capability in the visible light region where TiO_2 is inherently prohibited. Besides that, 2D SnS_2 demonstrates high stability under both ambient and electrolytic conditions, (Zhang et al., 2010) which endows its practical applications as an attractive visible-light-

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responsive photocatalyst (Zhong et al., 2012). Yu et al. (2014) reported a facial solvothermal approach to prepare monodisperse SnS_2 nanosheets, which exhibit much higher photocatalytic H_2 evolution activity than that of P25-TiO_2 under simulated sunlight irradiation. On the other hand, Sun et al. (2012) put forward a scalable liquid exfoliation strategy to obtain freestanding single-layer SnS_2 with an inspiring photon-to-current conversion efficiency up to 38.7%. Although great achievements have been realized on SnS_2 photocatalysts, it is suggested that combine SnS_2 photocatalyst with efficient co-catalytic graphene nanosheets can facilitates the charge transfer and improves the specific surface area. Chen et al. (2013) fabricated reduced graphene oxide/SnS_2 (rGO/SnS_2) composites, depicting favorable electrochemical and photocatalytic performances. Such unique structures are associated with high specific surface area and superior electronic conductivity, while the intimate contact and electrochemical effects in the interface between SnS_2 and graphene can benefit the charge transfer and provide more reaction sites, resulting in enhanced photocatalytic activities for hydrogen evolution. Inspired by the aforementioned investigations, the manufacture of graphene with ultrathin 2D SnS_2 can be a feasible approach for obtain photocatalysts with outstanding PEC activity and long-term stability.

Herein, we report a general and effective hydrothermal route to prepare 2D-2D SnS_2 nanosheet/rGO hybrid system and investigate the PEC properties of the as-prepared SnS_2/rGO hybrid nanosheets (HNs) by carefully controlling the bias potential and irradiation power density. The PEC measurements demonstrate the photocatalytic activity of SnS_2 is greatly improved by the combination of rGO. The remarkable PEC performance of SnS_2/rGO HNs can be attributed to the broadband absorption availability as well as the as co-catalyst effect from rGO. All the results imply that the obtained SnS_2/rGO HNs exhibits extraordinary PEC performance and may carry out potential advantages in practical applications.

2. Experimental section

2.1. Synthesis of materials

All the chemical reagents were of analytical grade and used without further purification. In a typical procedure, Graphene oxide (GO) was synthesized by using a modified Hummers method which has been reported previously. (Tan et al., 2015; Tang et al., 2015) Meanwhile, SnS_2/rGO HNs were synthesized by a two-steps hydrothermal method. In detail, 480 mg $SnCl_4{\cdot}5H_2O$ was dissolved in 100 mL N,N-dimethylformamide (DMF) solution, then 100 mg GO was mixed with the above solution with continuous stirring for 30 min to form a homogeneous dispersion. After that, 10 ml deionized (DI) water and 5 ml hydrochloric acid (HCl, 36–38 wt%) was added to the solution to maintain an acid condition. After heated at 80 °C for 12 h, a homogeneous mixture can be obtained after being centrifuged to remove the residual reagents after wash and filtration for three times using acetone and ethanol. Then, the obtained mixture was re-dispersed in 30 mL DI water with 330 mg of L-cysteine acid and transferred into 50 mL Teflon-lined stainless steel autoclaves at 180 °C for 18 h. The gray SnS_2/rGO HNs precipitates can be collected by centrifugation and washed with DI water and ethanol, and dried at 60 °C for 12 h in vacuum for further characterizations. Pure SnS_2 was prepared as control sample by the same procedures without adding GO.

2.2. Characterization

The crystal structures of the as-prepared samples were determined by X-ray diffraction (XRD) using Cu K_α radiation. Raman spectra were collected by using the Renishaw InVia Raman microscope, excited at room temperature with excitation laser wavelength of 532 nm. The morphologies and microstructures of the samples were characterized using field emission scanning electron microscopy (SEM, Tescan Vega3 SBH) and transmission electron microscopy (TEM, JEM 2100).

2.3. Preparation of working electrodes

The indium-tin oxide (ITO, 20 mm × 10 mm × 1 mm) conductor glass was used as the substrate of the working electrode, which was ultrasonically washed with acetone, ethanol and deionized water. Then, a small portion (1 mg) of as-prepared SnS_2/rGO was mixed with 1 mL ethanol solution to obtain evenly dispersed slurry. The working electrode was dried overnight under ambient conditions after the above slurry spread onto ITO substrate, yielding a catalyst loading of ~0.5 mg/cm^2 on the ITO glass;

2.4. Photoelectrochemical (PEC) measurements

The PEC tests were performed in 0.5 M Na_2SO_4 (pH = 7) electrolyte, using a standard three-electrode system operated with SnS_2 and SnS_2/rGO photoanodes. Meanwhile, an Ag/AgCl electrode was adopted as the reference electrode while Pt flake was utilized as cathode. Electrochemistry workstation CHI660E (CH Instruments, Inc., Shanghai) was used to control the bias potential and record the photocurrent generated. A 350 W Xenon arc lamp (Perfectlight Technology Co., Beijing) was placed 20 cm away from the reaction vessel, which working as a light source and no filter is used. The illumination intensity on the photoanode was fixed at 100 mW/cm^2. The linear sweep voltammograms of the different samples were measured at a scan rate of 10 mV/s. All the experiments were carried out at the same condition.

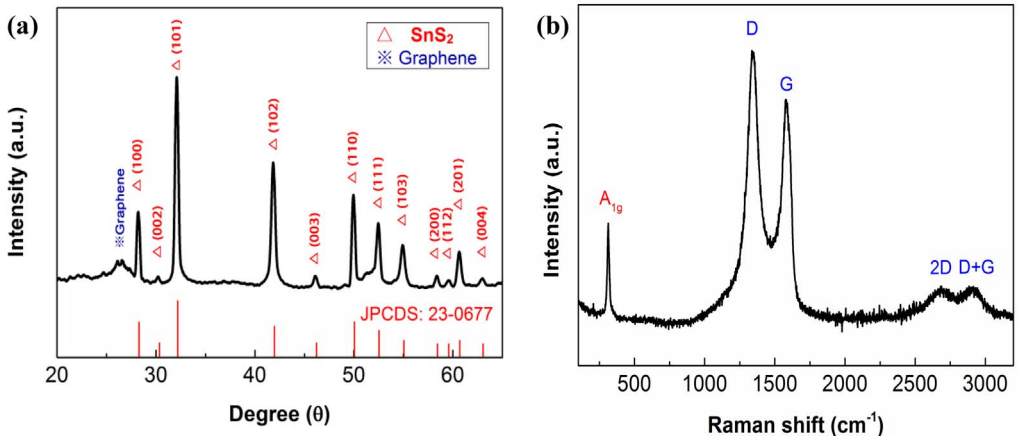

Fig. 1. (a) XRD pattern and (b) Raman spectra of as-prepared SnS_2/rGO hybrid nanosheets.