Solar Energy Materials and Solar Cells 174 (2018) 300–306

Contents lists available at ScienceDirect

Solar Energy Materials and Solar Cells

journal homepage: www.elsevier.com/locate/solmat

High photoelectrochemical activity and stability of Au-WS_2/silicon heterojunction photocathode

Longhui Zeng[1], Yang Liu[1], Shenghuang Lin, Wayesh Qarony, Lili Tao, Yang Chai, Xuming Zhang, Shu Ping Lau, Yuen Hong Tsang*

Department of Applied Physics and Materials Research Center, The Hong Kong Polytechnic University, Hung Hom, Kowloon, Hong Kong 99077, China

ARTICLE INFO

Keywords:
WS_2
WS_2/Si
Heterojunction
Photocathode
Photocatalyst

ABSTRACT

Although silicon has been widely employed as light harvesting antenna in photocatalysts due to its cost advantage, it suffers from low efficiency and poor stability due to photocorrosion of Si. To overcome this problem, a heterojunction photocathode was produced by coating a WS_2 thin-film on *p*-type Si. Our proposed method can further improve the photocatalytic activity and stability. The homogeneous WS_2 films with large surface area and tens-of-nanometers in thickness were prepared through magnetron and post-annealing process. This film not only functions as a protective layer to isolate the Si from the harsh electrochemical environment, but also forms a junction at the interface between WS_2 and *p*-type Si to facilitate the charge separation and transport processes. Additionally, further enhancement of visible photocatalytic performance was achieved by depositing Au film on WS_2/*p*-Si through thermal evaporation and the highest value of the photocurrent intensity achieved is up to ~ 4.5 μA/cm^2 at 0 V *versus* Ag/AgCl. Besides, photoelectrochemical instability of WS_2/*p*-Si electrodes can be minimized by adding Au coating. Our results suggest that adding the Au-WS_2 on *p*-Si can benefit carrier separation and providing physical protection of the Si layer. Therefore, it can further improve the overall photocatalytic activity and stability.

1. Introduction

The global energy crisis and many environmental problems could potentially be solved provided that photoelectrochemical (PEC) water splitting can be done in a cost effective way with high efficiency. PEC water splitting is a promising approach to generate clean and renewable energy source-hydrogen (H_2) and oxygen (O_2) by using solar energy. This research topic has gained extensive and increasing interests. The research works for searching for low cost, efficient and durable photoelectrode are particularly popular. Therefore, some common semiconductors such as Si, III–V, and II–VI have been extensively studied previously. Among these materials, silicon has attracted considerable attention due to its favorable properties and it has been widely applied in various fields such as electronics [1,2], thermoelectric [3], solar cell [4], and photo-electrochemical water splitting [5–7]. At room temperature, silicon with bandgap of 1.12 eV is considered to be one of the most promising candidates for photocathode because of efficient solar energy harvesting across the entire solar spectrum, low material cost and abundance (> 90% in the Earth's crust) [8]. For these reasons, silicon-based photoelectrodes and photocatalysts have been widely developed for solar energy harvesting and conversion. However, the poor photoelectrochemical stability is one of the key problems for the development of high performance Si-based photocatalysts as Si is thermodynamically vulnerable to photoactive dissolution, or photocorrosion [9]. In order to develop effective approaches to stabilize the photoactivity of Si, expensive metal and rare earth metals *e.g.* Pt [10], Ir/IrOx [11] were used for performance and stability enhancement preiously. Searching for the alternative low-cost and scalable strategies to solve stability issue is still an on-going and hot research topic with in the field.

Recently, the emergence of layered two-dimensional transition-metal disulfides (2D TMDs) has garnered much attention due to their favorable electrical and optical properties for fiber laser [12], photodetector [13], photocatalyst [14]. It is noted that 2D TMDs such as MoS_2, SnS_2, TiS_2, WS_2, $MoSe_2$, WSe_2 are emerging as important class of 2D materials for the photocatalysis applications [15]. For example, MoS_2-g-C_3N_4 hybrid photocatalyst was successfully fabricated using for the removal of NO [16]. WSe_2/RGO composite demonstrates high-efficiency in photocatalytic degradation of organic dye Rhodamine B under visible light irradiation [17]. By virtue of their attractive

* Corresponding author.
E-mail address: Yuen.Tsang@polyu.edu.hk (Y.H. Tsang).
[1] The first two authors contributed equally to this work.

http://dx.doi.org/10.1016/j.solmat.2017.07.042
Received 15 April 2017; Received in revised form 21 July 2017; Accepted 30 July 2017
Available online 19 September 2017

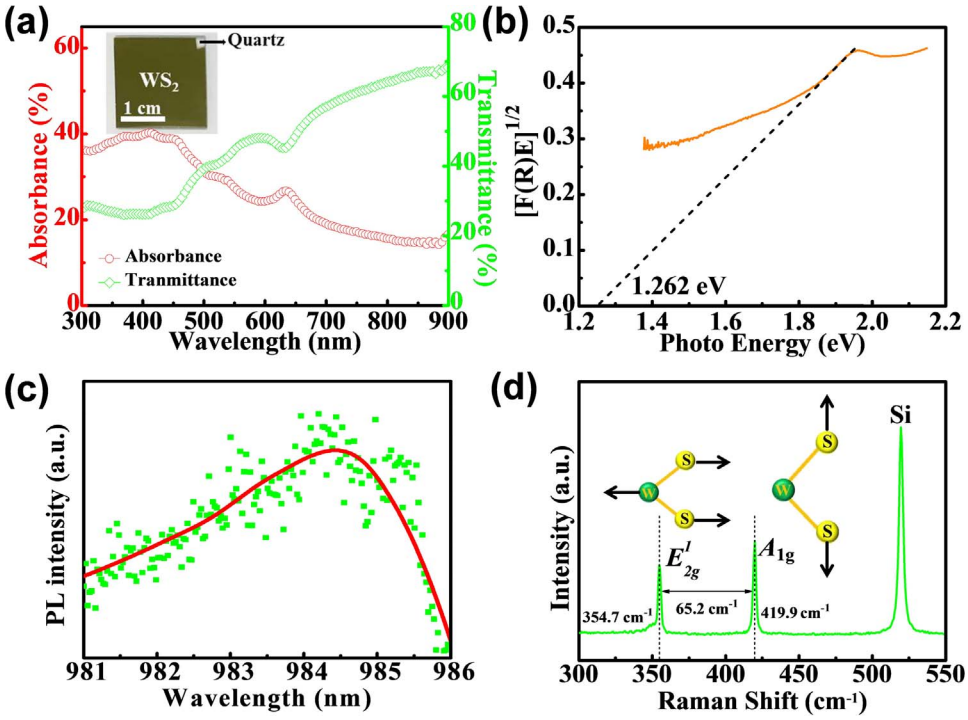

Fig. 1. (a) Measured UV–visible absorbance and transmittance of the WS_2 films. Inset in (a) shows the photograph of an annealed WS_2 film on quartz substrate (b) Plot transformed according to the Kubelka-Munk function *versus* photon energy (c) PL spectra of as-synthesized WS_2 films. (d) Raman spectrum of the WS_2 films on Si substrate. The insets show the illustration of different vibration modes.

properties for photocatalysts, TMDs are low cost and earth abundant and they can serve as promising materials to replace the more expensive Pt, Rh, and Ir suggested in the previous study. It has been reported that WS_2 and MoS_2 with suitable bandgaps (1.1–1.7 eV) matched well with the solar spectrum and possess high densities of active edge sites for photocatalysis [18,19]. Actually, WS_2 shows high thermal stability and wide operational temperature range as lubricants [20]. Moreover, WS_2 has excellent chemical stability and can serve as protecting barrier to prevent photocorrosion of Si. Furthermore, WS_2 could form a WS_2/*p*-Si heterojunction for performance enhancement of photocatalytic applications. It has been known that the induced electrical field between the WS_2 and Si could be very strong due to the difference in work function [18], which could facilitate the transport of the photogenerated electrons from Si to WS_2 and then to the electrolyte/solid interface.

Preparation of uniform and large area WS_2 thin film is one of the most important steps for high-quality device fabrication. However, WS_2 films reported in recent papers are usually acquired by exfoliation, solution-based syntheses, and chemical vapor deposition (CVD) [13,21]. In fact, it is difficult to control the uniformity of size and thickness and deposited into a thin film by using those WS_2 flakes fabricated by mechanical or chemical exfoliation [22]. Uniform and ultrathin WS_2 layers can be synthesized on oxide substrates by using CVD method, but the surface of CVD-grown WS_2 layers contains mainly electrochemically inactive basal planes [14]. The magnetron sputtering deposition method has some advantages over the CVD method including simplicity, low cost, high production speed and scalability. Therefore, to overcome these problems, direct magnetron sputtering deposition is employed to fabricate WS_2/*p*-type semiconductor heterojunctions.

In this study, a facile and simple method to functionalize Si photocathode with WS_2 thin films is reported. To further boost the device performance, Au film was coated on WS_2 to collect the electrons for high efficient photocurrent conduction. The as-prepared Au-WS_2/*p*-Si photocathode exhibited enhanced photo-activity with much higher photocurrent stability. The excellent performance of Au-WS_2/*p*-Si can not only offer strong potential for application of silicon-based photocatalysts/photoelectrodes for solar energy harvesting but also provide new insights for enhancing and stabilizing other photocatalytic systems.

2. Experimental section

2.1. WS_2 film deposition

WS_2 films on the *p*-Si substrate were produced by magnetron sputtering method. The WS_2 precursor film was first deposited on the clean *p*-Si substrate through sputtering by using sintered WS_2 target. The radio frequency (RF) power density, argon gas pressure, and substrate temperature were set to be 2.96 W/cm^2, 5 mTorr, and 200 °C, respectively; and deposition time of 5 mins. To improve the film crystallinity, the as-prepared WS_2 films were annealed in Ar atmosphere at 800 °C and kept stable for 2 h.

2.2. Device fabrication

To fabricate the Au-WS_2/*p*-Si photocathode, *p*-type (100) Si (resistivity 1–10 Ω cm) substrates were ultrasonically cleaned in alcohol, acetone and deionized water in sequence, and dried under a stream of nitrogen gas. WS_2 film was deposited under the conditions mentioned above. Afterward, Au (50 nm) films were deposited onto the WS_2 film by thermal evaporation.

2.3. Characterizations of materials and devices

UV–vis absorbance and transmittance spectra were measured by a SHIMADZU UV-2550 UV–vis spectrophotometer. The Raman spectra were carried out on an HR-800 Raman spectrometer with a 488 nm argon ion laser. The X-ray diffraction (XRD) pattern was recorded using a RigakuSmartLab X-ray diffractometer. The surface morphology and height profile of samples were obtained by atomic force microscopy (AFM, VeecoNanoscope V). The morphology, crystal structure, and chemical composition were investigated using a field emission transmission electron microscope (FETEM, JEOL Model JEM-2100F), equipped with an energy dispersive spectrometer (EDS). Additionally, the photocatalytic reaction was measured with an electrochemical workstation (CH Instruments, CHI 660E) in a stand and three-electrodes