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Enhanced visible light catalytic activity of $MoS_2/TiO_2/Ti$ photocathode by hybrid-junction

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ABSTRACT

In photoelectrochemical (PEC) water splitting systems, crucial obstacles limiting their performance are poor charge carrier dynamics and high recombination rate of photoexcited electron-hole pairs. Here, we report that this issue can be alleviated by engineering a hybrid-junction that is composed of homo- and hetero- junctions. This strategy is performed by facile hand-spraying MoS_2 over the surface of anatase/rutile homo-junction TiO_2 film on the Ti substrate to further form a hybrid-junction photocathode. By applying this photocathode into PEC reactor, enhanced catalytic activity is achieved under visible light (AM1.5 illumination of 300 W/m^2) with hydrogen evolution reaction (HER) potential of −114 mV versus reversible hydrogen electrode (RHE) at 10 mA/cm^2 and long-term stability of more than 10 times improvement comparing to ordinary electrode without the introduction of hybrid-junction. The hybrid-junction that effectively regulates charge separation and transfer pathways is proven to be responsible for the enhanced activity. As a novel exploration, this hybrid-junction system comprising of low-cost, efficient charge separation and transfer, and visible light responsivity offers a new path for relative materials to boost their PEC performance.

1. Introduction

Photoelectrochemical (PEC) water splitting system harvesting sunlight to drive uphill water splitting reactions has been the focus of attention due to its potential of converting sunlight into chemical fuels in a cost-economical and sustainable way [1–4]. In the past decades excellent advancement has been achieved, specially the metal oxide semiconductor has been invested greatly due to their intrinsic nature of the d orbital states, earth-abundance and superior PEC performance [5–8]. However, their PEC performance to the practical commercialization is still subjected to the limitations of poor charge-carrier dynamics and high recombination rate issues under the solar illumination [9,10]. To solve these issues, some efforts have been made to pursue reliable strategies in particular the search for hybrid systems [3,11–13].

Hetero- and homo-junctions are two distinctive approaches used in the hybrid systems [14,15]. The designing of hetero-junction is a well-established approach as it holds great potential to overcome the drawbacks of serious charge recombination and limited visible-light utilization [16], typically involving building an advanced two-step (Z-scheme) system. The Z-scheme system composed of two semiconductors with desired band gaps and energy positions ensure that the separated electrons and holes transport only in opposite directions toward the surface for preferred reactions, minimizing deleterious recombination and undesirable side reactions [17,18]. Z-scheme construction can not only regulate charge transfer pathways but also increase the sunlight utilization through the series connected two semiconducting materials with narrow bandgap absorbing visible light [19,20]. As an example, there have been reports that Z-scheme hetero-junction of MoS_2/TiO_2 with CdS quantum dots can effectively improve the catalytic activities under the visible light irradiation as the result of beneficial charge interaction in the interface [21]. Recent studies have also demonstrated that the excellent catalytic activity in the heterojunctions of MoS_2/TiO_2 is related to the strong interaction between the MoS_2 and TiO_2 [22–27].

On the other hand, the construction of homo-junction (phase-junction) is an alternative configuration access to charge-carrier separation because the formation of homo-junction between two distinct phases can adjust the transport of the charge carriers along the inter-phases band alignment [9]. For example, it has been reported that surficial

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phase-junction between the nanoparticles of anatase and rutile TiO_2 can enhance the water splitting activities [28]. The basic mechanism is that the surficial anatase/rutile phase junctions can guide the electrons or holes transferred between band structures of rutile and anatase TiO_2, thereby facilitating separation of electron-hole pairs and catalytic activities [28–30].

Although configuring hetero-junction or homo-junction is well explored, the potentials of integrating hybrid-junction comprising of hetero-junction and homo-junction into a single photoelectrode is still lack of investigation, especially in terms of the impact on charge carrier dynamics. In the heterogeneous system, the doping of foreign elements [31–33] was explored to provide multi-channel paths for improving the charge-carrier dynamics. In this study, we propose a facile strategy of building hybrid-junction to improve the catalytic activity of photocathode under visible light. We demonstrate that integration of homo-junction and hetero-junction on the bulk metal substrate as a simple but effective strategy could effectively fast the performance of charge separation, transfer and transportation dynamics at the interface and reduce charge carrier recombination in the bulk and at the surface.

We fabricated hybrid-junction of MoS_2/TiO_2 by hetero-coupling MoS_2 and homo-junction (mixed-phases) TiO_2 on the substrate of Ti foil. The hybrid-junction MoS_2/TiO_2 exhibits high activities under a visible light irradiation (AM 1.5 G illumination of 300 W/m^2) with hydrogen evolution reaction (HER) potential of −114 mV versus reversible hydrogen electrode (RHE) at 10 mA/cm^2, as well as long-term stability for more than 12 h at -0.3 V vs RHE while comparing to about 1 h without the introduction of hybrid-junction under same measurement conditions, more than 10 times improvement. The homo-junction TiO_2 thin layer on the substrate of Ti was synthesized through simple one-step thermal annealing process, different from traditional synthesis using hydrothermal or sol-gel methods [34–36]. The characterization on the HER activities suggest the homo-junction TiO_2 on the substrate of Ti could facilitate charge separation and transportation under the visible light illumination. After the hetero-coupling with MoS_2 constructed as hybrid-junction system, this cathode composite of MoS_2/TiO_2 on the substrate Ti exhibit higher activity and stability during the HER. The underlying charge transfer analysis elucidated that the hybrid-junction of Z-scheme hetero-junction and homo-junction plays important roles in the excellent performance.

2. Experimental section

2.1. Materials

Commercially Molybdenum disulfide (MoS_2) microflakes liquid-spraying was purchased from CRC Industries Americas Group. Titanium foils (Ti foils, 30 mm × 14 mm × 0.5 mm, 99.8% purity) were cut out from Ti sheet, which was purchased from Baoji Titanium Industry Co., LTD. Ethanol, acetone, isopropanol and deionized water were obtained from Sigma-Aldrich without further purification.

2.2. Preparation of homo-junction TiO_2 and MoS_2/TiO_2 composite electrodes

The fabrication consists of oxidation, spraying and annealing processes. Initially, Ti foils were cleaned by immersing the foils into the acetone rinsed by ultrasonic bath and subsequently dried in flowing nitrogen gas. After the initial cleaning step, Ti foils were oxidized at 400, 500 and 600 ℃ for 2 h with oxygen gas continually flowing through the quartz tube furnace to generate a thin layer of homo-junction TiO_2 on the surface of the Ti foil (Fig. S1). Following the oxidation step, commercial lubricating MoS_2 spray (CRC Industries) was applied to the TiO_2/Ti, followed by baking at 100 ℃ in the oven with ambient atmosphere for 10 h to ensure that all the solvent is evaporated. In the last annealing process, the pristine MoS_2/TiO_2/Ti foils were annealed at 500 ℃ for 1, 2, and 3 h, respectively in Nitrogen atmosphere under ambient pressure and cooled to the room temperature.

2.3. Physical characterization

Surface morphology of as-prepared samples was examined by field emission scanning electron microscopy (FESEM) (Hitachi, SU 8230) equipped with energy-dispersive X-ray spectrum (EDS) and electron backscatter diffraction (EBSD) microstructural-crystallographic characterization. Atomic force microscopy (AFM, Parker XE 200) was used to visualize surface the topography of samples on the nanometer scale. UV–vis light absorption spectra of the as-prepared samples were obtained using a SHIMADZU, UV-2600 spectrophotometer equipped with an integrated sphere assembly using diffuse reflection method. $BaSO_4$ was used as a reference to measure all samples in the wavelength range of 250–800 nm with a slit width of 1 nm. X-ray diffraction (XRD) patterns were collected on a Bruker D8-Advance diffractometer using Cu Kα radiation (λ = 1.5405 Å) in a range of 2-80° at a scan rate of 5°/min. Photoluminescence (PL) spectra were performed in the FS5 Spectrofluorometer of Edinburgh Instruments by focusing the laser radiation centered at 400 nm from an Xeon lamp onto the samples.

2.4. Photoelectrochemical measurement

PEC/Electrochemical measurements with/without simulated solar light illumination were performed and evaluated in a standard PEC three electrodes setup which is connected to electrochemical workstation (Zahner Elektrik IM6). The incident light was filtered through AM 1.5 G solar simulator over an adjustable 500 W Xeon lamp (AM 1.5 G, 300 W/m^2). The as-prepared composites, platinum gauze and Ag/AgCl with saturated KCl solution were used as working, counter and reference electrodes. In the text, the measured potentials *vs.* Ag/AgCl were all changed to the RHE scale based on the Nernst equation: $E_{RHE} = E_{Ag}/E_{AgCl} + pH * 0.059 + 0.1976$. All the current density reported in the work were calibrated using IR compensation, where the R (resistivity) was estimated by electrochemical impedance spectroscopy (EIS) with a frequency ranging from 10 Hz to 1 M Hz.

Linear scanning voltammetry measurements were carried out in 0.5 M H_2SO_4 at a constant scan rate of 20 mV/s over the potential range of -0.6 - 0 V (vs RHE). A long-term stability test for MoS_2/TiO_2 and MoS_2/Ti were conducted by an extended electrolysis (15 h) under dark or light conditions at a constant reduction potential of -0.3 V vs RHE. EIS test was carried out at open-circuit potential by applying an AC potential with an amplitude of 50 mV during the frequency range of 4×10^5 to 10^{-3} Hz in 0.5 M H_2SO_4 with/without the AM 1.5 G illumination (300 W/m^2). Mott-Schottky plots were obtained at frequencies of 5, 10 and 15 kHz and amplitude of 10 mV in 0.5 M H_2SO_4 solution under the dark or light conditions. In addition, current density-voltage (J-V) characteristic in an anodic direction was acquired at a scan rate of 20 mV/s. The measurements were carried out in a solution of Na_2SO_4 (pH 6.8) and subsequently in another solution of 1 M KOH (pH 13).

3. Results and discussion

3.1. Homo-junction TiO_2 on the substrate of Ti

Homo-junction TiO_2 was synthesized on the surface of Ti foil using simple one-step annealing process, as presented in the experimental section. The presence of homo-junction (mixed-phases) TiO_2 on the surface of Ti foil after the annealing process was determined by X-ray diffraction (XRD) and electron backscatter diffraction (EBSD). Fig. 1a shows the XRD patterns of TiO_2 at the temperature ranging from 400 ℃ to 600 ℃, in which both anatase or rutile TiO_2 could be observed (Fig. S2). Fig. 1b presents the EBSD mapping, clearly showing the mixed-phases orientation mapping on the surface with assorted colors.