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# Heterostructured SnS<sub>2</sub>/SnO<sub>2</sub> nanotubes with enhanced charge separation and excellent photocatalytic hydrogen production

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## ABSTRACT

SnO<sub>2</sub>, a promising candidate for photocatalytic water splitting, displays poor activity due to insufficient light utilization and rapid electron-hole recombination of charge carriers. Herein, one-dimensional heterostructures of SnO<sub>2</sub>/SnS<sub>2</sub> nanotubes was designed and synthesized through a facile electrospinning followed by vulcanized method. The unique heterostructured SnO<sub>2</sub>/SnS<sub>2</sub> could simultaneously promote photocarrier transport and suppress charge recombination through the uniquely coupled SnO<sub>2</sub>/SnS<sub>2</sub> heterogeneous interface. Additionally, the optimized type-II heterostructure could also improve light absorption and weak the barrier of photocharge transfer. As a result, the SnO<sub>2</sub>/SnS<sub>2</sub> exhibited excellent photocatalytic H<sub>2</sub> evolution performance under simulated light irradiation with high H<sub>2</sub> production rate of 50 μmol h<sup>-1</sup> without the use of any noble metal co-catalyst, which is 4.2 times higher than that of pure SnO<sub>2</sub> under the same condition.

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## Introduction

Hydrogen (H<sub>2</sub>) generation from semiconductor-driven photocatalytic water splitting has been considered as a feasible green route to tackle the energy crisis and environmental problems [1,2]. Therefore, the exploitation of efficient, scalable, and continual photocatalysts is extremely important for this intention [3–13]. Among plentiful existing photocatalysts, SnO<sub>2</sub> has drawn much attention due to its favorable band position, outstanding electron mobility (~100–200 cm<sup>2</sup> V<sup>-1</sup> s<sup>-1</sup>) as well as intrinsic stability [14–17]. On the other side, it also faces some drawbacks on account of its limited light utilization ability and fast charge carrier recombination, which seriously hinders the improvement of its photocatalytic activity.

Presently, diverse strategies have been promoted to boost the photoactivity of pristine SnO<sub>2</sub>. In addition to organic dye sensitization or elemental doping [7,14], constructing SnO<sub>2</sub>-based nanostructured heterojunction could improve the photocatalytic performance that could not be realized through conventional counterparts, profited by enhanced light absorption and inhibited electron-hole recombination [18–20]. Among the semiconducting metal sulfides, tin disulfide (SnS<sub>2</sub>) has attracted considerable attention [21–23]. SnS<sub>2</sub> has been demonstrated to be an efficient visible-light driven photocatalyst with a band gap of 2.18–2.44 eV. In addition, it can form a type II heterostructure with SnO<sub>2</sub> thanks to their matched band structure [8,24–31].

A couple of approaches have been adopted to synthesize SnO<sub>2</sub>/SnS<sub>2</sub> heterostructures, including hydrothermal-assisted

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self-hydrolysis route [30], wet-chemistry [32], microwave-assisted mean [33], hydrothermal method [34]. However, the existing methods is unable to regulate their structure and morphology. The in-situ sulfurized, a direct effective method, enables the effective transformation from one crystalline material to another with controllable morphology. In addition, One-dimensional (1D) nanotubes are considered to be optimal to promote charge transport, enhance light absorption, and provide more active sites for catalysis reaction [15,35,36].

Herein, a facile electrospinning combined with vulcanized method to fabricate  $\text{SnO}_2/\text{SnS}_2$  NTs heterostructure is put forward. Owing to the efficient charge separation and enhanced light absorption, the photocatalytic hydrogen evolution performance of  $\text{SnO}_2/\text{SnS}_2$  has been significantly improved compared to that of pristine  $\text{SnO}_2$  NTs under simulated light illumination. This work has demonstrated an effective strategy to construct heterogeneous structure through in-situ sulfurization to optimize the photocatalytic hydrogen evolution performance.

## Experimental section

### Materials synthesis

The  $\text{SnO}_2$  NTs were fabricated via a simple and versatile electrospinning technique. To prepare the precursor solution, tin chloride ( $\text{SnCl}_2$ , 1.125 g) and pyrrolidone (2 g, PVP,  $M_w = 1.3 \times 10^6 \text{ g mol}^{-1}$ ) were added into a mixture of ethanol (14 ml) and *N,N*-dimethylformamide (DMF, 11 ml) under vigorously stirring. Then, electrospinning was carried out with the solution at a DC voltage of 18 kV between the syringe needle and collector (aluminum foil) and a feeding rate of 0.5 ml/h. The as-spun  $\text{SnCl}_2/\text{PVP}$  composite nanofibers were calcined at 600 °C for 3 h with slow lamping rate (1 °C/min) under ambient condition to remove PVP and form  $\text{SnO}_2$  NTs.

In order to obtain the  $\text{SnO}_2/\text{SnS}_2$  heterostructure, the as-prepared  $\text{SnO}_2$  NTs were placed in the center of a quartz-tube furnace together with excess thiourea and sulfurized at 350 °C for 3 h with a heating rate of 1 °C/min in an inert environment.

### Characterization and measurement

The Crystal structure and morphology of catalysts were examined using X-ray diffraction (XRD, X'Pert PRO MPD, Philips) with a  $\text{Cu K}\alpha$  radiation ( $\lambda = 1.5418 \text{ \AA}$ ), field emission scanning electron microscopy (FE-SEM, FEI Nano SEM 450) and transmission electron microscopy (TEM, FEI Tecnai F30G<sup>2</sup>), respectively. Raman spectra were collected at room temperature on a Renishaw inVia Raman microscope with an excitation wavelength of 532 nm. The valence states of the elements and X-ray photoelectron spectroscopy (XPS) data and were acquired using a Physical electronics PHI-5802 equipped with a monochromatic  $\text{Al K}\alpha$  X-ray source in an ultrahigh vacuum environment. All the binding energies were calibrated by using the contaminant carbon (C 1s) 284.8 eV as a reference. Optical absorption spectra were recorded using an UV–vis spectrophotometer (Perkin-Elmer Lambda 35 UV-VIS-NIR). Photoluminescence (PL) spectra were measured at room temperature using a PL spectrophotometer (FLS 980).

The photocatalytic  $\text{H}_2$  evolution reaction was carried out in a top-irradiation photoreaction system. Photocatalyst powder (20 mg) was suspended by sonication in an aqueous solution (50 ml) containing 10 ml methanol. The photoreaction system was thoroughly degassed by pump to remove all air in the system prior irradiation by a 300 W Xe lamp. The light flux on the photoreactor was determined to be  $150 \text{ mW cm}^{-2}$  with an optical power meter (Perfect Light, PL-MW2000 Photoradiometer). The evolved  $\text{H}_2$  were analyzed by online gas chromatography (Shimadzu GC-2014c) equipped with a thermal conductivity detector (TCD) and a 5A molecular sieve column, using argon gas as the carrier gas. The temperature of the reaction chamber was maintained at 5 °C during the entire process.

The photoelectrochemical (PEC) measurements were performed with an electrochemical workstation (CHI 760E, CH Instruments) in a three-electrode cell with the photocatalyst-coated fluorine tin oxide (FTO) as the working electrode, Pt plate as the counter electrode, and an  $\text{Ag}/\text{AgCl}$  as the reference electrode. The 0.5 M  $\text{Na}_2\text{SO}_4$  aqueous solution pre-purged with nitrogen for 30 min was used as electrolyte without an additive. 10 mg of the as-synthesized sample was dispersed in ethanol (450  $\mu\text{L}$ ) and Nafion (50  $\mu\text{L}$ , 5%) mixed solution. The suspension was drop-casted onto FTO substrate and dried at room temperature. The working electrode surface area illuminated was controlled at  $1 \text{ cm}^2$  with Scotch tape. A solar simulator was used as the light source (AM 1.5G,  $100 \text{ mW cm}^{-2}$ ). Nyquist plots were recorded over the frequency range of 0.1 Hz– $10^5$  Hz. Mott-Schottky (M-S) plots were measured at a certain potential range with an AC amplitude of 5 mV and a frequency of 1 kHz under dark condition.

## Results and discussion

Fig. 1a, b shows SEM images of as-spun nanofibers before and after sulfurization, respectively. It can be seen that the as-spun  $\text{SnO}_2$  nanofibers are continuous and interconnected with a uniform diameter of approximately 100 nm (Fig. 1a). After sulfurization, the  $\text{SnO}_2/\text{SnS}_2$  displays a tubular structure with the diameter increasing up to ~180 nm (Fig. 1b). The microstructure of  $\text{SnO}_2/\text{SnS}_2$  is further investigated by TEM (Fig. 1c), the  $\text{SnO}_2/\text{SnS}_2$  displays a hollow structure, consisting with the SEM results. Fig. 1d shows the corresponding high-resolution TEM image of  $\text{SnO}_2/\text{SnS}_2$ . Both the  $\text{SnO}_2$  and  $\text{SnS}_2$  exhibit good crystallinity, and the lattice spacing of 0.335, 0.236, and 0.265 nm can be indexed to the (110), (200), and (101) planes of  $\text{SnO}_2$ , respectively. The other two sets of lattice fringes with the lattice spacing of 0.318 and 0.278 nm corresponds well to the (100) and (101) crystallographic planes of  $\text{SnS}_2$ , respectively [8,37]. Furthermore, the SEM elemental mappings of  $\text{SnO}_2/\text{SnS}_2$  show that the Sn, O, and S elements are uniformly distributed in  $\text{SnO}_2/\text{SnS}_2$  (Fig. 1e–h).

XRD and Raman characterizations have been adopted to analyze the crystalline phase of the as-prepared samples. As shown in XRD patterns (Fig. 2a), the major diffraction peaks at 26.6°, 33.9°, 37.9°, 39.1°, 51.8°, 54.8°, 57.9°, 62.0°, 64.8°, and 66.1° were observed for the as-prepared  $\text{SnO}_2$  and assigned to the diffraction of the (110), (101), (200), (111), (211), (220), (002),

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