Aqueous Solution Method towards \( \text{Sb}_2\text{S}_3 \) Thin Films for Photoanodes

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1. Experimental section

1.1. Preparation of \( \text{TiO}_2 \) arrays

The \( \text{TiO}_2 \) arrays were deposited on F-doped \( \text{SnO}_2 \) (FTO) coated glasses by a widely used hydrothermal method. This method consists of four steps. Firstly, 12 ml of hydrochloric acid was added into 12 ml of DI-water stirring for 10 min. Secondly, 0.4 ml of tetrabutyl titanate added in the above mixed solution forming a transparent solution. Thirdly, transfer the solution into a Teflon liner and put the cleaned FTO substrates vertically into the tank with the conductive surface facing adown. Last but not least, the autoclave was sealed and placed in the oven at 150 °C for different reaction time, then the samples were cooled naturally to room temperature after reaction.

1.2. Preparation of \( \text{Sb}_2\text{S}_3 \) films
The process of preparing Sb$_2$S$_3$ was as following. (a) polyethyleneimine (PEI) was used to bind antimony ions to form the homogeneous polymeric Sb$^{3+}$ precursor solution, and then the thiourea was added in it to form a uniform aqueous solution. To prepare a stable Sb$^{3+}$ precursor solution, 2.62 g of SbCl$_3$ was added to the aqueous solution with HF and 50 ml of deionized water, followed by dropwise add 5 g of PEI to the mixed solution. After a few minutes of continuous stirring, the solution was filtered by an Amicon ultrafiltration with a molecular weight of $< 10000$ g/mol for several times to filter out the uncomplexed Sb ions. Finally, the obtained aqueous precursor solution has a concentration of Sb$^{3+}$ ions of 24.8 mg/ml. (b) the aqueous precursor solution was spin-coated onto a substrate, such as SiO$_2$/Si, FTO and quartz (spin-coating method: 4000 rpm/s, 30 s). (c) The aqueous solution was spin-coated on cleaned substrates following annealing process which were performed in a furnace system. The temperature was set at 400 ºC for annealing 30 minutes in an argon (Ar) atmosphere, and then the samples were cooled to room temperature.

1.3. Preparation of Sb$_2$S$_3$/TiO$_2$ composite structures

The Sb$_2$S$_3$ films were grown onto TiO$_2$ arrays coated FTO substrates to prepare Sb$_2$S$_3$/TiO$_2$ composite structure. Firstly, we grew TiO$_2$ arrays on FTO substrate by hydrothermal method; Secondly, the prepared aqueous precursor solution of Sb$^{3+}$ with thiourea was spun on the TiO$_2$ arrays and then annealed in the furnace at 400 ºC to obtained Sb$_2$S$_3$/TiO$_2$ composite structure.

2. Characterization

2.1. Film characterization

The concentration of Sb$^{3+}$ in the precursor solution was evaluated by an inductively coupled plasma atomic emission spectrometer (ICP-AES, PerkinElmer Optima 8000). X-ray diffraction (XRD) patterns of the films were obtained with a Bruker Advance D8 diffraction system. The surface morphology of films was tested by scanning electron microscopy (SEM, Hitachi SU8010). The micro-structures of films were analyzed by high resolution transmission electron microscopy (HRTEM, FEI Tecnai F20). The valence state of the films was performed by X-ray photoelectron
spectroscopy (XPS, Thermo Fisher, Escalab 250Xi). The absorption spectrum of the films was measured with an ultraviolet-visible (UV-Vis) spectrometer (Shimadzu UV-2450). Photoluminescence Spectroscopy was tested on Horiba spectrofluorometer FM-4 (633 nm laser excitation). Raman Shift spectroscopy HR800 (Raman HORIBA Jobin Yvon) with a 532 nm excitation wavelength was employed to evaluate the as-grown thin films.

2.2. Device characterizations

All measurement of photoelectrochemical were conducted by an electrochemical workstation (CHI660D) with a 100 mW/cm² Xe lamp as light source and 0.1 M Na₂SO₄ solution (pH=7) as electrolyte. During the measurement, the as-prepared composite structure samples served as working electrode, a Pt wire as the counter electrode and an Ag/AgCl electrode as the reference electrode.

3 Results

**Fig. S1.** The XRD pattern of Sb-precursor without TU and Sb-precursor with TU annealed under Ar flow at 400 °C for 30min.

**Fig. S2.** the SEM images of Sb₂S₃ thin film with different magnification.
Fig. S3. (a) The energy level diagram of the FTO/TiO$_2$/Sb$_2$S$_3$ photoelectrodes, (b) The absorption spectra of TiO$_2$ and TiO$_2$ with Sb$_2$S$_3$ composite thin films.

Fig. S4. The photocurrent density of pure Sb$_2$S$_3$ photoanode with different thickness: (a) a single layer of Sb$_2$S$_3$ film and (b) 2-layer of Sb$_2$S$_3$ films on the FTO substrate.

Fig. S5. SEM of TiO$_2$ arrays grown under 20 h reaction time (top and cross view).
Fig. S6. The SEM figures of TiO$_2$ array under different hydrothermal reaction time.

Fig. S7. The photocurrent density of Sb$_2$S$_3$’ composite with 2 layer and 3 layer of Sb$_2$S$_3$.

Fig. S8. The morphology of composite photoelectrode (TiO$_2$ nanoarrays 5h, Sb$_2$S$_3$, 2layers).
Fig. S9. The stability of photocurrent density under light irradiation.