

In-situ deposition of Ag/Ag₂S hybrid nanoparticles onto TiO₂ nanotube arrays towards photoelectrodes with high visible light photoelectrochemical properties

Supporting Information

Wenguang Fan, Simon Jewell, Yiyi She and Michael K.H. Leung

Experimental Details

Preparation of TiO₂ nanotube arrays (TNA)

The TNAs were fabricated using the etching anodization method. Titanium (Ti) foil (Sigma-Aldrich, 99.7%, 0.25mm) was cut into 2.1cm*2.1cm squares and cleaned by sonication in a series of acetone, iso-propanol, ethanol and deionized (DI) water, for 30 minutes each. The foils were then rinsed with DI water and dried under a nitrogen (N₂) stream. The electrolyte for anodization was prepared by mixing 0.25 g sodium fluoride (Acros Organics, 99+%) with 47.25 g ethylene glycol (Sigma Aldrich, 99%) and 2.5 g DI water. After stirring for 6 hours, the electrolyte was transferred into a Teflon cell in which a Ti foil and a platinum foil were mounted as the anode and cathode, respectively. The distance between the anode and cathode was kept at 3 cm. Anodization was carried out at 40 V for 12 hours, without voltage ramping. The anodized foil was rinsed with ethanol and DI water and was pre-annealed at 100 °C for 30 minutes, followed by sonication in DI water for 15 minutes to remove the broken tubes and residue. Finally the foil was annealed at 500 °C for 6 h in air, with the ramping rate of 5 °C min⁻¹.

Deposition of the Ag/Ag₂S hybrid nanoparticles

Unless specially mentioned, all the procedures in this section were kept in dark conditions. In a 100 mL Teflon vessel, 30 mL of 20 mM silver nitrate (Strem, 99.9%) aqueous solution was mixed with 90 µL thioglycolic acid (Sigma Aldrich, 98%) where a light yellow precipitate was immediately formed. Subsequently 0.1 M NaOH (Sigma Aldrich, 97%) was added drop-wise into the vessel until the mixture turned to clear again and the pH reached 9.0. After stirring for 15 minutes, a TNA foil was bound to a 3 cm * 4 cm piece of glass using Teflon tape and placed in the vessel. The glass was tilted with the TNA facet facing down. The solution was purged with N₂ gas for 20 minutes before

adding 2 mL 0.1M sodium sulfide (Sigma Aldrich, >60%) solution to the vessel. The solution was then purged for another 20 minutes. The vessel was sealed in a stainless steel autoclave and was placed in a 120 °C oven. After 4 hours, the autoclave was removed and cooled to room temperature in ambient conditions. The foil was rinsed with DI water and dried under an N₂ stream.

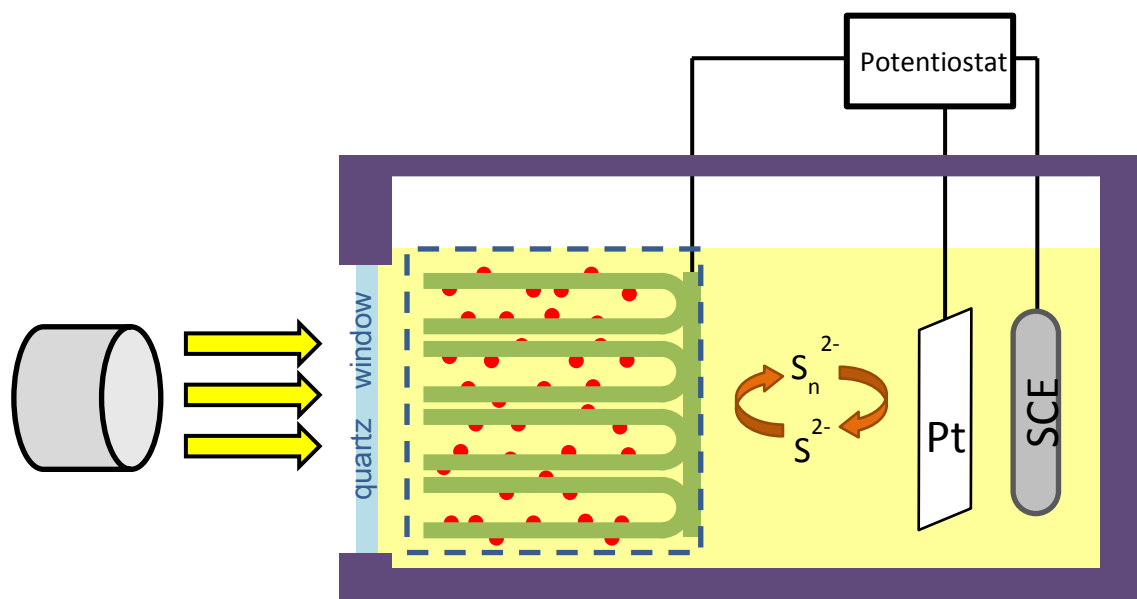
Characterization

Field emission-scanning electron microscopy (FE-SEM) was performed with a Hitachi S4800 with the accelerating voltage of 5.0 kV. High-resolution transmission electron microscope (HRTEM) images were obtained at 200 keV using a JEOL 2010F, equipped with energy-disperse X-ray spectroscopy (EDS) to analyze the elemental composition. Thin film X-ray diffraction (XRD) analysis was performed using Rigaku Smartlab X-ray diffractometer with Cu K α radiation. The scanning was performed from 2 θ of 20° to 100°, with steps of 0.01° and at intervals of 5° per minute. X-ray photoelectron spectroscopy (XPS) was carried out on Physical Electronics 5600 with Al K α as the excitation source to examine surface elemental composition and chemical state. Ultraviolet-visible diffuse reflectance spectra (UV-vis DRS) were recorded using a Shimadzu UV 2600 spectrophotometer with BaSO₄ as the reference.

Photoelectrochemical (PEC) Measurements

The PEC measurements were carried out in a typical three-electrode cell. The working photoanode was fabricated by attaching an electrical wire on the back side of the foil with conductive silver paint, followed by covering the entire surface with epoxy, except for the TNA or Ag/Ag₂S/TNA area. The uncovered working area was made approximately 1 cm². A platinum foil and a saturated calomel electrode (SCE) were employed as the counter electrode and reference electrode, respectively. A quartz window was mounted on the cell and the distance between the window and the anode was

kept constant (~2mm) for each measurement. The electrolyte was prepared by mixing 1 M sulfur with 1 M sodium sulfide solution. The light source was Newport 300 W Xe lamp. In measurements of the visible range, a 420 nm cut-off filter was mounted on the lamp. The data was collected with a Solartron analytical potentiostat.



Scheme S1 Illustration of the 3-electrode PEC cell used in this work

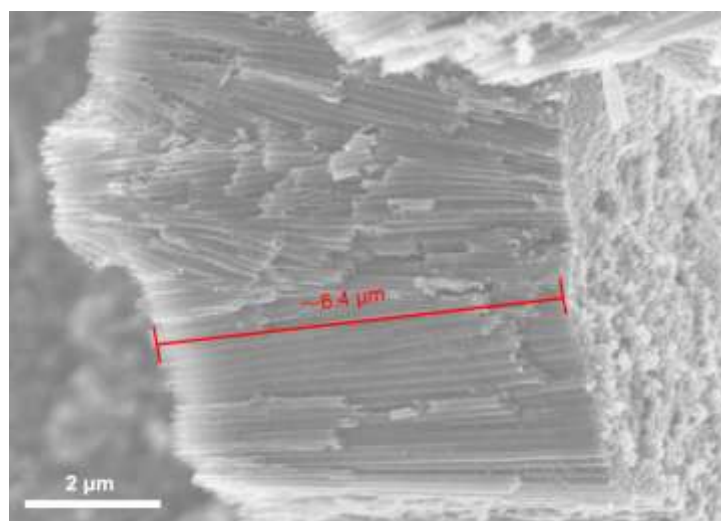
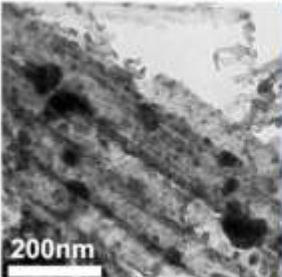


Figure S2 SEM image of cross-sectional view of bare TNA. The length of the nanotubes are measured as approximately 6.4 μm



Element	wt. %	atom. %	Error %
Ti	47.95	55.03	1.5
O	4.99	17.13	0.2
Ag	43.84	22.33	4.4
S	3.22	5.52	0.1

Table S1 EDS result of the general area of Ag/Ag₂S/TNA

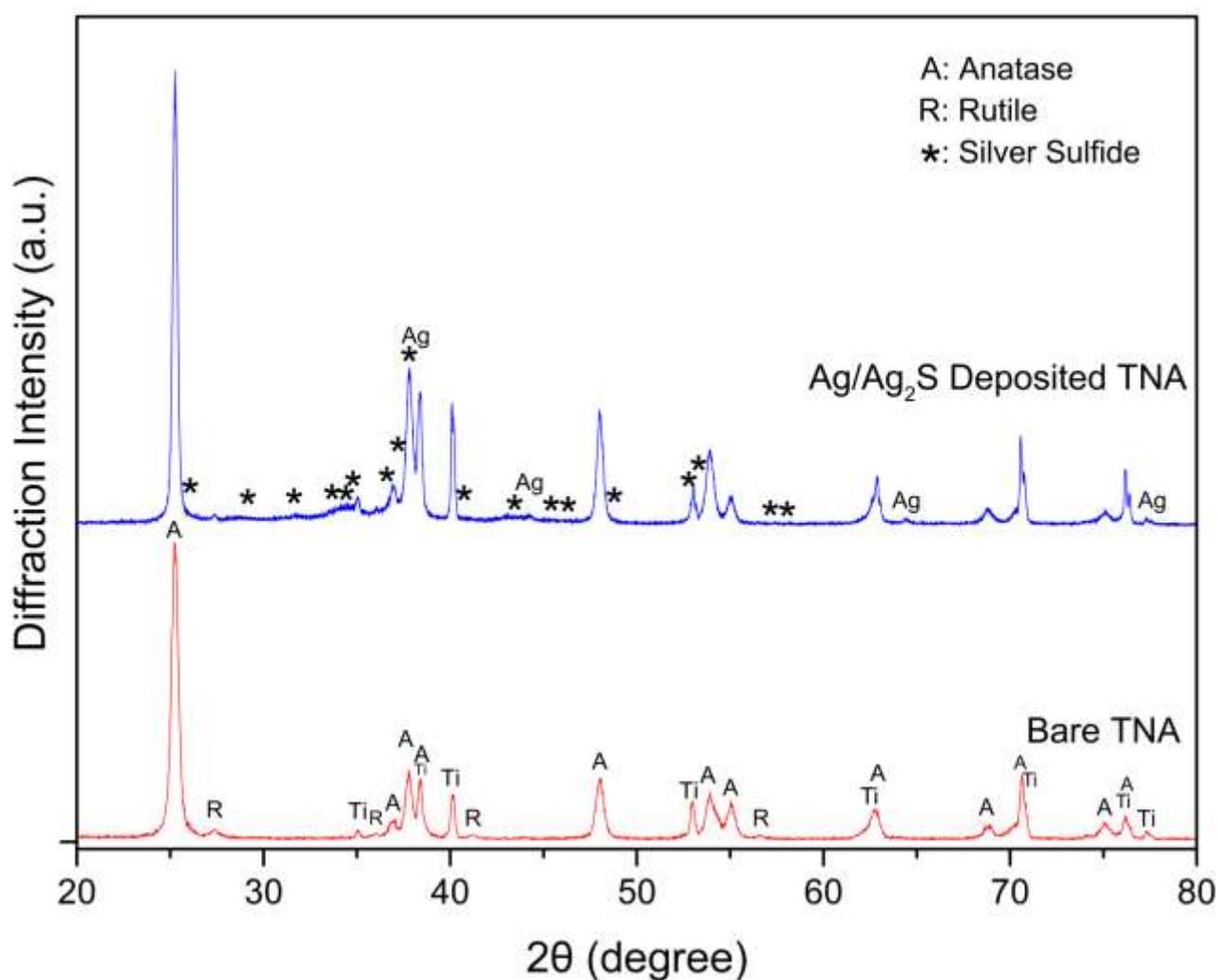


Figure S3 XRD patterns of bare TNA and Ag/Ag₂S/TNA (Ti, JCPDS card no. 65-3362; TiO₂, Anatase: JCPDS no. 21-1272, Rutile: JCPDS no. 21-1276; Ag, JCPDS no. 65-2871; Ag₂S, JCPDS no. 14-0072)

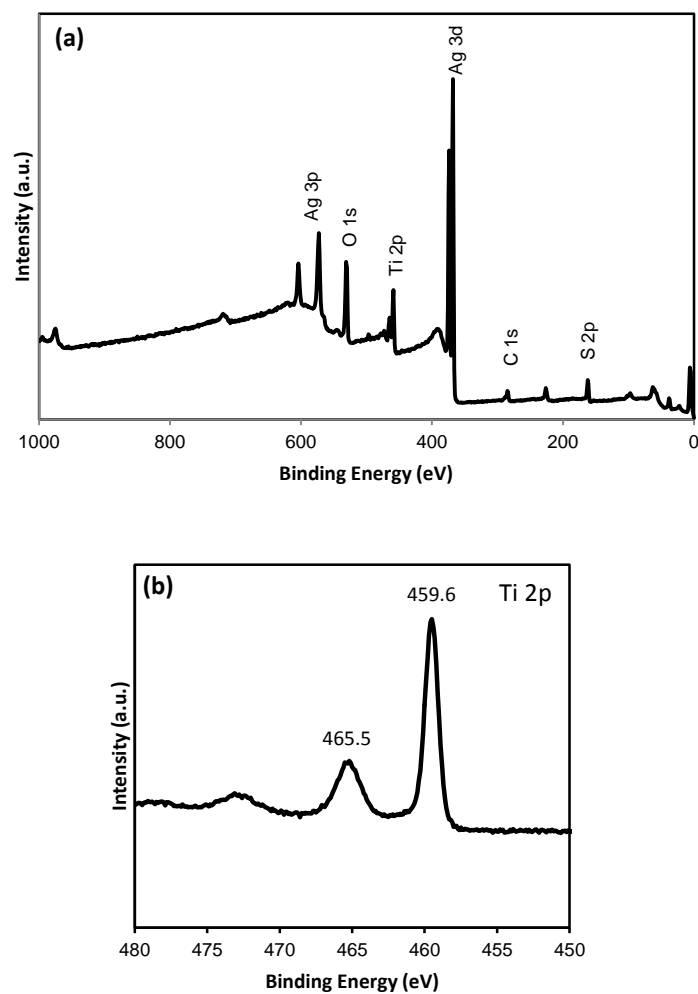


Figure S4 XPS spectra of as-prepared Ag/Ag₂S/TNA. (a) Wide survey spectrum. (b) Ti 2p binding energy spectrum

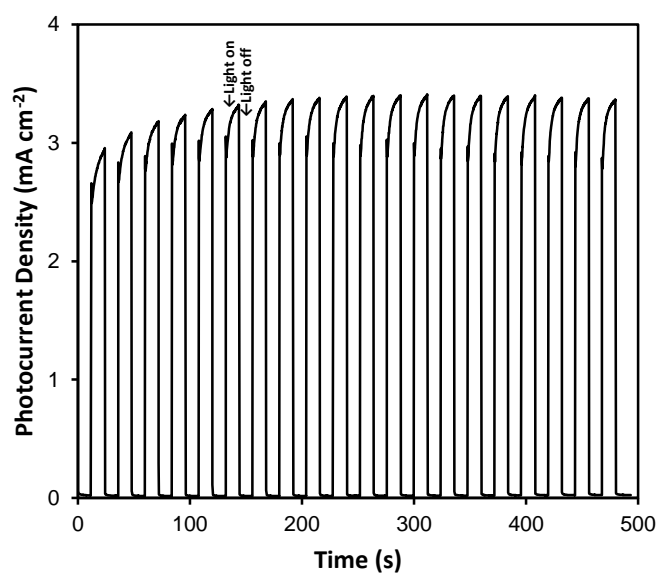


Figure S5 Photocurrent vs. time curve of Ag/Ag₂S/TNA electrode under repeated on-off illumination. Potential bias: 0 V vs. SCE