

Electronic Supplementary Information

Defect engineering of In₂S₃ nanoflowers through tungsten doping for ultrasensitive visible-light-excited photoelectrochemical sensor

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Experimental section

2.1 Chemicals and material

In(NO₃)₃·xH₂O was bought from Shanghai Titan Scientific Co., Ltd. (Shanghai, China). L-cysteine and 4-aminophenyl phosphate monosodium salt hydrate (4-APP) were purchased from Beijing J&K Scientific Co., Ltd. (Beijing, China). Na₂WO₄·2H₂O, 1, 4-benzenedicarboxylic acid, N, N-Dimethylformamide (DMF), H₂O₂, KCl, HCl, KH₂PO₄, Na₂HPO₄ were obtained from Chengdu KeLong Chemical Co., Ltd. (Chengdu, China). AgNO₃ was bought from Sinopharm Chemical Reagent Co., Ltd. (Beijing, China). Hexanethiol (HT) was bought from Sigma-Aldrich (St. Louis, MO, USA). Bst DNA Polymerase was obtained from Vazyme biotech Co. Ltd. (Nanjing, China) and deoxyribonucleoside triphosphates dNTPs was bought from Dingguo Changsheng Co., Ltd. (Beijing, China). The nicking enzyme was obtained from New England Biolabs Ltd. (Beijing, China). Tris(2-carboxyethyl) phosphine (TCEP), Streptavidin-alkaline phosphatase (SA-ALP), VEGF₁₆₅ were provided by Sangon Biotech Co. Ltd. (Shanghai, China). DNA oligonucleotides used in the

experiment were synthesized by Sangon Biotech Co. Ltd. (Shanghai, China) and the corresponding sequences were listed in Table S1. 0.1 M phosphate buffer solution (PBS) (pH = 7.0) containing 0.1 M KCl, 0.1 M KH₂PO₄ and 0.1 M Na₂HPO₄ was used throughout the experiment. [Fe(CN)₆]^{3-/4-} solution (pH = 7.4, 5.0 mM) was prepared by dissolving K₃[Fe(CN)₆] and K₄[Fe(CN)₆] in PBS solution (pH = 7.4). All chemicals were of analytical grade without further purification. Deionized water was used throughout the experiment.

2.2 Apparatus and characterization

The morphologies of the prepared nanomaterials were characterized by a transmission electron microscope (TEM, JEM-2100) and the elemental mapping images were recorded using EDX spectroscopy attached to TEM. The crystal phases of the samples were analyzed by powder X-ray diffraction (XRD) patterns on an XD-3 X-ray diffractometer with Cu K α radiation (Purkinje, China). UV-vis diffuse reflectance spectra (DRS) were obtained using a PE lambda 750S UV-vis-NIR spectrometer equipped with an integrating sphere and BaSO₄ was used as a reference. Photoluminescence (PL) spectra were acquired on Edinburgh Analytical Instruments FL/FSTCSPC920 coupled with a time-correlated single-photo-counting system at room temperature. X-ray photoelectron spectroscopy (XPS) results were acquired on a ThermoFisher ESCALAB 250Xi device with Mg K α ($h\nu = 1253.6$ eV) as the excitation source. Cyclic voltammetry (CV) and electrochemical impedance spectroscopy (EIS) measurements were performed with a CHI 760e electrochemistry workstation (Shanghai Chenhua Instrumentation, China). During the measurement process, a three-electrode system was adopted which was comprised of a platinum wire as the counter electrode, a saturated calomel electrode (SCE, saturated KCl) as the reference electrode, and a glassy carbon electrode (GCE, $\Phi = 4$ mm) as the working electrode.

PEC measurements were conducted with a PEC workstation (Ivium, Netherlands) and carried out in 5 mL of PBS containing electron donor ascorbic acid (AA, 0.1M) at room temperature. The excitation light source (wavelength: $\lambda = 460$ nm; radiant flux: $\Phi = 976$ mW) was provided by a light-emitting diode (LED) lamp and switched off-

on-off for 10-20-10 s and lasted 5 cycles without a bias voltage. CV measurements were performed in 2 mL of PBS solution (pH 7.0, 0.1 M) containing 5.0 mM $[\text{Fe}(\text{CN})_6]^{3-/4-}$ and 0.1 M KCl where the potential was between -0.2 and 0.6 V at a scan rate of 50 mV/s. EIS measurements were conducted in 2 mL of PBS (pH 7.0, 0.1 M) containing 5.0 mM $[\text{Fe}(\text{CN})_6]^{3-/4-}$ and 0.1 M KCl over a frequency range of 10 kHz to 0.1 Hz using an alternating current potential with an amplitude of 5 mV at a direct current potential of 0.22 V.

2.3 Preparation of In_2O_3

The In_2O_3 precursor was synthesized according to a previously reported method with minor modification.¹ Typically, 0.11 g $\text{In}(\text{NO}_3)_3 \cdot x\text{H}_2\text{O}$ and 0.11 g of 1,4-benzenedicarboxylic acid were dissolved in 30 mL of N,N-Dimethylformamide, and ultrasonicated for 5 min. The obtained mixture was then placed in a water bath at 140 °C for 50 min. After the temperature was cooled down to room temperature, the light yellow precipitate was collected by centrifugation, washed with water and ethanol alternatively for several times to remove the extra residuals and dried at 60 °C for 12 h. The as prepared powder was transferred to a crucible and calcinated in a muffle furnace at 350 °C for 2 h with a heating rate of 5 °C min^{-1} to obtain the In_2O_3 sample.

2.4 The reproducibility of the PEC sensor.

The reproducibility among electrodes was assessed by comparing the PEC response of the intra-assay and inter-assay under the same experiment conditions. The intra-assay was measured in the five same-batches of electrodes and inter-assay was carried out in five different batches of electrodes in the presence of 10 pM VEGF₁₆₅. As depicted in Fig. S8A, it can be seen that the PEC response of intra-assay variation was relatively small and the calculated RSD was 0.91 %. Meanwhile, Fig. S8B also showed small PEC response of inter-assay variation and the calculated RSD was 1.23 %. These results indicate that the proposed PEC strategy reflected an admirable reproducibility.

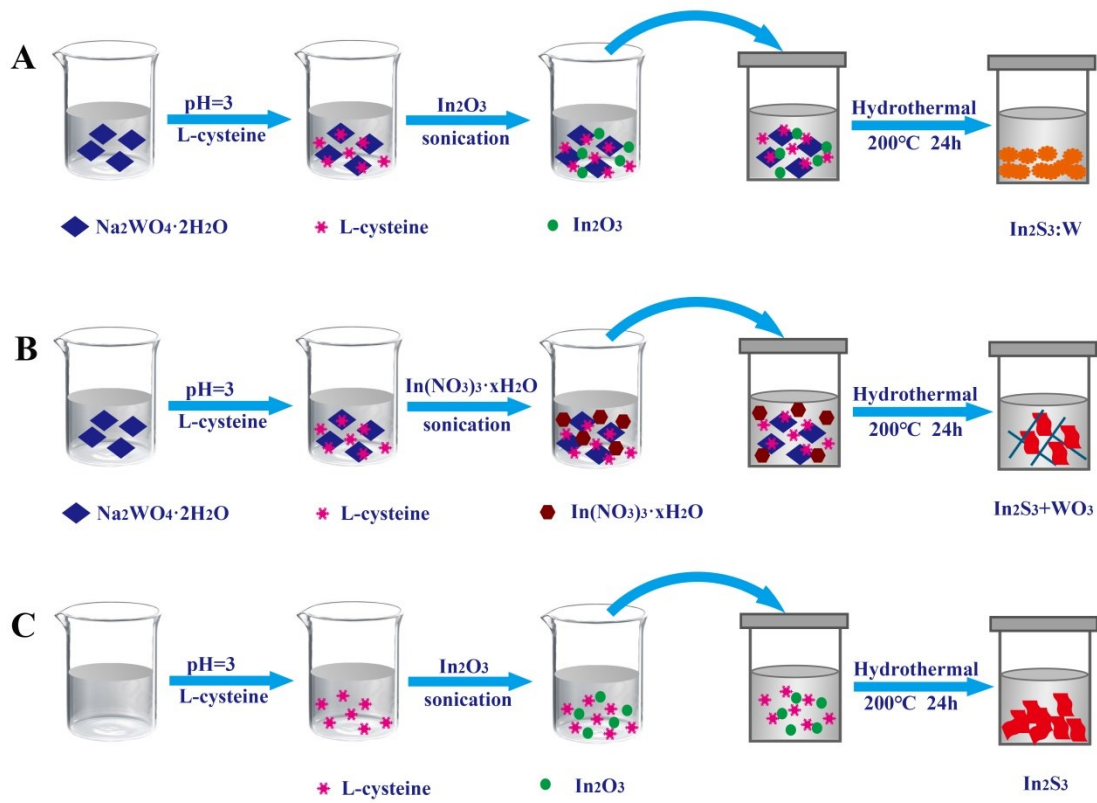


Figure S1. Schematic illustration of the formation process of $\text{In}_2\text{S}_3:\text{W}$ (A), $\text{In}_2\text{S}_3+\text{WO}_3$ (which prepared by replacing In_2O_3 with $\text{In}(\text{NO}_3)_3 \cdot x\text{H}_2\text{O}$) (B) and pristine In_2S_3 (C).

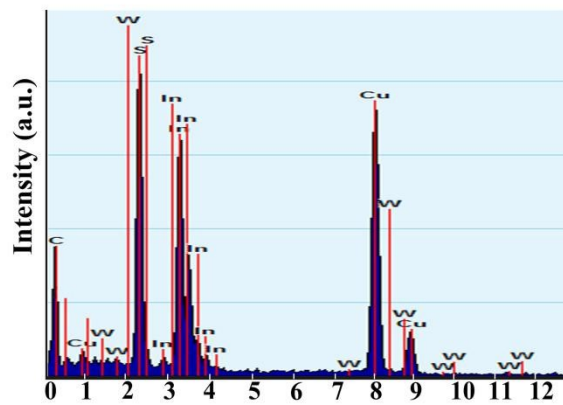


Figure S2 EDX mapping of $\text{In}_2\text{S}_3:\text{W}$ (D).

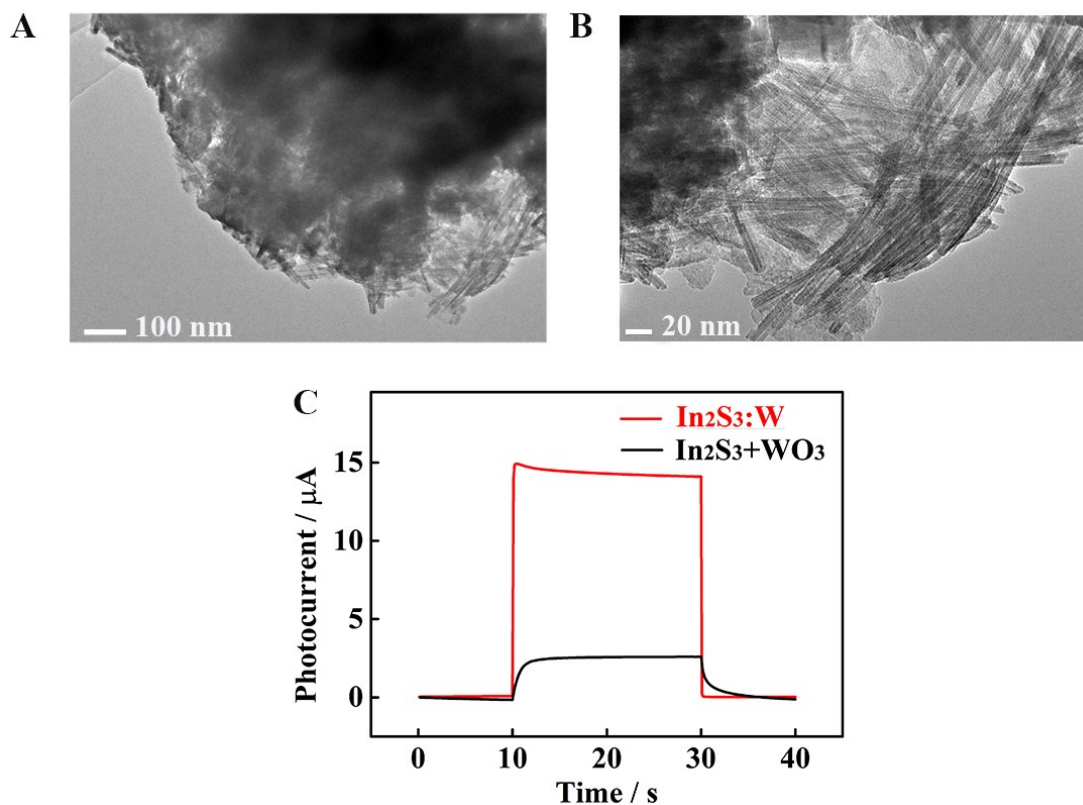


Figure S3 TEM images of $\text{In}_2\text{S}_3+\text{WO}_3$ which prepared by using $\text{In}(\text{NO}_3)_3 \cdot x\text{H}_2\text{O}$ as In source(A,B).

Photocurrent responses of $\text{In}_2\text{S}_3:\text{W}$ and $\text{In}_2\text{S}_3+\text{WO}_3$ (C)

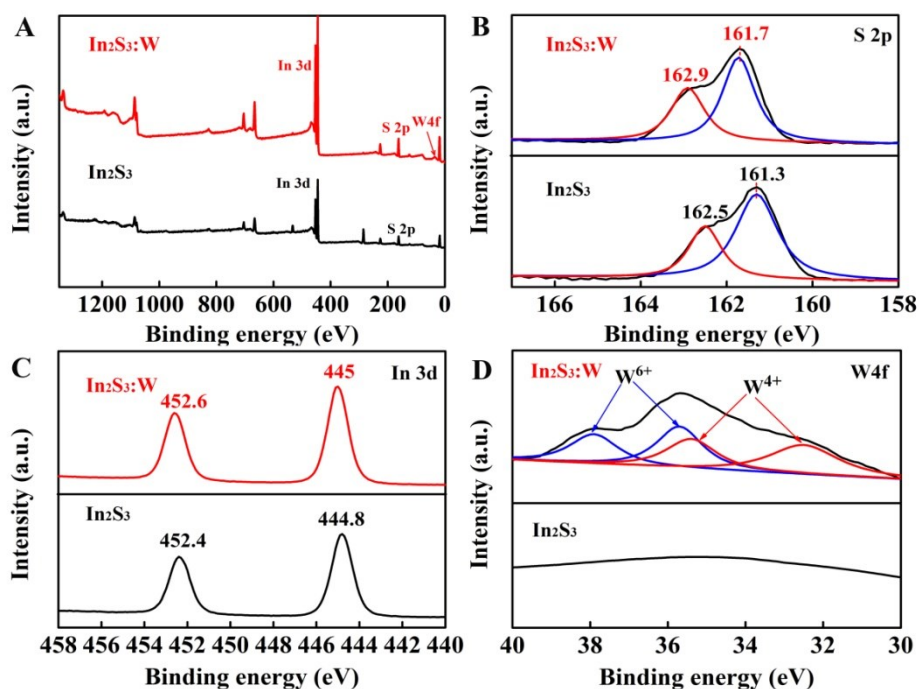


Figure S4 XPS survey of In_2S_3 and $\text{In}_2\text{S}_3:\text{W}$ (A), S 2p (B), In 3d (C), and W 4f (D) XPS spectra of In_2S_3 and $\text{In}_2\text{S}_3:\text{W}$ sample.

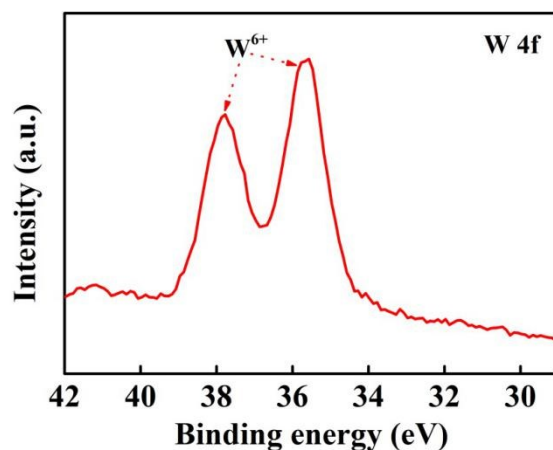


Figure S5 XPS W 4f spectrum of $\text{In}_2\text{S}_3+\text{WO}_3$ prepared by using $\text{In}(\text{NO}_3)_3 \cdot x\text{H}_2\text{O}$ as In source.

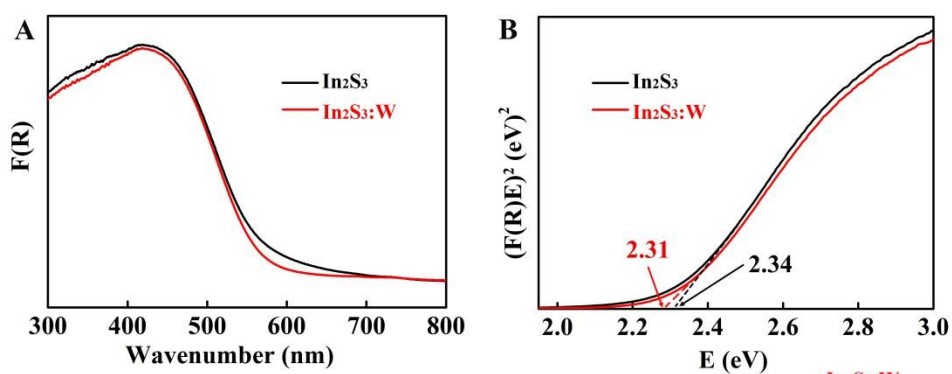


Figure S6 DRS of In_2S_3 and $\text{In}_2\text{S}_3:\text{W}$ (A). The corresponding Tauc plots of In_2S_3 and $\text{In}_2\text{S}_3:\text{W}$ (B).

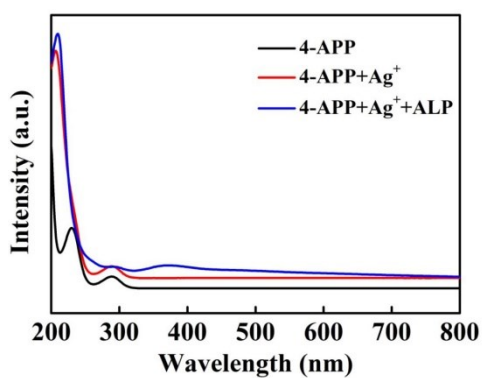


Figure S7 UV-vis spectra of 4-APP, mixture of 4-APP + Ag^+ , mixture of ALP, 4-APP and Ag^+ .

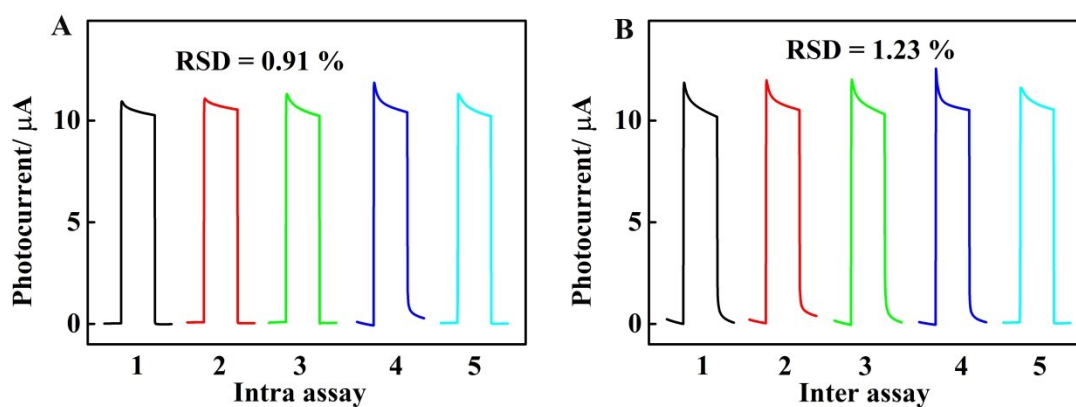


Figure S8 The PEC response of intra-assay (A) and inter-assay (B) incubating with 10 pM VEGF₁₆₅

Table S1. The oligonucleotide sequences used in the experiment.

name	Sequence (5'→3')
VEGF aptamer	CC GTC TTC CAG ACA AGA GTG CAG GG
T1	CAC TCT TGT CTG GAA GAC GG
template	CCC GAT TGT GAG TCG TAT TAA TC AACAA GACTC CC GTC TTC CAG ACA AGA GTG
HP	CAT TAA TAC GAT AT CCC GAT TGT GA GTC GTA TTA ATC
S1	ATA TCG TAT TAA TG GCT TCT CCC AGG AGC AGG
S2	GA TTA ATA CGA TAT CTG CTC CTG GGA GAA GCC

References

- (1) Wang, S.; Guan, B. Y.; Lou, X. W. D., *J. Am. Chem. Soc.* **2018**, *140* (15), 5037-5040.