

Electronic Supplementary Information

Embedded CuInS₂ nanoparticles in mesoporous TiO₂ nanofibers for boosted photocatalytic hydrogen production

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Experimental Procedure

Materials

Polyvinylpyrrolidone (PVP, MW \approx 1300000), tetrabutyl titanate (TBOT), Zinc acetate (ZnAC), dimethyl formamide (DMF), acetic acid (AC), diisopropyl azodiformate (DIPA), absolute ethyl alcohol, methanol (MEOH), 1-dodecanethiol, oleic acid, 1-octadecene, sodium sulfate (Na₂SO₄) and deionized water were purchased from Aladdin. The above chemicals were used directly and no further purification was carried out.

Preparation of TiO₂ mesoporous nanofibers

Foaming agent assisted electrospinning method was employed to synthesize the TiO₂ thoroughly mesoporous nanofibers. Firstly, a solution was prepared by dissolving 0.8 g of PVP and 3.0 g TBOT into a mixed solution of ethanol and acetic acid under vigorously stirring for 10 h. Then, 10 wt % of foamer (DIPA) were added into the above solution with continually vigorous stirring for 5 h to obtain a homogeneous precursor solution. Subsequently, the TBOT/PVP/DIPA precursor solution was transferred into a syringe pump with a stainless steel nozzle. The stainless steel nozzle was used as the anode for electrospinning, which is sized in \sim 0.2 mm in diameter. A metal cathode was used as the collector and the distance between the tip of the stainless steel nozzle and collector was fixed as 14 cm. For electrospinning of the precursor TBOT/PVP/DIPA fibers, an electrical potential of 14 kV and a flow rate of 1 mL h⁻¹ were applied in this process. Finally, the obtained TBOT/PVP/DIPA precursor fibers were heated up in a conventional tube furnace under air atmosphere. During this process, the heating rate, the target temperature, maintained time was 5 °C min⁻¹, 500 °C and 2 h, respectively.

Synthesis of CuInS₂ Quantum Dots:

Firstly, CuInS₂ quantum dots (QDs) were synthesized through a hot-injection method. In a typical synthetic procedure, CuI (0.076 g, 0.4 mmol) and In(OAc)₃ (0.464 g, 1.6 mmol) were mixed with 1-dodecanethiol (1 mL) in a 50 mL three-necked flask, which was followed by the addition of ODE (10 mL). The reaction mixture was degassed under vacuum for 20 min at 120 °C. Next, oleic acid (0.5 mL) was added into the reaction flask, and the solution was continuously degassed for 20 min. Then, they were purged with nitrogen for 20 min. Subsequently, the solution was heated to 210 °C for 60 min under nitrogen flow until a deep red colloidal solution was formed. Afterward, the reaction solution was cooled to room temperature and precipitated by adding excess acetone. The flocculent precipitate was centrifuged at 8500 rpm for 5 min and the supernatant decanted.

Preparation of TiO₂@CuInS₂ hybrid photocatalysts

TiO₂@ CuInS₂ hybrid photocatalysts were prepared by a liquid phase ultrasonic adsorption process. In a typical synthesis, 200 mg of TiO₂ mesoporous nanofibers was added into 20 mL of a trichloromethane solution consisting of 1 mmol CuInS₂ and then ultrasonicated for 2 h min to form a well-dispersed solution. The mixed solution was dried at 60 °C under stirring to obtain a TiO₂@CuInS₂ composite loaded with 10% content of CuInS₂. In comparison, TiO₂@CuInS₂ composites with CuInS₂ loaded content of 5% and 15% were also studied. All the as-prepared TiO₂@CuInS₂ composites were annealed under an argon atmosphere at 300 °C.

Characterization

The obtained TiO₂ and TiO₂@CuInS₂ samples were systematically characterized with field emission

scanning electron microscopy (FESEM, S-4800, Hitachi, Japan). X-ray powder diffraction (XRD, D8 Advance, Bruker, Germany) with Cu K α radiation ($\lambda=1.5406 \text{ \AA}$) was employed to analyze the phase structure of the TiO₂ and CuInS₂ samples. The porous properties of the TiO₂ samples were analyzed using N₂ adsorption at -195.8 °C on a specific surface area and porosity analyzer (ASAP 2020HD88, Micromeritics, USA). Transmission electron microscopy (TEM, JEM-2010F, JEOL, Japan) assembly with energy dispersive X-ray spectroscopy (EDX, Quantax-STEM, Bruker, Germany) was further applied to study the morphology and structural characteristics of the TiO₂@CuInS₂ sample products. The diffuse reflectance absorption spectra of the products were recorded on a UV-visible spectrophotometer (UV-3900, Hitachi, Japan) equipped with an integrated sphere attachment.

Photocatalytic Activity Measurements

Photocatalytic H₂ evolution of the sample products was performed in an inner-irradiation quartz annular reactor under UV-vis irradiation. A 300W Xenon lamp (CEL, HUL300) was used as the light source. Other components included a vacuum pump vacuumize, a recirculation pump, a gas collection and a water-cooled condenser. 0.1g of the as-synthesized samples was dispersed in 40 mL deionized water, and then 10 mL MEOH mixed solutions were added into the aqueous solution by an ultrasonic oscillator. Then, the mixture was transferred into a quartz reactor. The quartz reactor was deaerated by the vacuum pump and purged with N₂ for 30 min to further remove air. Finally, the photocatalytic water splitting reaction was irradiated under Xenon lamp. During the photocatalytic reaction, the temperature was maintained at 25 °C by a flow of cooling water. In comparison, the Xenon lamp was equipped a cutoff filter of UV-cut 420 and AM1.5 for different light source, in which the light intensities were both fixed at 150 mW/cm², respectively. The H₂ content was monitored by an online gas chromatography (GC,

7900) equipped with a thermal conductivity detector (TCD). The products were reused for 5 cycles to study the stability and recyclability.

Photoelectrochemical measurement

To study the photoelectrochemical performance, the photoelectrodes were firstly fabricated. Firstly, the slurry was prepared by grinding the mixture of 0.1 g sample products and 0.8 g ethanol. Then, a drop method was employed to coat the slurry onto an indium-tin oxide (FTO) glass. Afterwards, the FTO coated with slurry was dried in a vacuum oven and further calcined at 200 °C for 30 min to enhance the interface bonding. The photoelectrochemical performance of the sample products were studied in a standard three-electrode system, including an electrochemical analyzer (CHI 760e Instruments, Shanghai, China), Pt counter electrode, Ag/AgCl reference electrode and working electrode. A300W Xenon lamp (CEL, HUL300) light source equipped with a cutoff filter of AM1.5, in which the light intensity was fixed at 100 mW/cm². In addition, 0.5 M Na₂SO₄ solution was used as electrolyte.

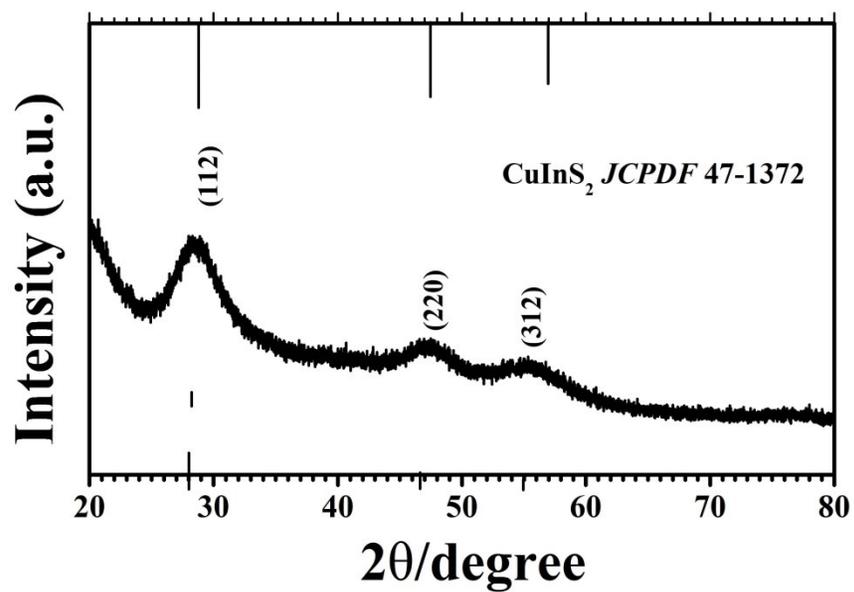


Fig. S1. XRD pattern of the as-prepared CuInS₂ QDs

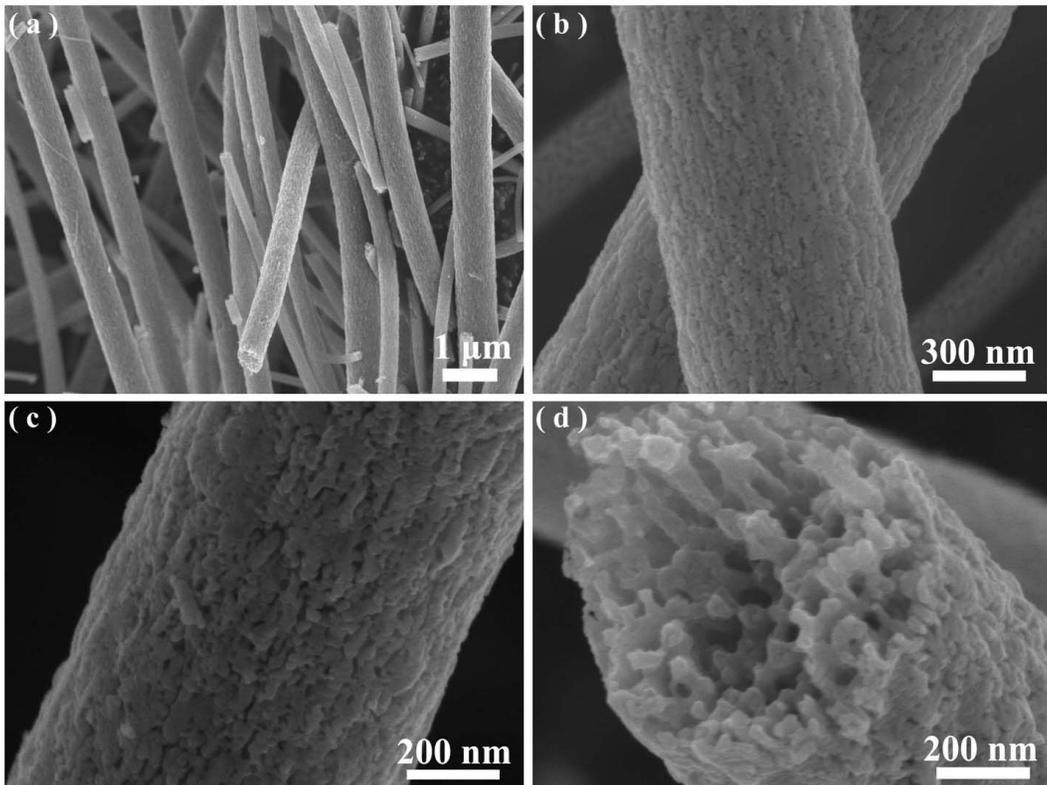


Fig. S2. (a-b) SEM images of the as-prepared mesoporous TiO₂ nanofibers

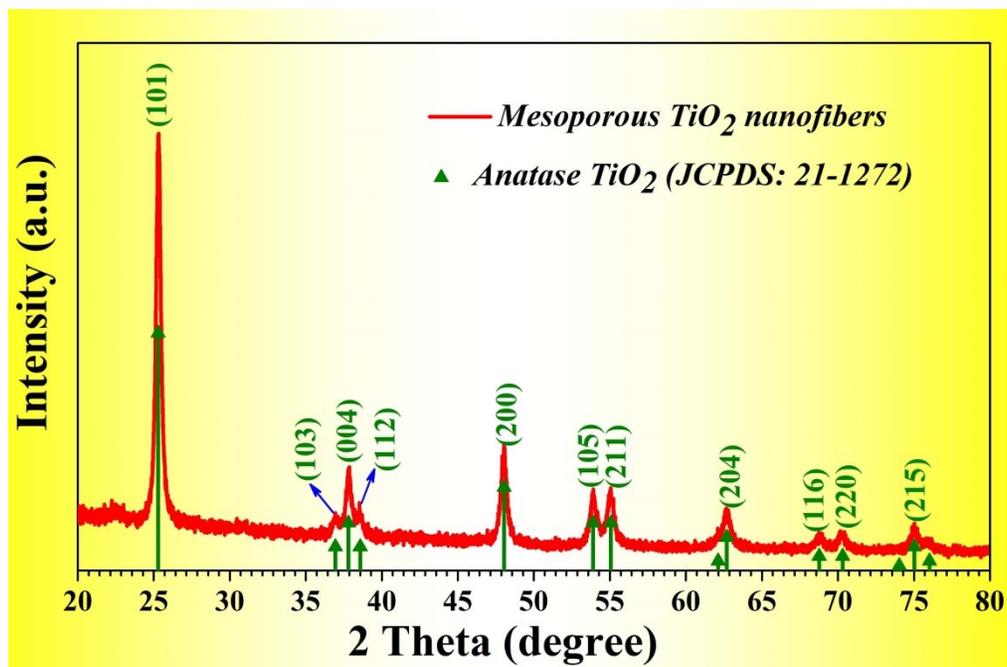


Fig. S3. (a-b) XRD pattern of the as-prepared mesoporous TiO₂ nanofibers

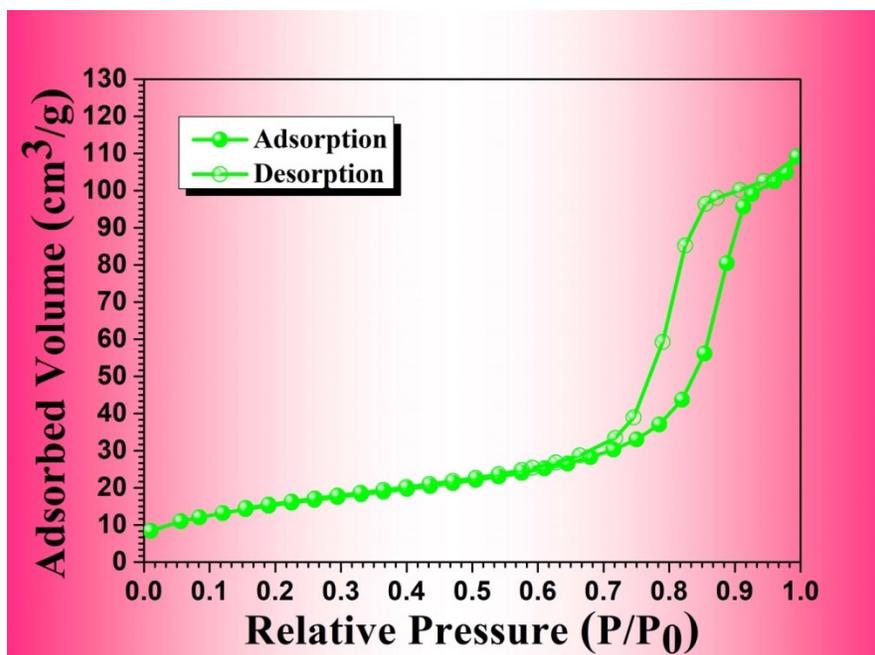


Fig. S4. N₂ adsorption-desorption curves of the as-prepared mesoporous TiO₂ nanofibers

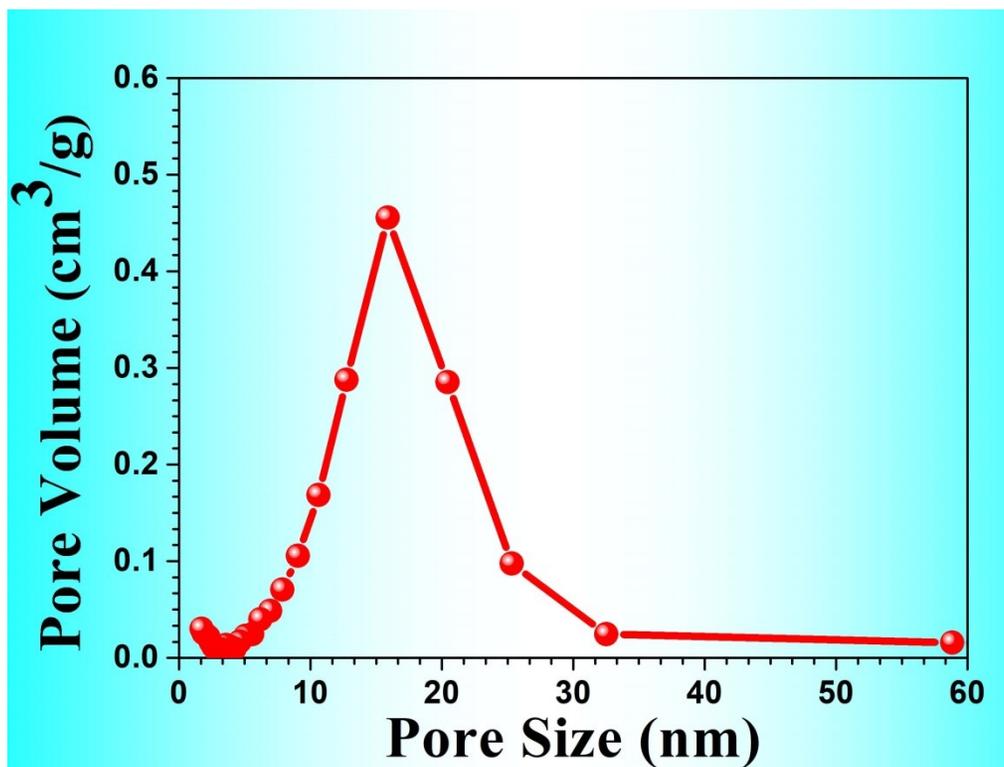


Fig. S5. Pore size distributions of the as-prepared mesoporous TiO₂ nanofibers

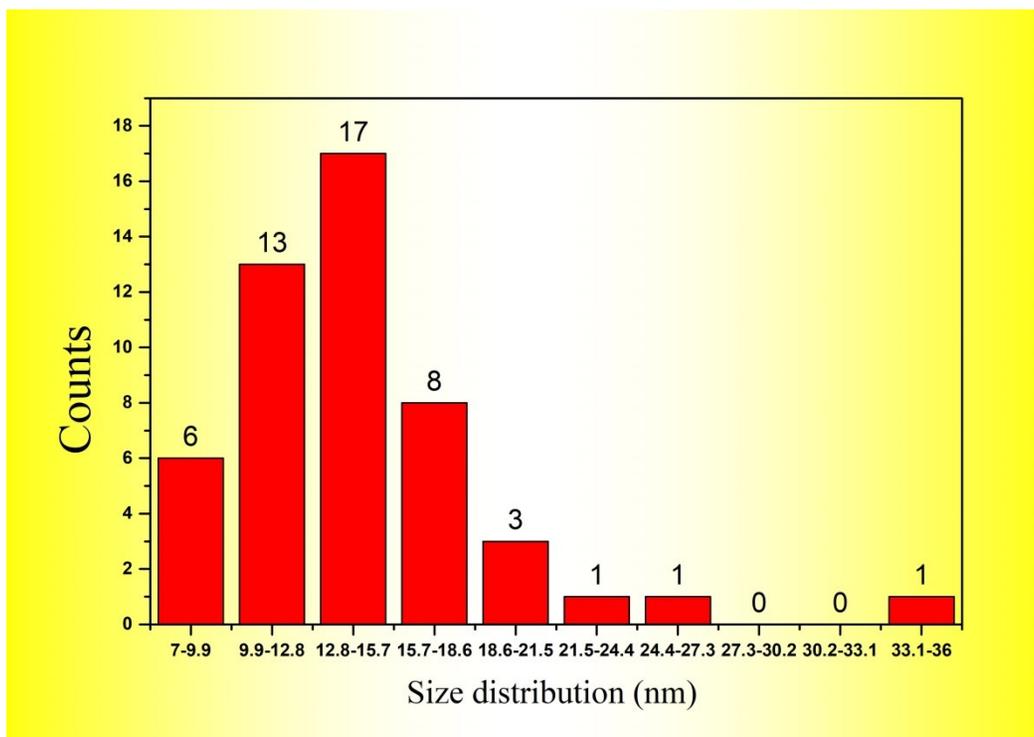


Fig. S6 Size distribution of the embedded CuInS₂ nanoparticles

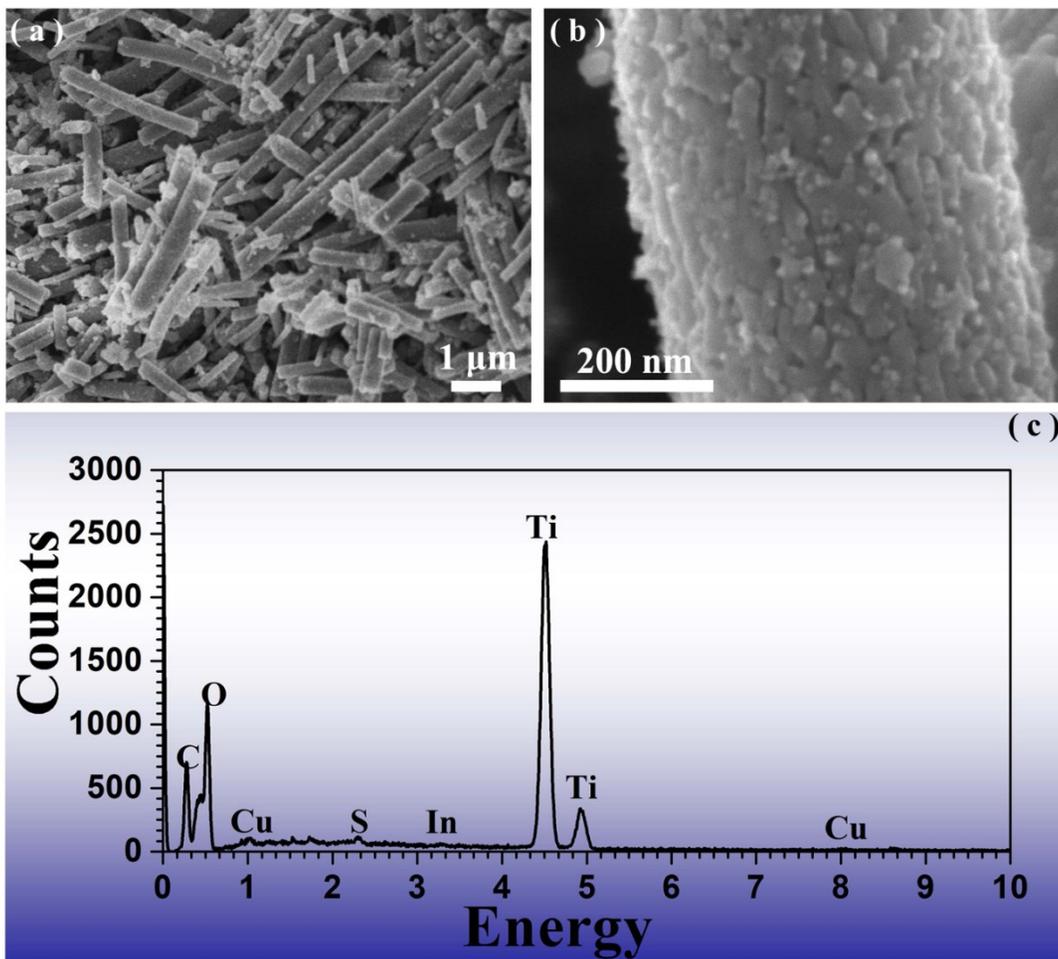


Fig. S7. (a-c) SEM images (a-b) and EDS pattern (c) of $\text{TiO}_2@\text{CuInS}_2$ (5%) sample.

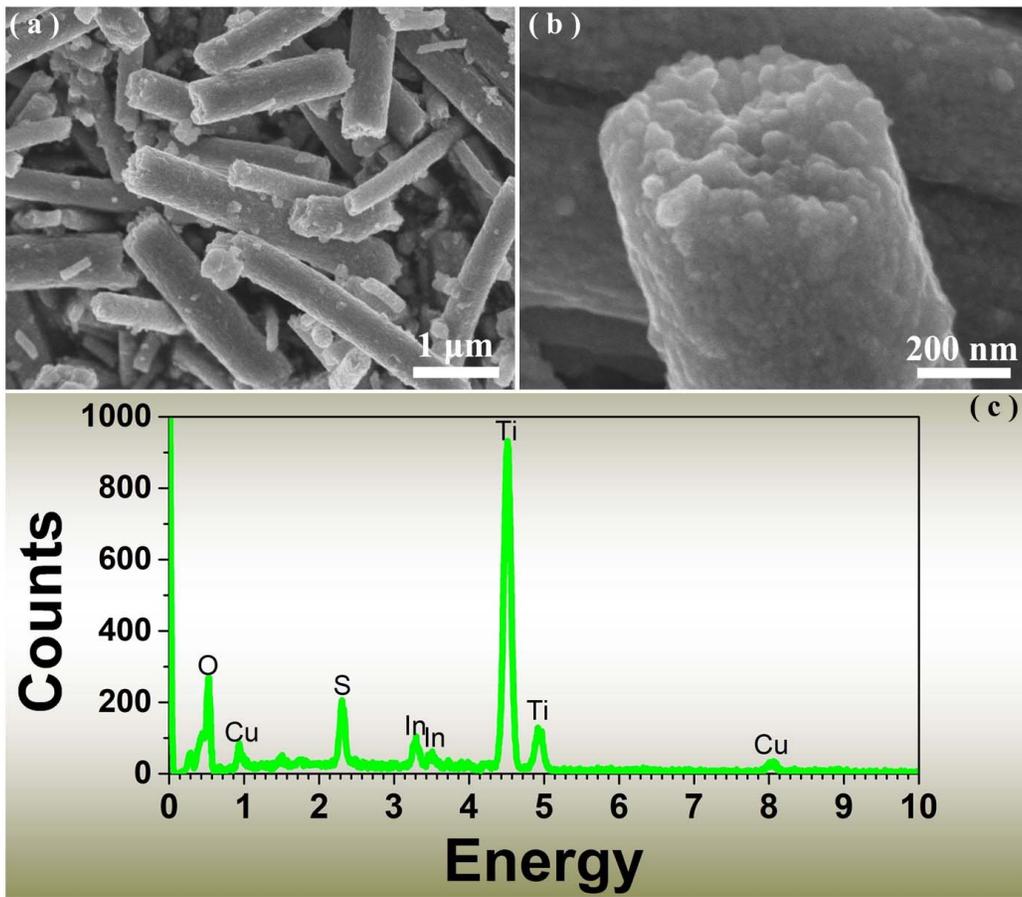


Fig. S8. (a-c) SEM images (a-b) and EDS pattern (c) of $\text{TiO}_2@\text{CuInS}_2$ (15%) sample.

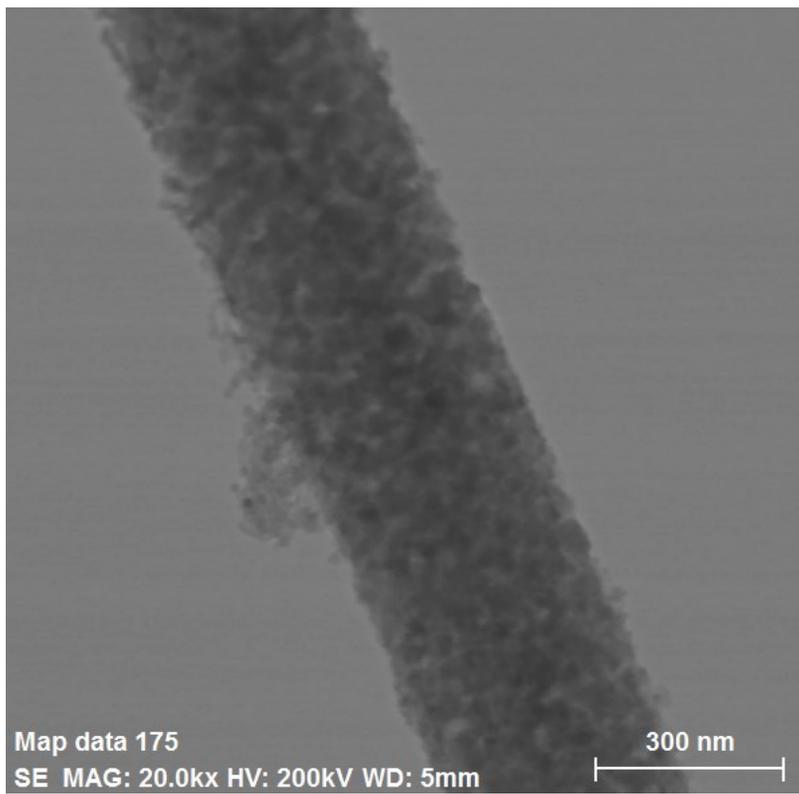


Fig. S9. STEM image of the TiO₂@CuInS₂ (10%) sample

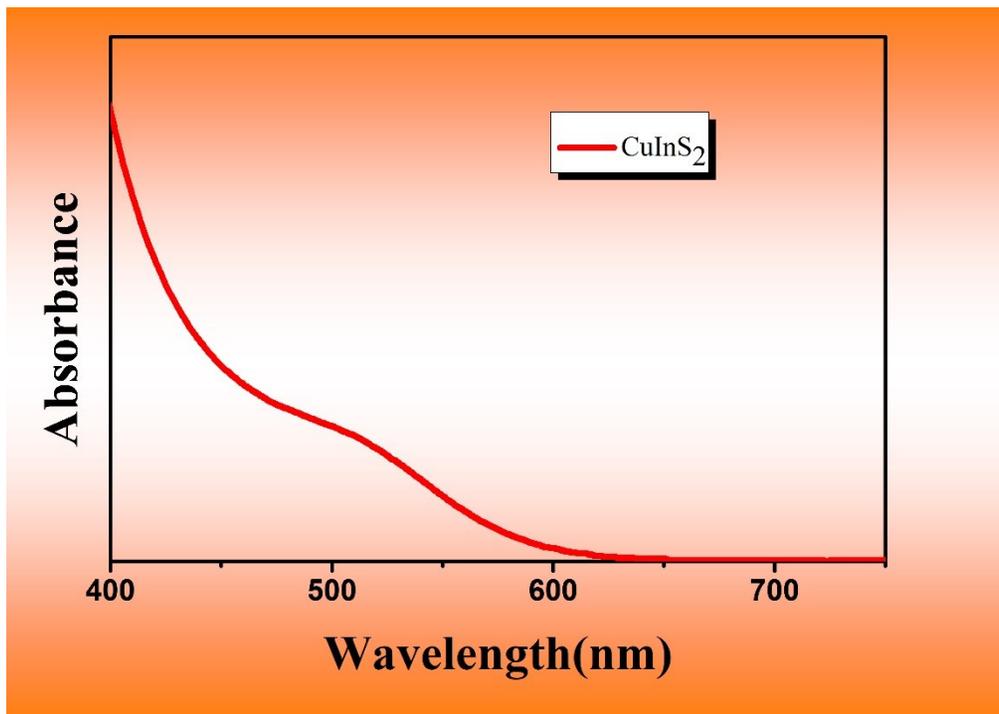


Fig. S10. UV-vis spectrum of bare CuInS₂ sample.

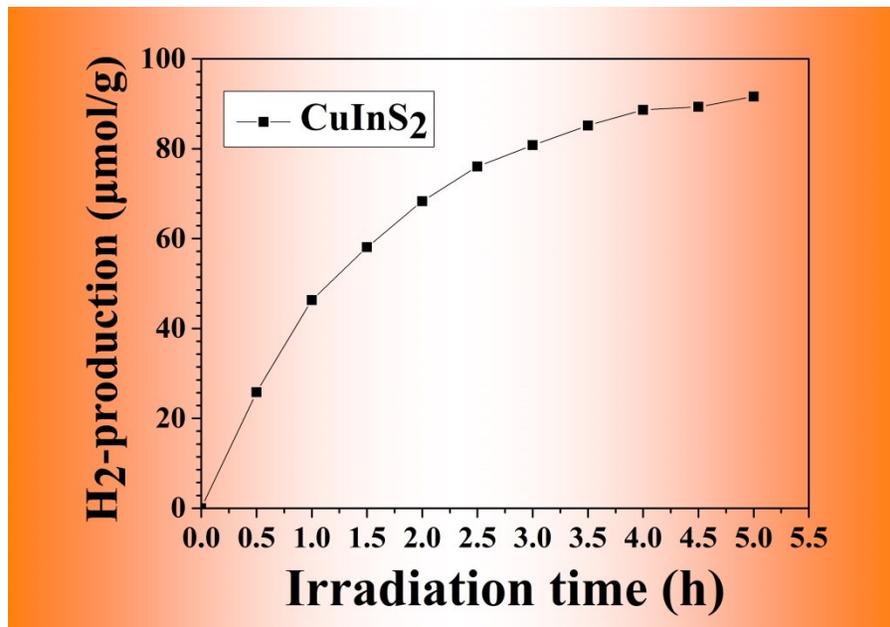


Fig. S11. Photocatalytic H₂ evolution activity over bare CuInS₂ photocatalysts under visible light irradiation.

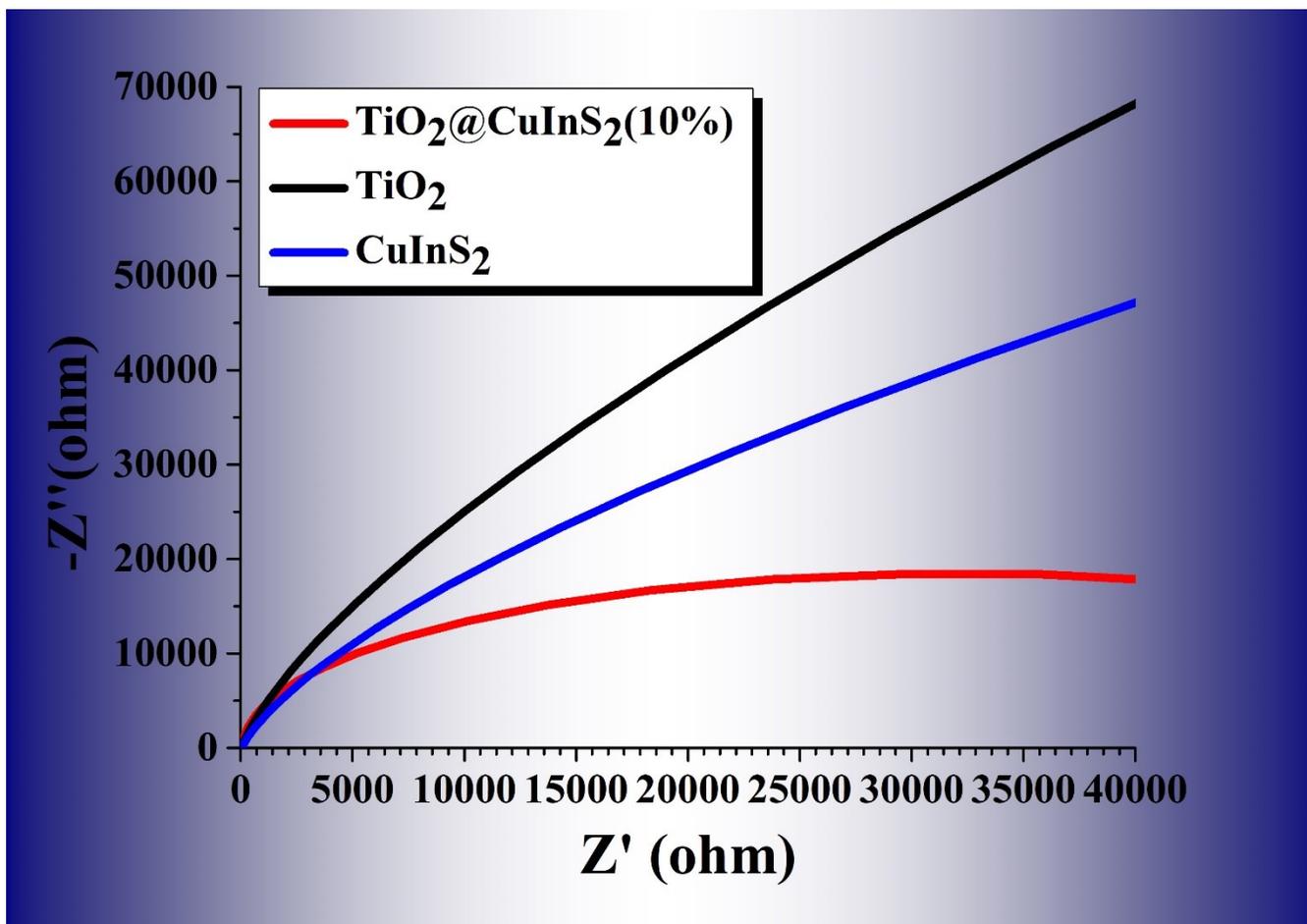


Fig. S12. EIS plots of the samples in 0.5 M Na₂SO₄ aqueous solution under AM 1.5 irradiation.

Table S1. Comparison of the related works for photocatalytic H₂ production

Material	Morphology	Cocatalyst	Irradiation conditions	Reaction solution	Activity ($\mu\text{mol g}^{-1}\text{h}^{-1}$)	Reference
TiO ₂ /CuInS ₂	Nanoparticles	---	300 W xenon lamp	Water+ethanol	273.25	[1]
TiO ₂ /CuInS ₂	Nanoparticles	MoS ₂	300 W Xenon lamp equipped with a UV cutoff filter ($\lambda > 420$ nm).	Water+Na ₂ S+MNa ₂ SO ₃	141	[2]
TiO ₂ /ZnO	Nanoparticles	Pt	300 W Xenon lamp	Water+MNa ₂ S+MNa ₂ SO ₃	1034	
TiO ₂ /ZnO	Nanoparticles	Pt	400 W mercury arc lamp	Water+MeOH	203	[3]
TiO ₂ /BiVO ₄	Mesoporous nanofibers	---	300 W Xenon lamp equipped with a UV cutoff filter ($\lambda > 420$ nm).	Water+MeOH	6.0	[4]
Fe doped TiO ₂	Mesoporous nanofibers	---	300 W Xenon lamp equipped with a UV cutoff filter ($\lambda > 420$ nm)	Water+MeOH	6.7	[5]
N-doped TiO ₂	Mesoporous nanofibers	---	300 W Xenon lamp equipped with a UV cutoff filter ($\lambda > 420$ nm)	Water+MeOH	39.5	[6]
ZnO	Mesoporous nanofibers	---	300 W Xenon lamp	Water+Na ₂ S+Na ₂ SO ₃	930	[7]
TiO ₂	Mesoporous hollow nanofibers	---	300 W Xenon lamp	Water+MeOH	499.1	[8]
	Hierarchical		500 W Xenon			

[11] Y. J. Yuan, D. Q. Chen, Y. W. Huang, Z. T. Yu, J. S. Zhong, T. T. Chen, W. G. Tu, Z. J. Guan, D. P. Cao and Z. G. Zou, *Chemsuschem*, 2016, **9**, 1003-1009.