Electronic Supplementary Information

In situ controlled growth of $ZnIn_2S_4$ nanosheets on reduced graphene oxide for enhanced photocatalytic hydrogen production performance

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Experimental section.

Graphene oxide sheets (GO) were prepared by a modified Hummer's method [S1]. In a typical procedure for the synthesis of reduced graphene oxide/$ZnIn_2S_4$ (RGO/$ZnIn_2S_4$) composite, 5 mg GO was dispersed into a mixed alcoholic solution that contained glycerol (5 mL) and ethanol (15 mL) by ultrasonication for 30 min. Then, 0.1910 g $In(NO)_3 \cdot 4.5H_2O$, 0.0550 g $Zn(AC)_2 \cdot 6H_2O$ and 0.2636 g L-cysteine hydrochloride monohydrate ($C_3H_7NO_2S \cdot HCl \cdot H_2O$, L-CHM) was added into the above solution under stirring one by one, followed by ultrasonication for another 30 min. Finally, the obtained yellow solution was transferred to a 50 mL Teflon-lined stainless steel autoclave, which was heated to 180 ^oC and maintained for 12 h. After cooling, the as-synthesized brown products were rinsed three times with ethanol and dried at 60 ^oC overnight. For comparison, bare RGO and the pure $ZnIn_2S_4$ were obtained under the same experimental conditions.

In order to obtain the detail content of RGO in the RGO/$ZnIn_2S_4$ composite, we added a certain amount of RGO/$ZnIn_2S_4$ composite into diluted hydrochloric acid (3 mol L^{-1}) and stirred overnight to ensure that $ZnIn_2S_4$ was dissolved completely. Then the black suspension was filtered, washed with distilled water several times. Subsequently, the clear filtrate was diluted and determined by ICP-AES to get the concentration of Zn^{2+} and In^{3+}, so the content of RGO and $ZnIn_2S_4$ in the composite can be calculated, respectively.

Characterization.

The X-ray diffraction (XRD) of powder samples was examined on a Bruker D8 X-ray diffractometer using Cu Ka radiation (λ = 0.15405 nm, 40 kV, 100 mA). Transmission electron microscopy (TEM) and high-resolution TEM (HRTEM) images of samples were recorded by using a JEOL 2100 microscope with a 200 kV accelerating voltage, Scanning electron microscopy (SEM) micrographs were taken using a Hitachi S-4800 instrument. UV-visible diffuse reflectance spectra (DRS) were determined by a UV/Vis/NIR Spectrometer (Perkin-Elmer Lambda950). The surface elements and their electronic states of the samples were analyzed using X-ray photoelectron spectroscopy (XPS, Kratos-AXIS UL TRA DLD, Al Ka X-ray source). Raman spectra were recorded on a Jobin Yvon HR 800 micro-Raman spectrometer at 457.9 nm. Fourier transform infrared spectra (FIIR) were collected using a Thermo Scientific Nicolet NICOLETiS10. The specific surface areas of the materials were calculated using the Brunauer–Emmett–Teller (BET) method. Zn^{2+} and In^{3+} concentrations of the samples were determined by Thermo ICAP6300 inductively coupled plasma-atomic emission spectrometry (ICP-AES).

Photocatalytic H_2 production.

The photocatalytic H_2 evolution from water was conducted in an online photocatalytic hydrogen production system (AuLight, Beijing, CEL - SPH2N). A certain amount of powder sample of the catalyst was suspended in a mixture of 100 mL of mixed aqueous solution containing 0.35 M Na_2S and 0.25 M Na_2SO_3. The reaction was carried out by irradiating the suspension with light from a 300 W Xe lamp (AuLight, CEL-HXF-300，Beijing) which was equipped with an optical filter (λ > 420 nm) to cut off the light in the ultraviolet region. Prior to the reaction, the mixture was deaerated by evacuation to remove O_2 and CO_2 dissolved in water. Gas evolution was observed only under photoirradiation, being analyzed by an on-line gas chromatograph (SP7800, TCD, molecular sieve 5 Å, N_2 carrier, Beijing Keruida Limited).

To evaluate the photostability, the photocatalyst after the first run of 3 h photochemical reaction was separated from the suspension, washed with water, and dried at 60° C, and then, the recovered photocatalyst was used for the next run of the photoreaction under the same conditions.

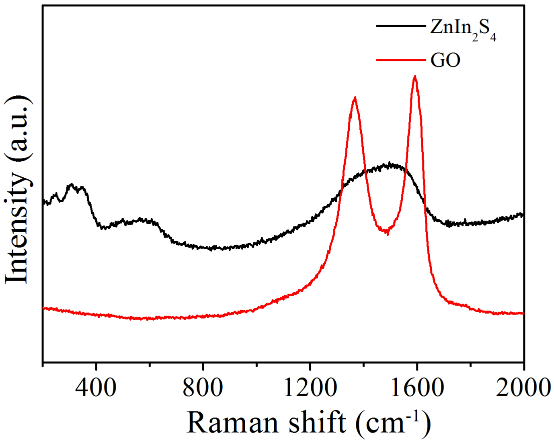

Fig. S1 Raman spectra of $ZnIn_2S_4$ and GO.

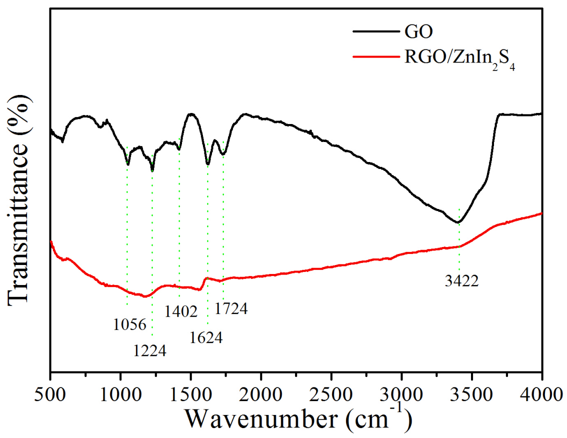

Fig. S2 FT-IR spectra of GO and RGO/ZnIn$_2$S$_4$ composite.

Fig. S2 shows the FT-IR spectra of GO and RGO/ZnIn$_2$S$_4$. The characteristic peaks of GO, including C-O stretching at 1056 cm^{-1}, C-OH stretching at 1224 cm^{-1}, carboxyl O-H deformation at 1402 cm^{-1}, skeletal vibration of unoxidized graphitic domains at 1624 cm^{-1} and C=O stretching at 1724 cm^{-1} were clearly observed in the spectrum recorded for GO.[S2,S3] The broad bands in the 3400-3800 cm^{-1} region and at 3422 cm^{-1} are related to physically adsorbed H_2O and CO_2 from the atmosphere, respectively. For the RGO/ZnIn$_2$S$_4$ composite, the peaks reflecting functional groups in GO are much less intense or absent, especially those at 1224 cm^{-1}, 1402 cm^{-1} and 1724 cm^{-1}, which are all assigned to the oxygen-containing groups. These results indicate that many oxygen-containing functional groups were removed during solvothermal reduction process.

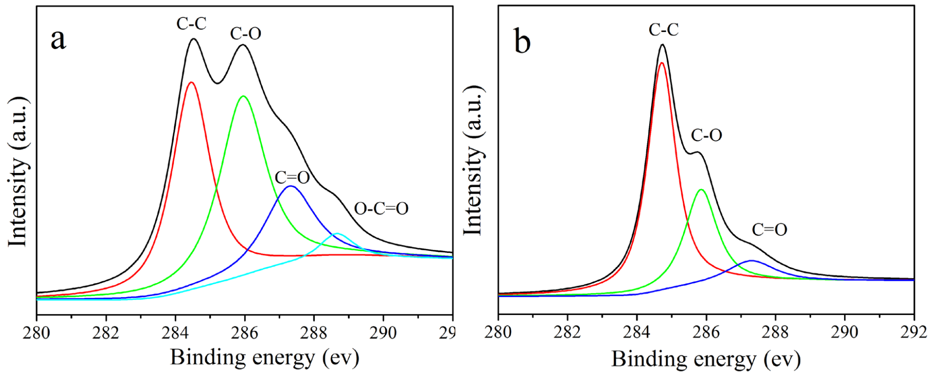

Fig. S3 High-resolution XPS spectra of C1s from: (a) GO and (b) RGO/ZnIn$_2$S$_4$.

As shown in Fig. S3a, the XPS spectrum of C1s from GO can be deconvoluted into four smaller peaks which are ascribed to the following functional groups: sp^2 bonded carbon (C-C, 284.9 eV), epoxy/hydroxyls (C-O, 286.5 eV), carbonyls (C=O, 287.3

eV), and carboxyl (O-C=O, 288.6 eV).[S4,S5] In comparison to the GO spectrum, the peak for O-C=O in the RGO/$ZnIn_2S_4$ (Fig. S3b) almost vanishes, and the peaks for C-O and C=O still exist but their intensities are much lower. The results reveal that the substantial reduction of GO occurred, which is in a good agreement with the FT-IR and Raman analysis.

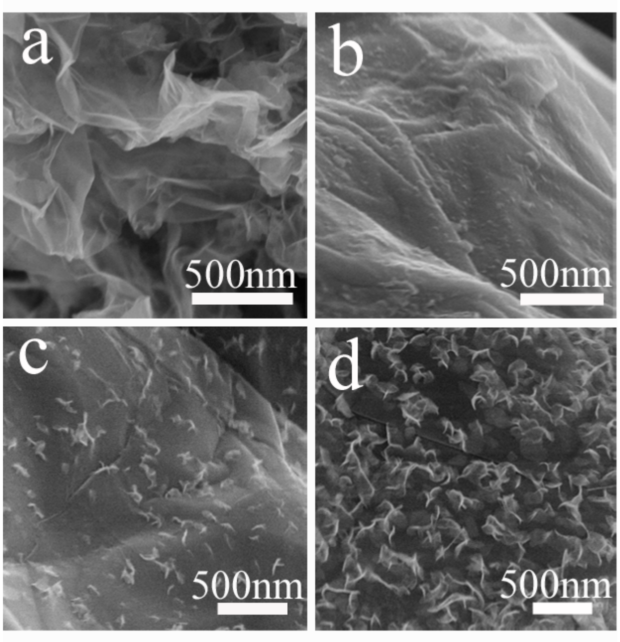

Fig. S4 SEM images of the RGO/$ZnIn_2S_4$ samples prepared from different solvothermal reaction time: (a) 0 h; (b) 0.5 h; (c) 3 h; (d) 12 h.

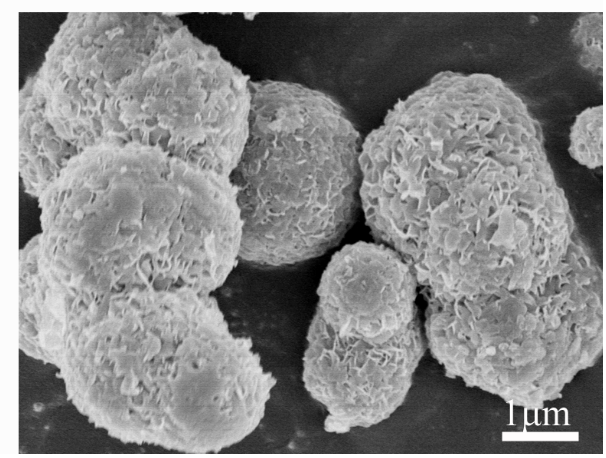

Fig. S5 SEM image of the as-prepared $ZnIn_2S_4$.

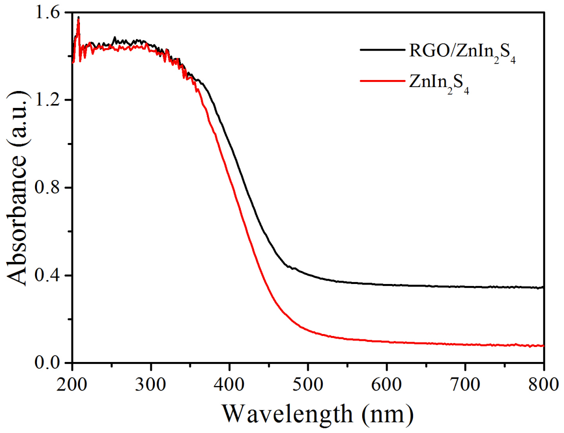

Fig. S6 UV-vis diffuse reflectance spectra of the RGO/ZnIn$_2$S$_4$ and ZnIn$_2$S$_4$ samples.

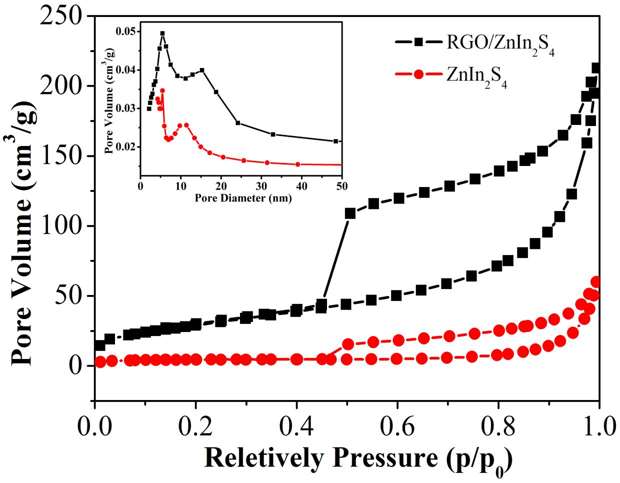

Fig. S7 Nitrogen adsorption-desorption isotherms and the corresponding pore size distribution curves (inset) of RGO/ZnIn$_2$S$_4$ and ZnIn$_2$S$_4$ samples.

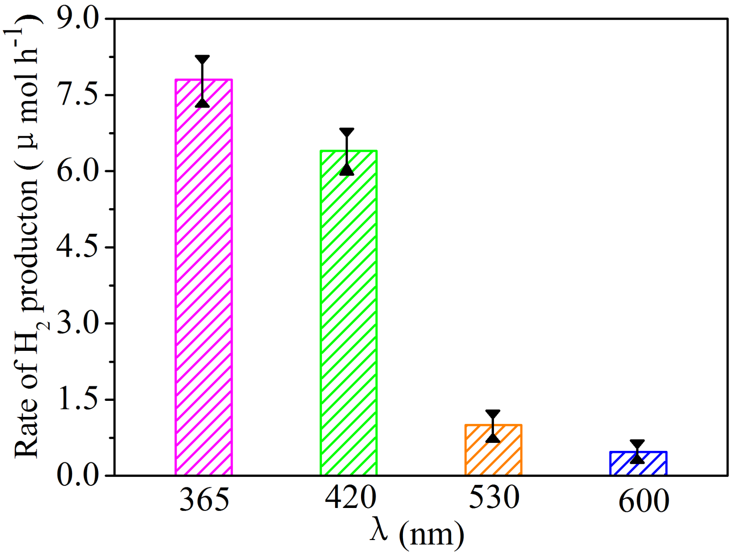

Fig. S8 H$_2$ production amount of RGO/ZnIn$_2$S$_4$ under different incident monochromatic light wavelength.

The H_2 production amount dependent on the incident monochromatic light wavelength was measured under the same photoreaction conditions, except for the incident light wave-length. The hydrogen yields of 1 h photoreaction under different light wavelengths (365, 420, 530 and 600 nm) were measured.

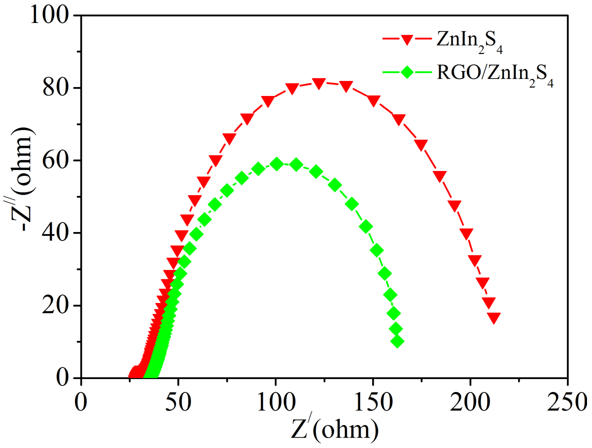

Fig. S9 Nyquist plots of $ZnIn_2S_4$ and RGO/$ZnIn_2S_4$ electrodes in 0.1 M Na_2S + 0.02 M Na_2SO_3 aqueous solution under visible light.

Electrochemical impedance spectra (EIS) analysis has become a powerful tool in studying the charge transfer process occurring in the three-electrode system and the EIS Nynquist plots of the two samples are shown in Figure S9. As has been reported that the intermediate-frequency response is associated with the electron transport and transfer at the $ZnIn_2S_4$/electrode interface.[S6,S7] The RGO/$ZnIn_2S_4$ sample shows smaller semicircle in the middle-frequency region in comparison to the $ZnIn_2S_4$, which indicates the fastest interfacial electron transfer.[S8] That is, because of the excellent conductivity, the introduction of RGO can benefit the charge transfer in the RGO/$ZnIn_2S_4$ system and thus lower the charge recombination. Overall, RGO can function as an electron collector and transporter in the composite and inhibit the charge recombination and thus significantly enhance the photocatalytic H_2-production activity.

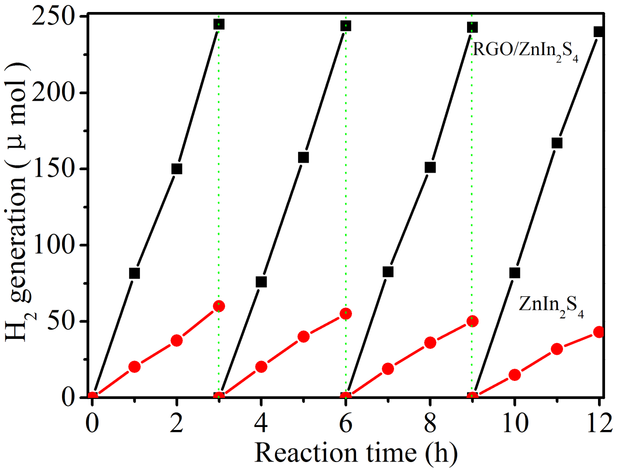

Fig. S10 Time course of photocatalytic H_2-production over $RGO/ZnIn_2S_4$ (0.050 g) and $ZnIn_2S_4$ (0.050 g).

References

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