Electronic Supplementary Material (ESI) for Physical Chemistry Chemical Physics.

Supporting Information

Hydrogenated $ZnIn_2S_4$ microspheres: boosting photocatalytic hydrogen evolution by sulfur vacancy engineering and mechanism insight

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Table S1. TRPL decay parameters of the pristine ZIS and H-ZIS.

Samples	**A_1**	**τ_1/ns**	**A_2**	**τ_2/ns**	**A_3**	**τ_3/ns**	**τ_{ave}/ns**
H-ZIS	0.39	18.25	0.50	42.60	0.54	86.26	67.38
ZIS	0.25	25.2955	0.33	47.08	0.42	19.58	35.01

Fig. S1

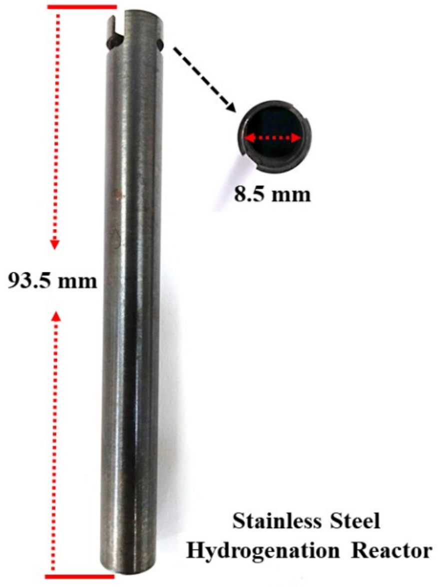

Fig. S1. The stainless steel hydrogenation reactor with a height of 93.5 mm and a diameter of 8.5 mm

Fig. S2

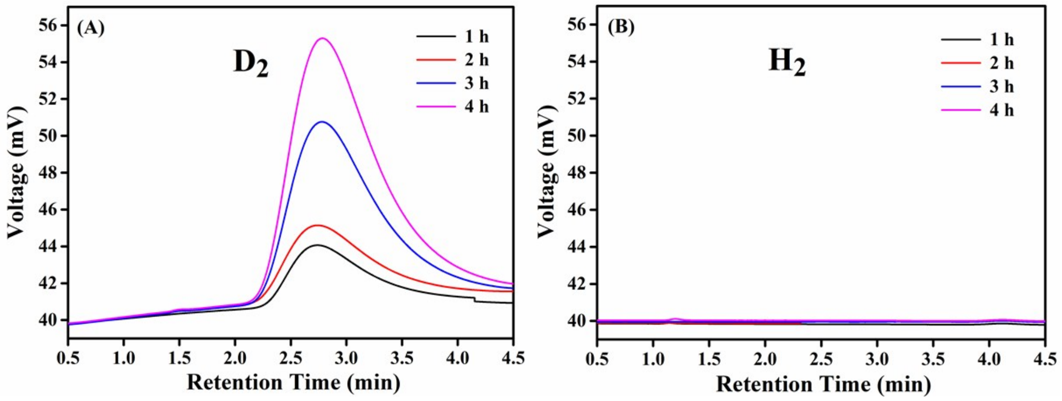

Fig. S2. Photocatalytic D_2O splitting over the H-ZIS sample under visible light: (A) the GC result of photocatalytic D_2 evolution; (B) the GC result of photocatalytic H_2 evolution

To test whether any hydrogen molecules were desorbed from the surface of the H-ZIS sample during the photocatalytic process, we used the H-ZIS sample to perform hydrogen evolution test in isotope D_2O, and used high-resolution Gas Chromatography Mass Spectrometer (GCT Premier, GC-MS) to detect the D_2. As shown in Fig. S2(A), after every 1 hour of sampling, a peak associated with D_2 was detected at a retention time of about 2.7 min, and with the increase of time, the D_2 amount produced from the photocatalytic D_2 evolution was also increased. This shows that the H-ZIS exhibited the photocatalytic activities in both D_2O and H_2O, and the D_2 or H_2 production amount was increased with the irradiation time. As a control, we also tested the amount of H_2 produced by H-ZIS in D_2O, and the results are shown in Fig. S2(B). It can be seen that no peak appeared during the whole retention time, indicating that H_2 could not be generated by H-ZIS in D_2O and no H_2 was desorbed from the H-ZIS surface during the photocatalytic process. This also proves that the adsorption of H_2 on the H-ZIS surface during hydrogenation treatment could be negligible.

Fig. S3

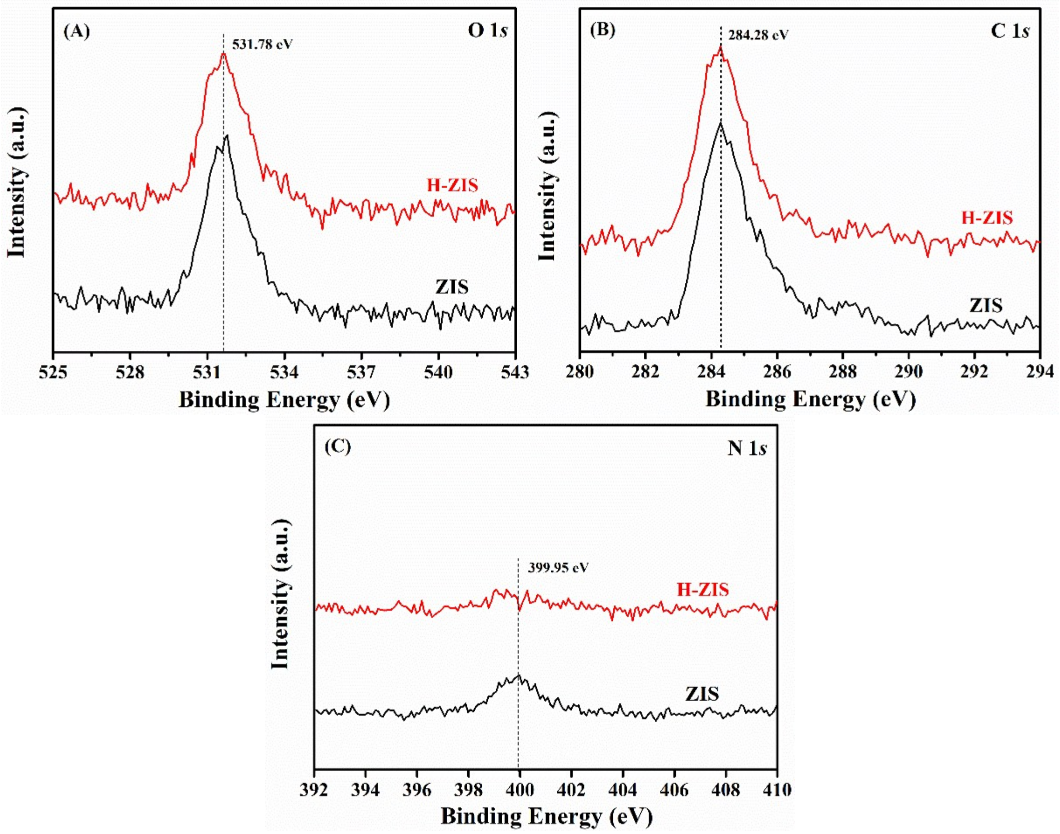

Fig. S3. XPS spectra of pristine ZIS and H-ZIS: (A) O 1*s*, (B) C 1*s*, and(C) N 1*s*

To further investigate the influence of hydrogenation process on the chemical composition of ZIS, the high-resolution XPS spectra of O 1s, C 1s and N 1s were also examined, as shown in Fig. S3. The peaks corresponding to O 1*s* and C 1*s* were detected at 531.78 and 284.28 eV (Fig. S3(A) and (B)), respectively, for both the pristine ZIS and H-ZIS samples, and there were no changes in peak position and peak intensity between these two samples, indicating that the peaks for O 1s and C 1s could be ascribed to adventitious oxygen and carbon during the XPS measurement. Meanwhile, the peaks at about 400.00 eV corresponding to N 1*s* was negligible for both the pristine ZIS and H-ZIS samples (Fig. S3(C)). These results confirm that the hydrogenation process would not introduce other impurities (such as: O, C, N) into the pristine ZIS.

Fig. S4

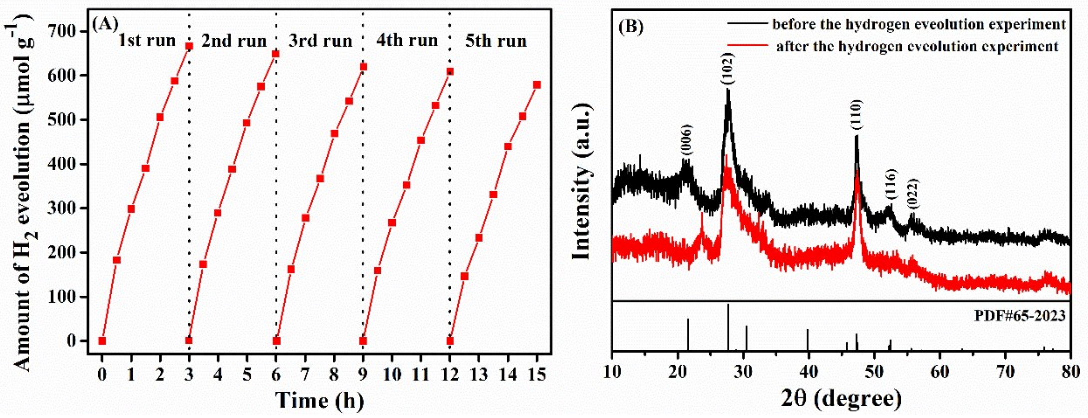

Fig. S4. (A) Photocatalytic H_2 evolution over the pristine ZIS for 5th cycles under visible light illumination; (B) XRD pattern of the pristine ZIS measured before and after photocatalytic cycling experiment

Fig. S5

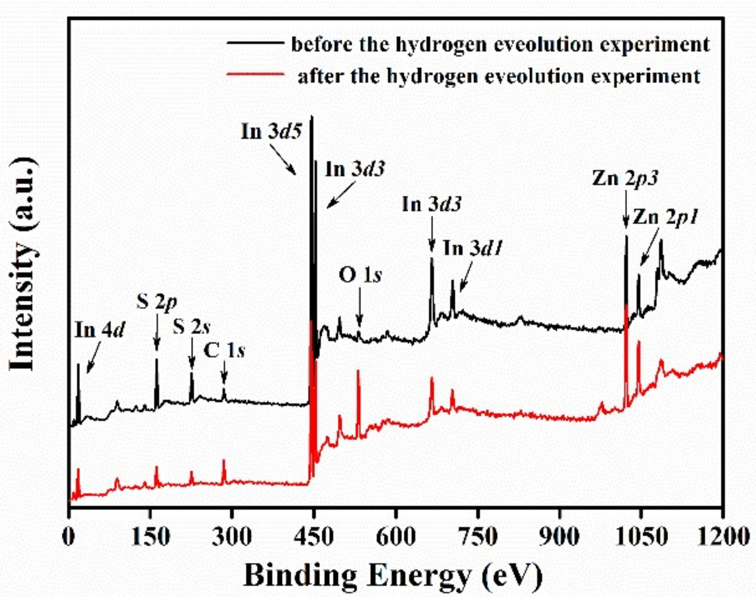

Fig. S5. The survey XPS spectra of H-ZIS measured before and after photocatalytic cycling experiment