Supporting Information

A "Uniform" Heterogeneous Photocatalyst: Integrated P-N Type $CuInS_2/NaInS_2$ Nanosheets by Partial Ion Exchange Reaction for Efficient H_2 Evolution

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Experimental Section

Materials: All the chemicals are analytical grade and used as received without further purification.

Synthesis of $NaInS_2$ nanocrystals: In a typical synthesis, 0.25 mmol $InCl_3$ and 1 mmol $Na_2S{\cdot}2H_2O$ were dispersed in 15 mL mixed solution of ethanol and methanol at a volume ratio of 1:1. After reaction under vigorous stirring for 30 minutes at room temperature, the formed precipitate was transferred into a 25 mL Teflon-lined stainless steel autoclave, then sealed and heated at 200 ^oC for 5 h. After reaction, the final obtained products were collected by centrifuging the mixture, washed with distilled water and absolute ethanol several times, before drying under a vacuum at 60 ^oC overnight.

Synthesis of $CuInS_2/NaInS_2$ Heterogeneous Nanosheets: $CuInS_2/NaInS_2$ heterostructures were synthesized by a cation exchange reaction using the above prepared $NaInS_2$ and CuCl as precursors. Typically, $NaInS_2$ was first dispersed in 5 mL dimethylformamide, and different amounts of CuCl in 10 mL dimethylformamide were added to the former solution. After stirring for 30 min, the mixture was transferred in to autoclave and maintained at 190 ^oC for 16 h, and then cooled to room temperature. The products were collected by centrifugation, washed with distilled water and absolute ethanol, and dried in a vacuum oven.

Synthesis of $NaInS_2/MgIn_2S_4$ Heterogeneous Nanosheets: The synthesis process of $NaInS_2/MgIn_2S_4$ heterostructures is similar to $CuInS_2/NaInS_2$, and $MgCl_2{\cdot}6H_2O$ was used instead of CuCl to react with$NaInS_2$. The reaction was occurred in 15 mL ethanol at 190 ^oC for 16 h, and then washed and fried for analysis.

Synthesis of $CuInS_2/MgIn_2S_4$ Heterogeneous Nanosheets: For the synthesis of $CuInS_2/MgIn_2S_4$ heterostructures, the $CuInS_2/NaInS_2$ was used as precursors and react with $MgCl_2{\cdot}6H_2O$. Typically, $CuInS_2/NaInS_2$ was first dispersed in 15 mL ethanol and 1 mmol $MgCl_2{\cdot}6H_2O$ were added to the former solution. After stirring for 30 min, the mixture was transferred in to autoclave and maintained at 190 ^oC for 16 h. After the heat treatment, it was cooled to room

temperature and the obtained products were washed with distilled water and absolute ethanol, and dried in a vacuum oven.

Synthesis of $ZnIn_2S_4/MgIn_2S_4$ Heterogeneous Nanosheets: $ZnIn_2S_4/MgIn_2S_4$ heterostructures were synthesized by a two-step cation exchange reaction. First, 1 mmol of synthesized $NaInS_2$ was reacted with x mmol of $ZnCl_2$ in absolute ethanol and then cation exchanged with (2-x) mmol $MgCl_2 \cdot 6H_2O$at 190 ^oC for 16 h by a solvothermal reaction.

Synthesis of $CuInS_2$ nanoparticle decorated $NaInS_2$ nanosheets: $NaInS_2$ nanoparticles were first synthesized by hydrothermal reaction between $InCl_3$ and Na_2S in 15 mL ethylenediamine at 190 ^oC for 16 h. Cation exchange reaction was conducted, i.e. transferring $NaInS_2$ to $CuInS_2$. The as-synthesized $CuInS_2$ nanoparticles were further mixed with $NaInS_2$ nanosheets and calcined at 300 ^oC for 2 h to adhered $CuInS_2$ onto the surface of $NaInS_2$ nanosheets.

Characterization: The morphologies and structure analyses of obtained samples were carried out by field emission scanning electron microscope (FESEM, JEOL JSM-7600F) and transmission electron microscope (TEM, JEOL JEM-2100F). XRD patterns were recorded from a Shimadzu XRD-6000 X-ray diffractometer with the 2θ range from 10 to 90^o. UV−vis absorption spectra were recorded on a Lambda 750 UV/Vis/NIR spectrophotometer (Perkin–Elmer, USA). Photoluminescence spectra of synthesized heterogeneous nanosheets were obtained by a Shimadzu RF-5301PC spectrophotometer using an excitation wavelength of 325 nm. The chemical composition was determined by an inductively coupled plasma atomic emission spectrometer (ICP-AES, Optima 5300DV, Pekin-Elmer).

Flatband Potential Measurement: The flatband potentials were measured by impedance spectroscopy using Mott−Schottky plots. The test films were first prepared by directly drop-casted of corresponding aqueous samples on fluorine-tin oxide (FTO) glass substrate, dried at room temperature before calcining at 400 ^oC in inert atmosphere for an hour. Mott−Schottky measurements were carried out by Gamry electrochemical impedance spectroscopy in 0.1 M of NaOH solution. Sample films, Pt electrode and Ag/AgCl electrode were used as working electrode, counter electrode and reference electrode, respectively.

Photocatalytic Hydrogen Testing: The photocatalytic hydrogen evolution was performed in a 25 mL glass reactor. In a typical test run, 10 mg of synthesized products were suspended in 15 mL of aqueous solution containing 0.1 M ascorbic acid as the sacrificial reagent and without co-catalyst. The reactor was then sealed up and purged with nitrogen gas to remove any residual air. Subsequently, the reactor was irradiated with a300 W Xe lamp (200 mW/cm^2, MAX-302, Asahi Spectra, USA) coupled with a UV cut-off filter (λ > 420 nm). The

photocatalytic H_2 evolution rate was quantitatively analyzed by an Agilent 7890A gas chromatograph.

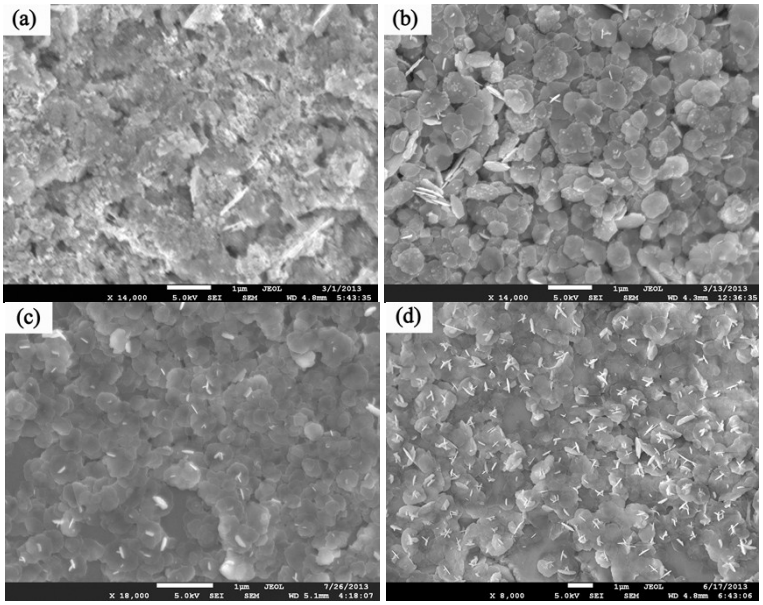

Figure S1 Typical morphological evolution of $NaInS_2$ nanoparticles with different reaction times: (a) 20 min., (b) 1 h, (c) 5 h and (d) 12h.

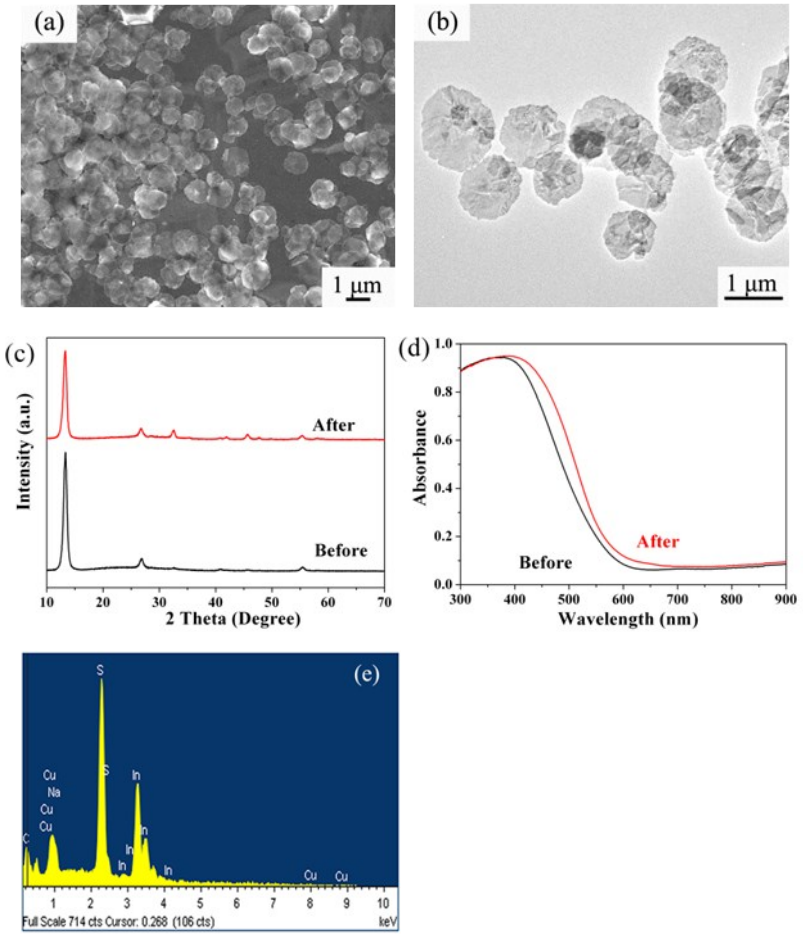

Figure S2 (a) SEM and (b) TEM images, (c) XRD, (d) UV-vis and (e) EDX pattern of obtained nanosheets reacted with 5 % Cu^{+} ions at room temperature.

Table S1. Compositional analysis of $NaInS_2/CuInS_2$ heterogeneous nanosheets

Sample	Calculated molar ratio Cu/Na	ICP-AES Cu/Na
Cu-0.3	0.30	0.42
Cu-1	1.00	1.19
Cu-3	3.00	3.13
Cu-5	5.00	5.09

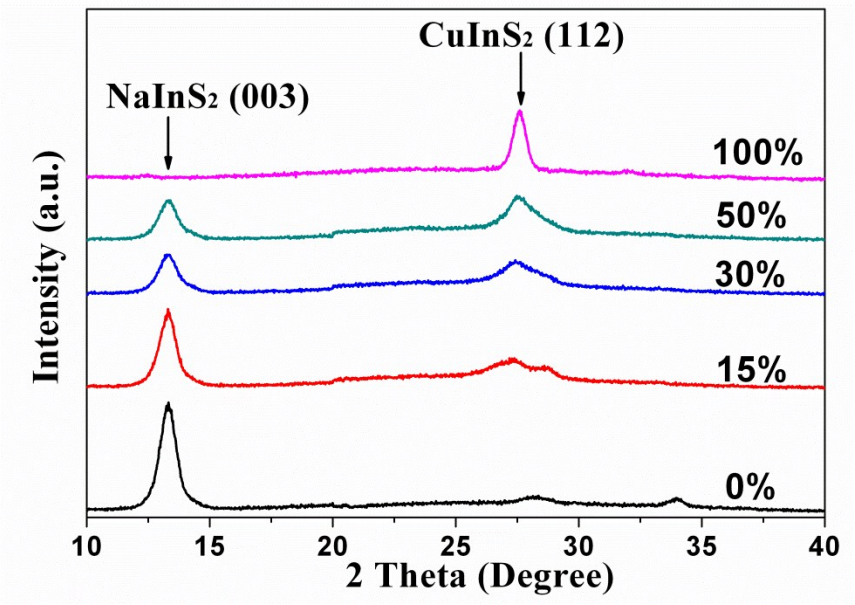

Figure S3 XRD patterns of heterogeneous nanosheets with different molar ratio of Cu/Na by an ion exchange reaction.

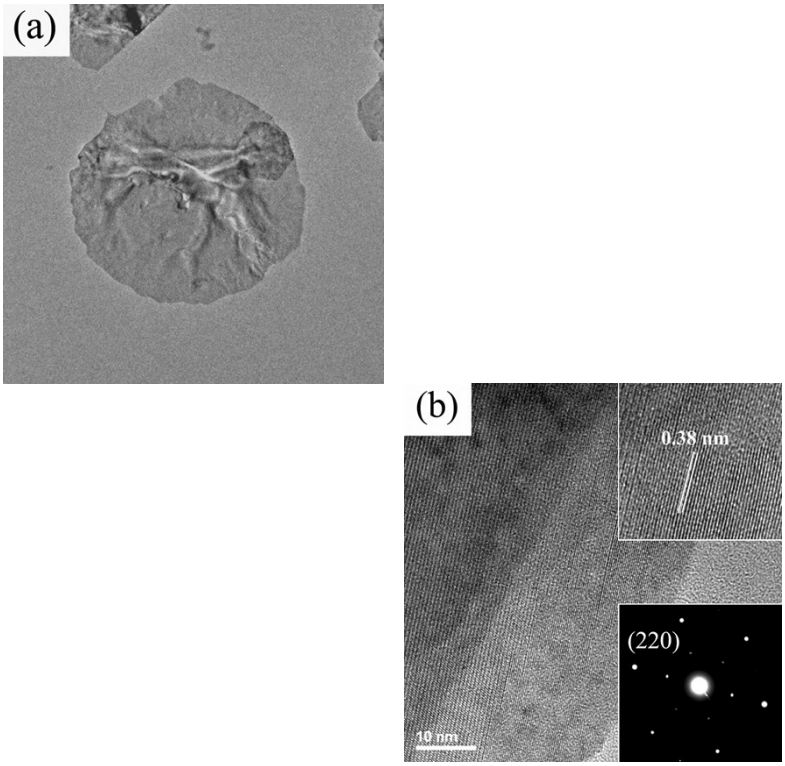

Figure S4 (a) TEM and (b) HRTEM of $NaInS_2$ nanosheets.

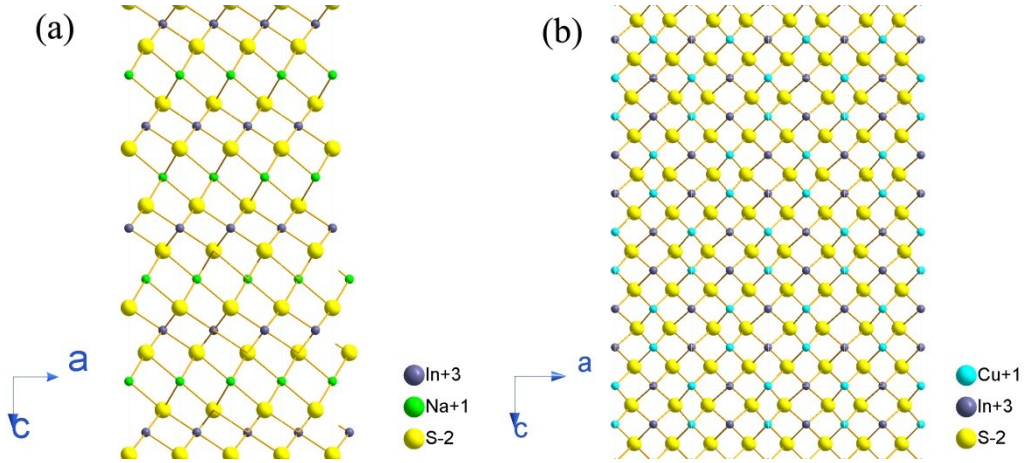

Figure S5 The schematic illustration of the atom arrangement of (a) $NaInS_2$ and (b) $CuInS_2$,with (010) plane.

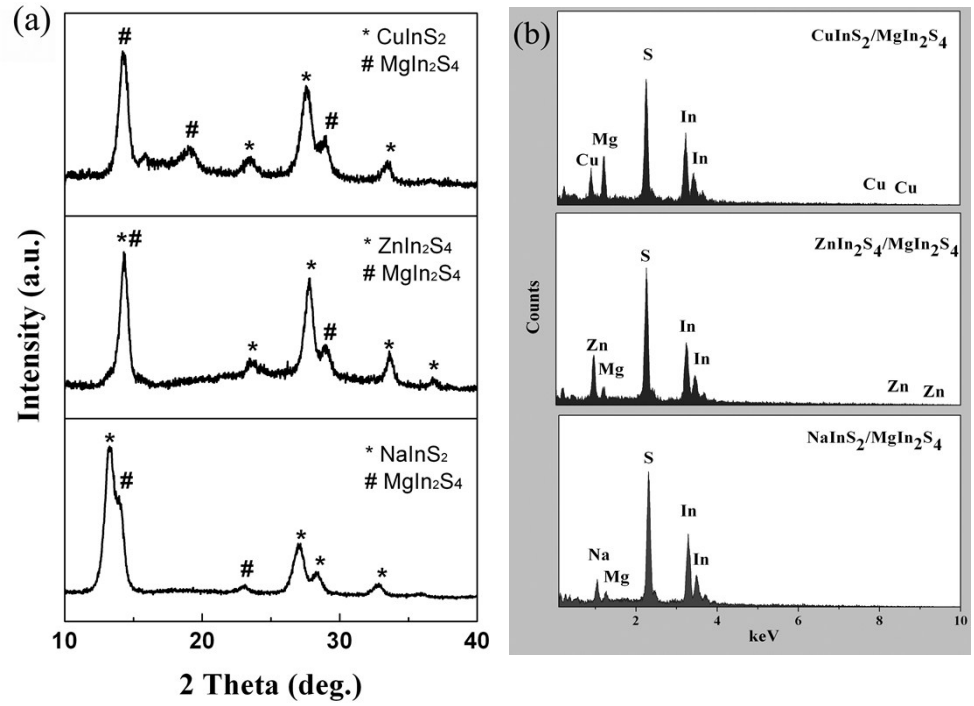

Figure S6 (a) XRD and (b) EDX spectra of other ternary sulfideheterogeneous structures $CuInS_2/MgIn_2S_4$, $ZnIn_2S_4/MgIn_2S_4$and $NaInS_2/MgIn_2S_4$.

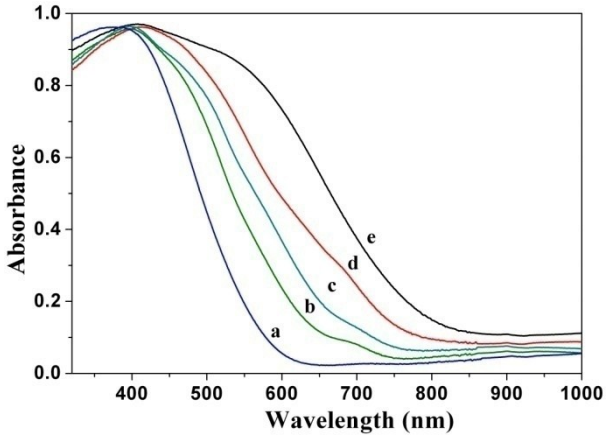

Figure S7 UV-vis spectra of heterogeneous nanosheets with different molar ratio of Cu/Na by ion exchange reaction: (a) 0 %, (b) 0.3 %, (c) 0.5 %, (d) 1 % and (e) 1.5%.

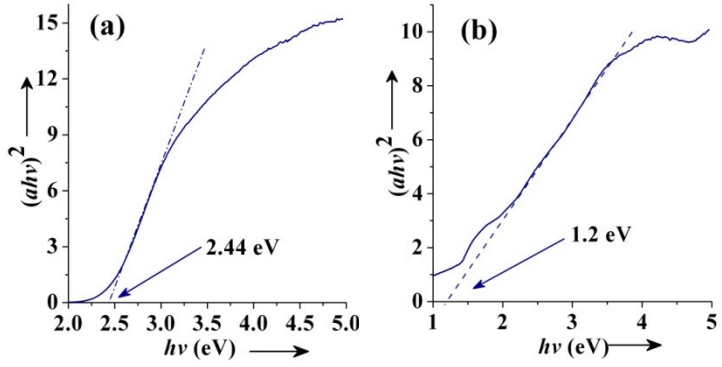

Figure S8 (a) bandgap energy of the pure $NaInS_2$ and b) $CuInS_2$.

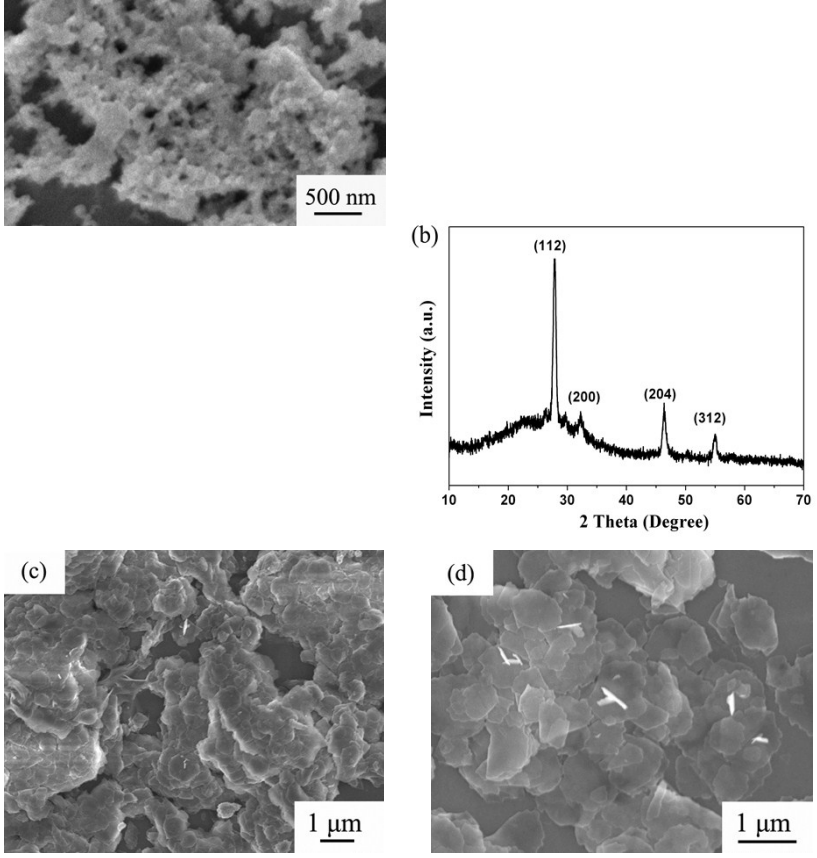

Figure S9 (a) SEM image and (b) XRD pattern of synthesized $CuInS_2$ nanoparticles, (c) and (d) SEM images of obtained $CuInS_2$ nanoparticles (0.5%) decorated $NaInS_2$ heterogenerous photocatalysts.

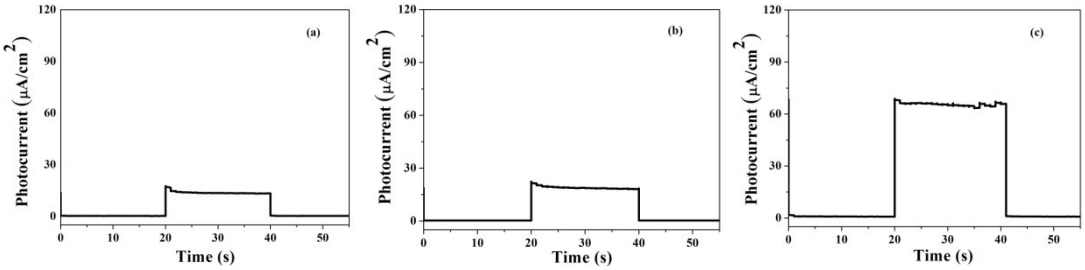

Figure S10 Photocurrent-time plots for the working electrodes of (a) pure $NaInS_2$, (b) $CuInS_2$ nanoparticles decorated $NaInS_2$ and (c) $CuInS_2/NaInS_2$ integrated heterostructures, with a bias of 0.2 V in 0.1 M K_2SO_4 chopped AM1.5 illumination, 100 mW/cm^2.