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

Peng Hu, Chee Keong Ngaw, Yee Yan Tay, Shaowen Cao, James Barber, Timothy Thatt Yang Tan,* Say Chye Joachim Loo*.

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$_2$S·2H$_2$O 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 °C 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 °C 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 °C 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$_2$S$_4$ Heterogeneous Nanosheets:** The synthesis process of NaInS$_2$/MgIn$_2$S$_4$ heterostructures is similar to CuInS$_2$/NaInS$_2$, and MgCl$_2$·6H$_2$O was used instead of CuCl to react with NaInS$_2$. The reaction was occurred in 15 mL ethanol at 190 °C for 16 h, and then washed and fried for analysis.

**Synthesis of CuInS$_2$/MgIn$_2$S$_4$ Heterogeneous Nanosheets:** For the synthesis of CuInS$_2$/MgIn$_2$S$_4$ heterostructures, the CuInS$_2$/NaInS$_2$ was used as precursors and react with MgCl$_2$·6H$_2$O. Typically, CuInS$_2$/NaInS$_2$ was first dispersed in 15 mL ethanol and 1 mmol MgCl$_2$·6H$_2$O were added to the former solution. After stirring for 30 min, the mixture was transferred in to autoclave and maintained at 190 °C for 16 h. After the heat treatment, it was cooled to room temperature.
temperature and the obtained products were washed with distilled water and absolute ethanol, and dried in a vacuum oven. *Synthesis of ZnIn$_2$S$_4$/MgIn$_2$S$_4$ Heterogeneous Nanosheets:* ZnIn$_2$S$_4$/MgIn$_2$S$_4$ 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$_2$·6H$_2$O at 190 °C 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$_2$S in 15 mL ethylenediamine at 190 °C 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 °C 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°. 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 °C 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 a 300 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) 12 h.
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

<table>
<thead>
<tr>
<th>Sample</th>
<th>Calculated molar ratio</th>
<th>ICP-AES Cu/Na</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cu-0.3</td>
<td>0.30</td>
<td>0.42</td>
</tr>
<tr>
<td>Cu-1</td>
<td>1.00</td>
<td>1.19</td>
</tr>
<tr>
<td>Cu-3</td>
<td>3.00</td>
<td>3.13</td>
</tr>
<tr>
<td>Cu-5</td>
<td>5.00</td>
<td>5.09</td>
</tr>
</tbody>
</table>
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 sulfide heterogeneous structures CuInS$_2$/MgIn$_2$S$_4$, ZnIn$_2$S$_4$/MgIn$_2$S$_4$ and NaInS$_2$/MgIn$_2$S$_4$. 
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$_2$SO$_4$ chopped AM1.5 illumination, 100 mW/cm$^2$. 