**Electronic Supplementary Information**

**MAPbI$_3$ microcrystals integrated with Ti$_3$C$_2$T$_x$ MXene nanosheets for efficient visible-light photocatalytic H$_2$ production**

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1. Experimental section

1.1 Chemicals and materials

All chemicals were of analytical grade and used as received without further purification. Methylammonium iodine (MAI, ≥99.5%) and PbI₂ (≥99.99%) were obtained from Xi’an Polymer Light Technology Corp. HI (55~57 wt.% in water) was purchased from Shanghai Titan Scientific Co. Ltd. H₃PO₂ (50 wt.% in water) was received from Shanghai Aladdin Biochemical Technology Co. Ltd. Ti₃AlC₂ powders were purchased from Beijing Dk Nano technology Co., Ltd. LiF was purchased from Aladdin Industrial Corporation. All solutions used throughout the experiments were prepared with ultrapure water (18.2 MΩ cm).

1.2 Preparation of Ti₃C₂Tₓ nanosheets (Ti₃C₂Tₓ NSs)

Ti₃C₂Tₓ NSs were synthesized according to a reported procedure. 2.4 g of LiF was added into 30 mL of 9 M HCl and the solution was allowed to mix thoroughly at room temperature for 10 min. After that, 1.5 g of Ti₃AlC₂ powder was slowly added to above-prepared LiF-HCl aqueous solution to avoid initial overheating due to exothermic nature of the reaction. Then, the temperature was increased to 35 ℃ and the reaction allowed to proceed under continuous stirring for 24 h. The powder was repeatedly washed with water until almost neutral pH (≥6). The freshly produced powder was then dispersed in 100 mL of water and exfoliated with an aid of ultrasonication for 1 h under continuous N₂ bubbling to minimize oxidation. Then, the resulted suspension solution was centrifuged at 3500 rpm for 1 h and the supernatant was collected and freeze-dried to obtain Ti₃C₂Tₓ NSs powders.
1.3 Preparation of MAPbI₃ and MAPbI₃-saturated HI-H₃PO₂ solution

MAPbI₃ was synthesized by the reaction of MAI (2.56 g) and PbI₂ (7.43 g) in a 25mL of aqueous solution of H₃PO₂ (50 wt %) and HI (57 wt %) at a volume ratio of 1:4. The solution was then heated at 100 °C for 1 h and cooled to room temperature to obtain the saturated solution with MAPbI₃ precipitates. The MAPbI₃ precipitates were separated from the MAPbI₃-saturated solution by centrifugation and dried at 60 °C for 48 h in a vacuum oven to get MAPbI₃ powders, and the obtained MAPbI₃-saturated HI-H₃PO₂ solution was preserved for photocatalytic experiments and photoelectrochemical measurements.

1.4 Preparation of MAPbI₃-Ti₃C₂Tx NS composite photocatalysts

MAPbI₃-Ti₃C₂Tx NS composite photocatalysts were synthesized by a simple in-situ integration method as follows: 100 mg of MAPbI₃ powder and a certain amount of Ti₃C₂Tx NSs (2, 4, 6, 8, 10, or 12 mg) were added to a reaction cell (65 mL) containing 5 mL of MAPbI₃-saturated HI-H₃PO₂ solution. The resulting mixture were ultrasonicated for 5 min. The MAPbI₃-Ti₃C₂Tx NS composite photocatalysts were then either collected by centrifugation for further characterizations or directly used for following photocatalytic H₂ evolution experiment.

1.5 Characterization

X-ray diffraction (XRD) patterns were investigated with a Rigaku Smartlab diffractometer with a nickel filtrated Cu Ka radiation. Scanning electron microscopy (SEM) images were taken with a ZEISS EVO 10 scanning electron microscope. Transmission electron microscopy (TEM) and high-resolution TEM (HRTEM) images
were taken with a Tecnai-G²-F30 field emission transmission electron microscope. Atomic force microscopy (AFM) was carried out on a AFMWorkshop TT2-AFM atomic force microscope in tapping mode. X-ray photoelectron spectroscopy (XPS) measurements of the samples were performed on a Thermo Scientific Escalab-250Xi electron spectrometer using an Al Ka X-ray source. Binding energies were referenced to the C 1s peak (set at 284.8 eV) of the sp² hybridized (C=C) carbon from the sample. UV-vis diffuse reflectance spectra were recorded on a PerkinElmer Lambda-750 UV-vis-near-IR spectrometer equipped with an integrating sphere and BaSO₄ powders were used as a reflectance standard. UV-vis absorption spectra were taken with a Thermo Scientific Evolution 220 spectrophotometer. Photoluminescence spectra were determined by a Horiba Scientific FluoroMax-4 spectrofluorometer spectrometer.

1.6 Photocatalytic H₂ evolution experiments

Photocatalytic H₂ evolution experiments were performed with a PCX50C Discover multichannel photocatalytic reaction system (Beijing Perfectlight Technology Co. Ltd.) with white-light LED lamps (10 W×9, 370 nm≤λ≤780 nm) as the light source. Then, the reaction solution was thoroughly degassed by repeated evacuation N₂ filling, and finally refilled with N₂ to reach ambient pressure. After that, the reaction solution was irradiated under continuous stirring. The amount of H₂ produced was manually taken out by a gastight syringe (Agilent, 1.0 mL) and analyzed at given time intervals with a precalibrated gas chromatography (Tech comp; GC-7900) with a thermal conductivity detector, a 5 Å molecular sieve column (4 mm×5 m), and with N₂ as carrying gas.

1.7 Determination of solar-to-hydrogen energy conversion efficiency

The solar HI splitting efficiency, so-called solar-to-hydrogen (STH) conversion
efficiency, is the ratio of solar light converted to break the chemical bonding of HI. The standard hydrogen reduction potential is 0 V vs. NHE, and the I\(^-\) oxidation potential to I\(_3^-\) is 0.53 V vs. NHE. Because the concentration of I\(_3^-\) ion in the 5.7 M HI aqueous solution was 1.9 M and the pH of the solution was 0.4, the redox potential could be determined from the Nernst equation as follows:\(^1\)

\[
E (2H^+ + 2e^- \rightarrow H_2) = 0 - 0.0592 \times 2 \times \log \left( \frac{1}{[H^+]} \right) = 0 - 0.0592 \times \text{pH} = 0.0236 \text{ V vs. RHE}
\]

\[
E (3I^- \rightarrow I_3^- + 2e^-) = 0.53 + \frac{0.0592}{2} \times \log \left( \frac{[I_3^-]}{[I^-]^3} \right) = 0.53 + \frac{0.0592}{2} \times \log \left( \frac{1.9}{5.7^3} \right) = -0.47 \text{ V vs. RHE}
\]

For this reason, the total potential for the HI splitting in 5.7 M of HI solution could be calculated as 0.0236 V + 0.47 V = 0.493 V, thus the STH of photocatalytic HI splitting can be calculated as follows:

\[
\text{STH (\%)} = \frac{\text{Evolved } H_2 (\text{mol}) \times 6.02 \times 10^{23} \times 2 \times 0.493 \text{ (eV)} \times 1.6 \times 10^{-19}}{P_{\text{sol}} (\text{W cm}^2) \times S (\text{cm}^2) \times t (s)} \times 100\%
\]

where the \(P_{\text{sol}} (\text{W cm}^2)\) is the light irradiation flux, the \(S (\text{cm}^2)\) represents the irradiation area, and the \(t (s)\) is irradiation time for \(H_2\) evolution.

According to above equations, in the case of the MAPbI\(_3\) (100 mg)/Ti\(_2\)C\(_2\)T\(_x\) (10 mg), 314.2 \(\mu\)mol of \(H_2\) was evolved after 6 h of light irradiation at 95 mW cm\(^{-2}\). The light irradiation area was 9.62 cm\(^2\), the STH was calculated to be 0.15%.

1.8 Electrochemical and photoelectrochemical measurements

The electrochemical and photoelectrochemical measurements were carried out in a standard three-electrode electrochemical set-up using a CS3103 (Wuhan Corrtest Instruments Corp., Ltd) electrochemical workstation. For the fabrication of working electrode, the catalyst suspension was prepared by dispersing 40 mg of catalyst into 5 mL
of toluene solution with a ultrasonication of 30 min. Afterward, the as-prepared catalyst suspension was drop-coated on one side of carbon paper (HESEN, HCP030P, thickness, 0.3 mm) in a glove box. Then, 20 μL of 0.5 wt% Nafion ethanol solution was drop-coated onto the surface of formed catalyst film and the resulted electrode was transferred to a vacuum oven and dried at 60 °C for 6 h. For photocurrent measurements, a saturated Ag/AgCl and a Pt mesh (1 cm×1 cm) were used as reference electrode and counter electrode, respectively. A 60 mL of dichloromethane (CH₂Cl₂) solution containing 0.1 M tetrabutylammonium hexafluorophosphate (TBAPF₆) solution was used as the supporting electrolyte. A 300-W white Xe lamp equipped with a cut-off filter of 420 nm was used as the light source. Photocurrent response was recorded by using an amperometric current-time technique at a bias of -0.423 V vs. Ag/AgCl. For electrochemical measurements, a saturated Ag/AgCl and a graphite rod (Diameter: 6 mm) were used as reference electrode and counter electrode, respectively. Potentiostatic electrochemical impedance spectroscopy (EIS) measurements were carried out at a bias of -0.423 V vs. Ag/AgCl with an AC amplitude of 5 mV in the frequency range of 10 mHz to 100 kHz in CH₂Cl₂ solution containing 0.1 M TBAPF₆ as electrolyte. Linear sweep voltammetry (LSV) measurements were carried out in a MAPbI₃-saturated aqueous HI/H₃PO₂ mixed solution at scan rate of 5 mV s⁻¹.
2. Additional figures and tables

**Fig. S1** (a) TEM image of Ti$_3$C$_2$T$_x$ NSs. (b) AFM image and (c) the corresponding height profiles of Ti$_3$C$_2$T$_x$ NSs.

**Fig. S2** (a) XRD patterns of Ti$_3$AlC$_2$ and Ti$_3$C$_2$T$_x$ NSs. The appearance of characteristic
diffraction peaks of the (002), (004), (006), (008), (0010), and (0012) planes in the XRD pattern Ti$_3$C$_2$Tx NSs shows the successful transformation of Ti$_3$AlC$_2$ MAX into Ti$_3$C$_2$Tx MXene nanosheets. (b) The easy dispersion of Ti$_3$C$_2$Tx NSs in MAPbI$_3$-saturated HI-H$_3$PO$_2$ solution showing an obvious Tyndall effect.

**Fig. S3** (a) XRD patterns of Ti$_3$C$_2$Tx NSs, M-Ti$_3$C$_2$Tx, and bulk Ti$_3$AlC$_2$. (b) SEM image of M-Ti$_3$C$_2$Tx. (c) AFM image and (d) the corresponding height profiles of M-Ti$_3$C$_2$Tx. (e) Photocatalytic H$_2$ evolution on the Ti$_3$AlC$_2$ (10 mg), MAPbI$_3$ (100 mg)-M-Ti$_3$C$_2$Tx (10 mg), and MAPbI$_3$ (100 mg)-Ti$_3$C$_2$Tx NS (10 mg). Photocatalytic reaction conditions: MAPbI$_3$-saturated aqueous HI-H$_3$PO$_2$ mixed solution, 5 mL; Light source, 10-W LED lamp, 370≤λ≤780 nm; reaction time: 24 h.

In order to clarify the effect of the thickness of the Ti$_3$C$_2$Tx on the photocatalytic HER activity, multilayer Ti$_3$C$_2$Tx (M-Ti$_3$C$_2$Tx) was also prepared by etching bulk Ti$_3$AlC$_2$ crystals with a LiF/HCl mixed solution without exfoliation and integrated with MAPbI$_3$ microcrystals for photocatalytic H$_2$ evolution. The XRD patterns in Fig. S3a show that the Al-layer has been effectively removed from the M-Ti$_3$C$_2$Tx, but the M-Ti$_3$C$_2$Tx is not
fully exfoliated. SEM image of Fig. S3b indicates that the M-Ti$_3$C$_2$Tx is layered thick sheet. AFM (Fig. S3c) analysis shows that the thickness of the M-Ti$_3$C$_2$Tx is 332.1 nm, which corresponds to ca. 339 layers. As a result, the MAPbI$_3$-M-Ti$_3$C$_2$Tx shows much inferior photocatalytic H$_2$ evolution activity to MAPbI$_3$-Ti$_3$C$_2$Tx NS composite (Fig. S3d). This result clearly indicates that the ultrathin feature of the Ti$_3$C$_2$Tx NSs is crucial to enhance the photocatalytic performance of the MAPbI$_3$ microcrystals. The ultrathin Ti$_3$C$_2$Tx NSs cannot only supply large surface area to ensure an intimate contact with MAPbI$_3$ microcrystals for efficient electron transfer, but also greatly shorten the the electron transfer distance from excited MAPbI$_3$ to the active sites, all of which but also, all of which are beneficial for suppressing the charge recombination and thus enhancing the activity of photocatalytic H$_2$ evolution.

**Fig. S4** Time courses of photocatalytic H$_2$ evolution on MAPbI$_3$ (100 mg) integrated with different amounts of Ti$_3$C$_2$Tx NSs under visible light irradiation. The reaction conditions are kept same as employed for Fig. 1a.
Table S1 Comparison of photocatalytic H<sub>2</sub> evolution of MAPbI<sub>3</sub>-Ti<sub>3</sub>C<sub>2</sub>T<sub>x</sub> NS composite with other MAPbI<sub>3</sub>-based photocatalysts under visible light.

<table>
<thead>
<tr>
<th>Catalyst</th>
<th>Reactant solution</th>
<th>Light source</th>
<th>H&lt;sub&gt;2&lt;/sub&gt; evolution activity (μmol h&lt;sup&gt;−1&lt;/sup&gt;)</th>
<th>Stability</th>
<th>Ref.</th>
</tr>
</thead>
<tbody>
<tr>
<td>MAPbI&lt;sub&gt;3&lt;/sub&gt;-Ti&lt;sub&gt;3&lt;/sub&gt;C&lt;sub&gt;2&lt;/sub&gt;T&lt;sub&gt;x&lt;/sub&gt; NS</td>
<td>HI solution</td>
<td>10 W LED Lamp (380 nm≤λ≤780 nm)</td>
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<td>&gt; 120 h</td>
<td>This work</td>
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<tr>
<td>MAPbI&lt;sub&gt;3&lt;/sub&gt;/MoS&lt;sub&gt;2&lt;/sub&gt; NSs</td>
<td>HI solution</td>
<td>10 W LED Lamp (380 nm≤λ≤780 nm)</td>
<td>206.1</td>
<td>&gt; 150 h</td>
<td>2</td>
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<tr>
<td>MAPbI&lt;sub&gt;3&lt;/sub&gt;/Pt/C</td>
<td>HI solution</td>
<td>10 W LED Lamp (380 nm≤λ≤780 nm)</td>
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<tr>
<td>MAPbI&lt;sub&gt;3&lt;/sub&gt;/Pt</td>
<td>HI solution</td>
<td>Solar simulator (λ≥475 nm)</td>
<td>11.4</td>
<td>160 h</td>
<td>3</td>
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<td>MAPbI&lt;sub&gt;3&lt;/sub&gt;/rGO</td>
<td>HI solution</td>
<td>300 W Xe lamp (λ≥420 nm)</td>
<td>93.9</td>
<td>200 h</td>
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<td>MAPbI&lt;sub&gt;3&lt;/sub&gt;/Ni&lt;sub&gt;3&lt;/sub&gt;C</td>
<td>HI solution</td>
<td>300 W Xe lamp (λ≥420 nm)</td>
<td>116.3</td>
<td>200 h</td>
<td>5</td>
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<td>MAPbI&lt;sub&gt;3&lt;/sub&gt;/BP</td>
<td>HI solution</td>
<td>300 W Xe lamp (λ≥420 nm)</td>
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<td>MAPbI&lt;sub&gt;3&lt;/sub&gt;/Pt/TiO&lt;sub&gt;2&lt;/sub&gt;</td>
<td>HI solution</td>
<td>300 W Xe lamp (λ≥420 nm)</td>
<td>72.8</td>
<td>12 h</td>
<td>7</td>
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Fig. S5 Enlarged XRD patterns of pristine Ti<sub>3</sub>C<sub>2</sub>T<sub>x</sub> NSs, pristine MAPbI<sub>3</sub>, and MAPbI<sub>3</sub>-Ti<sub>3</sub>C<sub>2</sub>T<sub>x</sub> NS composite.
**Fig. S6** XPS survey spectra of Ti$_3$C$_2$T$_x$ NSs, MAPbI$_3$ and MAPbI$_3$-Ti$_3$C$_2$T$_x$ NS composite.

![XPS survey spectra of Ti$_3$C$_2$T$_x$ NSs, MAPbI$_3$ and MAPbI$_3$-Ti$_3$C$_2$T$_x$ NS composite.](image)

**Fig. S7** XPS spectra (a) C 1s of pristine Ti$_3$C$_2$T$_x$ NSs and MAPbI$_3$-Ti$_3$C$_2$T$_x$ NS composite and (b) I 3d of pristine MAPbI$_3$ and MAPbI$_3$-Ti$_3$C$_2$T$_x$ NS composite.

![XPS spectra (a) C 1s of pristine Ti$_3$C$_2$T$_x$ NSs and MAPbI$_3$-Ti$_3$C$_2$T$_x$ NS composite and (b) I 3d of pristine MAPbI$_3$ and MAPbI$_3$-Ti$_3$C$_2$T$_x$ NS composite.](image)

**Fig. S8** LSV curves of HER over Pt/C and Ti$_3$C$_2$T$_x$ NSs coated on carbon paper (CP) recorded in a MAPbI$_3$-saturated aqueous HI-H$_3$PO$_2$ mixed solution at scan rate of 5 mV s$^{-1}$.

![LSV curves of HER over Pt/C and Ti$_3$C$_2$T$_x$ NSs coated on carbon paper (CP) recorded in a MAPbI$_3$-saturated aqueous HI-H$_3$PO$_2$ mixed solution at scan rate of 5 mV s$^{-1}$.](image)
**Fig. S9** SEM images of MAPbI$_3$-Ti$_3$C$_2$Tx NS composite after 120 h of photocatalytic H$_2$ evolution and the corresponding EDS elemental maps of N, Ti, Pb, and I elements.

**Fig. S10** Comparison of XRD patterns of MAPbI$_3$-Ti$_3$C$_2$Tx NS composite before and after stability test.
**Fig. S11** XPS spectra (a) Pb 4f, (b) I 3d, (c) Ti 2p, and C 1s of MAPbI$_3$-Ti$_3$C$_2$T$_x$ NS composite after stability test.

**References**


