Electronic Supplementary Information

Coupling of $MAPbI_3$ microcrystals with conductive polyaniline for efficient visible-light-driven H_2 evolution

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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 PbI_2 (≥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. H_3PO_2 (50 wt% in water) was received from Shanghai Aladdin Biochemical Technology Co. Ltd. $(NH_4)_2S_2O_8$ (APS), and aniline monomer were purchased from Shanghai Titan Scientific Co. Ltd. Aniline was purified twice under reduced pressure and stored below in a refrigerator prior to use. Toluene was purchased from Sinopharm Chemical Reagent Co., Ltd

1.2 Characterization

X-ray diffraction (XRD) patterns were investigated with a Rigaku smartlab diffractometer with a nickel filtrated Cu *Kα* radiation. Scanning electron microscopy (SEM) images were taken with a ZEISS EVO 10 scanning electron microscope. Transmission electron microscopy (TEM) images were taken with a Tecnai-G^2-F30 field emission transmission electron microscope. X-ray photoelectron spectroscopy (XPS) measurements of the samples were performed on an X-ray photoelectron spectrometer (Thermo Scientific Escalab-250Xi) equipped with a monochromatic Al Ka X-ray source. Binding energies were referenced to the C 1s peak (set at 284.4 eV) of the sp^2 hybridized (C=C) carbon from the PANI NWs sample and $MAPbI_3$, $MAPbI_3$-PANI NW referenced to the C 1s peak (set at 284.8 eV). Ultraviolet-visible (UV-vis) transmission spectroscopy was performed using a Shimadzu UV-1800 spectrophotometer. Photoluminescence spectra were determined by a Horiba Scientific FluoroMax-4 spectrofluorometer spectrometer.

1.3 Preparation of catalysts

1.3.1 Preparation of $MAPbI_3$ and $MAPbI_3$-saturated HI/H_3PO_2 solution[1,2]

$MAPbI_3$ was synthesized by the reaction of MAI (2.56 g) and PbI_2 (7.43 g) in a 25mL of mixed solution containing HI (57 wt %) and H_3PO_2 (50 wt %) at a volume ratio of 4 to 1. The solution was then heated at 100 °C for 1 h and cooled to room temperature to obtain the saturated solution with $MAPbI_3$ precipitates. The $MAPbI_3$ precipitates were separated from the saturated solution by centrifugation and dried at 60 ^{o}C for 48 h in a vacuum oven to get $MAPbI_3$ powders, and the obtained $MAPbI_3$-saturated HI/H_3PO_2 solution was preserved for photocatalytic experiments.

1.3.2 Preparation of polyaniline nanowires (PANI NWs)

The HCl-doped PANI NWs were synthesized by a facile interfacial polymerization method at room temperature.[3] 3.2 mmol of aniline (ANI) was dissolved in chloroform (CH_2Cl_2, 10 mL), while ammonium peroxydisulfate ($(NH_4)_2S_2O_8$, 0.8 mmol) was dissolved in 10 mL of 1 M HCl. After that, the HCl solution containing $(NH_4)_2S_2O_8$ was carefully poured onto the CH_2Cl_2 solution containing aniline monomer to generate a clear interface between the two layers. After an induction period of 3~5 min, green PANI formed at the interface and then gradually diffused into the aqueous phase. After a 24 h reaction, the as-prepared HCl-doped PANI NWs in aqueous phase were collected by high-speed centrifugation, washed with water, and dried at 60 °C for 12 h in a vacuum oven. The dedoped PANI NWs were obtained by reacting HCl-doped PANI NWs with $NH_3 \cdot H_2O$ (1 M) at room temperature to obtained followed by washing with water and dried at 60 °C for 12 h in a vacuum oven.

1.3.3 Preparation of $MAPbI_3$-PANI NW composite photocatalysts

$MAPbI_3$-PANI NW composite photocatalysts were synthesized by directly mixing 100 mg of $MAPbI_3$ microcrystals with different amounts of dedoped PANI NWs (2, 4, 6, 7, 8 and 10 mg) in a reaction cell (65 mL) containing 5 mL of $MAPbI_3$-saturated aqueous HI/H_3PO_2 (v/v=4/1) solution. After removing the dissolved oxygen by evacuation, the reaction solution containing the mixture of $MAPbI_3$ and PANI NWs was subjected to the of visible light for 6 h. At the end of the reaction, the resulted $MAPbI_3$-PANI NW composite photocatalysts were collected by centrifugation and dried at 60 °C for 48 h in a vacuum oven.

1.4 Photocatalytic H_2 evolution measurements

Photocatalytic H_2 evolution experiments were performed with a PCX50C Discover multichannel photocatalytic reaction system (Beijing Perfectlight Technology Co. Ltd.)

with white-light LED lamps (10 W, 380 nm≤λ≤780 nm) as the light source. Then, the reaction solution was thoroughly degassed by repeated evacuation-N_2 filling process, and finally refilled with N_2 to reach ambient pressure. After that, the reaction solution was irradiated under continuous stirring. The amount of H_2 produced was manually taken out by a gas-tight syringe (Agilent, 1.0 mL) and analyzed at given time intervals with a gas chromatography (Tech comp; GC-7900) with a thermal conductivity detector, a 5 A molecular sieve column (4 mm×5 m), and with N_2 as carrying gas. The apparent quantum efficiency (AQE) of H_2 evolution was measured under the same photocatalytic reaction conditions with irradiation light at 420 nm, and the AQE was calculated according to Eq. (1):

$$\mathrm{AQE}(\%) = \frac{2\ \text{number of evolved } \mathrm{H_2} \text{ molecules}}{\text{number of incident photons}} \times 100\% \qquad (1)$$

1.5 Electrochemical and photoelectrochemical measurements

All the electrochemical and photoelectrochemical measurements were performed on a CS3103 (Wuhan Corrtest Instruments Corp., Ltd) electrochemical workstation in a three-electrode cell. For the fabrication of working electrode, the catalyst suspension was prepared by dispersing 100 mg of catalyst into 1 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 ℃ 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 (CH_2Cl_2) solution containing 0.1 M tetrabutylammonium hexafluorophosphate ($TBAPF_6$) 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. For electrochemical measurements, a saturated Ag/AgCl and a Pt mesh (1 cm×1 cm) were used as reference electrode and counter electrode, respectively. Potentiostatic electrochemical impedance spectroscopy (EIS) measurements were carried out at a bias of -0.52 V vs. Ag/AgCl with an AC amplitude of 5 mV in the frequency range of 10 mHz to 100 kHz in CH_2Cl_2 solution containing 0.1 M $TBAPF_6$ as electrolyte. For Mott-Schottky (M-S) measurements were carried out in CH_2Cl_2 solution containing 0.1 M $TBAPF_6$ at a frequency of 1 kHz. The cyclic voltammetry (CV) curve of PANI were measured in HI/H_3PO_2 or H_3PO_2 solution with a scanning rate of 10 mV s^{-1}. The PANI-modified glassy carbon (GC, 3 mm) electrode was prepared as follows: 5 mg of PANI were dispersed in 100 μL of 5 wt% Nafion solution by at least 30 min sonication to form a homogeneous suspension. Then 10 μL of suspension was loaded onto a GC electrode. The linear sweep voltammetry (LSV) were measured at a scan rate of 5 mV s^{-1} in $MAPbI_3$-saturated aqueous HI/H_3PO_2 mixed solution. A saturated Ag/AgCl and a graphite rod (Diameter: 6 mm) were used as reference electrode and counter electrode, respectively. For the fabrication of working electrode, the catalyst suspension was prepared by dispersing 5 mg of catalysts into 5 mL of ethanol/H_2O (4/1, v/v) mixed solution containing 100 μL of 0.5 wt% Nafion solution by ultrasonication for 30 min. Afterward, the as-prepared catalyst suspension was loaded onto carbon paper. The loading amount of PANI NWs on carbon paper was controlled to be 2.5 mg cm^{-2}.

2. Additional figures and tables

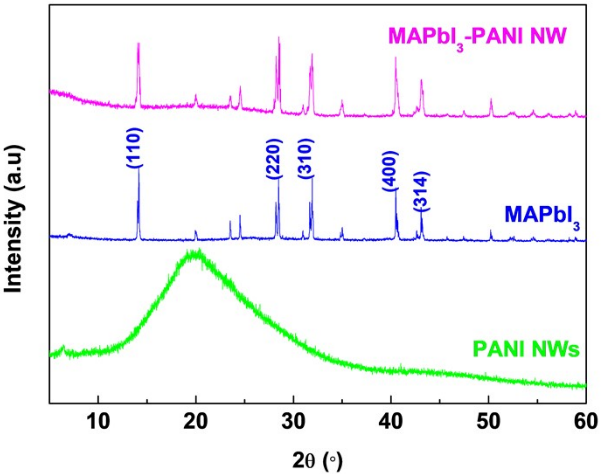

Fig. S1 XRD patterns of pristine $MAPbI_3$, PANI NWs, and $MAPbI_3$-PANI NW composite photocatalyst.

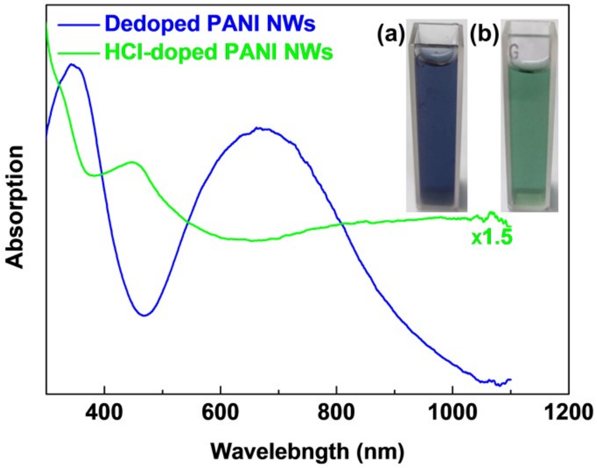

Fig. S2 UV-vis absorption spectra of HCl-doped PANI NWs (green line+inset a) and dedoped PANI NWs via reacting with ammonium hydroxide (blue line+inset b).

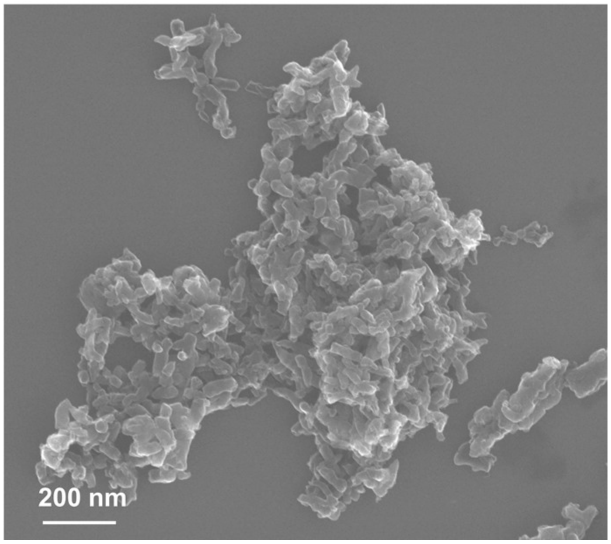

Fig. S3 SEM image of PANI NWs.

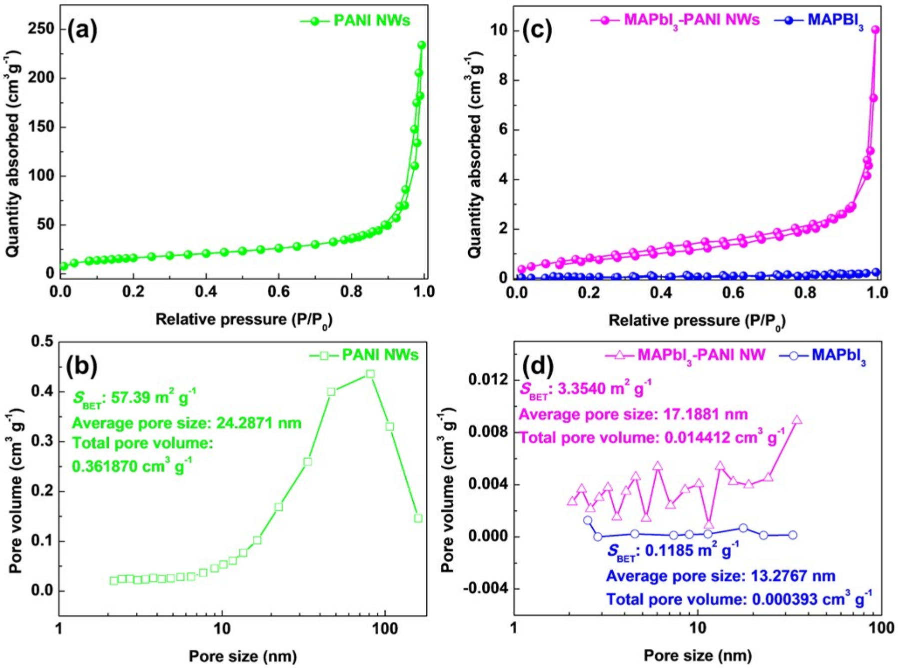

Fig. S4 N_2 adsorption-desorption isotherms (a, c) and corresponding pore size distribution curve (b, d) of PANI NWs, MAPbI$_3$-PANI NW and MAPbI$_3$.

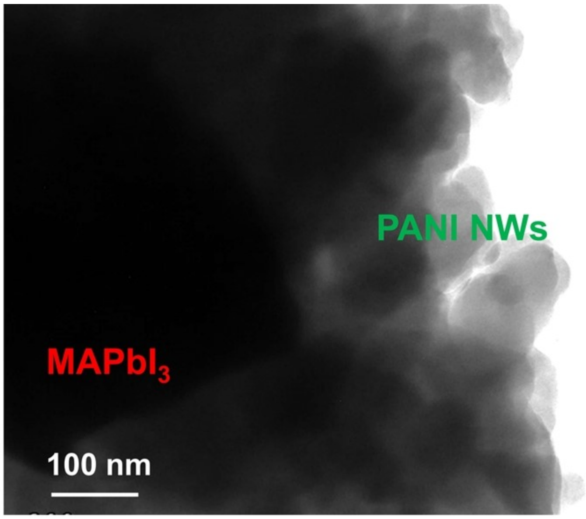

Fig. S5 TEM image of MAPbI$_3$-PANI NW composite photocatalyst.

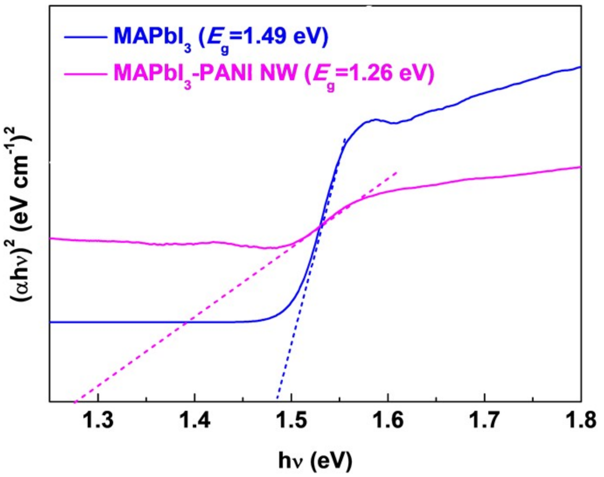

Fig. S6 Tauc plots of pristine MAPbI$_3$ and MAPbI$_3$-PANI NW composite photocatalyst.

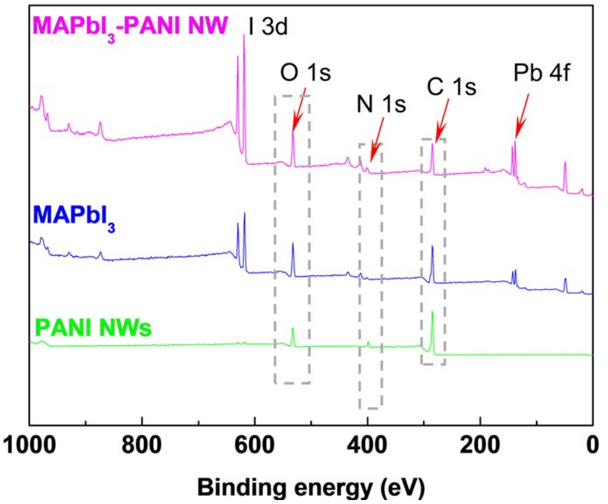

Fig. S7 XPS survey spectra of PANI NWs, pristine MAPbI$_3$, and MAPbI$_3$-PANI NW composite photocatalyst.

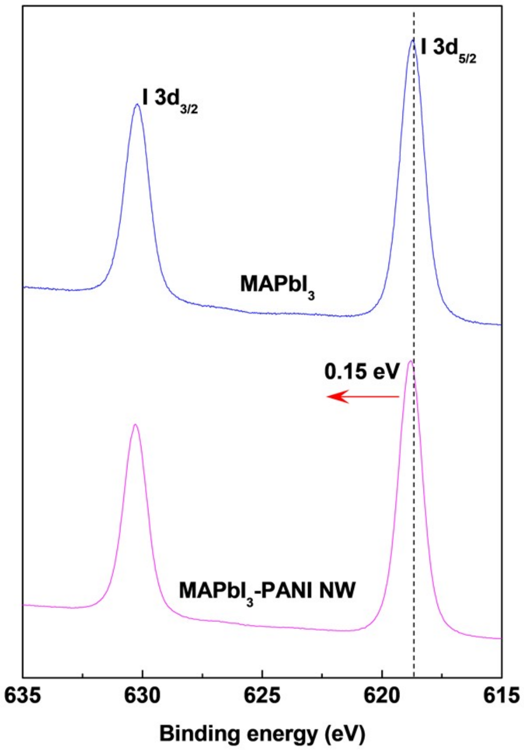

Fig. S8 I 3d XPS spectra of pristine MAPbI$_3$ and MAPbI$_3$-PANI NW composite photocatalyst.

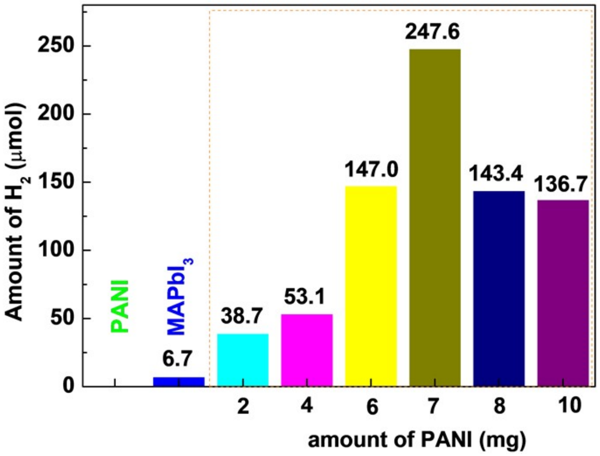

Fig. S9 The amount of H$_2$ evolved on pristine MAPbI$_3$, PANI NWs, and MAPbI$_3$-PANI NW composite photocatalysts prepared from 100 mg of MAPbI$_3$ with different adding amounts of PANI NWs in a 6 h reaction. Reaction conditions: MAPbI$_3$-saturated aqueous HI/H$_3$PO$_2$ mixed solution, 5 mL; Light source, 10-W LED lamp, $370 \leq \lambda \leq 780$ nm.

Table S1 Comparison of photocatalytic H$_2$ evolution of MAPbI$_3$-PANI NW composite with other MAPbI$_3$-based photocatalysts under visible light

Catalyst	Reactant solution	Light source	H_2 evolution activity (μmol h^{-1})	Stability	Ref.
$MAPbI_3$/PANI NW	HI solution	10 W LED Lamp (380 nm≤λ≤780 nm)	38.8	42 h	This work
$MAPbI_3/MoS_2$ NSs	HI solution	10 W LED Lamp (380 nm≤λ≤780 nm)	206.1	＞150 h	1
$MAPbI_3/Ti_3C_2T_x$ NSs	HI solution	10 W LED Lamp (380 nm≤λ≤780 nm)	64.61	＞120 h	2
$MAPbI_3$/Pt/C	HI solution	10 W LED Lamp (380 nm≤λ≤780 nm)	68.5	N/A	1
$MAPbI_3$/Pt	HI solution	Solar simulator (λ≥475 nm)	11.4	160 h	4
$MAPbI_3$/rGO	HI solution	300 W Xe lamp (λ≥420 nm)	93.9	200 h	5
$MAPbI_3/Ni_3C$	HI solution	300 W Xe lamp (λ≥420 nm)	116.3	200 h	6
$MAPbI_3$/BP	HI solution	300 W Xe lamp (λ≥420 nm)	748.4	200 h	7
$MAPbI_3/Pt/TiO_2$	HI solution	300 W Xe lamp (λ≥420 nm)	72.8	12 h	8
$MAPbI_3$/1T-2H $MoSe_2$	HI solution	300 W Xe lamp (λ≥420 nm)	60.8	36 h	9
$MAPbI_3$/MoC	HI solution	300 W Xe lamp (λ≥420 nm)	38.4	18 h	10

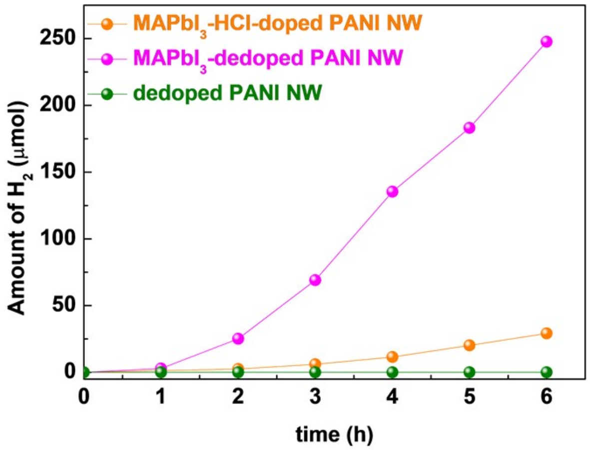

Fig. S10 Time courses of photocatalytic H_2 evolution on $MAPbI_3$-PANI NW composite photocatalyst prepared from $MAPbI_3$ (100 mg) with HCl-doped PANI NWs or dedoped PANI NWs (7 mg). Reaction conditions: $MAPbI_3$-saturated aqueous HI/H_3PO_2 mixed solution, 5 mL; Light source, 10-W LED lamp, 370≤λ≤780 nm.

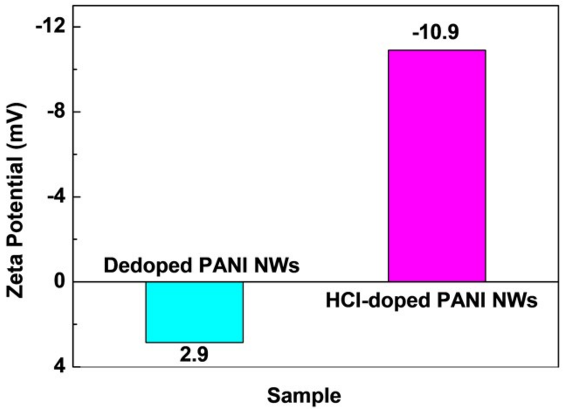

Fig. S11 Zeta potentials of HCl-doped PANI NWs and dedoped PANI NWs in $MAPbI_3$-saturated HI solution.

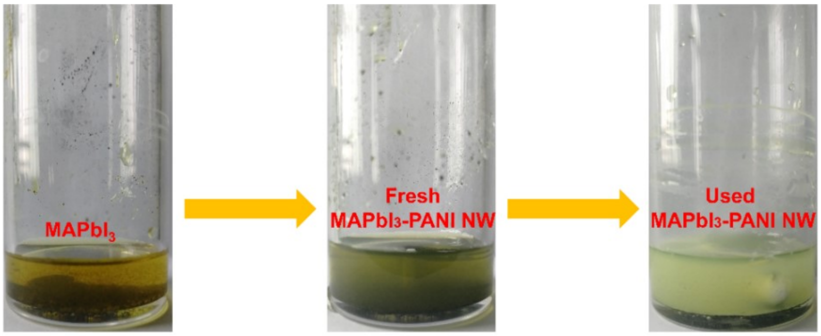

Fig. S12 The optical photos of $MAPbI_3$-PANI NW composite photocatalyst during the preparation and after stability test.

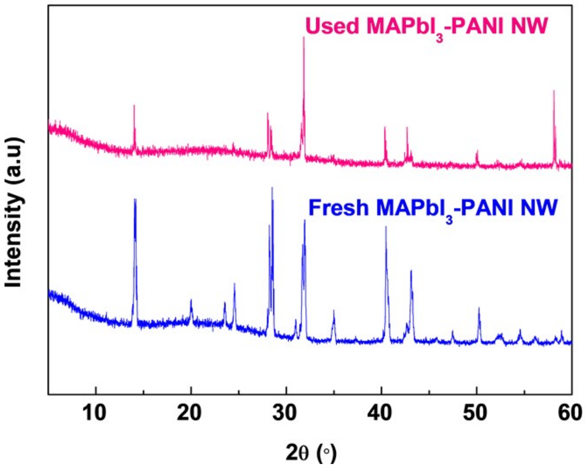

Fig. S13 XRD patterns of $MAPbI_3$-PANI NW composite photocatalyst before and after stability test.

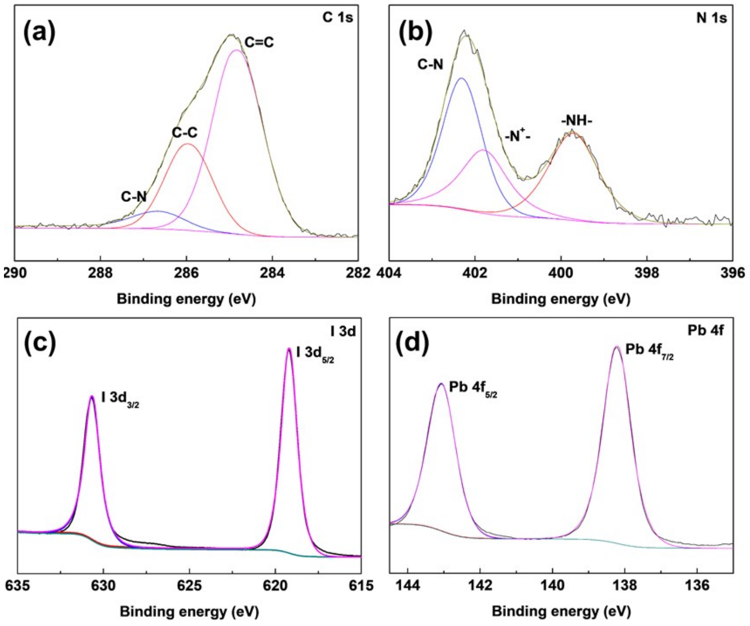

Fig. S14 XPS spectra of $MAPbI_3$-PANI NW composite photocatalyst after stability test.

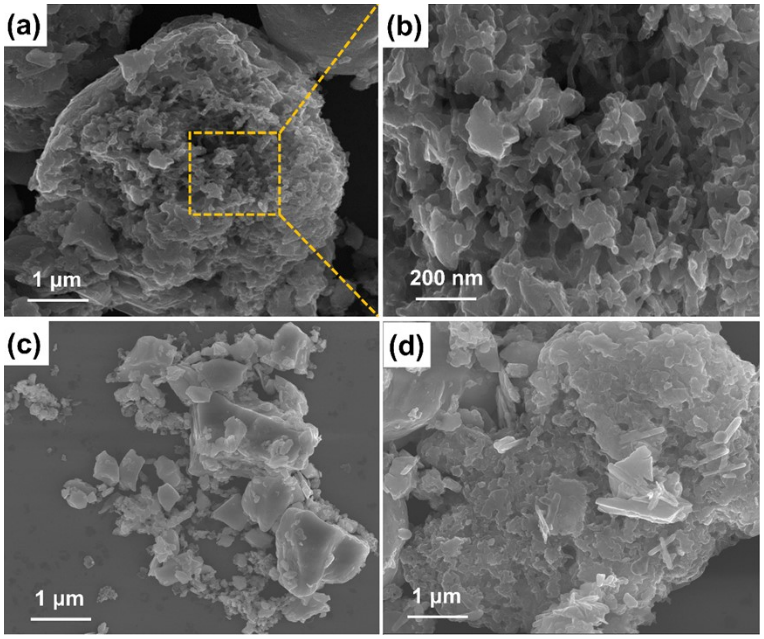

Fig. S15 SEM spectra of $MAPbI_3$-PANI NW composite photocatalyst after stability test.

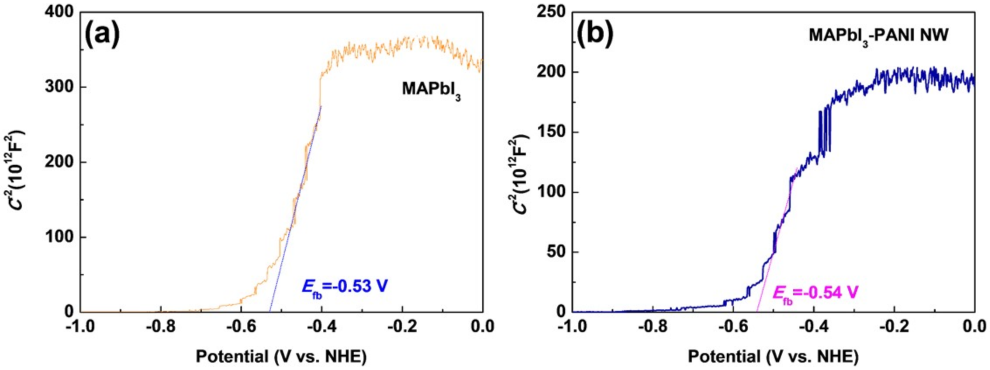

Fig. S16 Mott-Schottky plots of pristine MAPbI$_3$ and MAPbI$_3$-PANI NW.

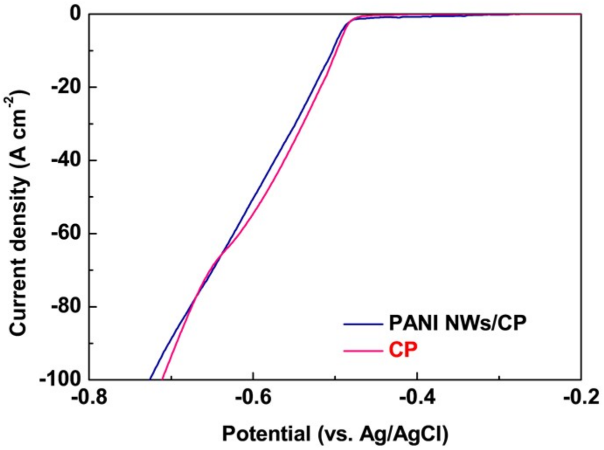

Fig. S17 LSV curves of H$_2$ evolution on carbon paper (CP) and PANI NWs coated CP (PANI NWs/CP) recorded in HI/H$_3$PO$_2$ solution.

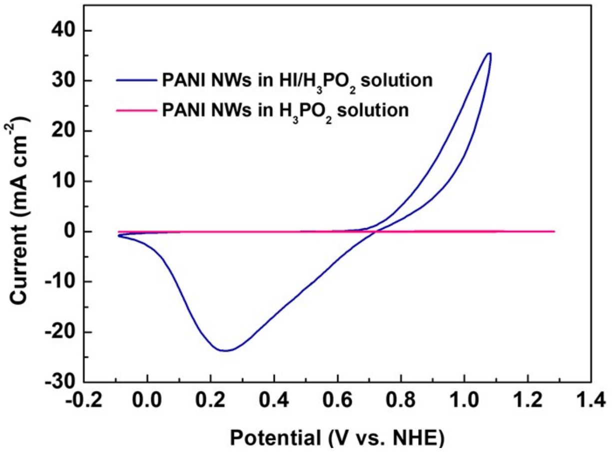

Fig. S18 CV curves of PANI NWs coated on glass carbon in a H$_3$PO$_2$ solution with and without HI.

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