

Supporting Information

NiCoP Modified Lead-free Double Perovskite Cs₂AgBiBr₆ for Efficient Photocatalytic Hydrogen Generation

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Characterizations

The Zeta potential of the sample was measured using a multi-angle particle size potential analyzer, the instrument model is Nanobrook Omni. X-ray powder diffraction (XRD) measurement was performed by an Ultima IV diffractometer (Japan) equipped with Cu-K α radiation ($\lambda = 0.15406$ nm). Transmission electron microscopy (TEM) images and high-resolution transmission electron microscopy (HRTEM) images were taken on JEOL-JEM-2010 with an acceleration voltage of 200 kV. High-angle annular dark-field scanning TEM (HAADF-STEM) and elemental mapping analyses were acquired on a FEI Tecnai G2 F30 S-TWIN microscope equipped with a field-emission gun working at 300 kV. X-ray photoelectron spectroscopy (XPS) measurement was performed on a Perkin-Elmer PHI 5000C ESCA system with Al K α radiation operated at 250 W. Optical absorption spectra (UV-vis DRS) of the samples were measured by a Shimadzu UV-2600 spectrometer. Photoluminescence (PL) spectra of the samples was measured using a Fluoromax-4 fluorescence spectrometer (Horiba) at room temperature. Time-resolved PL spectrum was also recorded on FLS1000 using a supercontinuum 400 nm blaze as the light source, and the excitation wavelength is 375 nm. The decay curves detected at 650 nm were fitted by a tri-exponential decay function using Fluoracle software. The electrochemical measurements were acquired on a CHI660D electrochemical workstation using a conventional three electrodes cell with a working electrode, a Pt plate and a Ag/AgCl electrode as the counter electrode and reference electrode, respectively. The working electrode was prepared through a clean FTO deposited with a sample film of 0.5*0.5 cm. CH₂Cl₂ solution containing 0.1 M tetrabutylammonium hexafluorophosphate (TBAPF₆) was used as the electrolyte.

1. Photocurrent measurements were carried out under a 300 W Xenon lamp coupled with a UV cutoff filter ($\lambda > 420$ nm). Set the voltage parameter to 1.0 V, and test the light on and off the sample at an interval of 100 s.
2. In EIS measurements, set the open circuit voltage, high frequency 10 kHz, low frequency 0.1 Hz.

3. In Mott-Schottky plots measurements, set frequency 1000 Hz, amplitude 10 mV. The voltage is set to open circuit voltage ± 0.8 V.

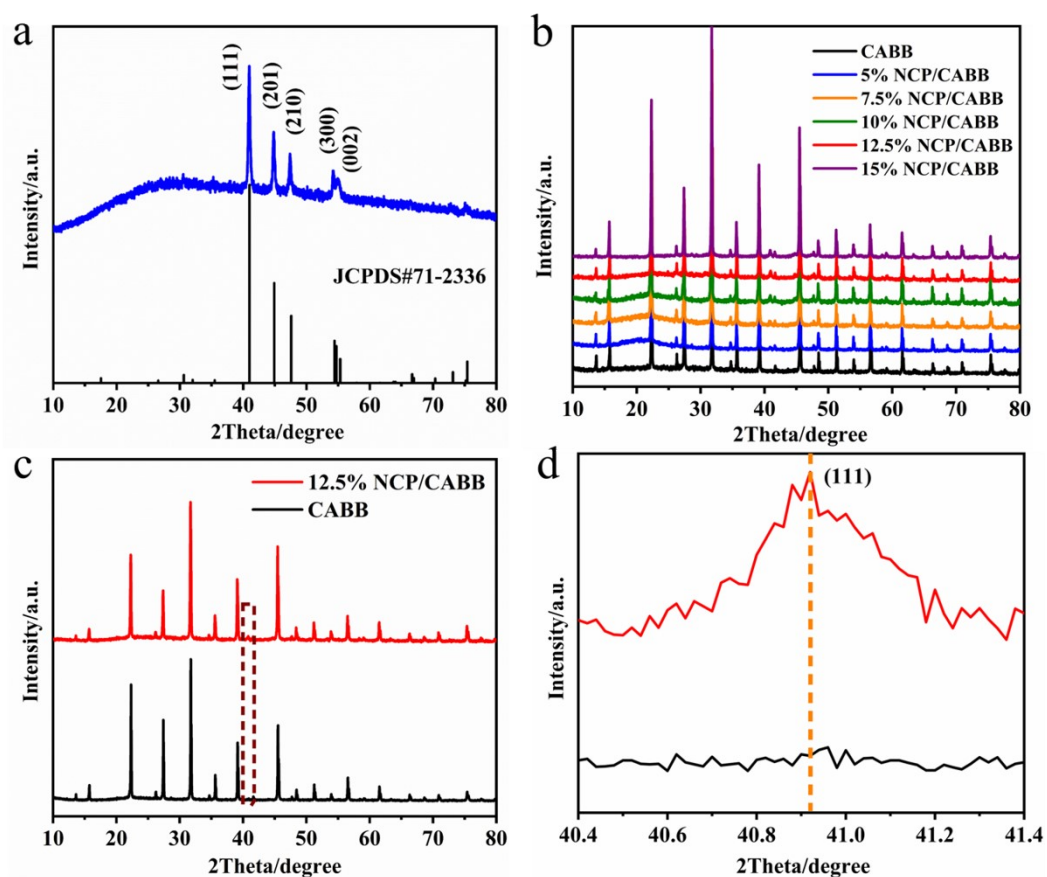


Figure S1. (a) XRD pattern of NCP, (b) XRD patterns of x% NCP/CABB samples, (c) XRD patterns and (d) magnified peaks at (111) of 12.5% NCP/CABB and CABB.

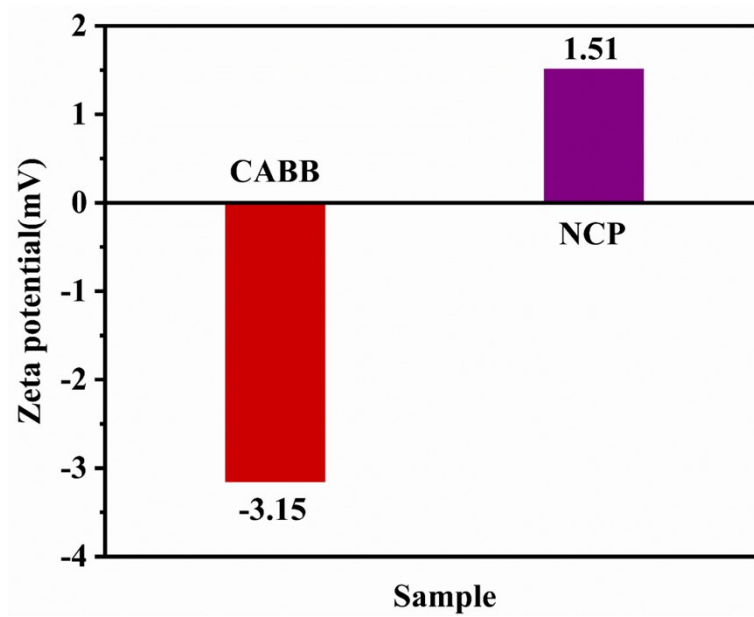


Figure S2. Zeta potentials of CABB and NCP.

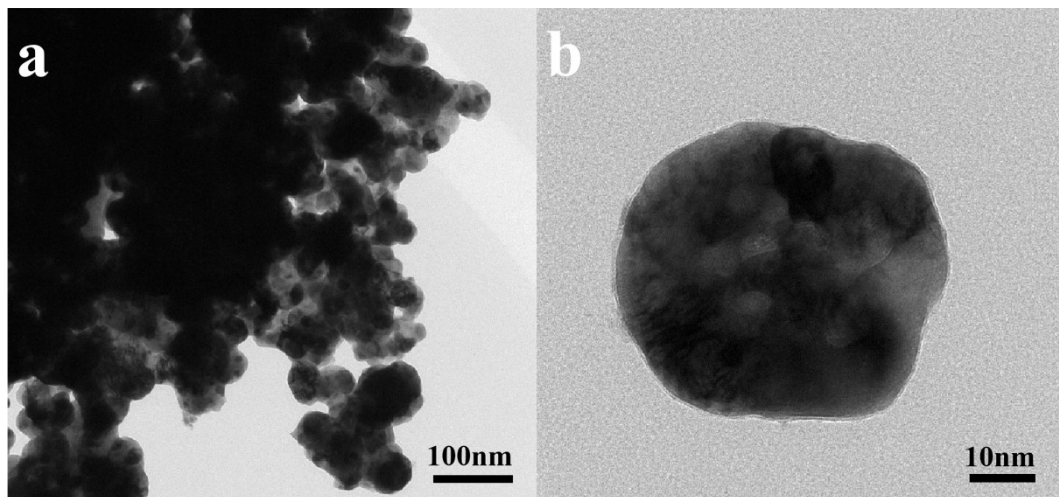


Figure S3. (a & b) TEM images of NCP.

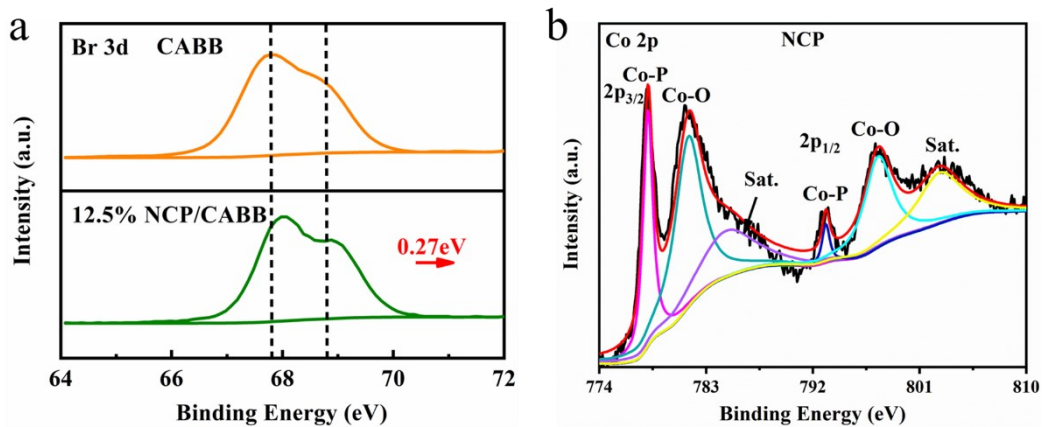


Figure S4. (a) Br 3d spectra of CABB and 12.5% NCP/CABB, (b) Co 2p spectra of NCP.

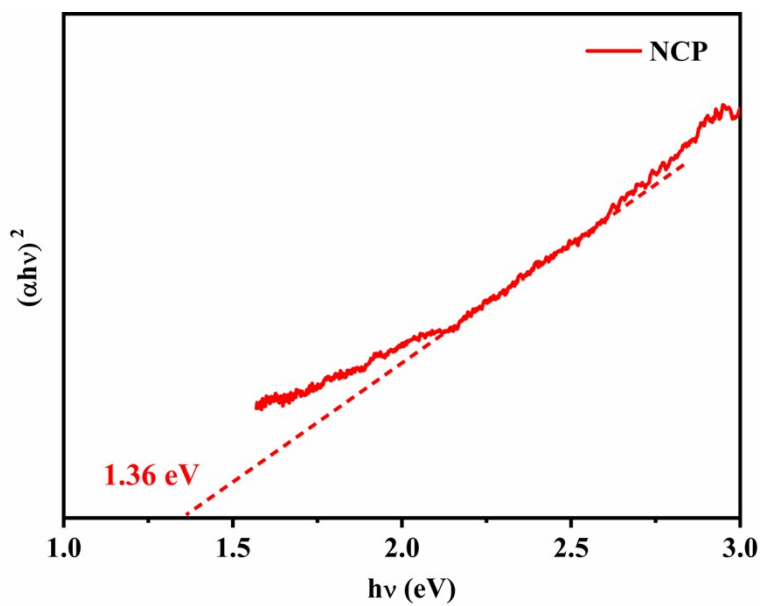


Figure S5. The Tauc plots of NCP.

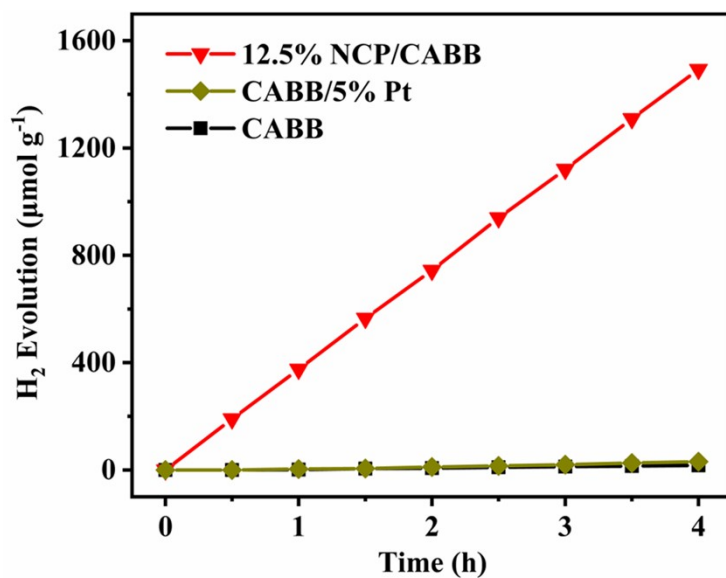


Figure S6. Photocatalytic H₂ evolution activities of CABB, 12.5% NCP/CABB and CABB/5% Pt.

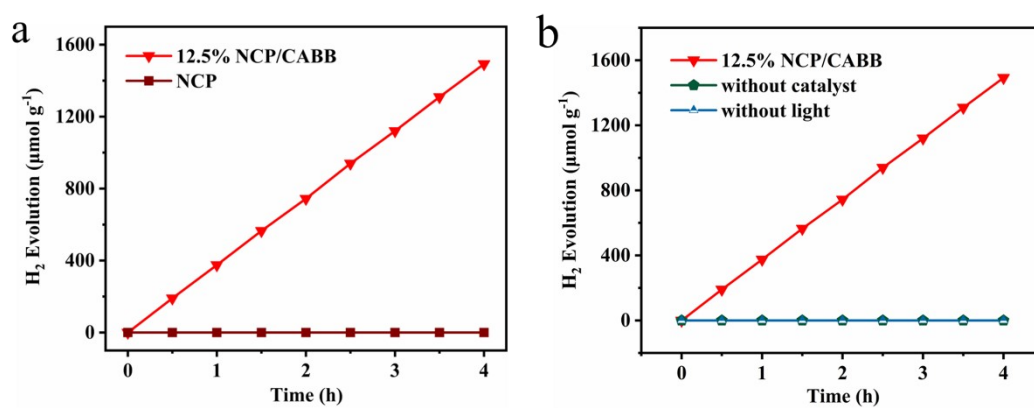


Figure S7. Comparison of H₂ evolution activities (a) NCP and (b) without light irradiation and without photocatalyst.

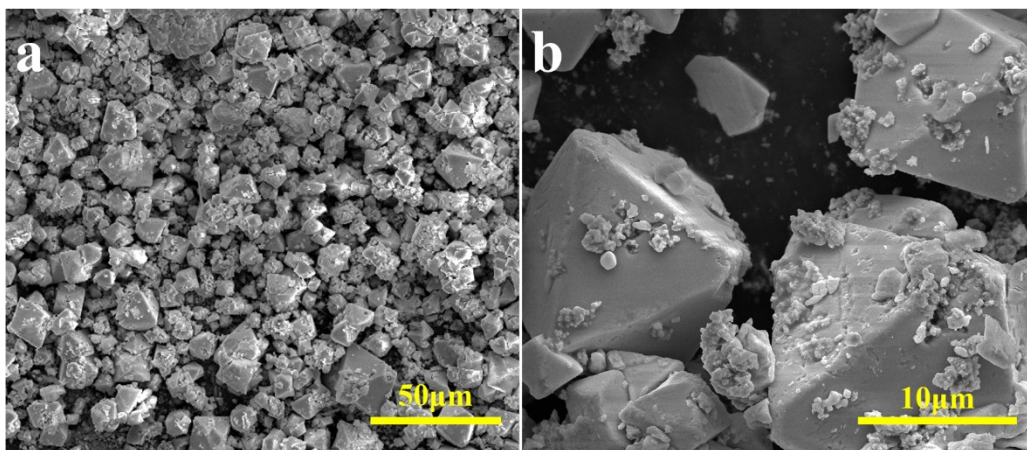


Figure S8. (a & b) SEM images of 12.5% NCP/CABB composites after 16 h of photocatalytic H₂ evolution.

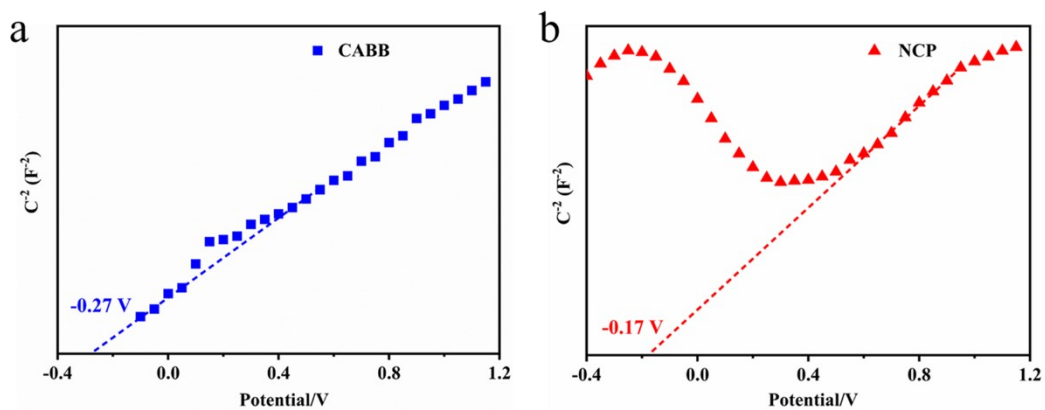


Figure S9. Mott-Schottky plots for (a) CABB and (b) NCP photocatalysts in CH₂Cl₂ solution containing 0.1 M tetrabutylammonium hexafluorophosphate (TBAPF₆).

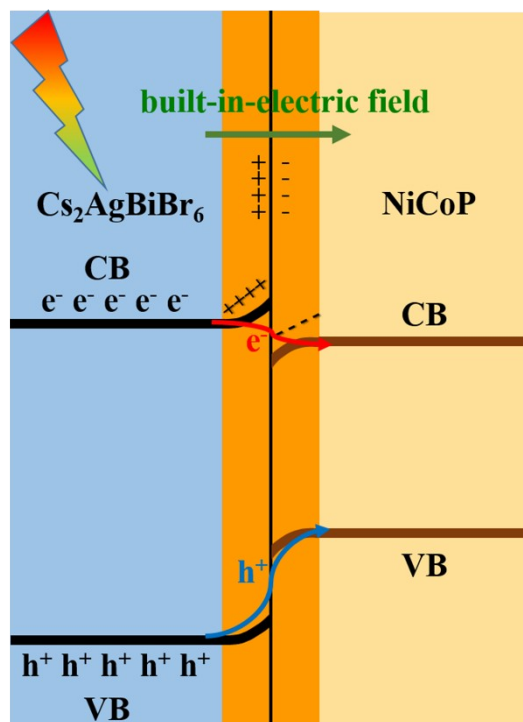


Figure S10. Schematic diagram of band bending on NCP/CABB.

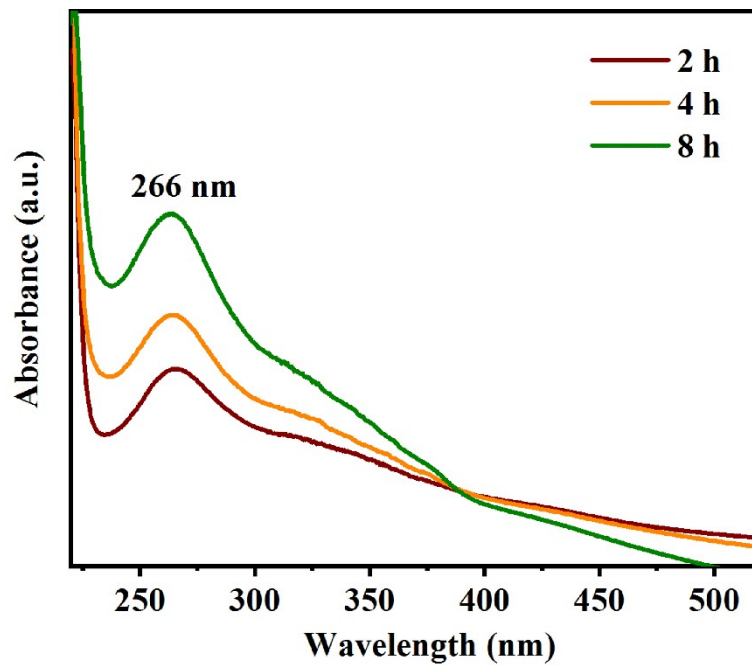


Figure S11. Time-dependent UV-Vis spectra of Br_3^- for photocatalytic HBr splitting reaction of 12.5% NCP/CABB.

Table S1. Comparison of H₂ evolution over reported lead-free perovskite photocatalysis.

Materials	Reactant solution	Light source	H ₂ activity (μmol g ⁻¹ h ⁻¹)	Stability (h)	Ref
Pure Cs ₂ AgBiBr ₆	HBr/H ₃ PO ₂ solution	300 W Xe lamp (λ ≥ 420 nm)	4.23		This work
Cs ₂ AgBiBr ₆ /5% Pt	HBr/H ₃ PO ₂ solution	300 W Xe lamp (λ ≥ 420 nm)	7.78		This work
NiCoP/Cs ₂ AgBiBr ₆	HBr/H₃PO₂ solution	300 W Xe lamp (λ ≥ 420 nm)	373.16	16	This work
RGO/Cs ₂ AgBiBr ₆	HBr/H ₃ PO ₂ solution	300 W Xe lamp (λ ≥ 420 nm)	48.9	120	1
N-C/Cs ₂ AgBiBr ₆	HBr/H ₃ PO ₂ Solution	300 W Xe lamp (λ ≥ 420 nm)	380	24	2
Cs ₂ AgBiBr ₆ /MoS ₂	HBr/H ₃ PO ₂ solution	300 W Xe lamp (λ ≥ 420 nm)	87.5	500	3
PtI _x /[(CH ₃) ₂ NH ₂] ₃ [BiI ₆]	HI/H ₃ PO ₂ solution	9 mW LED lamp (λ = 465 nm)	47	100	4
DMASnBr ₃ @g-C ₃ N ₄	10% TEOA, Pt 3 wt%	1500 W Xe lamp, (300-800 nm)	1730		5
PEA ₂ SnBr ₄ /g-C ₃ N ₄	10% TEOA, Pt 3 wt%	1500 W Xe lamp, (300-800 nm)	1613		6
Cs ₃ Bi _{2x} Sb _{2-2x} I ₉ /Pt	HI/H ₃ PO ₂ solution	300 W Xe lamp (λ ≥ 420 nm)	926	50	7
Cs ₃ Bi ₂ Br ₉ /g-C ₃ N ₄ (3wt% Pt)	10% TEOA, Pt 3 wt%	1500 W Xe lamp, (300-800 nm)	1050		8

Table S2. PL decay fitting parameters of CABB and 12.5% NCP/CABB using triexponential decay kinetics.

Materials	τ_1 (ns)	B_1 (%)	τ_2 (ns)	B_2 (%)	τ_3 (ns)	B_3 (%)	τ_{avg} (ns)
CABB	1.24	11.12	26.23	22.48	134.94	66.40	126.73
12.5% NCP/CABB	0.58	59.98	3.15	23.16	32.02	16.86	27.08

References

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