

Supporting Information

Encapsulating Halide Perovskite Quantum Dots in Metal-Organic Frameworks for Efficient Photocatalytic CO₂ Reduction

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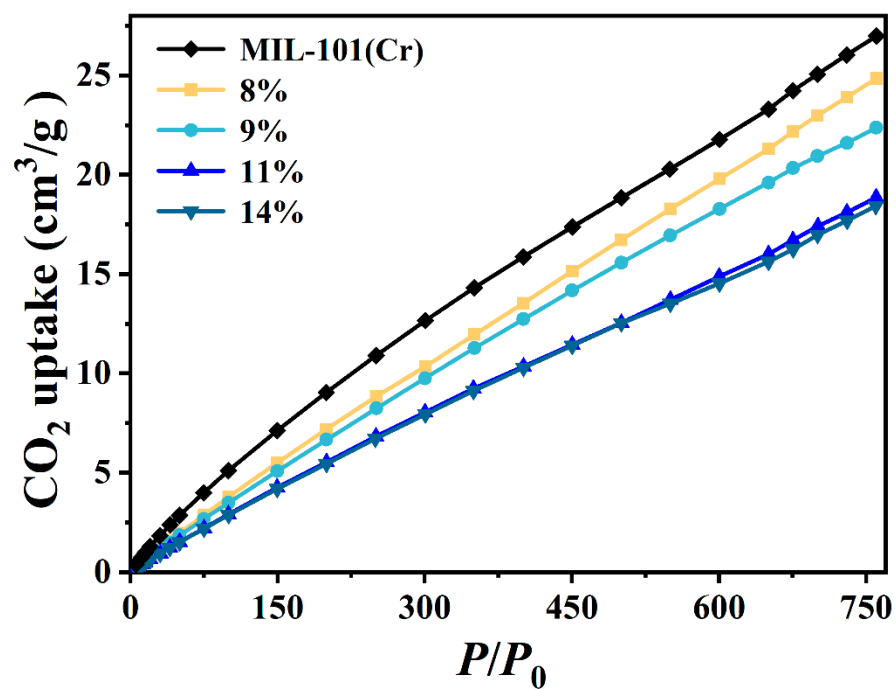


Figure S1 CO₂ adsorption isotherms of MIL-101(Cr) and x MAPbBr₃@MIL-101(Cr) at 298 K.

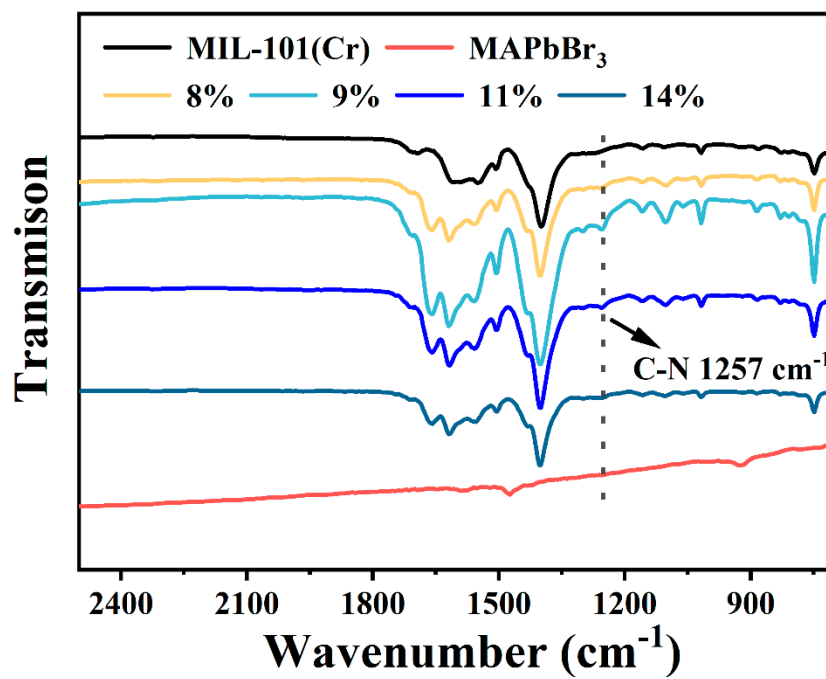


Figure S2 FTIR spectra of MAPbBr₃, MIL-101(Cr) and xMAPbBr₃@MIL-101(Cr).

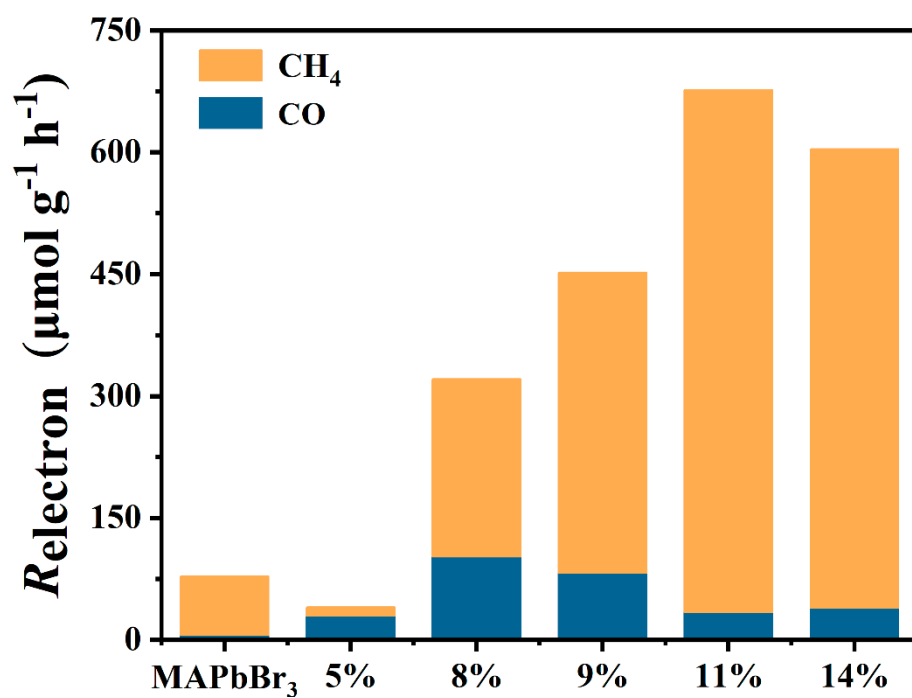


Figure S3 Electron transfer rate of the $x\text{MAPbBr}_3@\text{MIL-101}(\text{Cr})$ and MAPbBr_3 in a 9-h photocatalytic CO_2 reduction reaction.

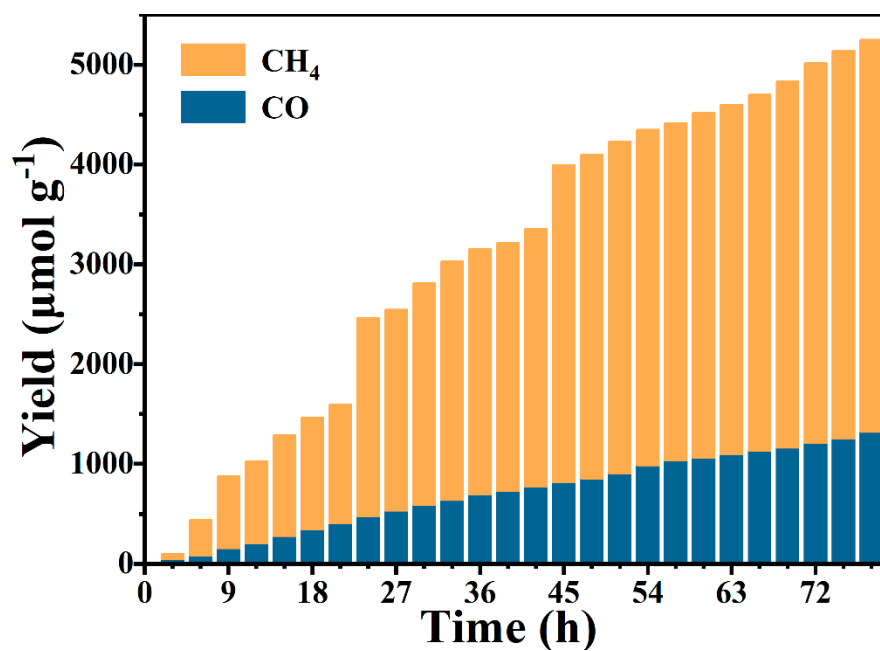


Figure S4 The yields of CH₄ and CO in a 78-h photocatalytic CO₂ reduction with 11%MAPbBr₃@MIL-101(Cr).

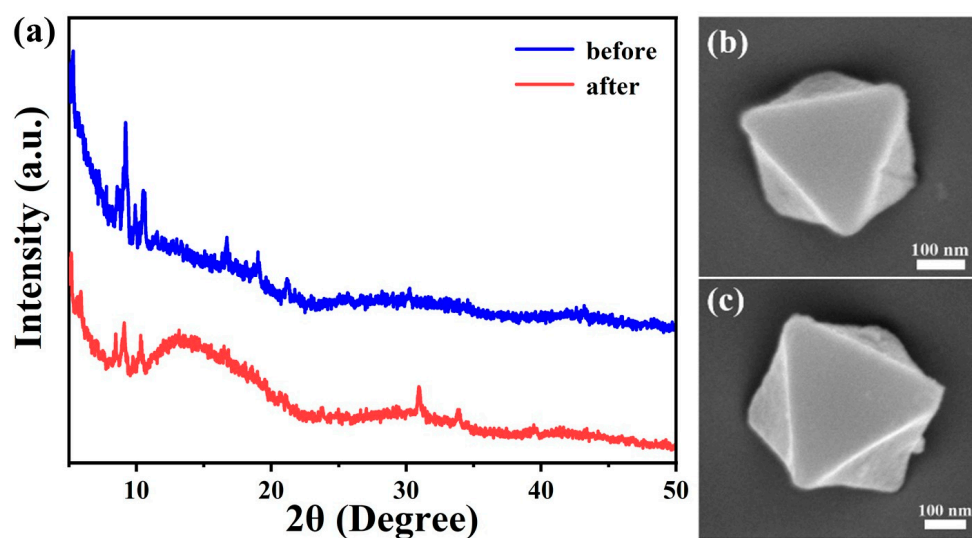


Figure S5 (a) PXRD patterns and (b, c) SEM images of 11%MAPbBr₃@MIL-101(Cr) before (b) and after (c) 78 h photocatalytic CO₂ reduction.

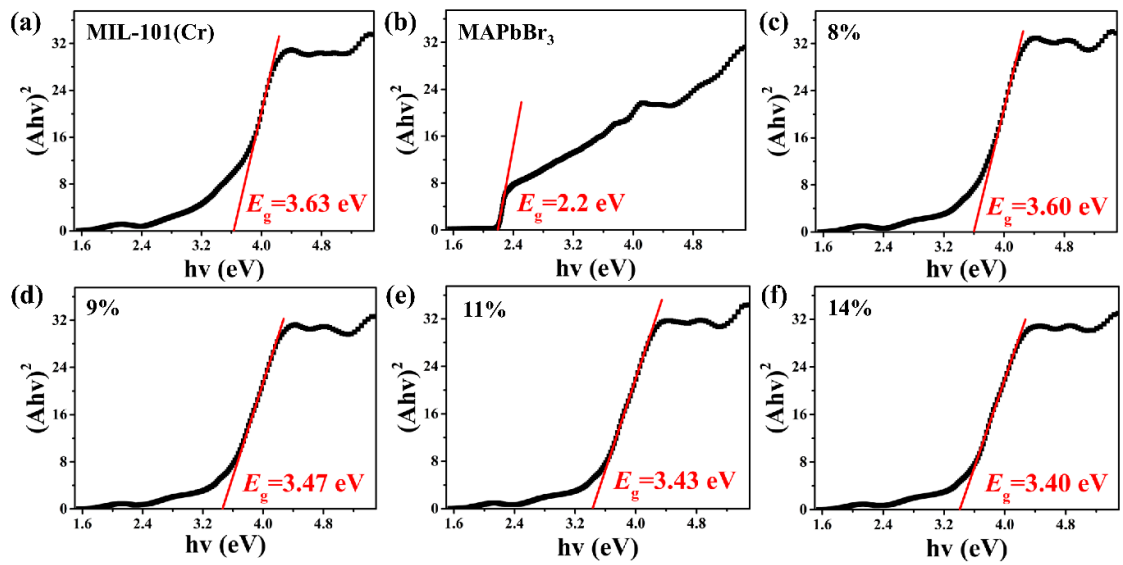


Figure S6 Tauc plot of MIL-101(Cr) (a), MAPbBr₃ (b) and x MAPbBr₃@MIL-101(Cr) (c-f).

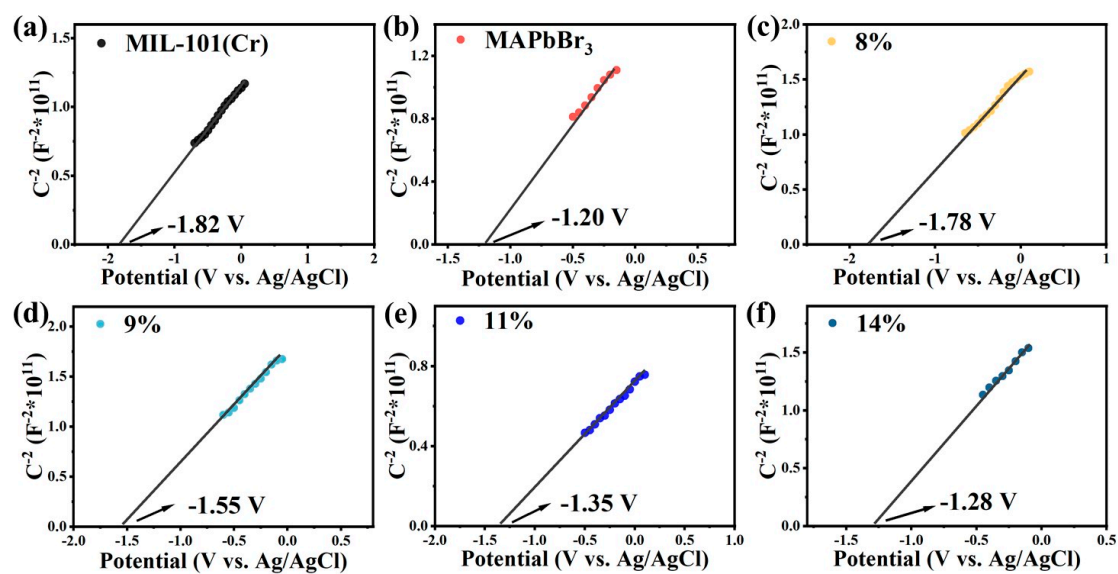


Figure S7 Mott–Schottky plots (vs. Ag/AgCl) of MIL-101(Cr) (a), MAPbBr₃ (b), and xMAPbBr₃@MIL-101(Cr) (c-f).

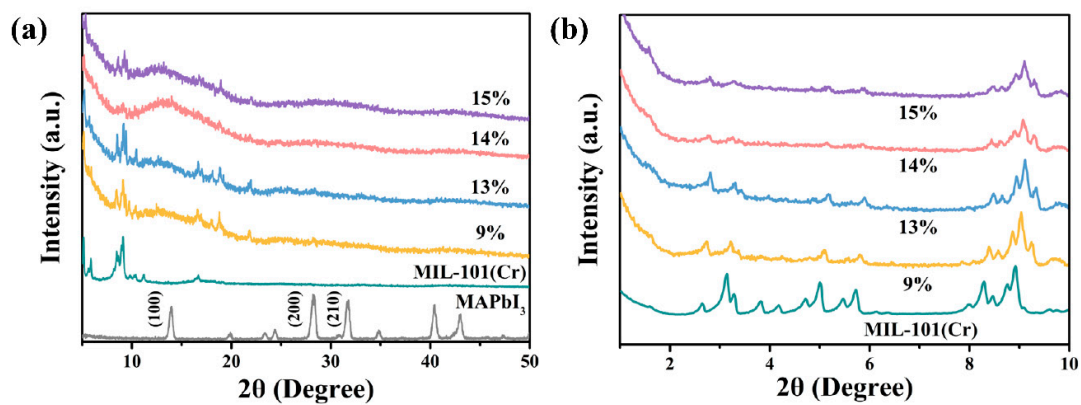


Figure S8 (a) PXRD patterns and (b) Small-angle XRD patterns of MIL-101(Cr), MAPbI₃, and x MAPbBr₃@MIL-101(Cr) samples.

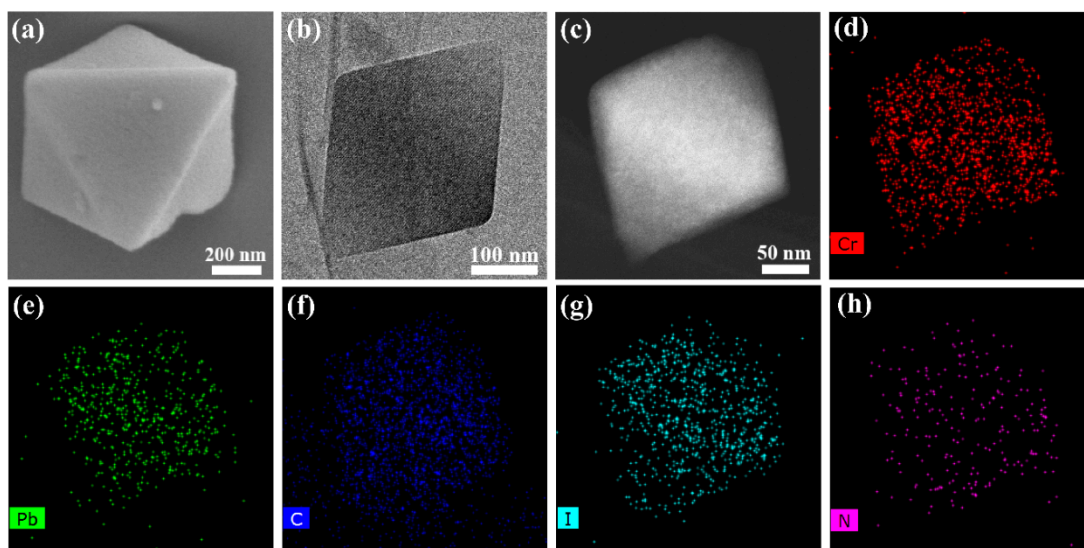


Figure S9 (a) SEM, (b) TEM, (c) HAADF-STEM images, and (d-h) Elemental mappings of 14%MAPbI₃@MIL-101(Cr).

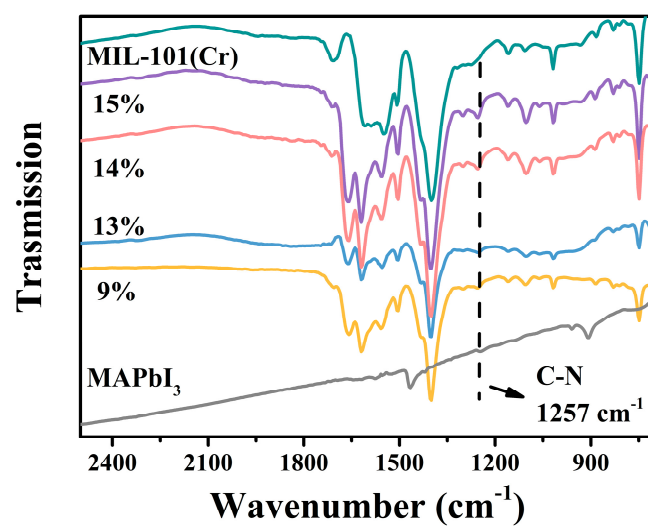


Figure S10 FTIR spectra of MAPbI₃, MIL-101(Cr) and x MAPbI₃@MIL-101(Cr).

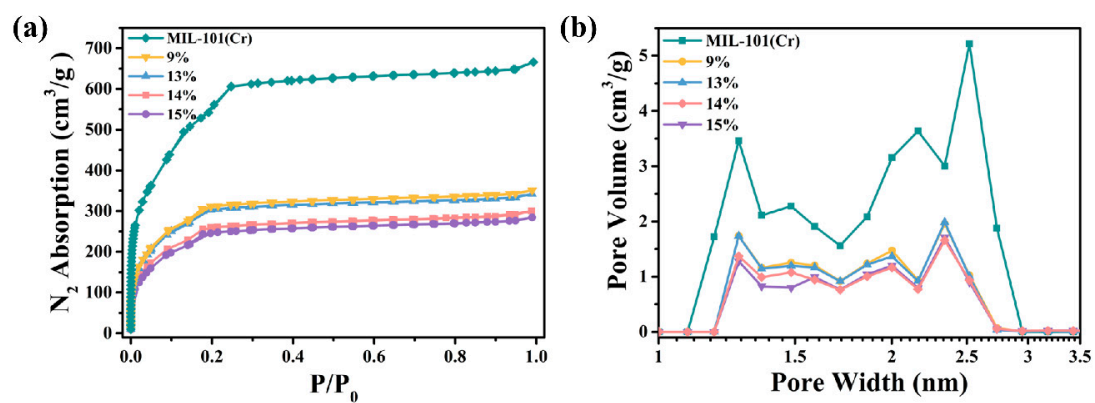


Figure S11 (a) N_2 sorption isotherms at 77 K and (b) Pore size distribution of MIL-101(Cr) and $xMAPbI_3@MIL-101(Cr)$.

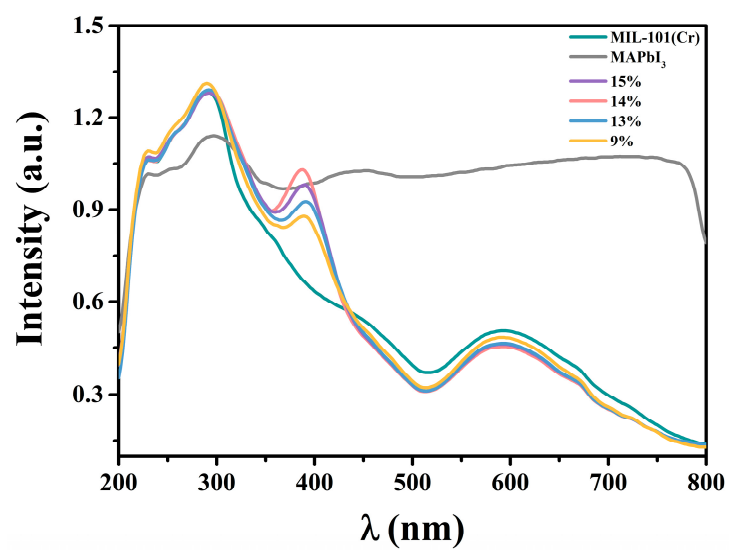


Figure S12 UV-vis spectra of MIL-101(Cr), MAPbI₃ and xMAPbI₃@MIL-101(Cr).

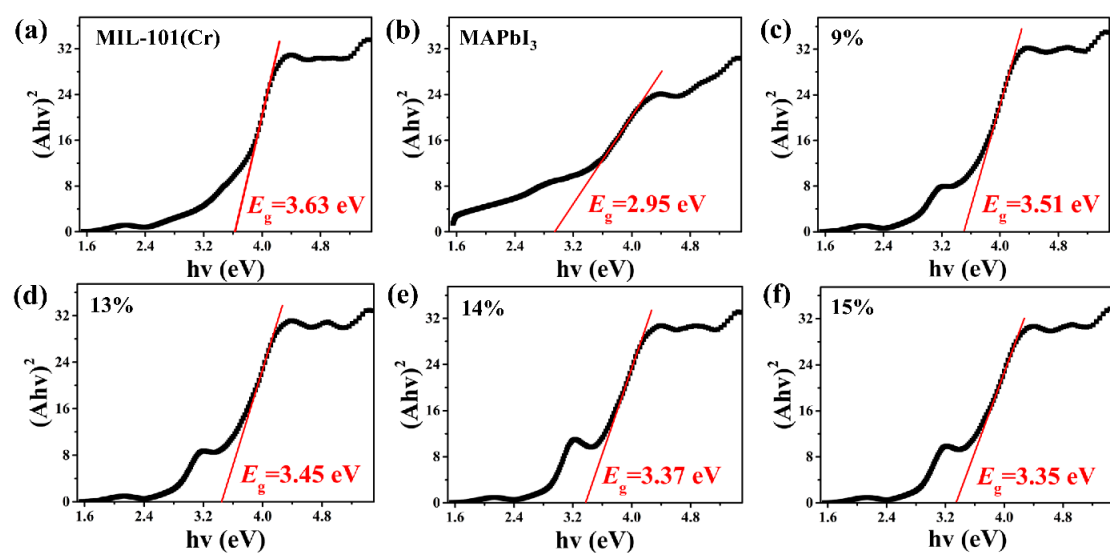


Figure S13 Tauc plot of MIL-101(Cr) (a), MAPbI₃ (b) and x MAPbI₃@MIL-101(Cr) (c-f).

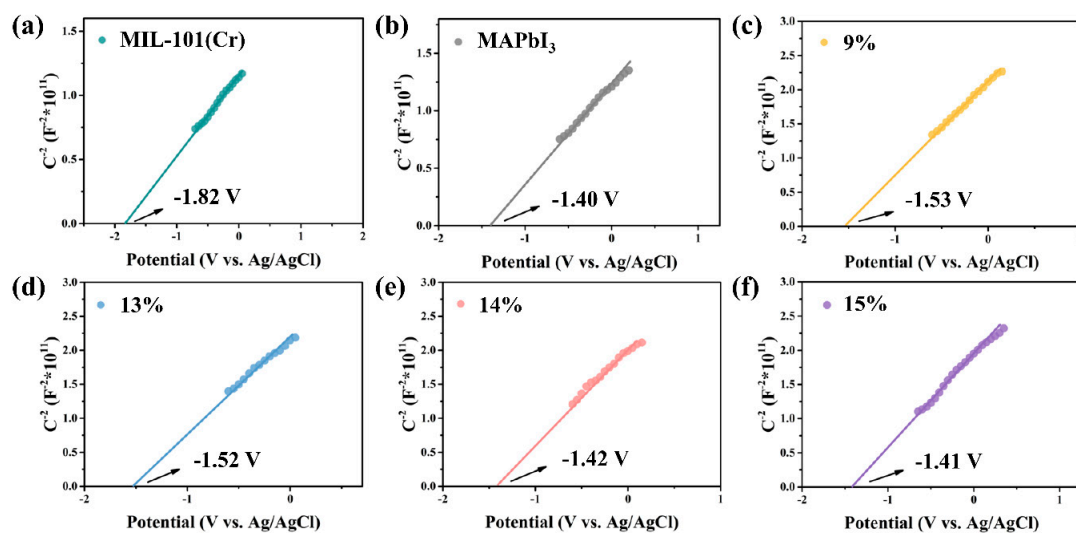


Figure S14 Mott-Schottky plots (vs. Ag/AgCl) of MIL-101(Cr), MAPbI₃ and x MAPbI₃@MIL-101(Cr).

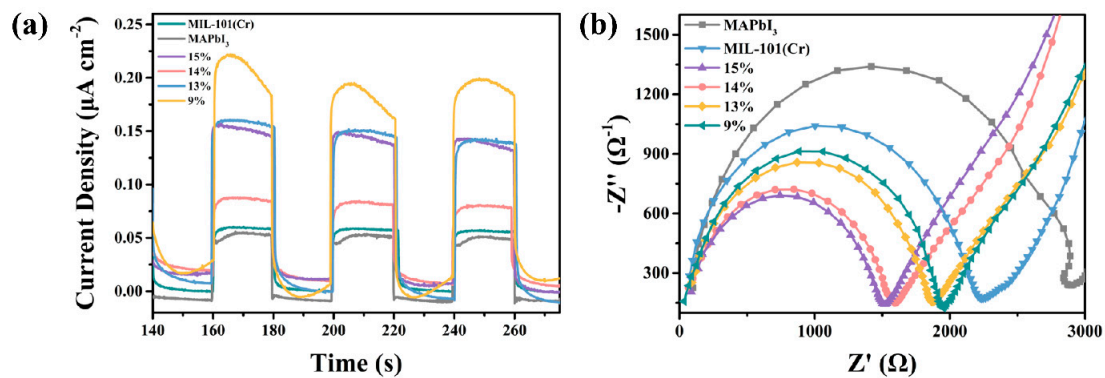


Figure S15 (a) Photocurrent density curves plotted at 0.2 V (vs. Ag/AgCl) under light and dark, and (b) Electrochemical impedance spectra of MIL-101(Cr), MAPbI₃ and $x\text{MAPbI}_3@\text{MIL-101(Cr)}$.

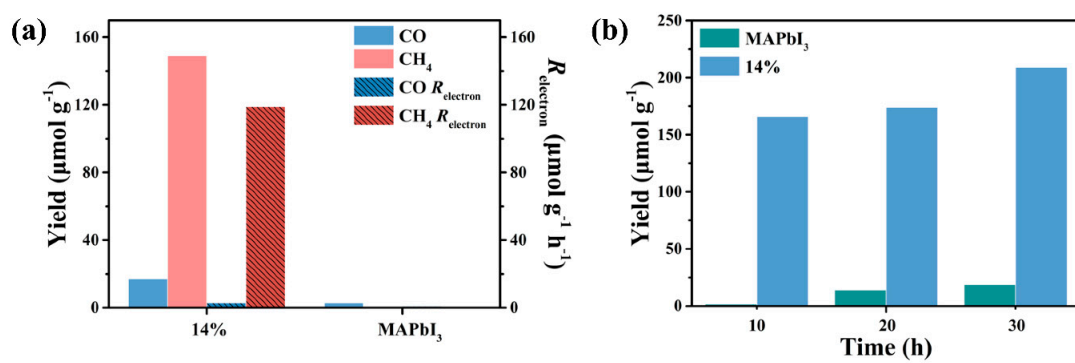


Figure S16 (a) Yields and R_{electron} in a 10-hour reaction, and (b) Stable test of MAPbI₃ and 14%MAPbI₃@MIL-101(Cr).

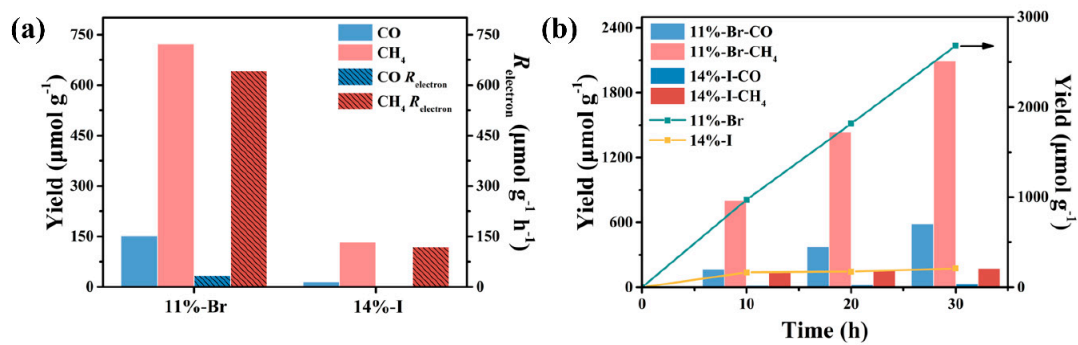


Figure S17 (a) The comparison of yields and electron consumption rates in a 9-hour reaction, and (b) stability tests in a 30-hour reaction of 11%MAPbBr₃@MIL-101(Cr) and 14%MAPbI₃@MIL-101(Cr).

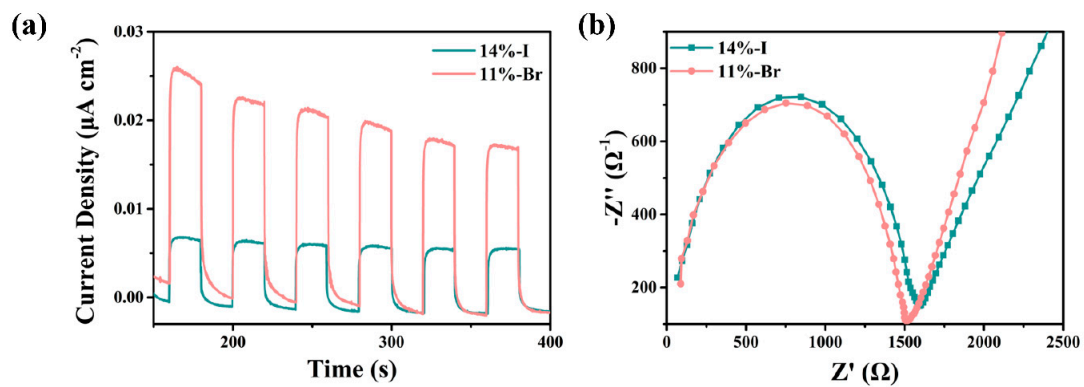


Figure S18 The comparison of 11MAPbBr₃@MIL-101(Cr) and 14%MAPbI₃@MIL-101(Cr) (a) Photocurrent density curves under light and dark. (b) Electrochemical impedance spectra.

Table S1 Elemental Analysis results of $x\text{MAPbX}_3@\text{MIL-101}(\text{Cr})$

| Sample | Cr | Pb | MAPbX ₃ |
|-------------------------------------|--------------------|--------------------|--------------------|
| | (wt%) ^a | (wt%) ^a | (wt%) ^b |
| 8%MAPbBr ₃ @MIL-101(Cr) | 9.52 | 3.58 | 8.29 |
| 9%MAPbBr ₃ @MIL-101(Cr) | 8.32 | 3.90 | 9.02 |
| 11%MAPbBr ₃ @MIL-101(Cr) | 8.31 | 4.83 | 11.17 |
| 14%MAPbBr ₃ @MIL-101(Cr) | 8.54 | 6.03 | 13.95 |
| 9%MAPbI ₃ @MIL-101(Cr) | 7.79 | 2.93 | 8.77 |
| 13%MAPbI ₃ @MIL-101(Cr) | 8.24 | 4.36 | 13.07 |
| 14%MAPbI ₃ @MIL-101(Cr) | 6.89 | 4.50 | 13.47 |
| 15%MAPbI ₃ @MIL-101(Cr) | 7.70 | 4.71 | 14.09 |

^a Measured by ICP-OES. ^b Calculated according to Equation S1

$$wt(\text{MAPBX}_3)\% = wt_{\text{Pb}}\% / \left(\frac{207}{12+6+14+207+80 \times 3} \right) \quad (\text{Equation S1})$$

Table S2 Pore volumes of different pores of $x\text{MAPbX}_3@\text{MIL-101}(\text{Cr})$ and $\text{MIL-101}(\text{Cr})$

| Sample | Pore volume ^a (cm ³ /g) | Micropore (cm ³ /g) | Mesopore (cm ³ /g) |
|-------------------------------------|--|-----------------------------------|----------------------------------|
| MIL-101(Cr) | 1.28 | 0.57 | 0.71 |
| 8%MAPbBr ₃ @MIL-101(Cr) | 0.72 | 0.41 | 0.31 |
| 9%MAPbBr ₃ @MIL-101(Cr) | 0.63 | 0.41 | 0.22 |
| 11%MAPbBr ₃ @MIL-101(Cr) | 0.49 | 0.26 | 0.23 |
| 14%MAPbBr ₃ @MIL-101(Cr) | 0.47 | 0.24 | 0.23 |
| 9%MAPbI ₃ @MIL-101(Cr) | 0.53 | 0.28 | 0.71 |
| 13%MAPbI ₃ @MIL-101(Cr) | 0.52 | 0.28 | 0.24 |
| 14%MAPbI ₃ @MIL-101(Cr) | 0.45 | 0.22 | 0.23 |
| 15%MAPbI ₃ @MIL-101(Cr) | 0.43 | 0.22 | 0.21 |

^a Total pore volume was determined by using the adsorption branch of the N₂ isotherm at $P/P_0 = 0.995$.

Table S3 Summary of the photocatalytic CO₂ reduction performance over various halide perovskite-based photocatalysts.

| Photocatalyst | Products | Light source | R_{electron}^a | Ref. |
|--|---|-------------------------------------|-------------------------|------------------|
| 11%MAPbBr ₃ @MIL-101(Cr) | CO, CH ₄ | 300 W Xe | 677 | This work |
| 14%MAPbBr ₃ @MIL-101(Cr) | CO, CH ₄ | 300 W Xe | 122 | This work |
| CsPbBr ₃ /UiO-66(NH ₂) | CO, CH ₄ | 300 W Xe | 18.5 | [S1] |
| CsPbBr ₃ /GO | H ₂ , CO, CH ₄ | 100 W | 29.8 | [S2] |
| MAPbI ₃ @PCN-221(Fe _{0.2}) | CO, CH ₄ | 300 W Xe >400 nm | 112 | [S3] |
| CsPbBr ₃ /g-C ₃ N ₄ | CO | 300 W Xe >420 nm | 148.9 | [S4] |
| CsPbBr ₃ @ZIF-8 | CO, CH ₄ | 100 W Xe lamp | 15.498 | [S5] |
| CsPbBr ₃ @ZIF-67 | CO, CH ₄ | 100 W Xe lamp | 29.63 | [S5] |
| Cs ₂ SnI ₆ | CH ₄ | 150 mW cm ⁻² > 400 nm | 16.24 | [S6] |
| Pt-g-C ₃ N ₄ /NaNbO ₃ | CH ₄ | 300W Xe Lamp > 420 nm | 51.2 | [S7] |
| CsPbBr ₃ /Au/TiO ₂ | CO, CH ₄ | AM 1.5 G 100 mW·cm ⁻² | 44.3 | [S9] |

^a The calculation of the total electron consumption rate is based on Equation S2:

$$R_{\text{electron}} = 2R_{\text{CO}} + 8R_{\text{CH}_4} \quad \text{(Equation S2)}$$

where R_{CO} and R_{CH_4} represents the generation rate of CO and CH₄, respectively.

^b EA = ethyl acetate

Table S4 TRPL decay parameters of MAPbBr₃, 11%MAPbBr₃@MIL-101(Cr) and MIL-101(Cr).

| Catalyst | A ₁ | τ ₁ /ns | A ₂ | τ ₂ /ns | τ/ns |
|--|----------------|--------------------|----------------|--------------------|----------------------|
| MAPbBr ₃ | 68.32 | 1.72 | 0.25 | 8.06 | 1.82 |
| 11%MAPbBr ₃ @MIL-101 (Cr) | 0.10 | 25.21 | 26.98 | 2.18 | 3.17 |
| MIL-101 (Cr) | 0.16 | 25.50 | 32.75 | 2.03 | 3.39 |
| $\tau = \frac{(A_1\tau_1^2 + A_2\tau_2^2)}{(A_1\tau_1 + A_2\tau_2)}$ | | | | | (Equation S3) |

References

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