Electronic Supplementary Material (ESI) for CrystEngComm.

Supporting Information

Construction of $CsPbBr_3$/Carboxyl-modified rGO Heterostrucures for Efficient Photocatalytic Reduction of CO_2 to Methanol

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Table S1 The preparation conditions of samples

Sample	$CsPbBr_3$ NCs (2 μM)	rGO-COOH (2.825 mg/mL)
1	0.5 mL	2 mL
2	1 mL	2 mL
3	1.5 mL	2 mL
4	2 mL	2 mL
5	4 mL	2 mL

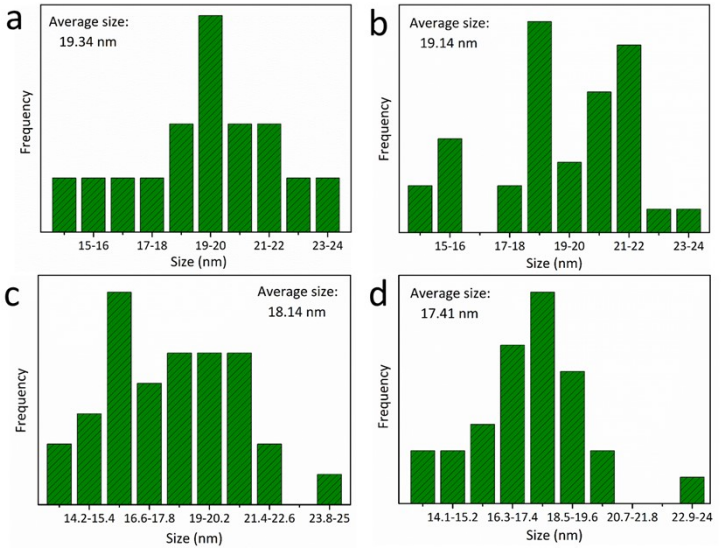

Figure S1 The size-distribution histograms of sample 1-4.

Table S2 Summary of the ICP-MS analysis results of the sample 4.

	Cs	Pb	Br
ppm	0.184	0.328	0.416
μmol/L	1.38	1.58	5.20

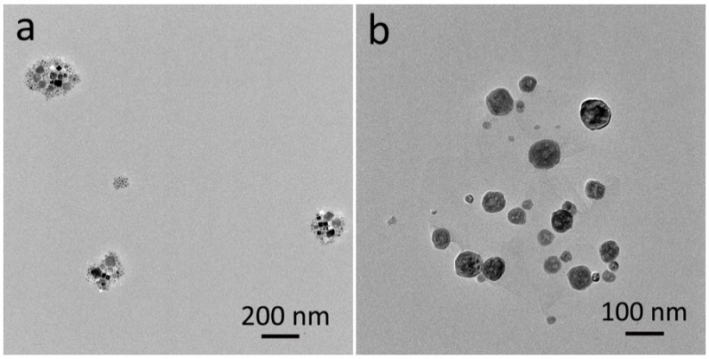

Figure S2 TEM image of the contrast sample which was prepared with the same conditions with sample 4 except using rGO without the decoration of -COOH.

Table S3 Raman information of samples

Sample	I_D	I_G	I_D/I_G
rGO	147.63	130.48	1.131
rGO-COOH	204.56	153.03	1.337
4	360.00	317.00	1.356

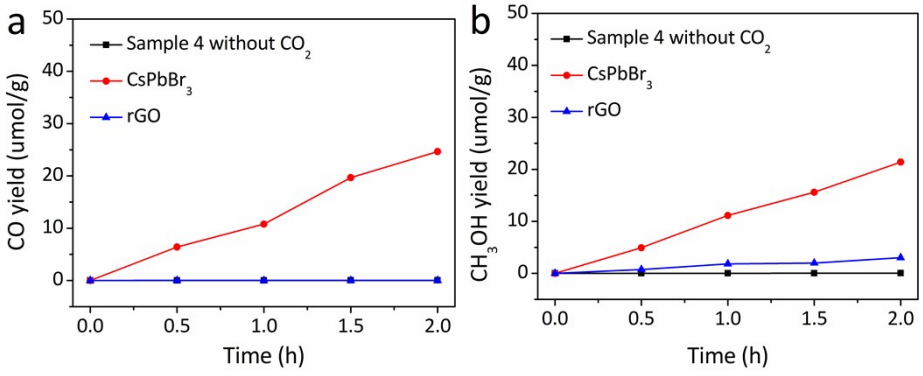

Figure S3 CO (a) and CH_3OH (b) yield plots of $CsPbBr_3$, rGO, and the blank experiment as the function of reaction time.

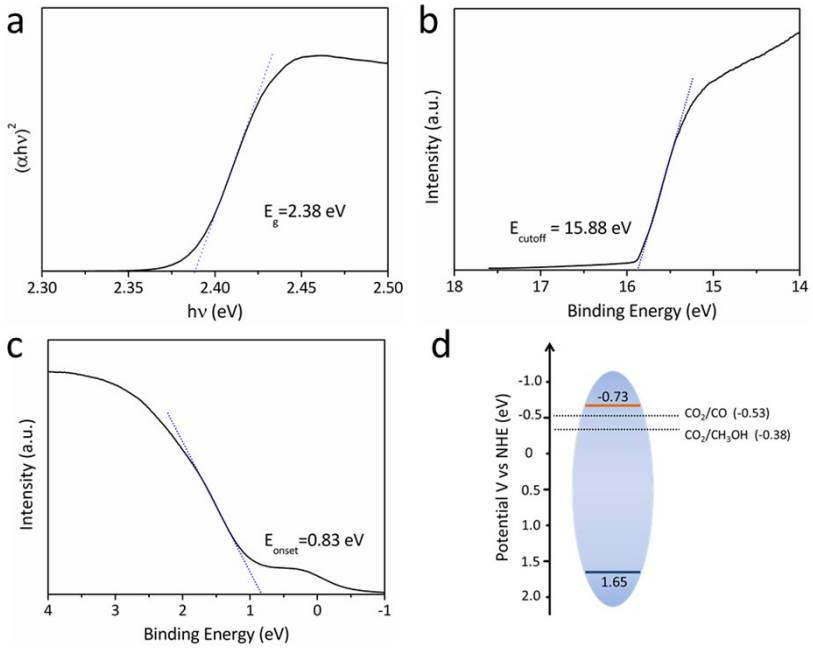

Figure S4 Tauc plot (a), UPS spectra of the secondary edge region (b) and the HOMO region (c), schematic illustration of energy band structure (d) for sample 4. The Tauc plot was obtained from the corresponding UV-vis diffuse reflectance spectrum according to the formula 1 where α, h, υ, A, and E_g, is absorption coefficient, Planck constant, light frequency, constant, and band gap, respectively. The value of n is 1/2 for direct band gap semiconductor. The UPS measurement was carried out using a He I (*hv*= 21.2eV) source. $E_{HOMO/VBM}$ was calculated using formula 2.

$$(\alpha hv)^{\frac{1}{n}} = A(hv - E_g) \quad (1)$$

$$E_{HOMO/VBM} = hv - (E_{cutoff} - E_{onset}) \quad (2)$$

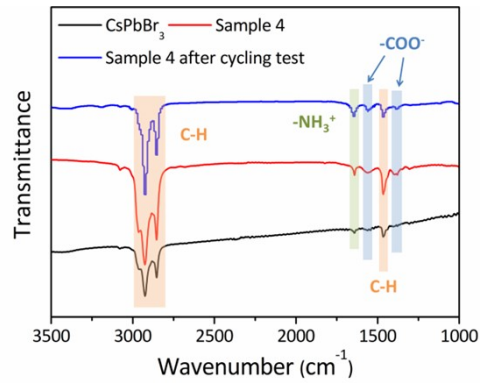

Figure S5 FTIR spectra of the parent $CsPbBr_3$ NCs, sample 4 before and after 10th cycling test.

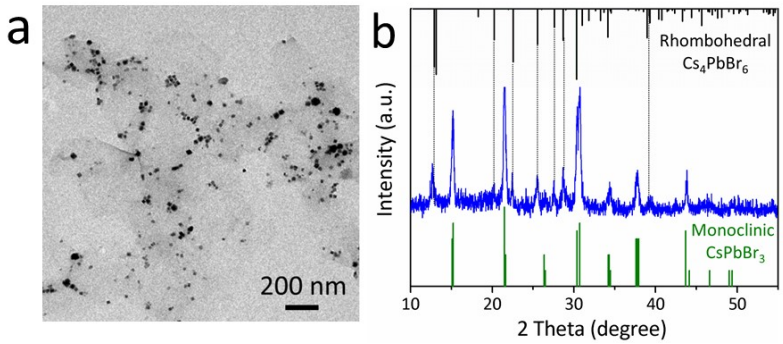

Figure S6 TEM image (a) and XRD pattern (b) of sample 4 after 10th cycling test.

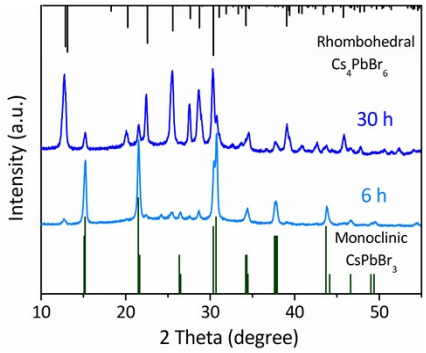

Figure S7 XRD patterns of sample 4 with different exposure time at 70% relative humidity and room temperature.

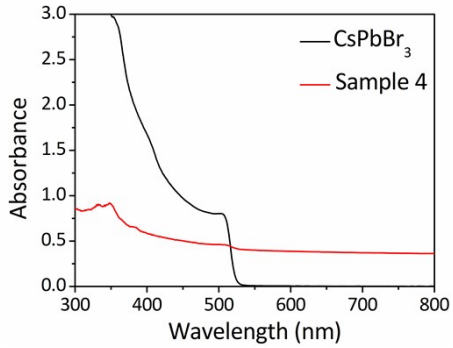

Figure S8 The absorption spectra of the parent $CsPbBr_3$ NCs and sample 4.

Table S4 Components B_1 and B_2, time constants τ_1 and τ_2, and average lifetime τ of the parent $CsPbBr_3$ NCs and sample 4.

Sample	τ_1	B_1	τ_2	B_2	$\tau_{average}$ (ns)
$CsPbBr_3$	9.37	25.12	48.06	74.88	45.68
4	1.15	7.14	72.74	27.26	5.34

* A biexponential function was applied to fit the decay curves:

$$F(t) = A + B_1 \exp\left(-t/\tau_1\right) + B_2 exp(-t/\tau_2)$$

in which B_1 and B_2 is the normalized amplitudes of each component. τ_1 and τ_2 represent the time constants. The shorter lifetime component is assigned to the exciton recombination and the longer lifetime component is associated with the surface related emission.

The average lifetime ($\tau_{average}$) was calculated by:

$$\tau_{average} = (B_1\tau_1^2 + B_2\tau_2^2)/(B_1\tau_1 + B_2\tau_2)$$

Calculation of CO_2 conversion efficiency.

CO_2 conversion efficiency was calculated by the C content of products and the total amount of CO_2 in the reaction system.

$$CO_2\ conversion\ efficiency = \frac{n(C_{product})}{n(C_{total\ CO_2})} = \frac{n(CO) + n(CH_3OH)}{n(CO_2)}$$

The reaction chamber was 40 mL filled with 1.4*101325 Pa CO_2. The temperature is 353 K. Calculated by Ideal Gas Law (PV=nRT), CO_2 is 0.0019 mol. After reaction 2h, according to the yield of CO and CH_3OH, CO_2 conversion efficiency of sample 1, 2, 3, 4 was 0.008%, 0.014%, 0.021%, 0.028%.