

Supplementary Materials

g-C₃N₄-Stabilised Organic–Inorganic Halide Perovskites for Efficient Photocatalytic Selective Oxidation of Benzyl Alcohol

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Method&Materials

Formamidinium hydrobromide (FABr, 98 wt.%, Tokyo Chemical Industry Co., LTD), *N,N*-dimethylformamide (DMF, 99.8%, Sigma Aldrich), trifluorotoluene (anhydrous, 99%, Sigma Aldrich), lead(II) bromide (PbBr₂, Tokyo Chemical Industry Co., LTD), melamine (C₃N₃(NH₂)₃, 99%, Aladdin), toluene (C₇H₈, 99.5%, Guangzhou Chemical Reagent Factory). All the above chemicals were used as received.

The preparation of g-C₃N₄ refers to a modified reported method⁷. In detail, a 10 mL unsealed sample vial filled with melamine was heated up to 550 °C for 4 h with a heating rate of 2.3 °C min⁻¹ under air in muffle furnace. The as-prepared g-C₃N₄ was subsequently employed for the fabrication of composite materials in the next step.

FAPbBr₃ precursor solution were synthesized by typical two-step method. Briefly, FABr and PbBr₂ with the same mole ratio were dissolved in 5 ml DMF respectively. The two solutions were then mixed and ultrasonicated until completely dissolved to give the precursor solution. Pure FAPbBr₃ crystals were obtained by adding 35 mL methylbenzene and then drying the part of precursor at certain temperature. For details, the *ca.* 3 μm perovskite is obtained at 58 °C and the *ca.* 20 μm perovskite is prepared at 25 °C in a furnace oven, respectively. The g-C₃N₄ powder of different masses were added to the four equal FAPbBr₃ precursor to prepare FAPbBr₃/C₃N₄ hybrids with 5, 10, 20, and 30 wt % of FAPbBr₃. Then ultrasonication ending up with a uniform dispersion. The dispersion turned into yellow after 35 ml methylbenzene was added, indicating that the FAPbBr₃ nanocrystals were precipitated on the surface of g-C₃N₄. The obtained yellow dispersion was then dried at 60 °C overnight under air to obtain the final C₃N₄/FAPbBr₃ composite materials with different weight ratio of FAPbBr₃. The as-prepared WO₃/FAPbBr₃ samples were obtained using the similar approach.

Characterization

SEM images were obtained using a Hitachi scanning electron microscope. Powder samples are stuck to an aluminium stub using carbon sticky tape. Diffuse reflectance UV-vis spectra were recorded on an Ocean Optics HR2000+ High Resolution Spectrometer with DH-2000-BAL Deuterium/Helium light source (200-1100 nm). Spectra are recorded in Spectra Suite software using an integration time of 10 seconds, box car smoothing width of 30, and 10 scans to average. Wide angle PXRD patterns were recorded on a Bruker-AXS D8 Advance instrument with Lynx eye detector, using Cu K α radiation (1.54 Å) with a 1 mm slit on the source and 2.5 mm detector slit. Data was collected from 10 – 60 ° 2 θ , with 0.02 ° step size and a scan speed of 0.1 seconds per step. Samples are deposited on a quartz sample holder. For the activity tests, samples are irradiated by a 150 W Xe lamp with irradiance of *ca.* 100 mW cm⁻² with 380 nm filter. For the GC tests, the samples are prepared as following: 10 mg FAPbBr₃/C₃N₄ hybrids of different weight percentages of FAPbBr₃ and pure FAPbBr₃ nanocrystals are dispersed in 1.5 mL trifluorotoluene. The dispersions are ultrasonicated for 5 h before the measurement. ESR spectra were recorded on a Bruker ESP 300 E electron paramagnetic resonance spectrometer. PL spectra (Olympus U-TLU) was recorded from 380 to 700 nm with 1.0002 seconds exposure time and 120 pin hole, under an excitation wavelength of 360nm. X-ray photoelectron spectroscopy (XPS, AXIS-HSi). TEM images were obtained from JEM-200, using an accelerating voltage of 200 kV. The energy dispersive x-ray spectroscopy (EDX) was recorded on a FEI Talos F200S instrument. Electron spin resonance spectra were obtained over Bruker ESP 300 E electron paramagnetic resonance spectrometer.

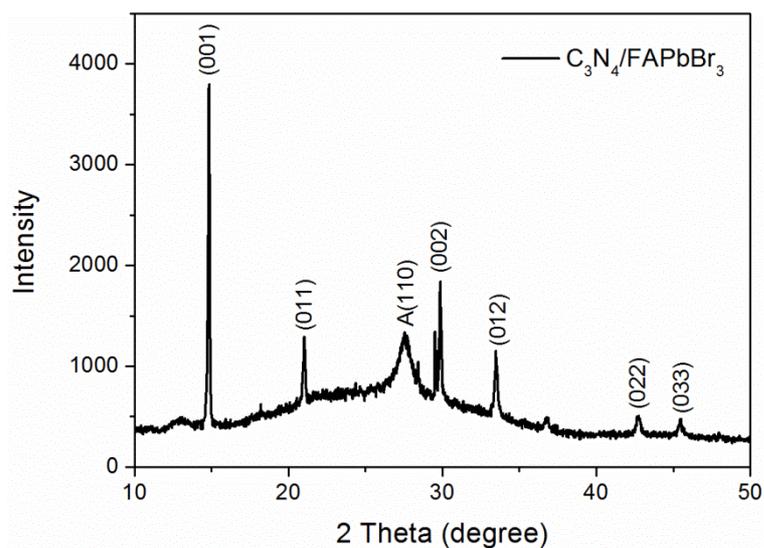


Figure S1. PXRD of $FAPbBr_3/C_3N_4$ hybrids, where A = diffraction pattern from (110) of g- C_3N_4 (JCPDS# 87-1526), the rest of the diffraction patterns are consistent with $FAPbBr_3$ from a previous report [1].

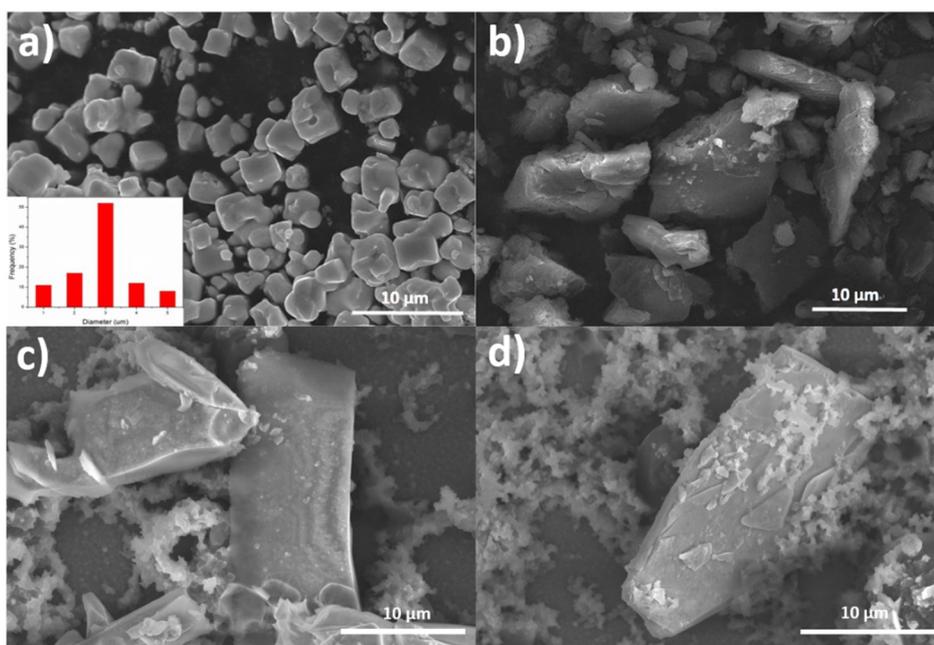


Figure S2. SEM images of (a) prinstin $FAPbBr_3$ crystals synthesis through anti-solvent method and their size distribution; (b-d) $FAPbBr_3/C_3N_4$ hybrids materials.

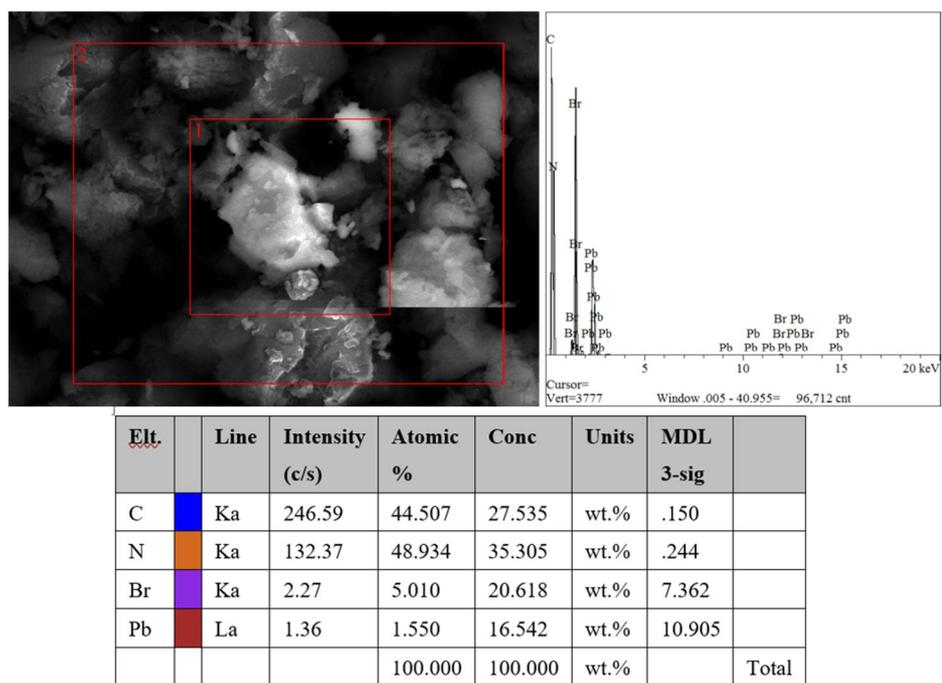


Figure S3. Selected area EDX analysis of the as-prepared FAPbBr₃/C₃N₄ samples, with detailed elemental distribution.

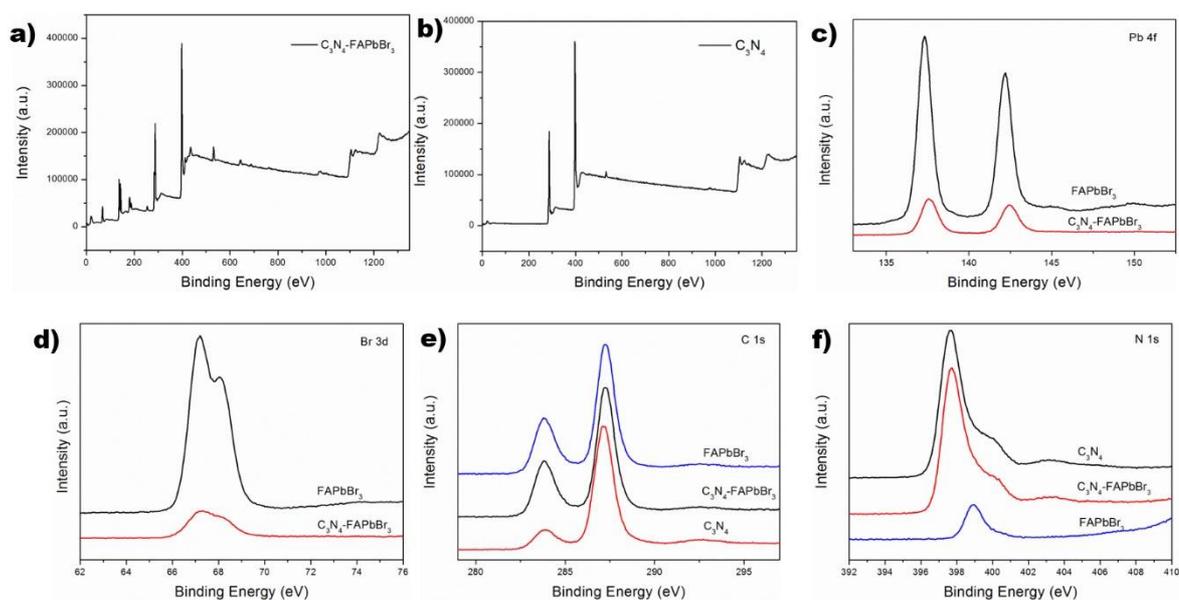


Figure S4. XPS spectrum of (a) C₃N₄/FAPbBr₃ hybrids materials; (b) pristine g-C₃N₄; (c-f) bind energy of Pb 4f orbitals, Br 3d orbitals, C 1s orbitals and N 1s orbitals, respectively.

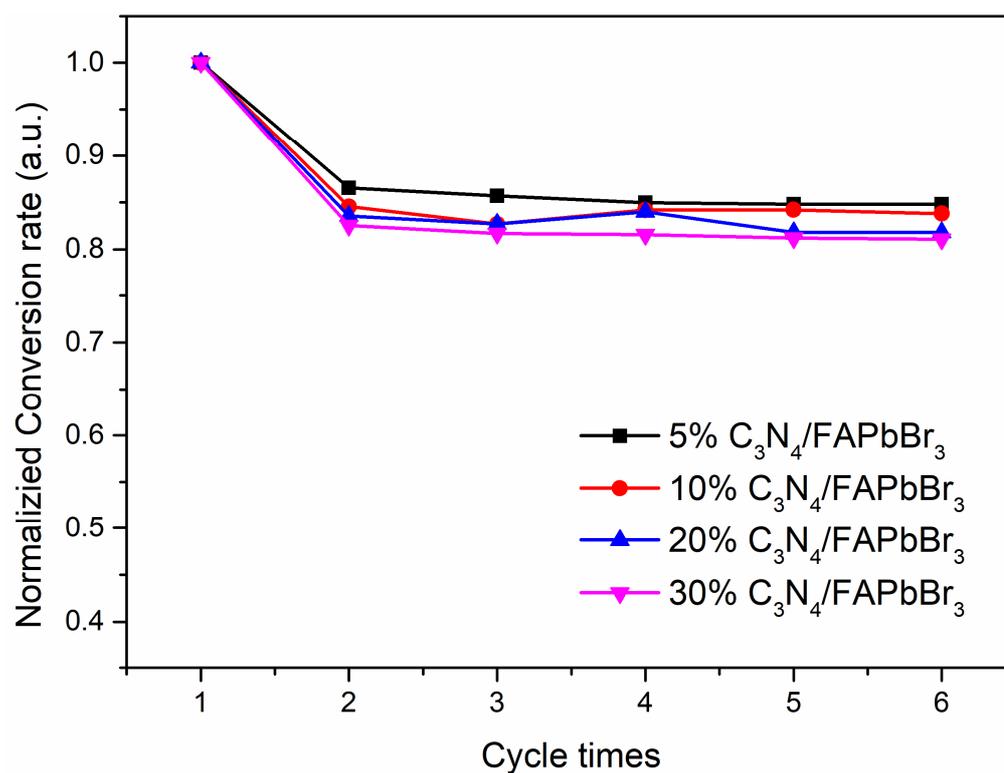


Figure S5. The photoactivity of C₃N₄/FAPbBr₃ hybrids materials with respect to the photoactivity in the first cycle of each. The reaction conditions are consistent with other tests.

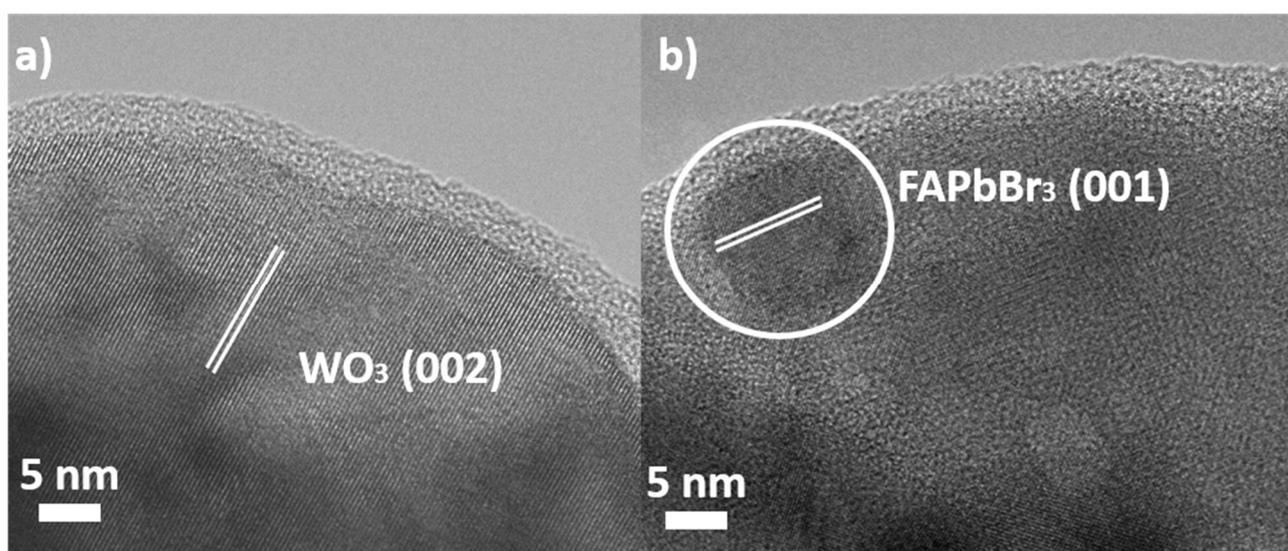


Figure S6. HRTEM of (a) WO₃ nanoplate and (b) WO₃/FAPbBr₃ hybrids materials.

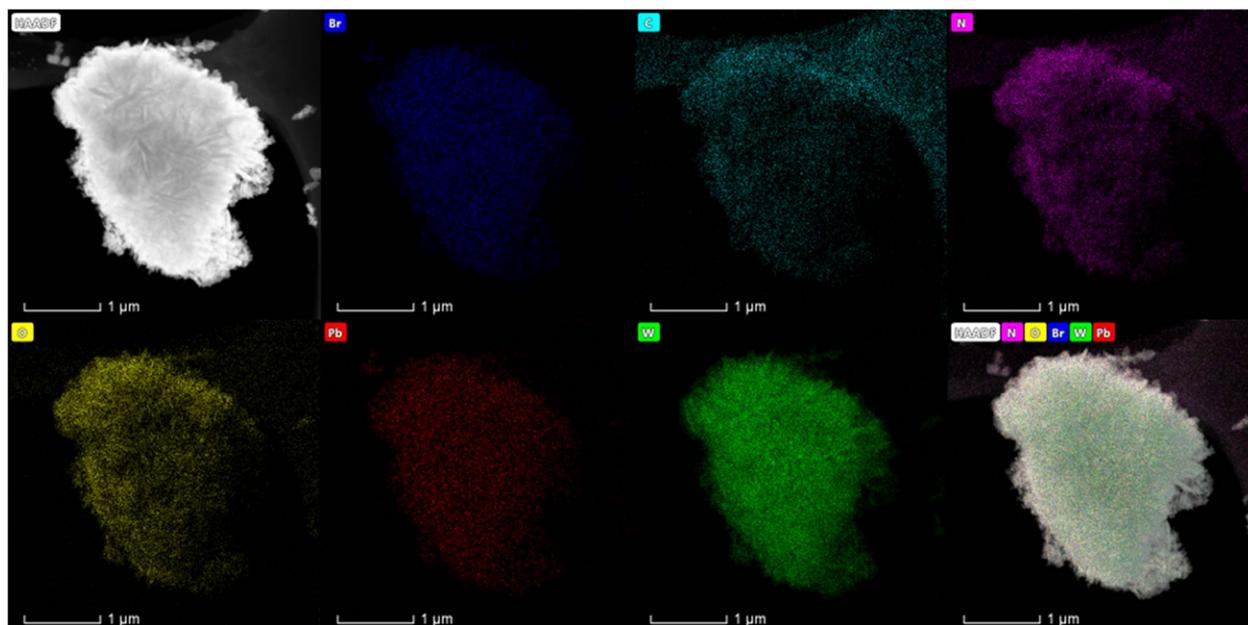


Figure S7. TEM-HAADF image and according elemental mapping of $\text{WO}_3/\text{FAPbBr}_3$ hybrids materials.

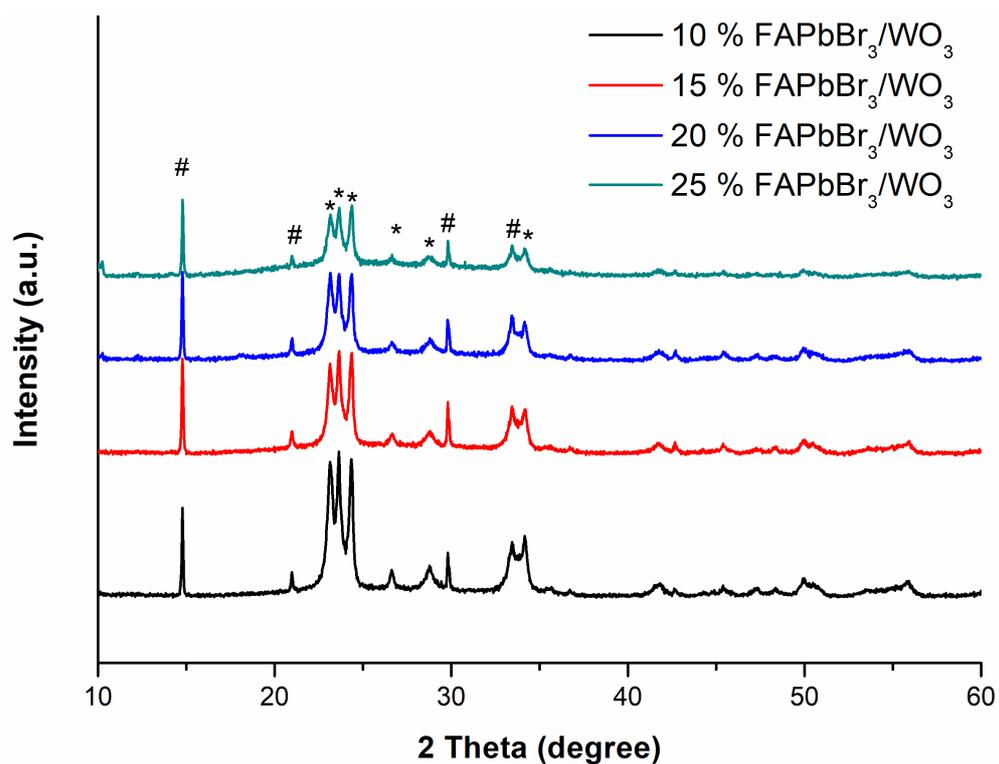
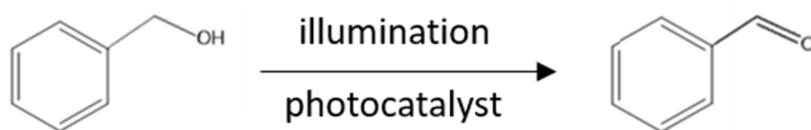


Figure S8. PXRD of $\text{WO}_3/\text{FAPbBr}_3$ hybrids with different FAPbBr_3 weight ratios, in which # = FAPbBr_3 and * = WO_3 (JCPDS# 43-1035), respectively.



Reaction conditions: 10 mg photocatalysts, 1.5 mL toluene as solvent with 0.1 mmol benzylic alcohol, saturated with oxygen under dark before the experiment, Xe lamp (100 mW cm⁻²) as simulated solar light irradiation (4 h). The conversion rate and selectivity to products are calculated using the below formulas:

$$\text{Conversion (\%)} = (C_B - C_A)/C_B \times 100$$

$$\text{Selectivity (\%)} = 100 \times C_P/(C_B - C_A)$$

C_B , C_A and C_P are corresponding to the concentrations of reactant before and after the photocatalytic reactions, and the amount of target products, respectively.

Table S1. Photocatalytic oxidation of benzylic alcohol using a series of samples.

Sample	Conversion (%)	Selectivity (%)
FAPbBr ₃ (ca. 3μm) dark	0	0
FAPbBr ₃ (ca. 3μm)	14.6	99
FAPbBr ₃ (ca. 20μm)	6.8	99
g-C ₃ N ₄	1.8	92
5% C ₃ N ₄ /FAPbBr ₃	23.1	99
10% C ₃ N ₄ /FAPbBr ₃	30.2	99
20% C ₃ N ₄ /FAPbBr ₃	46.6	99
30% C ₃ N ₄ /FAPbBr ₃	35.8	99
WO ₃	5.4	94
5% WO ₃ /FAPbBr ₃	11.5	99
10% WO ₃ /FAPbBr ₃	18.9	99
20% WO ₃ /FAPbBr ₃	24.6	99
30% WO ₃ /FAPbBr ₃	21.2	99

Table S2. Photocatalytic oxidation of benzylic alcohol using a series of samples with long-pass filter (420 nm, 450 nm and 500 nm).

Sample	X (%)	Y (%)
FAPbBr ₃ (ca. 3μm)	73.6	7.2
* FAPbBr ₃ (ca. 3μm)	79.3	6
# FAPbBr ₃ (ca. 3μm)	83.5	5.6
& FAPbBr ₃ (ca. 3μm)	91	4.8
20% C ₃ N ₄ /FAPbBr ₃	82.2	16.9
*20% C ₃ N ₄ /FAPbBr ₃	82.6	16.3
#20% C ₃ N ₄ /FAPbBr ₃	83.8	5.3
&20% C ₃ N ₄ /FAPbBr ₃	90.2	4.5
20% WO ₃ /FAPbBr ₃	74	7
*20% WO ₃ /FAPbBr ₃	80.1	5.7
#20% WO ₃ /FAPbBr ₃	84	5
&20% WO ₃ /FAPbBr ₃	90.5	4.2

X: the photoactivity of photocatalysts after 6 reaction cycles relative to its original conversion rate (in the first cycle)

Y: the photoactivity loss after the first reaction cycles

The applied 420 nm, 450 nm and 500 nm long-pass filter are labeled by *, # and &, respectively.

References

- [1] Wang J, Song C, He Z, Mai C, Xie G, Mu L, et al. All-Solution-Processed Pure Formamidinium-Based Perovskite Light-Emitting Diodes. *Advanced Materials*. 2018; 30(39):e1804137.