

Supplementary Information for:

A highly photoconductive composite prepared by incorporating polyoxometalate into perovskite for photodetection application

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Experimental Section

S1. Materials and Synthesis.

The $\text{CH}_3\text{NH}_3\text{PbI}_3$ precursor was prepared according to reported procedure with a little modification: Hydroiodic acid (38mL, 0.227mol, 45 wt. % in water, Sinopharm) and methylamine (23mL, 0.273mol, 40 wt. % in water, Amethys.) were stirred in the ice bath for 2h. After stirring at 0°C for 2h, the resulting solution was evaporated at 50°C until the solvent completely evaporated and white chemicals ($\text{CH}_3\text{NH}_3\text{I}$) synthesized. The precipitate was washed three times with diethyl ether and dried at 60°C under vacuum and used without further purification. To prepare $\text{CH}_3\text{NH}_3\text{PbI}_3$ precursor, the synthesized $\text{CH}_3\text{NH}_3\text{I}$ (0.8g) and PbI_2 (2.3g, 98% Sinopharm) were mixed in N,N-Dimethylformamide (DMF, 7.3mL, 99.5% Aladdin) at 60°C for overnight with stirring. PW_{12} was prepared according to literature method.¹ The $\text{CH}_3\text{NH}_3\text{PbI}_3/\text{PW}_{12}$ composite precursor was prepared by adding 0.05g PW_{12} into 1ml $\text{CH}_3\text{NH}_3\text{PbI}_3$ precursor under continuous stirring until the PW_{12} was completely dissolved.

S2. Fabrication of photoconductive device.

Indium tin oxide coated glass (ITO glass) was patterned by chemical etching (Zn powder and 2 M HCl) with the bridging-gap width of roughly 50 μm and length of

1.5cm. Each piece of the ITO was adopted as an electrode. Then, the etched substrate was cleaned with surfactant and rinsed with acetone and ethanol and deionized water and finally dried by air flow.

Photoconductive devices were fabricated by spin-coating the as-prepared $\text{CH}_3\text{NH}_3\text{PbI}_3/\text{PW}_{12}$ composite or pristine $\text{CH}_3\text{NH}_3\text{PbI}_3$ precursor onto the pre-cleaned ITO electrodes at a rate of 1500 rpm for 60s and consequently heating at 100 °C for 30min. All these procedures were carried out on naturally ambient air and room temperature.

Characterization.

Infrared spectra (IR) were recorded with a Nicolet Magna 560 FT-IR Spectrometer. X-ray diffraction (XRD) analyses were performed with a Rigaku D/max-3c X-ray diffractometer, using CuK α 1 radiation ($\lambda=1.5405\text{\AA}$). Field-emission scanning electron microscopy (Hitachi SU-8010 FE-SEM) was used to investigate the surface morphology. All electrochemical experiments were performed on a CHI660C Electrochemical Workstation (Shanghai Chenhua Instrument Corp., China) at on naturally ambient air and room temperature. A two-electrode system was employed with each piece of the ITO as an electrode. The photoconductivity of the samples was measured by monitoring their photocurrent response under light irradiation. All photocurrent experiments were carried out at a constant bias of 3 V. A 300 W xenon lamp ($320\text{ nm} \leq \lambda \leq 780\text{ nm}$) was used as a white light source. The different wavelength (300nm to 800nm) lights from a 300 W Xe lamp were focused through a monochromator. The incident power light was measured by a power meter. The fluorescence spectra were recorded on the FL900/FS920 steady-state fluorescence spectrometer. The UV-vis diffuse reflectance spectroscopy (DRS) was recorded with a UV-Vis-NIR Spectrophotometer (Varian).

Figures

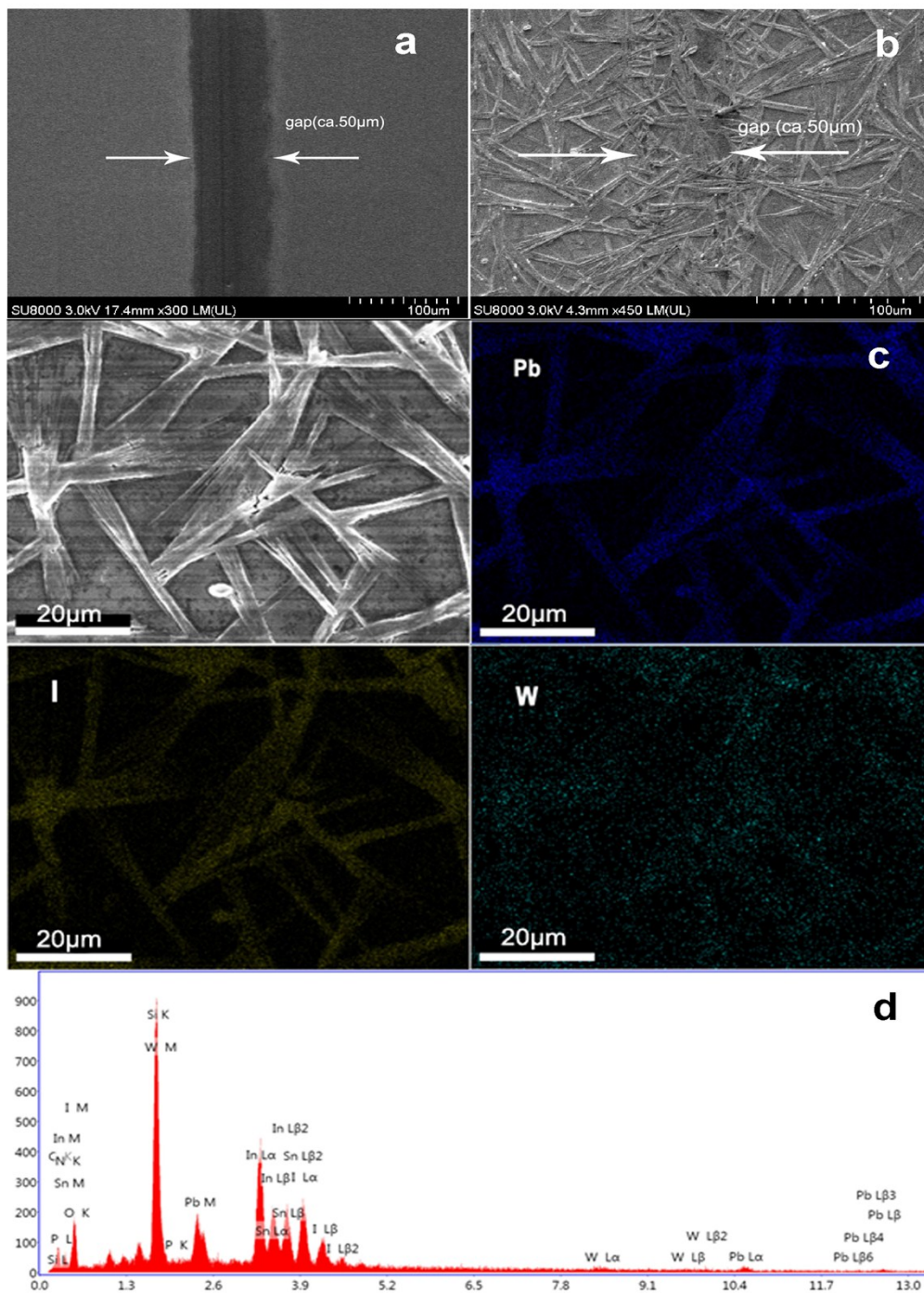


Fig. S1 SEM of detached ITO (a), after deposition of $\text{CH}_3\text{NH}_3\text{PbI}_3$ (b), elements mapping (c), and EDX analysis (d).

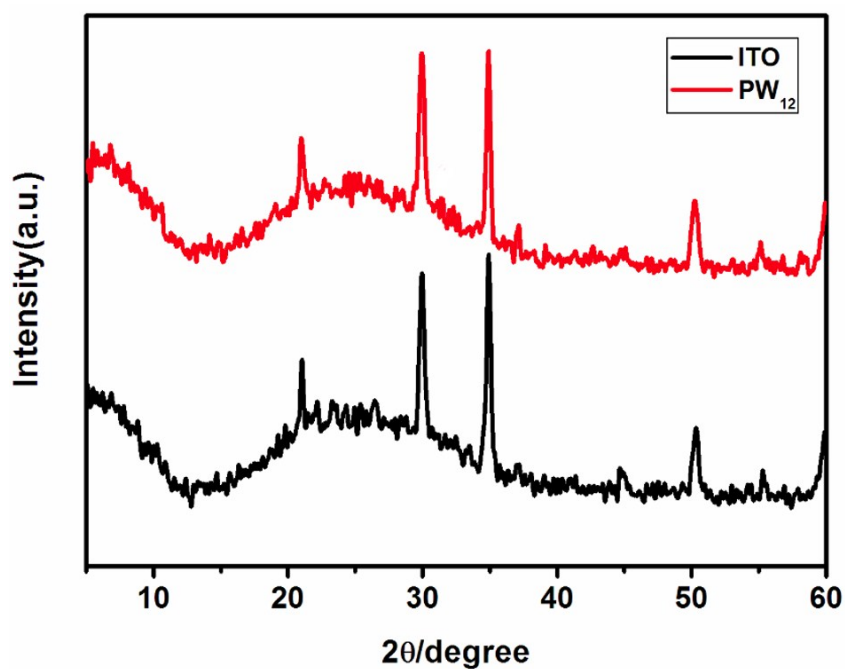


Fig. S2 XRD of ITO substrate and PW_{12} film deposited on ITO

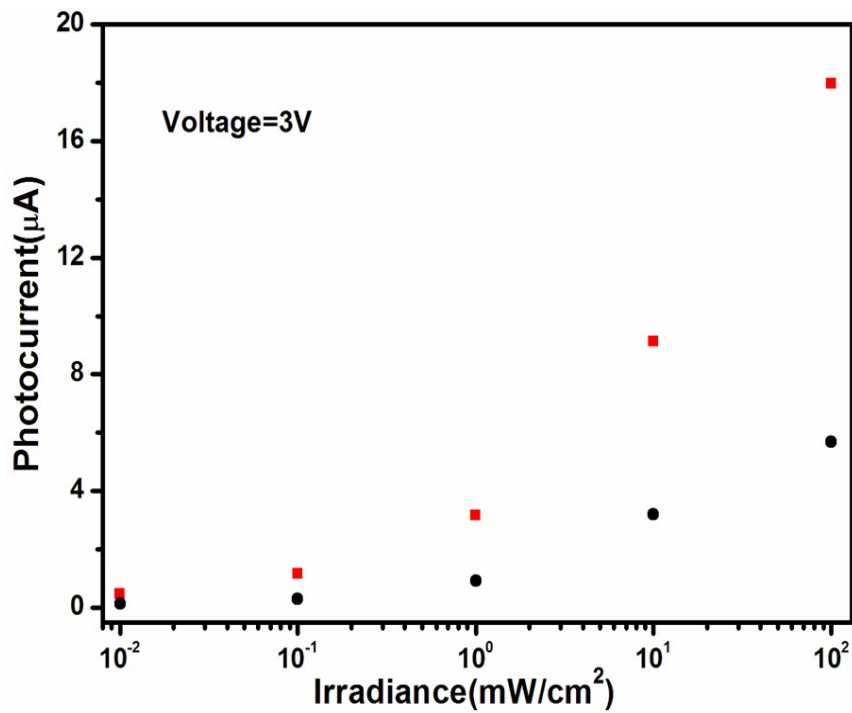


Fig. S3 photocurrent of different irradiance $\text{CH}_3\text{NH}_3\text{PbI}_3$ (black) and the $\text{CH}_3\text{NH}_3\text{PbI}_3/\text{PW}_{12}$ composite (red)

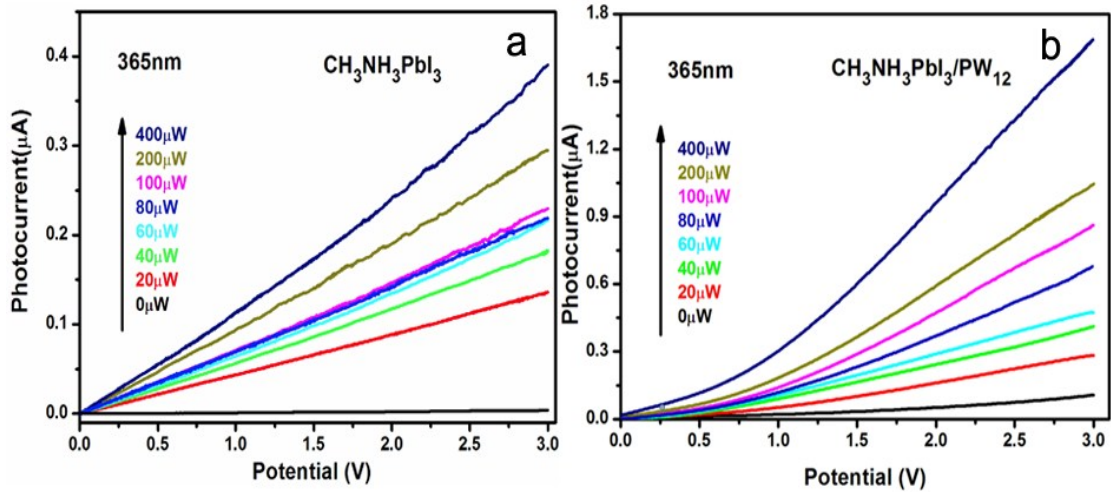


Fig. S4 the 365nm I-V curves of $\text{CH}_3\text{NH}_3\text{PbI}_3$ (left) and the $\text{CH}_3\text{NH}_3\text{PbI}_3/\text{PW}_{12}$ composite (right)

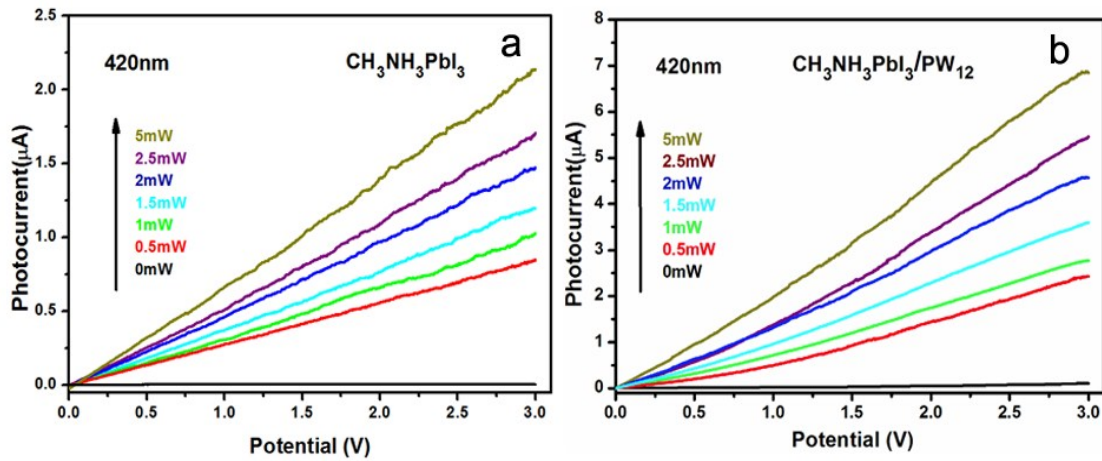


Fig. S5 the 420nm I-V curves of $\text{CH}_3\text{NH}_3\text{PbI}_3$ (left) and the $\text{CH}_3\text{NH}_3\text{PbI}_3/\text{PW}_{12}$ composite (right)

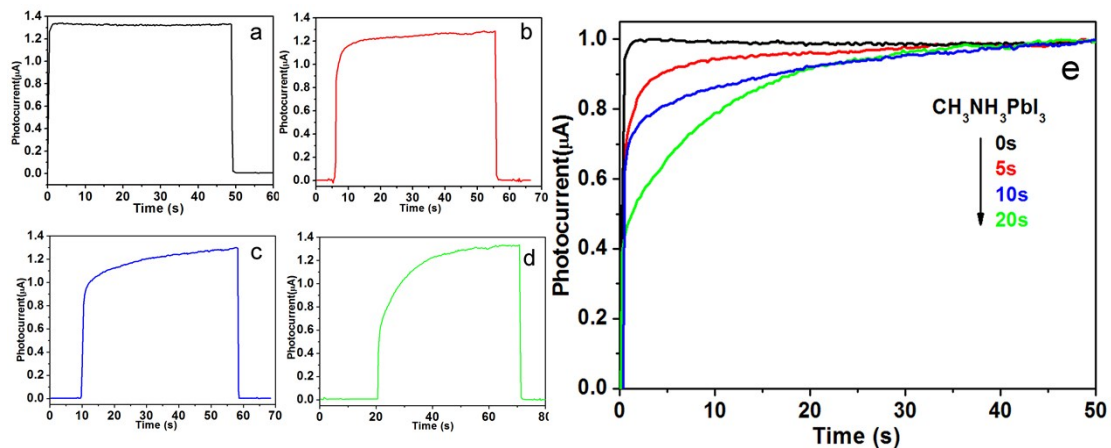


Fig. S6 I-T curves of $\text{CH}_3\text{NH}_3\text{PbI}_3$ under 1V bias before illumination for 0s (a), 5s (b), 10s (c), and 20s (d), normalized current derived from a-d (e), respectively.

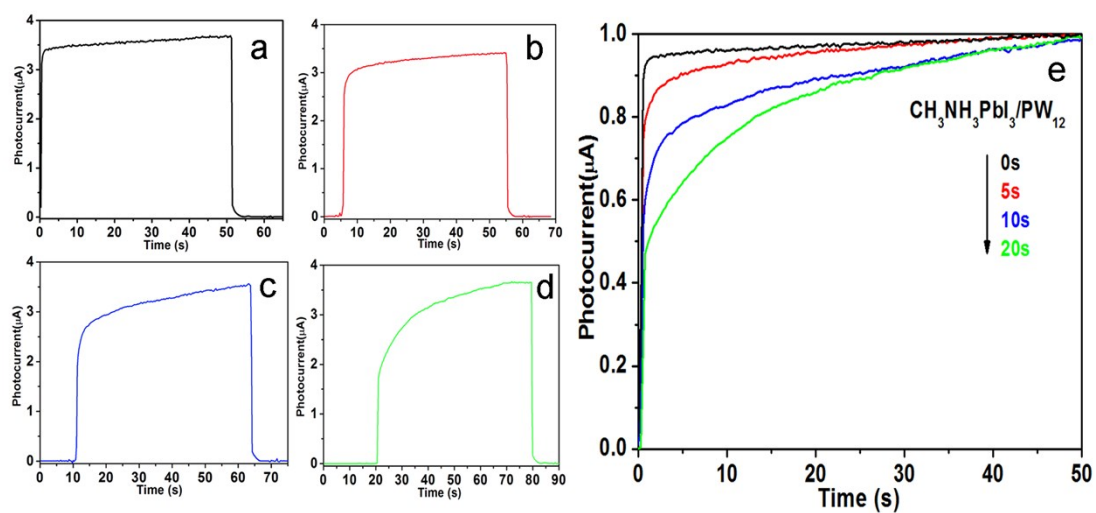


Fig. S7 I-T curves of $\text{CH}_3\text{NH}_3\text{PbI}_3/\text{PW}_{12}$ under 1V bias before illumination for 0s (a), 5s (b), 10s (c), and 20s (d), normalized current derived from a-d (e), respectively.

References

1. H. Wu, *J. Biol. Chem.*, 1920, **43**, 189.