Electronic Supplementary Information

All-inorganic perovskite quantum dot/mesoporous TiO_2 composite-based photodetectors with enhanced performance

Lin Zhou[a], Kai Yu[a], Fan Yang[a], Jun Zheng[a], Yuhua Zuo[*a],Chuanbo Li[a], Buwen Cheng[a] and Qiming Wang[a]

[a]State Key Laboratory on Integrated Optoelectronics, Institute of Semiconductors, Chinese Academy of Sciences, Beijing 100083, China

Experimental Section

Materials Preparation: All the reagents were purchased from Aladdin or Alfa Aesar and were used directly without further purification unless noted otherwise. As reported by Protesescu et al.,[1] Cs_2CO_3 (0.814 g) was loaded into a 250 mL 3-necked flask along with octadecene (ODE, 40 mL) and oleic acid (OA, 2.5 mL), dried for 1 h at 140 °C, and then heated under N_2 to 200 °C until all the Cs_2CO_3 reacted with OA. Because Cs-oleate precipitates out of ODE at room temperature, it was preheated to 100 °C before injection. ODE (5 mL), oleylamine (OAm, 0.5 mL), dried OA (0.5 mL), and $PbBr_2$ (0.069 g) were loaded into a 250 mL 3-necked flask and the temperature was increased to 120 °C under N_2. After complete solubilization of the $PbBr_2$ salt, the temperature was increased to 180 °C and a Cs-oleate solution (0.4 mL, 0.125 M in ODE, prepared as described above and preheated before injection) was quickly injected, and 5 s later, the reaction mixture was cooled using an ice-water bath. After centrifugation at 8000 rpm for 10 min, the supernatant was discarded and the particles were re-dispersed in n-hexane forming stable solutions of colloidal $CsPbBr_3$ QDs.

Device Fabrication: the glass substrates were cleaned successively using acetone, isopropanol, and de-ionized water. The planar interdigitated Ti/Au (50/200 nm) electrodes were fabricated using standard photolithography to pattern the photoresist for subsequent metallization and lift-off. We defined the channel length as 10 µm, while the finger widths and the channel widths were 10 µm and 2 mm, respectively. Then, the mesoporous TiO_2 (mp-TiO_2) was deposited on top of the substrate by spin-coating TiO_2 paste (Dyesol 18NR-T), which was diluted 4 times by absolute ethyl alcohol, at a rate of 2000 rpm for 30s. The layer was then sintered in air at 500 °C for 30 min. The thicknesses of the mp-TiO_2 films were controlled to ~200 nm. The above the $CsPbBr_3$ QDs solution (~1 mg/mL) was deposited on the substrate (2000 rpm, 10 s) by spin-coating (3 times) and finally washing with pure 2-propanol (2000 rpm, 10s). This device was named MSM II. For device MSM I, the $CsPbBr_3$ QD solution was drop-cast directly on a glass substrate with pre-patterned gold electrodes and annealed at 200 °C for 30 min in a N_2 atmosphere.

Characterization: The UV-Vis spectra of the nanocrystal solution were collected using a Shimadzu UV3600PLUS UV-Vis-NIR spectrophotometer over an excitation range of 400–600 nm, at 0.5 nm intervals. Photoluminescence (PL) spectra and time-resolved PL decay spectra were measured using the Edinburgh Instruments (EI) FLS980 lifetime and steady state spectrometer. High-resolution transmission electron microscopy (HR-TEM) of the nanocrystals of the $CsPbBr_3$ perovskites was performed using a FEI Tecnai G2 F20 S-TWIN field emission transmission electron microscope. X-ray diffraction (XRD) measurements of the perovskite nanocrystals powder was performed using a BRUKER, AXS D8 ADVANCE X-ray powder diffractometer using monochromatized Cu-Kα radiation (λ = 1.5406 Å). Film morphologies of the mp-TiO_2 films were characterized by field emission scanning electron microscopy (FEI, Nova NanoSEM650). The current-voltage characteristics and time response of the perovskite devices were recorded using a semiconductor device analyzer (Agilent B1500A, USA). A 150 W halogen lamp (MLC-150C, Motic Asia, Hong Kong) was used as the light source for the photovoltaic (I-V) and time response measurements. Photoresponsivity (R) was calculated by measuring the photocurrent I_{ph} and dividing this value by the incident power P_{inc}, such that $R = I_{ph}/P_{inc}$. The spectral photocurrent was measured using a Stanford Research Systems SR830 lock-in amplifier. The monochromatic illumination was provided by a monochromator (Zolix, Omni-λ500) supplied with a tungsten-halogen light source (Zolix, LSH-T150). The light intensities (P_{inc}) of the different wavelengths were measured by a photodiode power sensor (Thorlabs, S130VC). The light excitation was chopped at a frequency of 180 Hz. The device was biased using a Keithley 2611A system source meter. The detector was kept in a dark, shielded environment. And all characterizations were performed in air at room temperature.

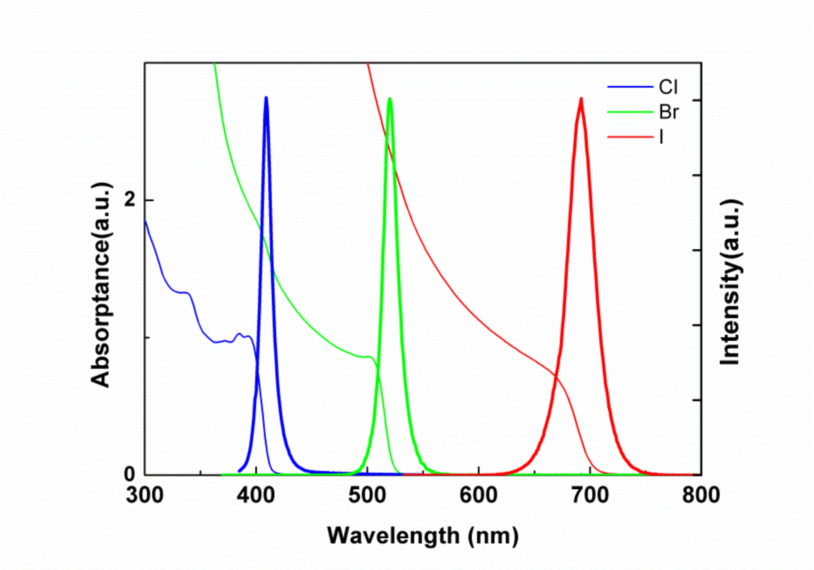

Fig. S1 Absorption and photoluminescence (PL) spectra of $CsPbX_3$ (X = Cl, Br, or I) QDs in solution.

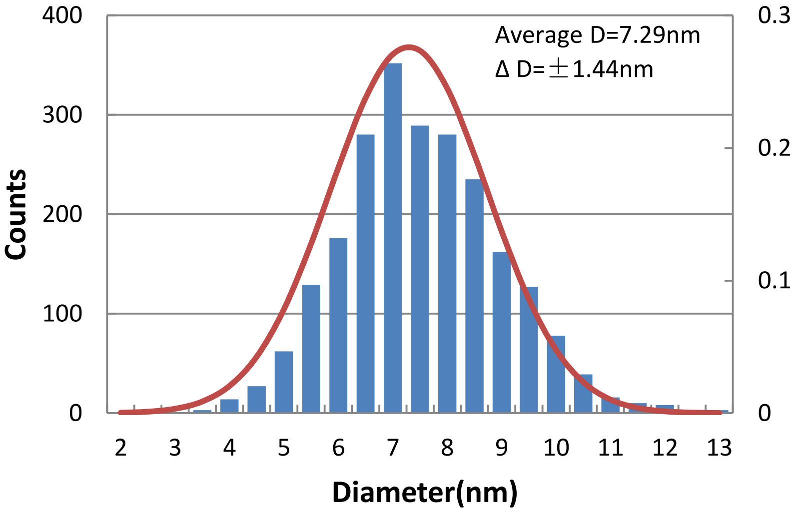

Fig. S2 Analysis of size distribution for the sample shown in Fig. 1(c).

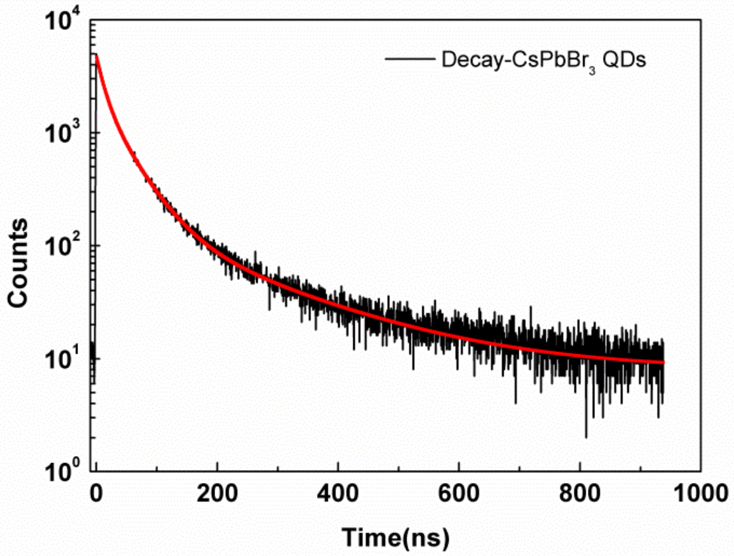

Fig. S3 Time-resolved PL decay and radiative lifetime of $CsPbBr_3$ QDs in n-hexane solution.

Sample	τ_1 (ns)	Ratio1	τ_2 (ns)	Ratio2	τ_3 (ns)	Ratio3	$\tau_{ave}{}^{\#}$
pure QDs film	1.5	38.3%	7.5	39.3%	57.1	22.4%	16.31ns
QDs on mp-TiO_2	1.0	37.2%	4.0	46.4%	16.5	16.4%	4.93ns
QDs in n-hexane solution	12.3	21.3%	42.4	56.4%	189.0	22.3%	68.68ns

$^{\#}\tau_{ave}$ = Ratio1*τ_1+ Ratio2*τ_2+ Ratio3*τ_3

Table S1. Values for TRPL characteristics of pure QDs film after annealing, QDs on mp-TiO_2, and QDs in n-hexane solution.

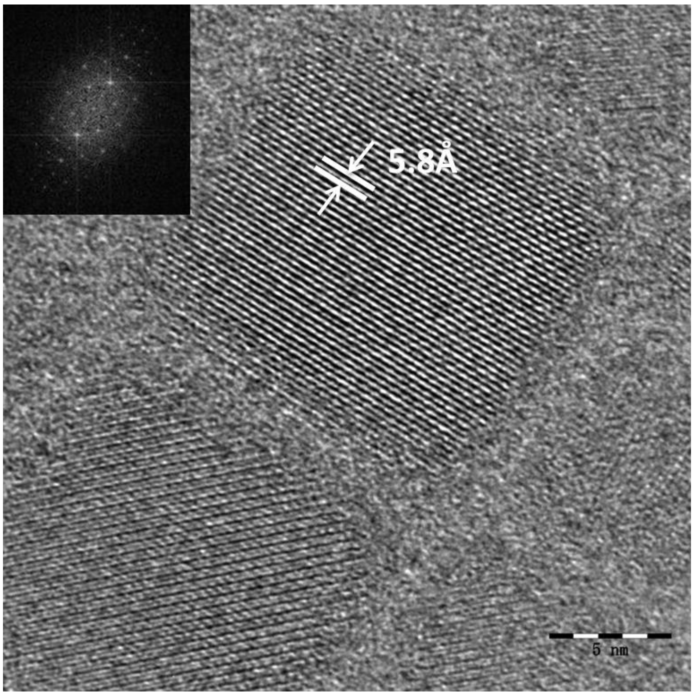

Fig. S4 HRTEM images of a typical $CsPbBr_3$ QDs QDs (scale bar 5 nm). The insets in the top left corner are the corresponding FFT images.

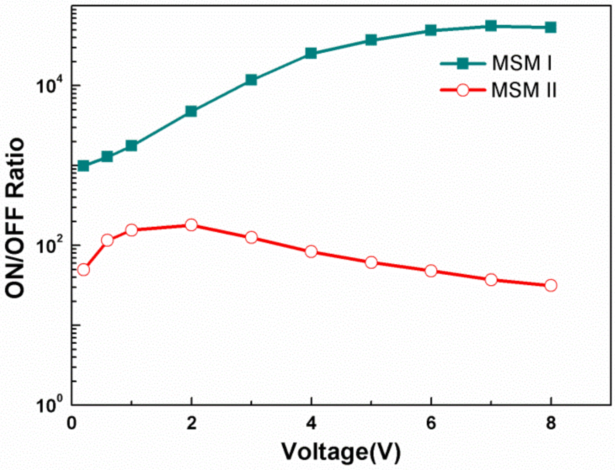

Fig. S5 On/off ratios of the devices at different bias.

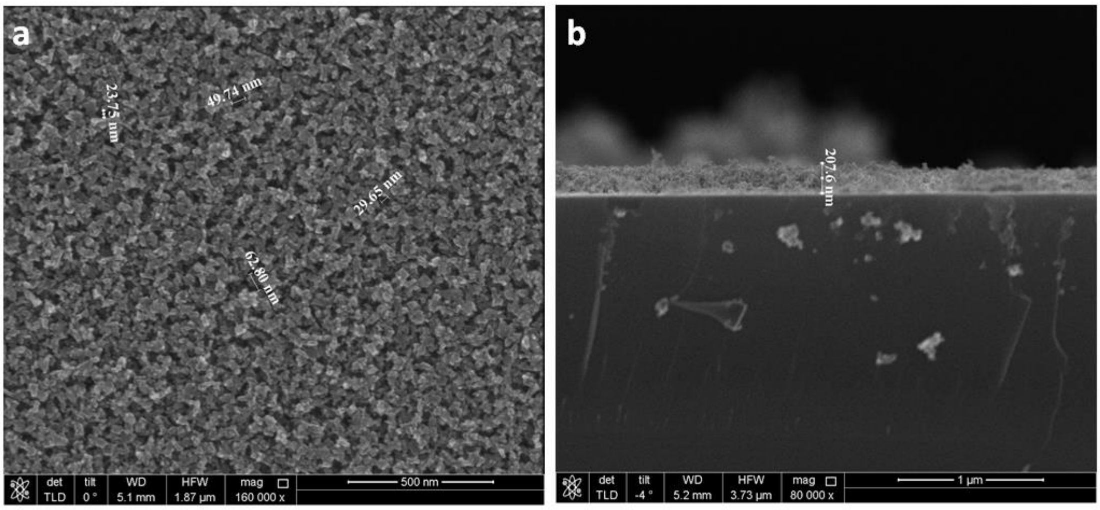

Fig. S6 Morphology of the mp-TiO_2 film on Si substrate. a) Top view SEM images. b) SEM cross-sectional images of the mp-TiO_2 film.

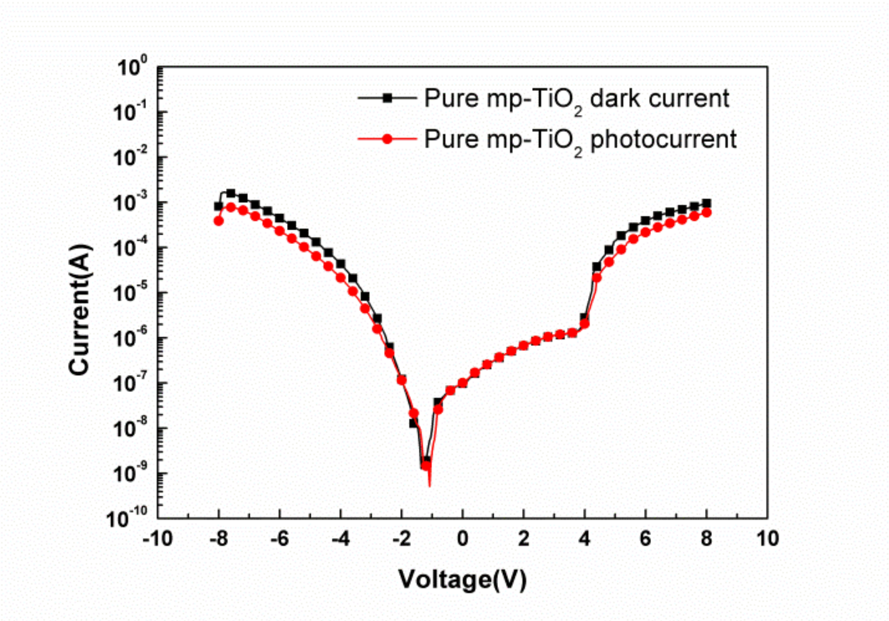

Fig. S7 Dark and photocurrent I-V curves of our fabricated mp-TiO_2-based photodetectors.

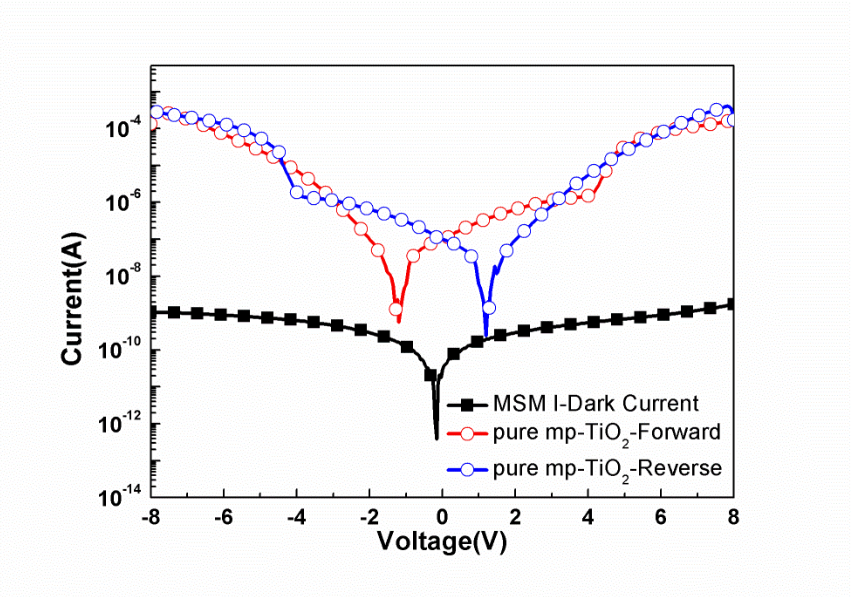

Fig. S8 Dark current curves of the device MSM I and the pure mp-TiO_2 device.

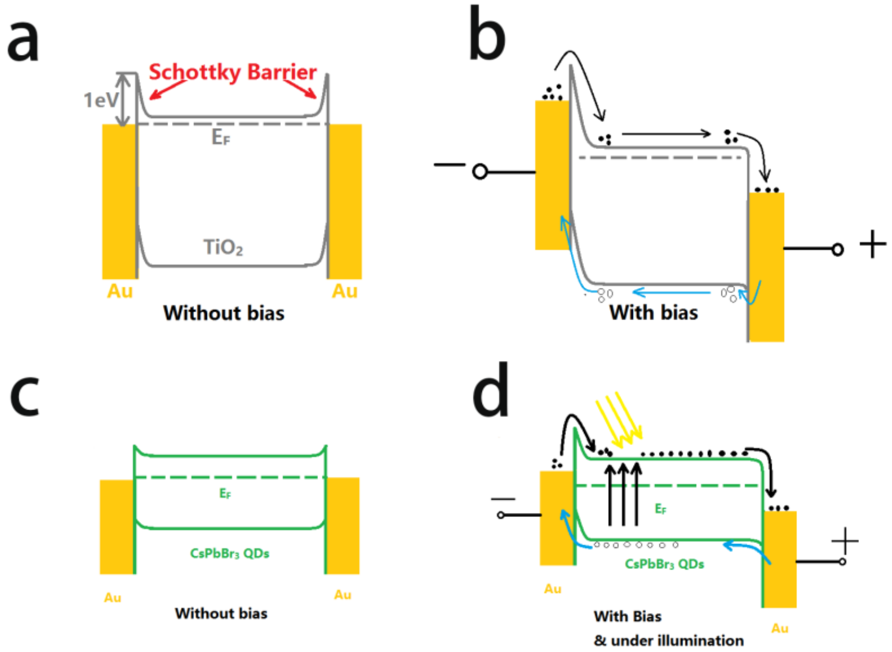

Fig. S9 Schematic energy-band diagrams of MSM I. a) Au/$CsPbBr_3$ QDs/Au MSM device without external bias. b) The device MSM I with external bias under illumination.

1. L. Protesescu, S. Yakunin, M. I. Bodnarchuk, F. Krieg, R. Caputo, C. H. Hendon, R. X. Yang, A. Walsh and M. V. Kovalenko, *Nano letters*, 2015, **15**, 3692-3696.