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., $Cs_2CO_3$ (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 ($\lambda = 1.5406$ 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 CsPbX₃ (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 CsPbBr₃ QDs in n-hexane solution.

<table>
<thead>
<tr>
<th>Sample</th>
<th>τ₁ (ns)</th>
<th>Ratio₁</th>
<th>τ₂ (ns)</th>
<th>Ratio₂</th>
<th>τ₃ (ns)</th>
<th>Ratio₃</th>
<th>τave</th>
</tr>
</thead>
<tbody>
<tr>
<td>pure QDs film</td>
<td>1.5</td>
<td>38.3%</td>
<td>7.5</td>
<td>39.3%</td>
<td>57.1</td>
<td>22.4%</td>
<td>16.31ns</td>
</tr>
<tr>
<td>QDs on mp-TiO₂</td>
<td>1.0</td>
<td>37.2%</td>
<td>4.0</td>
<td>46.4%</td>
<td>16.5</td>
<td>16.4%</td>
<td>4.93ns</td>
</tr>
<tr>
<td>QDs in n-hexane solution</td>
<td>12.3</td>
<td>21.3%</td>
<td>42.4</td>
<td>56.4%</td>
<td>189.0</td>
<td>22.3%</td>
<td>68.68ns</td>
</tr>
</tbody>
</table>

τave = Ratio₁*τ₁ + Ratio₂*τ₂ + Ratio₃*τ₃

Table S1. Values for TRPL characteristics of pure QDs film after annealing, QDs on mp-TiO₂, 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.