[Supporting information]

High Performance Hybrid Graphene-$CsPbBr_{3-x}I_x$ Perovskite Nanocrystals Photodetector

Do-Hyun Kwak, Da-Hye Lim, Hyun-Soo Ra, Parthiban Ramasamy, Jong-Soo Lee*

[a]*Department of Energy Systems Engineering, DGIST, Daegu 711-873, Republic of Korea*

Experimental Section.

Materials:

Cesium carbonate (Cs_2CO_3, 99.9%), Lead(II) bromide ($PbBr_2$, 99.999%), Lithium iodide (LiI, 99%) were all used as received from Sigma Aldrich. 1-octadecene (ODE, 90%), Hexane (95%, anhydrous grade) and Ethanol (anhydrous grade, 99.5%) were purchased from Sigma-Aldrich and used without further purification. Oleic acid (OA, 90%) and Oleylamine (OAm, 70%) were purchased from Sigma-Aldrich and dried under vacuum.

Preparation of Cs-oleate:

0.207 g of Cs_2CO_3 was mixed with 10 mL of ODE and 625 μL of OA in a three neck flask. The mixture was dried under vacuum at 120 °C for 1 h. Then the mixture was heated to 150 °C under N_2 until all Cs_2CO_3 reacted with OA and kept at 100 °C.

Synthesis of $CsPbBr_3$ Nanocrystals:

0.069 g of $PbBr_2$ and 5 mL of ODE were loaded into 25 mL 3-neck flask and dried under vacuum for 1h at 120 ºC. Dried OAm (0.5 mL) and dried OA (0.5 mL) were injected at 120 ºC under N_2. After complete solubilisation of a $PbBr_2$ salt, the temperature was raised to 160 °C. Then 0.4 mL of above mentioned Cs-oleate solution was injected quickly and 5s later, the reaction mixture was cooled by the ice-water bath. The NCs were precipitated using ethanol, re-dispersed in 30 mL of hexane and filtered through 0.2 μm PTFE filter.

Anion exchange reactions:

All the exchange reactions were carried out at room temperature in air. Typically. 10mg LiI powder was added to 1mL of above prepared $CsPbBr_3$ NCs in hexane. Then the mixture was shaken vigorously which produced a color change from green to red. The whole exchange reaction was completed in less than 5 seconds. Then the mixture was filtered through 0.2 µm PTFE filter.

Characterization

X-Ray Diffraction (XRD). X-ray diffractograms were obtained by using a Rigaku MiniFlex 600 diffractometer, equipped with a Cu Kα X-ray source (λ=1.5418 Å). Samples for XRD analysis were prepared by depositing a hexane dispersions NCs on a microscopic glass substrate.

Transmission electron microscopy (TEM) images were recorded on a Hitachi HF-3300 microscope operating at 300 kV. Samples were prepared by dropping a diluted nanosheet solution onto carbon coated copper grids.

UV-vis Absorption Spectroscopy. Absorption spectra of NCs dispersed in hexane were measured in 1 cm path length quartz cuvettes using a Cary 5000 UV-vis-NIR (Agilent Technologies) spectrophotometer. Photoluminescence Spectroscopy. PL spectra of NCs dispersed in hexane were measured using Cary Eclipse fluorescence spectrophotometer. (λ_{exc} = 350 nm for all samples).

A Raman spectrometer (NICOLET ALMECA XR, Thermo scientific) equipped with a 532-nm laser was used to characterize the thickness of the graphene. The scanning range was high resolution from 1200 to 3000 Raman shift (cm^{-1}).

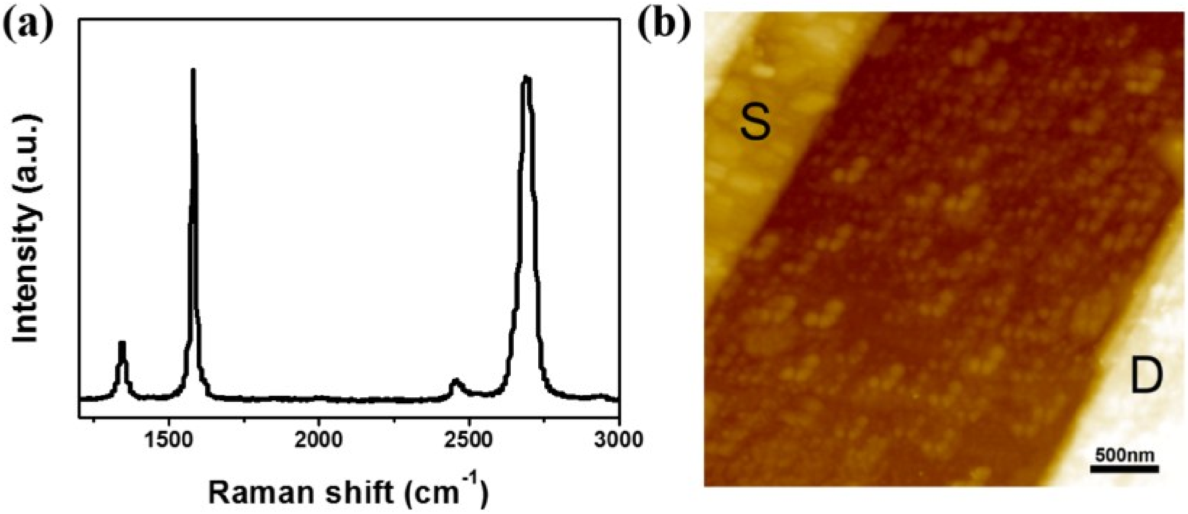

Fig. S1. (a) Raman spectra of graphene used in the study. The 2D peak and G peak of the graphene are similar intensity, which indicates bilayer graphene. (b) Top-view AFM image of graphene-CsPbBr$_{3-x}$I$_x$ NCs photodetector.

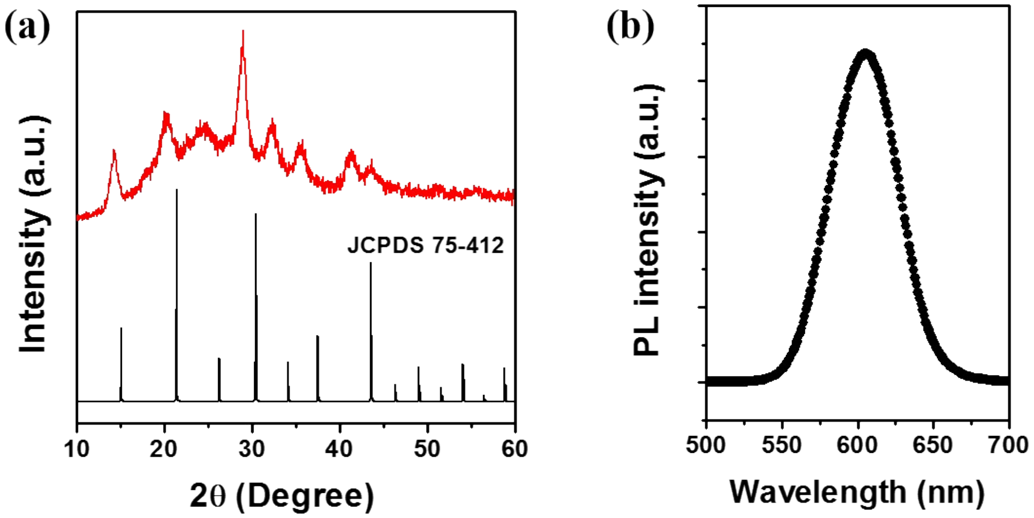

Fig. S2. (a) XRD pattern of $CsPbBr_{3-x}I_x$ NCs (up) and $CsPbBr_3$ (down). The peaks of $CsPbBr_{3-x}I_x$ NCs are shifted to low angle at comparing peaks of the $CsPbBr_3$ NCs. Doping large I atom to $CsPbBr_3$ NCs results in the extend lattice. (b) PL spectra of $CsPbBr_{3-x}I_x$ NCs.

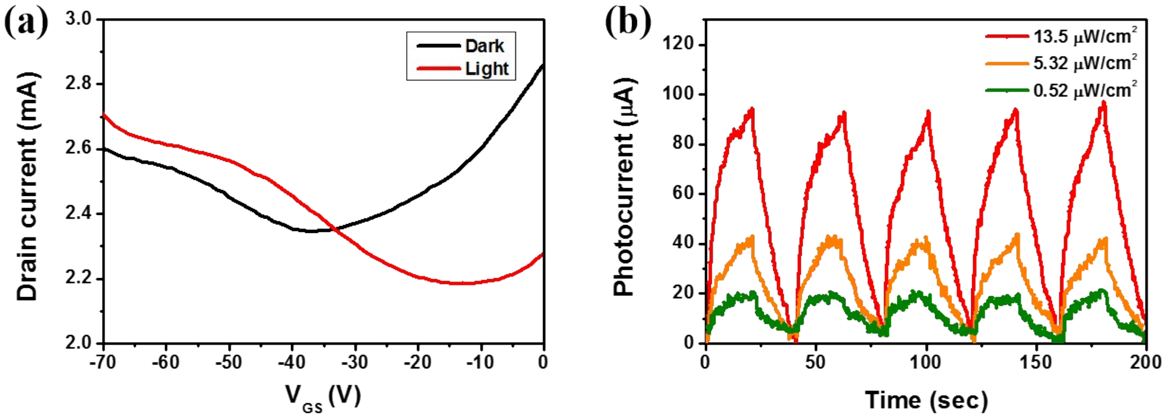

Fig. S3. (a) Transfer curve of graphene-$CsPbBr_{3-x}I_x$ NCs photodetector as a function of gate-source voltage at 1 V_{DS}. (b) Temporal response of graphene-$CsPbBr_{3-x}I_x$ NCs photodetector for on/off illumination at bias 1 V_{DS} and -60 V_{GS}.