Supporting Information

Plasmonic-Enhanced Perovskite-Graphene Hybrid Photodetectors

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Material Preparation and Characterization: Au-NPs with a diameter of ~ 40 nm were synthesized according to a modified sodium citrate reduction method.[1] Specifically, 100ml aqueous solution of $HAuCl_4$ (0.25 mM) was heated to boiling. 0.5 ml aqueous solution of sodium citrate (1 wt%) was added into the $HAuCl_4$ solution under strong stirring. The color of the mixture changed from transparent to blue, then to deep red in a few minutes. The final solution was purified by centrifugation and then dispersed in ethanol just before use. Single-layer graphene was grown on copper foils by CVD and then transferred onto substrates by methods reported before.[2, 3] $CH_3NH_3PbI_3$ precursor

solution in dimethylformamide (DMF) was prepared according to a previously reported method.[4, 5]. First, CH_3NH_3I was synthesized by reacting 10 ml methylamine (33 wt% in absolute ethanol, Aldrich) and 10 ml hydroiodic acid (57 wt% in water, Aldrich) in a 150 ml round-bottomed flask in an ice bath during 2 hours and then at room temperature for another 1 hour with magnetic stirring. The precipitate was then recovered by rotatory evaporation at 50 °C. The product was further purified twice by precipitation in diethylether and re-dissolution in ethanol. The obtained white solid was dried at 60 °C in a vacuum oven for 24 hours. The $CH_3NH_3PbI_3$ precursor solution of 40 wt% concentration was prepared by mixing CH_3NH_3I powder with PbI_2 (Aldrich) at a 1:1 molar ratio in DMF at 60 °C with magnetic stirring for 12 hours. This solution was ready for use after twice filtration by PTFE syringe filters (0.45 μm pore size). All UV-Visible absorption spectra presented were recorded by a Varian Cary-5E spectrometer. Raman spectrum of graphene was acquired by a Horiba Jobin-Yvon XploRA ONE™ Raman microscope with excitation laser of 532 nm. X-ray diffraction (XRD) spectrum of CH3NH3PbI3 was measured using a PANalytical Philips X'pert system (Cu K-alpha radiation).

SONM measurements: A fluorescent nanoparticle (f-NP) was glued at the end of a sharp AFM tip that scans the sample surface in a tapping mode. The tip/f-NP/sample region was illuminated with a 658 nm laser diode in a transmission mode at normal incidence from the bottom of the sample as described in previous works[6, 7]. The fluorescence signal from the f-NP was recorded simultaneously with the topography

signal. When this f-NP is near the Au-NPs, its fluorescence increases due to enhanced local electromagnetic field boosted by the plasmonic effect of Au-NPs.

Device Fabrication and Characterization: To fabricate phototransistor devices, gold electrodes were first defined onto bare Si/SiO_2 substrates by photolithography and thermal evaporation. In a P-G-Au devices, Au-NPs were bonded on the Si/SiO_2 substrate (the thickness of SiO_2 = 300 nm) through a self-assembled monolayer of 3-aminopropyl-triethoxysilane (APTES) according to a reported method.[8] Specifically, a substrate was first cleaned in a sonication bath of acetone, ethanol and water respectively. The dried substrate was then treated with oxygen plasma. It was then immersed into an APTES solution for 12 hours. After being rinsed with ethanol and dried, the substrate was placed into an Au-NPs water solution for 1 hour. The substrate was further dipped into ethanol for five minutes and dried gently before use. The resulted transistor patterns have a channel length (W) of 40 μm and a channel width (L) of 2 cm. Graphene was transfer onto either the bare or the Au-NPs bonding Si/SiO_2 substrates. The perovskite films were formed by spin-coating $CH_3NH_3PbI_3$ precursor solution followed by 1 hour of annealing at 100 °C. The Scanning Electron Microscope images of Au-NPs on substrates were acquired using FEI MAGELLAN 400 SEM with field emission gun source. The photoresponse of devices were characterized using a laser (wavelength = 532 nm) and a computer-controlled Keithley 2612B Source Measurement Unit.

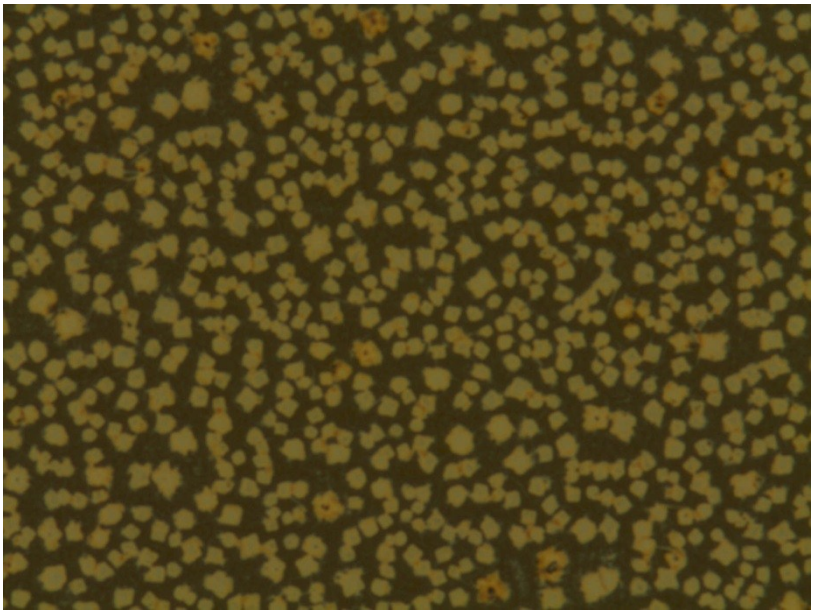

Figure S1. Optical microscope image of the $CH_3NH_3PbI_3$ layer, indicating isolated island-like morphology.

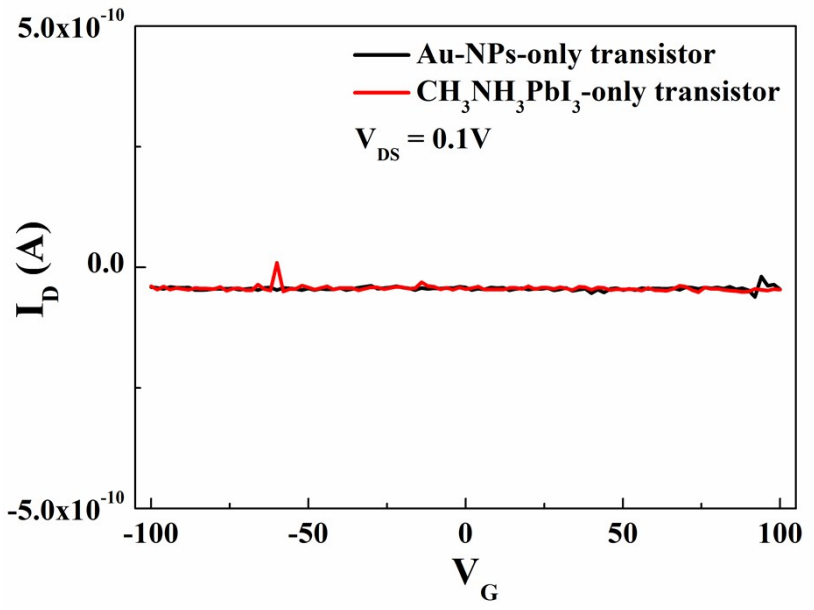

Figure S2. Transfer characteristics of the transistor with only Au-NPs or with only $CH_3NH_3PbI_3$ deposited on the Si/SiO_2 substrates.

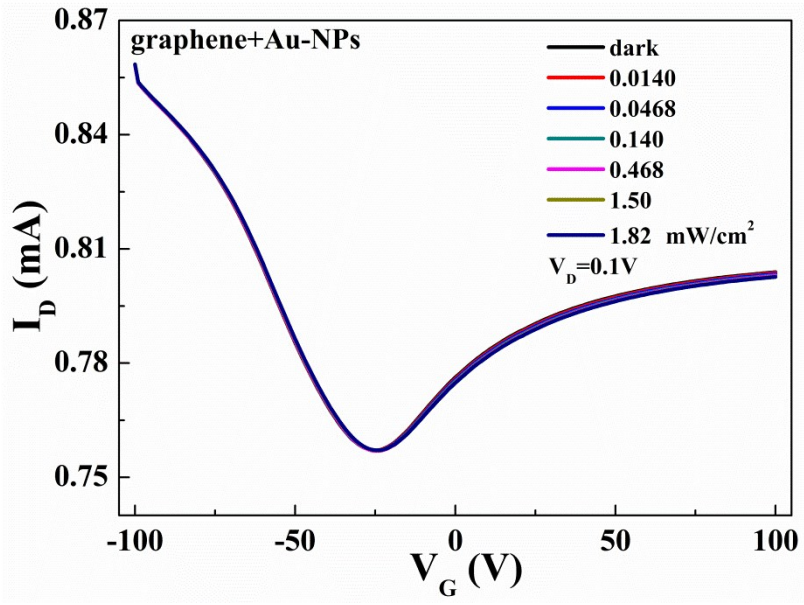

Figure S3. Transfer characteristics of the graphene-Au-NPs device under a V_{DS} bias of 0.1 V and under an illumination of a wavelength of 532 nm at different light intensities

Reference

1. B. V. Enustun and J. Turkevich, *J Am Chem Soc*, 1963, **85**, 3317.
2. S. P. Pang, Y. Hernandez, X. L. Feng and K. Mullen, *Adv Mater*, 2011, **23**, 2779-2795.
3. Z. K. Liu, J. H. Li and F. Yan, *Adv Mater*, 2013, **25**, 4296-4301.
4. J. H. Heo, S. H. Im, J. H. Noh, T. N. Mandal, C. S. Lim, J. A. Chang, Y. H. Lee, H. J. Kim, A. Sarkar, M. K. Nazeeruddin, M. Gratzel and S. I. Seok, *Nat Photonics*, 2013, **7**, 487-492.
5. M. M. Lee, J. Teuscher, T. Miyasaka, T. N. Murakami and H. J. Snaith, *Science*, 2012, **338**, 643-647.
6. L. Aigouy, P. Prieto, A. Vitrey, J. Anguita, A. Cebollada, M. U. Gonzalez, A. Garcia-Martin, J. Labeguerie-Egea and M. Mortier, *J Appl Phys*, 2011, **110**.
7. A. Vitrey, L. Aigouy, P. Prieto, J. M. Garcia-Martin and M. U. Gonzalez, *Nano Lett*, 2014, **14**, 2079-2085.
8. A. P. Kulkarni, K. M. Noone, K. Munechika, S. R. Guyer and D. S. Ginger, *Nano Lett*, 2010, **10**, 1501-1505.