†Electronic Supplementary Information

Plasmon Resonance Scattering at Perovskite $CH_3NH_3PbI_3$ Coated Single Gold Nanoparticle: Evidence for Electron Transfer†

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Experimental Section

Chemicals and Reagents.

Gold chloride trihydrate ($HAuCl_4 \cdot 3H_2O$, >99.0%) and lead diiodide (PbI_2, >99.999%) were obtained from Sigma-Aldrich. Sodium citrate and hydroxylamine hydrochloride ($NH_2OH \cdot HCl$) were bought from Shanghai Lingfeng Chemical Reagent Co., Ltd. (China). N-dimethylformamide (DMF) was purchased from Sinopharm Chemical Reagent Co., Ltd. (Shanghai, China). Methylammonium iodide (MAI, >99.5%) was purchased from Shanghai MaterWin New Materials Co., Ltd. (China). The indium tin oxide (ITO) slides were purchased from Zhuhai Kaivo Optoelectronic Technology Co., Ltd. (China). All chemicals were analytically pure. Ultrapure water (resistivity = 18.2 MΩ cm) produced from a Milli-Q apparatus was used throughout the experiments.

Preparation of 62 nm Gold Nanoparticles.

Gold particle seeds with diameters of 14 nm were synthesized by the citrate-mediated reduction of $HAuCl_4$. 50 mL of 0.01 wt.% $HAuCl_4$ was heated with a condenser under vigorous stirring and then added 5 mL of 38.8 mM sodium citrate rapidly. The solution was heated for 15 min, and the solution was stirred for another 15 min after heat treatment. These gold particle seeds were then used for the synthesis of the 62 nm gold nanoparticles (GNPs). 1 mL seed nanoparticles and 100 μL of 0.2 M $NH_2OH \cdot HCl$ were mixed into 25 mL water. Then 3.0 mL of 0.1 wt.% $HAuCl_4$ was added under vigorous stirring. Colloidal particles with average diameters of 62 nm were characterized by an absorption maximum at 537 nm by using UV-vis spectrometry.[1]

Synthesis of Organic-Inorganic Hybrid Perovskite $CH_3NH_3PbI_3$.

To obtain a uniform perovskite precursor, MAI and PbI_2 was mixed at a 1:1 molar ratio and dissolved in anhydrous DMF (40% w/w) under vigorous magnetic stirring for 12 h. This solution was reacted and stored under a dry nitrogen atmosphere. Then, the as-prepared precursor was coated on the ITO slides and annealed at 100 °C for 1 h in N_2 to get the $CH_3NH_3PbI_3$ sample.[2]

Preparation of the Samples.

The surface of ITO slides were cleaned in an ultrasonic bath by using ethanol, acetone and water to remove oil matter and water-soluble matter, respectively. Each step was maintained for more than one hour. The cleaned ITO slides were placed in the diluted gold colloid solution (20 times) for 2 minutes. Then, the GNPs-modified ITO slides were rinsed with water, dried under a steam of nitrogen and coated with $CH_3NH_3PbI_3$ precursor. To facilitate the dark-field observation, the superfluous solution was removed with pipette. Finally, the modified ITO slides were annealed at 100 °C for 1 h in N_2.

Dark-Field Microscope and Scattering Spectroscopy.

The dark-field measurements were performed on an inverted microscope (eclipse Ti-U, Nikon, Japan) that was equipped with a dark-field condenser (0.8 <NA <0.95) and a 40×objective lens (NA = 0.8). The white light source was a 100 W halogen lamp, which applied to excite the GNPs and produced plasmon resonance scattering light. A true-color digital camera (Nikon DS-fi, Japan) was used to capture the dark-field color images. A monochromator (Acton SP2300i) equipped with a grating (grating density: 300 lines/mm; blazed wavelength: 500 nm) and recorded by a spectrometer CCD (PIXIS 400, Princeton Instruments, USA) were applied to obtain the scattering spectra of single nanoparticle.

Material Characterizations.

TEM images were recorded with a transmission electron microscope (JEOL, JEM-1400) at 120 kV. UV-vis spectrum was carried out on an Ocean Optics USB 2000+ UV-vis spectrophometer. SEM characterizations of the samples were performed on a scanning electron microscope (Hitachi, S-4800) at 15 kV, equipped with a Bruker QUANTAX 400-30 EDS analyzer. XRD spectra were obtained on a Bruker D8 FOCUS X-ray diffraction in range of 10°–80°. TOF-SIMS chemical analysis is carried out with a TOF-SIMS V instrument (IONTOF GmbH, Germany).

Reference

1. L. Shi, C. Jing, W. Ma, D. W. Li, J. E. Halls, F. Marken and Y. T. Long, *Angew. Chem. Int. Edit.,* 2013, **52**, 6011-6014.

2. D. W. de Quilettes, S. M. Vorpahl, S. D. Stranks, H. Nagaoka, G. E. Eperon, M. E. Ziffer, H. J. Snaith and D. S. Ginger, *Science*, 2015, **348**, 683-686.

Figure S1-S10

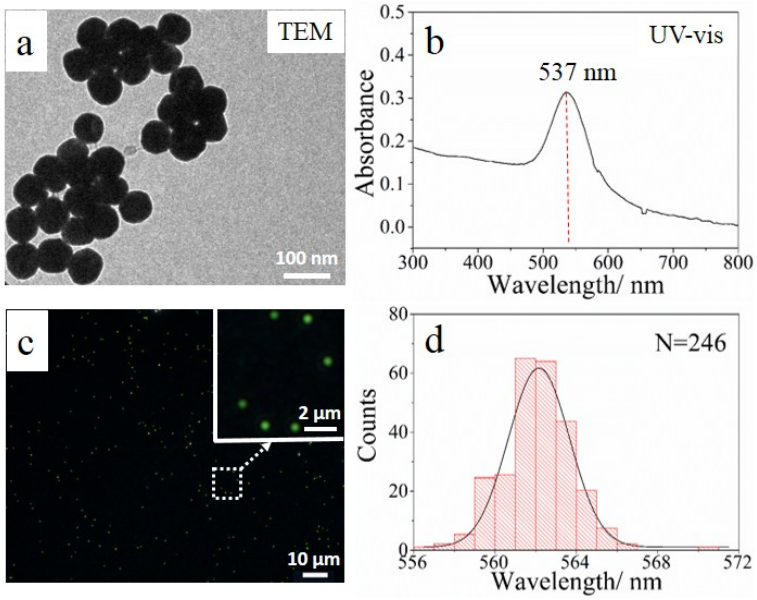

Figure S1. TEM image (a), UV-vis spectrum (b), dark-field images (c) of the synthesized GNPs and statistic peak wavelength distribution calculated by nanoparticleAnalysis program (d).

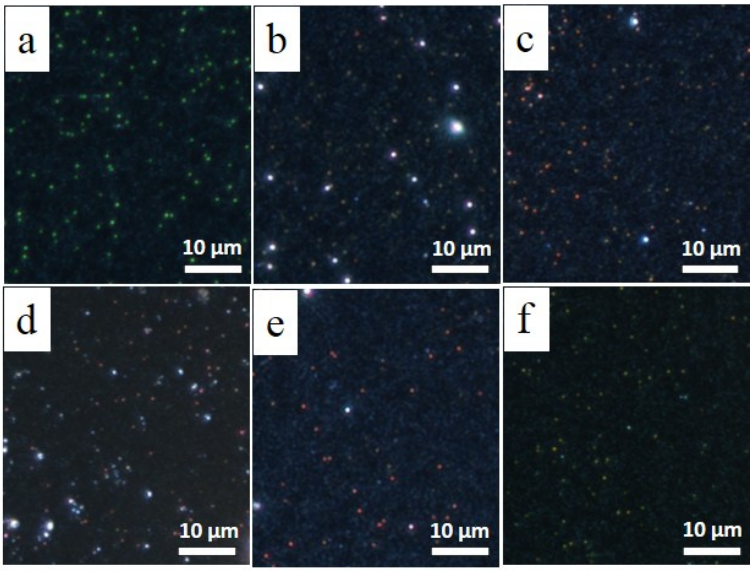

Figure S2. Dark-field images of the GNPs before (a) and after annealing with 5, 10, 20, 30, 40 wt.% (b-f) $CH_3NH_3PbI_3$ in N_2.

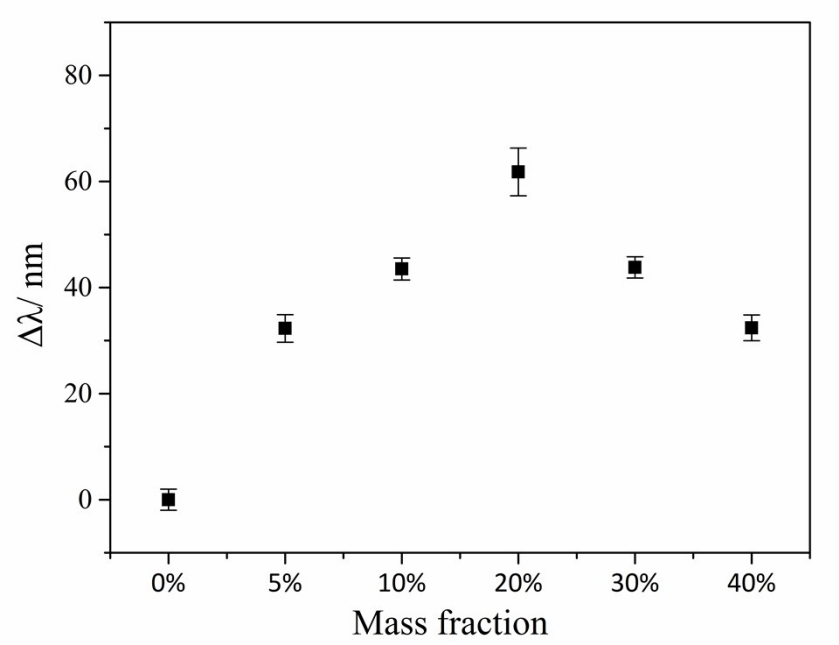

Figure S3. Plots of peak shift for GNPs acquired from Gaussian fitting of the histogram before (0 wt.%) and after annealing with $CH_3NH_3PbI_3$ of 5, 10, 20, 30 and 40 wt.%.

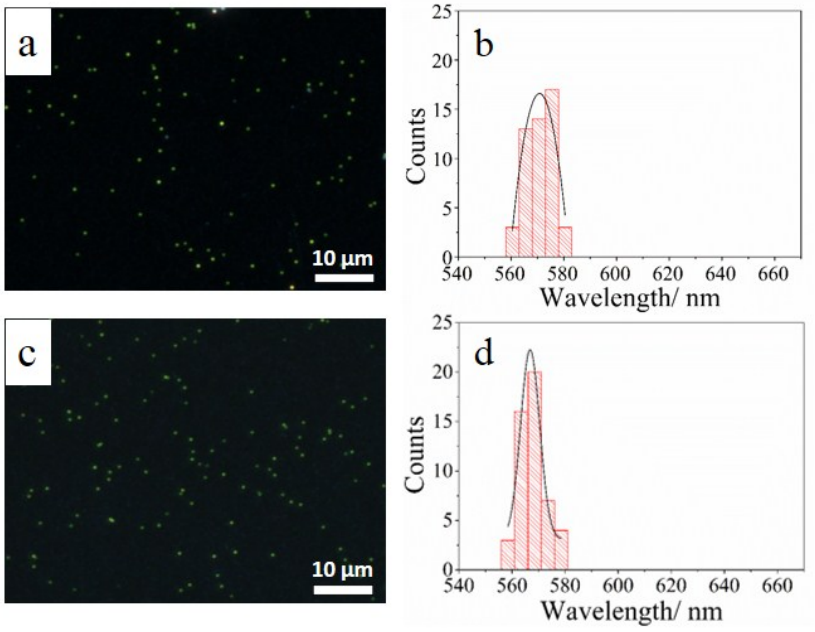

Figure S4. The dark-field images and scattering peak wavelength of GNPs after annealing in the absence (a, b) and presence (c, d) of DMF.

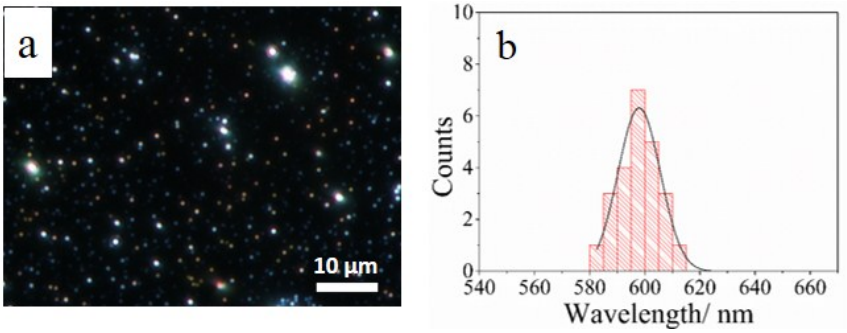

Figure S5. The dark-field image and scattering peak wavelength of GNPs after annealing with 40 wt.% $CH_3NH_3PbI_3$ on the glass.

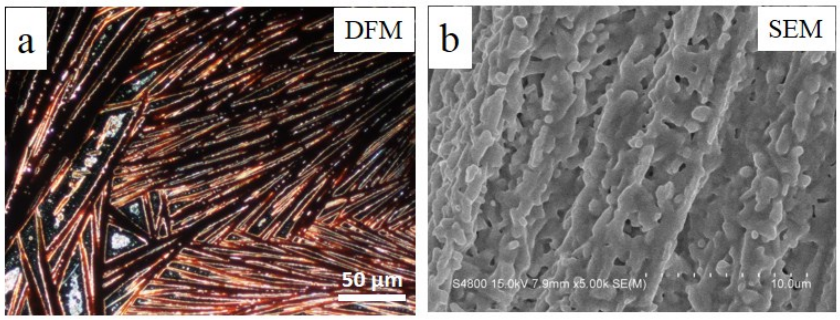

Figure S6. The DFM images (a) and SEM images (b) of $CH_3NH_3PbI_3$ thin film (40 wt.%).

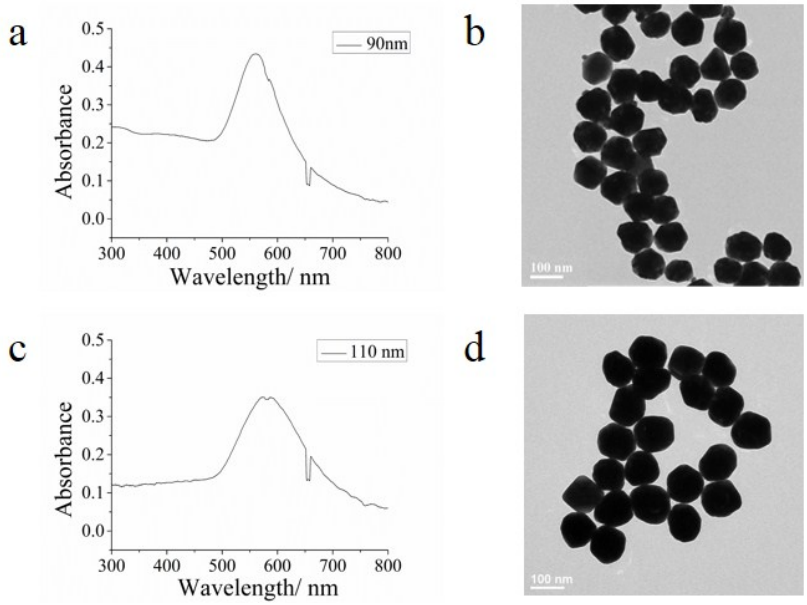

Figure S7. UV-vis spectra and TEM images of 90 nm (a, b) and 110 nm (c, d) GNPs.

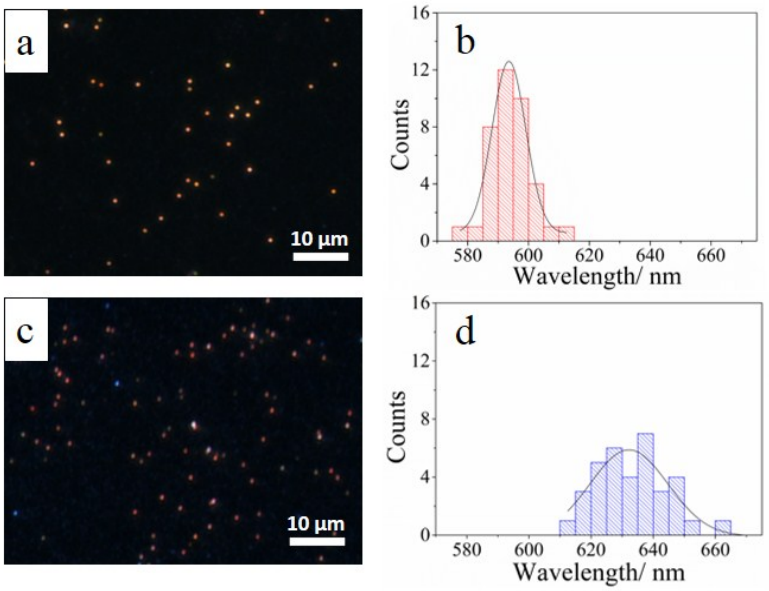

Figure S8. The dark-field images and scattering peak wavelength of 90 nm GNPs before (a, b) and after (c, d) annealing with 20 wt.% $CH_3NH_3PbI_3$.

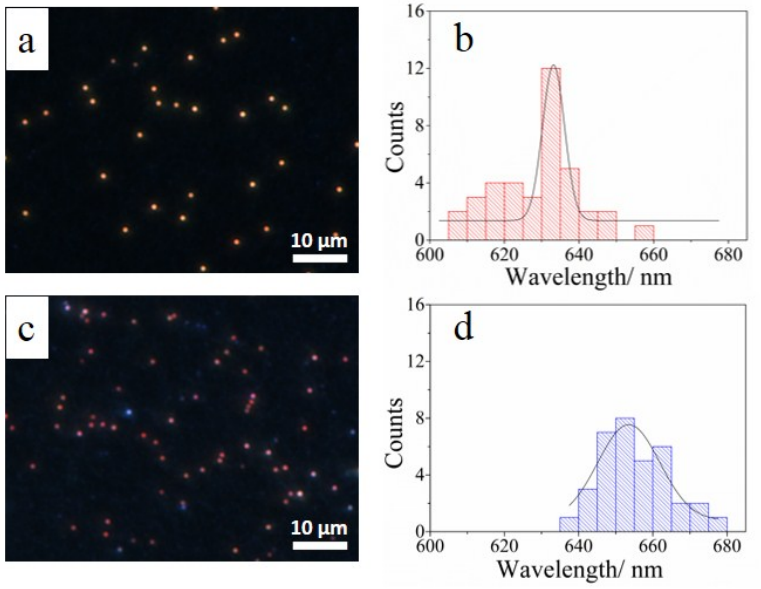

Figure S9. The dark-field images and scattering peak wavelength of 110 nm GNPs before (a, b) and after (c, d) annealing with 20 wt.% $CH_3NH_3PbI_3$.

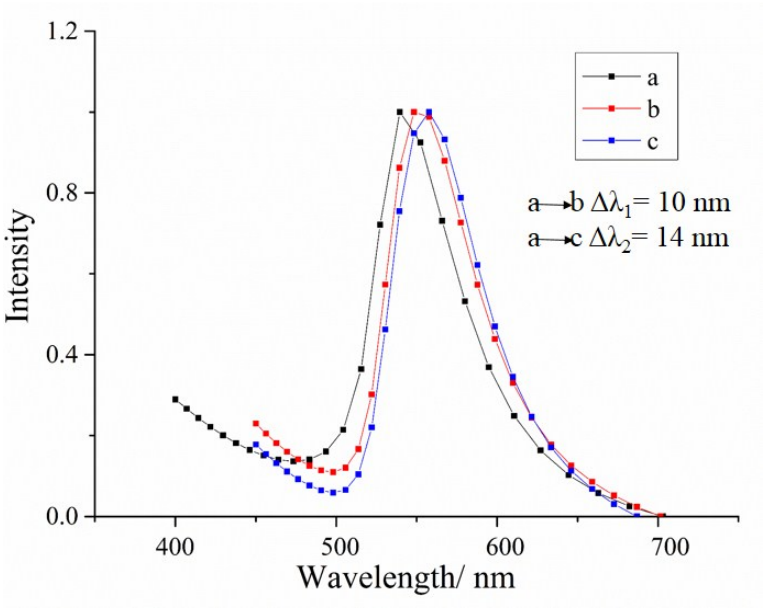

Figure S10. Scattering peak simulation of 62 nm GNPs before (a) and after coated with 5 nm (b) and 10 nm (c) $CH_3NH_3PbI_3$.