

Supporting Information

Au Nanoparticles on Ultrathin MoS₂ Sheets for Plasmonic Organic Solar Cells

Xi Yang,[‡] Wenqing Liu,[‡] Min Xiong, Yingying Zhang, Tao Liang, Jingting Yang, Mingsheng Xu,*
Jian Ye* and Hongzheng Chen*

Experimental Section

Gold Nanoparticle Synthesis: Tetrachloroauratetrihydrate (HAuCl₄·3H₂O) and sodium citrate were purchased from Aldrich and used as received. Au NPs were synthesized according to the standardized sodium citrate reduction method, which was followed by the surface functionalization of Polyvinylpyrrolidone (PVP).¹⁰⁻¹² Typically, the PVP and the colloidal solutions were mixed and stirred for 24 h at room temperature. The resultant Au nanoparticles were purified through high-speed centrifugation and re-dispersion, which were repeated more than 5 times. The final Au NPs solutions were concentrated into 3 mg/mL in deionized water.

MoS₂ nanosheet Synthesis: Chemically exfoliated MoS₂ nanosheets were synthesized through Li intercalation.³³ 0.3 g pristine MoS₂ crystals (Sigma-Aldrich) were immersed in 3 mL of 1.6 M butyllithium solution in hexane for 2 days in glovebox. The Li_xMoS₂ was filtrated and washed with hexane to remove excess lithium and organic residues. Exfoliation was achieved immediately by ultrasonicing Li_xMoS₂ in water (10 mg/mL) for 2 h. Exfoliated MoS₂ solution was then dialyzed using MW 10,000 cut-off membranes for 5 days, followed by 4000 rpm centrifugation to remove any un-exfoliated aggregates.

MoS₂@Au composite Synthesis: The aqueous solution of Au NPs and MoS₂ nanosheets were mixed together with vigorous stirring for 5 min and the resulted mixture was purified through high-speed centrifugation and re-dispersion to remove any unattached Au NPs. MoS₂@Au composite with different decoration coverage was realized by tuning the added volume of Au NPs solutions into the MoS₂ solution.³² Typically, a decoration coverage read as 5 vol% was obtained by mixing 10 μ L 2 mg/mL Au NPs with 200 μ L 2 mg/mL MoS₂. The MoS₂@Au composite thin film was deposited by multi-step spin-coating. For the HTL deposition in OSC devices, 3 times spin-coating was used to fully cover the ITO substrate.

Device fabrication: Prior to device fabrication, the ITO substrates were cleaned by sonication using detergent, deionized water, acetone, and isopropanol sequentially for every 15 min followed by 15 min of ultraviolet ozone treatment. The MoS₂ or MoS₂@Au composite was spin-coated onto ITO for 3 times from their aqueous solution without further annealing. Then the substrates were transferred into a glovebox for spin coating of PTB7:PC₇₁BM (1:1.5) active layer with a thickness of about 90 nm. PFN was deposited as electron transporting layer to extract electron to the cathode. Subsequently, samples were loaded into a vacuum deposition chamber (background pressure $\approx 5 \times 10^{-4}$ Pa) to deposit a 120 nm thick aluminum cathode with a shadow mask (device area of 4 mm²). The J - V curves were measured with Keithley236 measurement source units at room temperature in air. The photocurrent was measured under a calibrated solar simulator (Abet 300 W) at 100 mW cm⁻², and the light intensity was calibrated with a standard photovoltaic reference cell. External quantum efficiency (EQE) spectrum was measured with Stanford lock-in amplifier 8300 unit.

Theoretical simulation: All calculated optical spectra and the electric field distribution profiles were obtained from the FDTD method using the program of FDTD Solutions (Lumerical Solutions, Inc., Canada). A 20 nm size Au nanoparticle embedded in the media of H₂O, PEDOT:PSS or PTB7:PC₇₁BM is illuminated with a total-field scattered-field (TFSF) source, which propagates along the Z direction with a polarization along the

X direction. The simulation region is $800 \times 800 \times 800 \text{ nm}^3$ with a non-uniform mesh adapted to the structure plus a uniformly meshed region $30 \times 30 \times 30 \text{ nm}^3$ with a grid size of 0.5 nm. A value of 1.33 was used for the refractive index of H_2O . We have used the Lumerical's multi-coefficient model (MCM) to fit the empirical dielectric function of Au, PEDOT:PSS and PTB7:PC₇₁BM for obtaining a better simulation.³⁶⁻³⁸

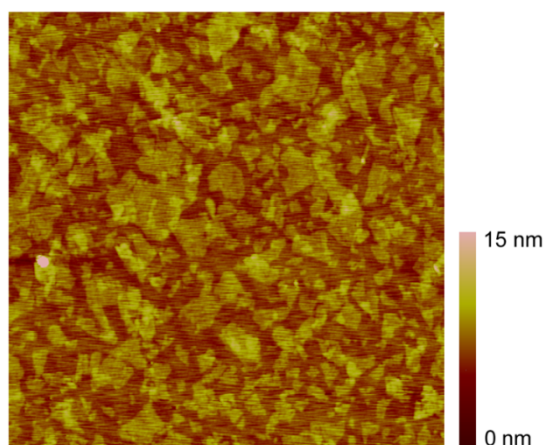


Figure S1. AFM image of the chemically exfoliated MoS₂ nanosheets on SiO₂/Si.

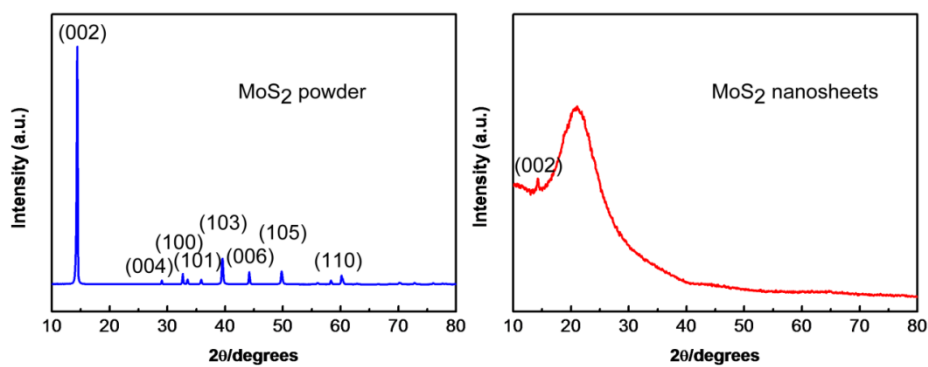


Figure S2. Powder X-ray diffraction (XRD) patterns of bulk MoS₂ powder and chemically exfoliated MoS₂ nanosheets. The samples were deposited on quartz substrates for testing.

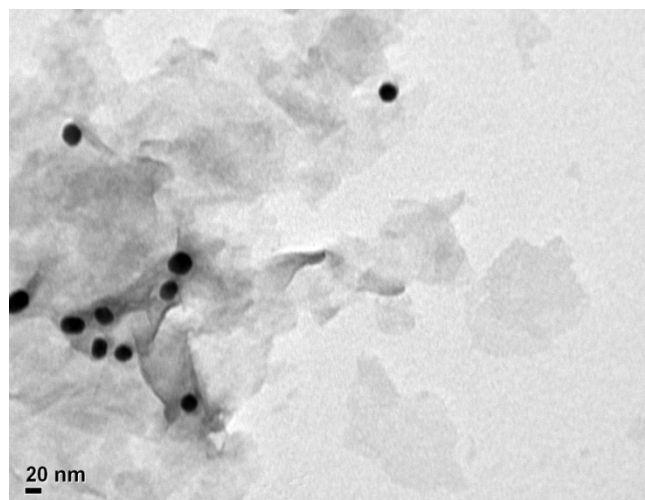


Figure S3. Higher magnification TEM image of MoS₂@Au composites with Au decoration of 12.5 vol%

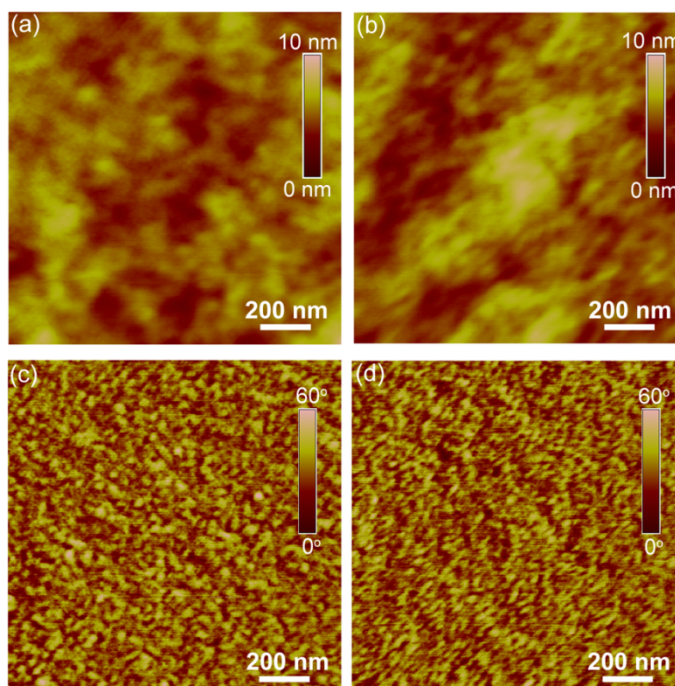


Figure S4. Height (a, b) and phase (c, d) images of active layer on MoS₂ (a, c) and MoS₂@Au (b, d).