ADVANCED MATERIALS

Supporting Information

for *Adv. Mater.,* DOI: 10.1002/adma.202209968

Fully Optical in Operando Investigation of Ambient Condition Electrical Switching in MoS_2 Nanodevices

*Joanna Symonowicz, Dmitry Polyushkin, Thomas Mueller, and Giuliana Di Martino**

Supporting Information

Title: Fully optical in operando investigation of ambient condition electrical switching in MoS_2 nanodevices

*Joanna Symonowicz, Dmitry Polushkin, Thomas Mueller, and Giuliana Di Martino**

J. Symonowicz, G. Di Martino
Department of Materials Science and Metallurgy, University of Cambridge, 27 Charles Babbage Rd, Cambridge, CB3 0FS, United Kingdom
E-mail: gd392@cam.ac.uk

D. Polyushkin, T. Mueller
Vienna University of Technology, Institute of Photonics, Gusshausstrasse 27-29 / 387, Vienna, 1040, Austria

(A) Electrical contacting setup

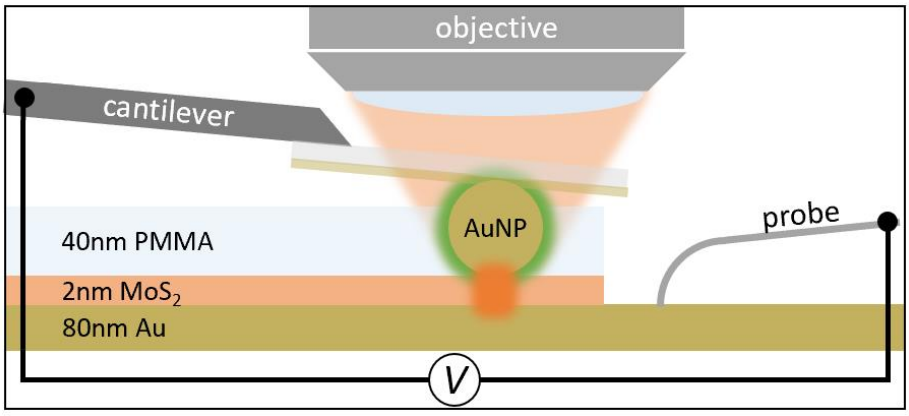

Figure S1. A schematic representation of electrical contacting setup.

(B) Transfer residues and ligands characterization

Here, we study adlayers present in the tested MoS_2 nanosheet. First, we investigate citrate ligands surrounding the Au nanoparticle (AuNP). We prepare a control sample by drop casting AuNPs directly onto Au substrate (**Figure S2a** - inset). Raman spectroscopy (633 nm excitation) confirms the presence of a molecular layer around AuNP (**Figure S2a)** and dark

field spectroscopy (DF) aims to understand its thickness. The resulting DF spectra of 30 control devices reveal two peaks at ~750 nm and ~920 nm (**Figure S2b)**, which correspond to about 0.5-0.75 nm as confirmed by finite-difference time-domain (FDTD) simulations (**Figure S2c)** using *Lumerical* software.[1]

Moreover, we do not observe quenching of MoS_2 PL by a direct contact with Au[3] (**Figure 1b** - main manuscript), hence we expect a layer of transfer residues separating MoS_2 from Au substrate. Atomic force microscopy (AFM) confirms the presence of polymer droplets on Au in vicinity of MoS_2 (**Figure S3a**). To confirm that the irregularities, which we ascribe to residues, are not simply due to Au damage, we present AFM scan of the smooth Au substrate where MoS_2 is not present (**Figure S3b**).

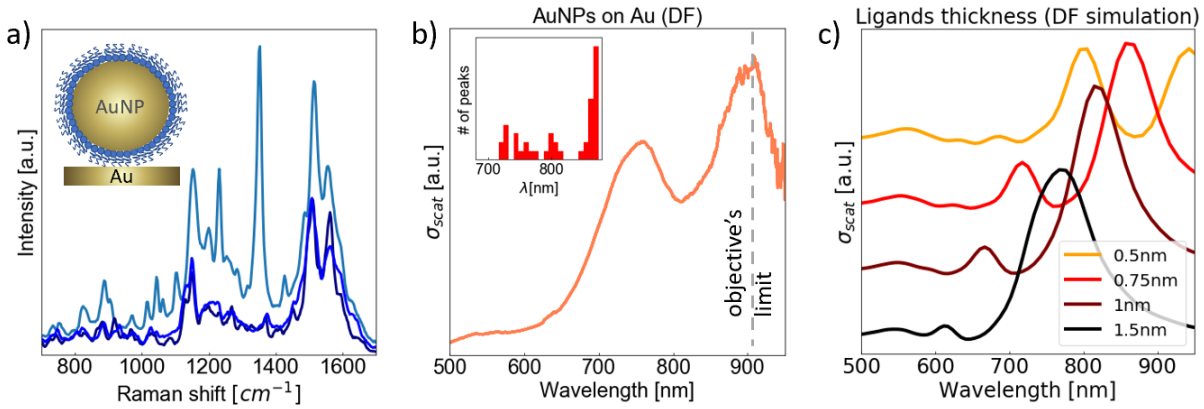

Figure S2. Study of citrate ligands thickness using a control sample: a) collected Raman signals revealing organic species around AuNP,[2] as depicted in the insert. b) Measured dark field scattering (DF) data with the insert displaying statics of resonance wavelengths for 30 control devices; c) simulation of resonances for a range of ligand thicknesses calculated by FDTD method.

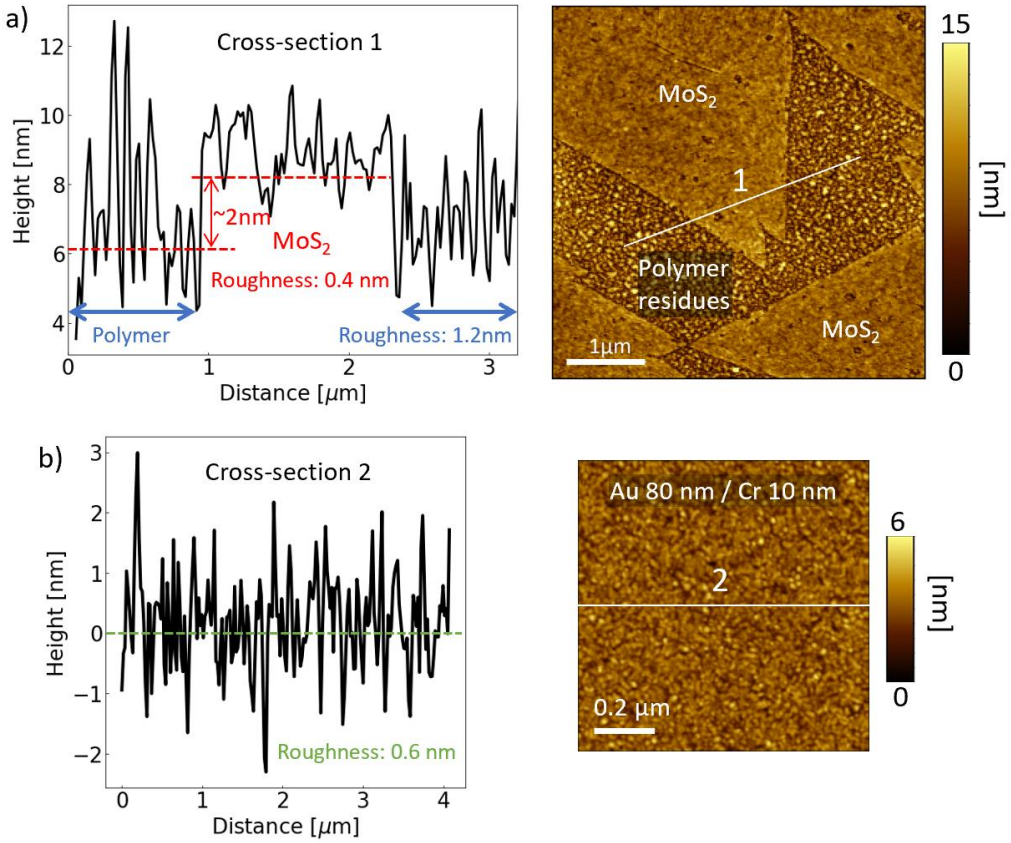

Figure S3. Atomic force microscopy (AFM) study of MoS_2's thickness. a) *Cross-section 1* (indicted on the AFM map to the right) shows the change in height of ~2 nm, corresponding to 3 layers of MoS_2.[5] b) *Cross-section 2* of the substrate without transferred MoS_2. The roughness of Au substrate is 0.6 nm, suggesting that the irregularities (roughness ~1.2 nm) detected under MoS_2 are associated with polystyrene polymer residues.[4]

(C) FDTD simulations

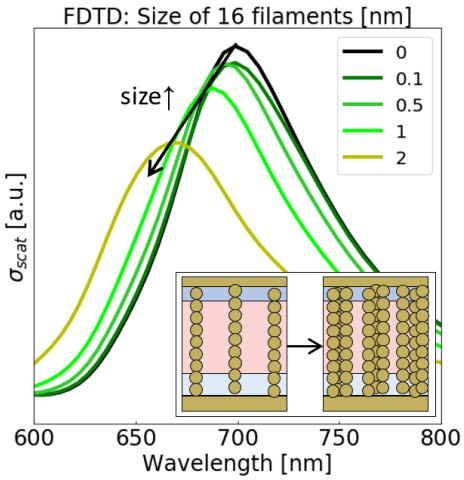

Figure S4. FDTD simulations linking the growth of 16 Au filaments in size with the blue-shift of gap mode's resonance.

(D) MoS_2 growth

The sapphire substrates were cleaned consecutively in acetone, 2-isopropanol, piranha solution (3:1 H_2SO_4:H_2O_2), DI water, and oxygen plasma for 10 min at 300 W. Then the substrate is placed face-down 15 mm above a crucible containing ~3 mg of MoO_3 (99.998% *Alfa Aesar*) and loaded into a split-tube two-zone CVD furnace with a 30 mm outer diameter quartz tube. CVD growth was performed at atmospheric pressure using ultra-high-purity argon as the carrier gas. A second crucible containing 1 g of sulfur (99.9% purity, *Sigma-Aldrich*) was loaded upstream from the growth substrates and kept at the temperature of 140 ^{o}C during the growth. The tube is flushed with Ar at room temperature before starting the growth. First, the furnace is preheated up to 750 ^{o}C and kept at this temperature for a few hours for temperature stabilization. Later the substrate and MoO_3 precursor are loaded into the growth area of the furnace. During the growth, the Ar is supplied with a flow of 10 sscm. After 10 min of growth at 750 ^{o}C, the furnace is opened for a fast cooling with keeping the tube under an argon atmosphere.

The CVD furnace delivers 1 cm^2 MoS_2 films grown on sapphire. These films are of good quality and allow the fabrication of NMOS electronics. Measurements of the single transistors show excellent performance with small hysteresis, ON/OFF ratios exceeding eight orders of magnitude, and average mobilities around 10 cm^2/Vs with values reaching up to almost 20 cm^2/Vs, subthreshold swing (SS) of 130 mV/dec, and adequate saturation.

(E) Electrical measurements

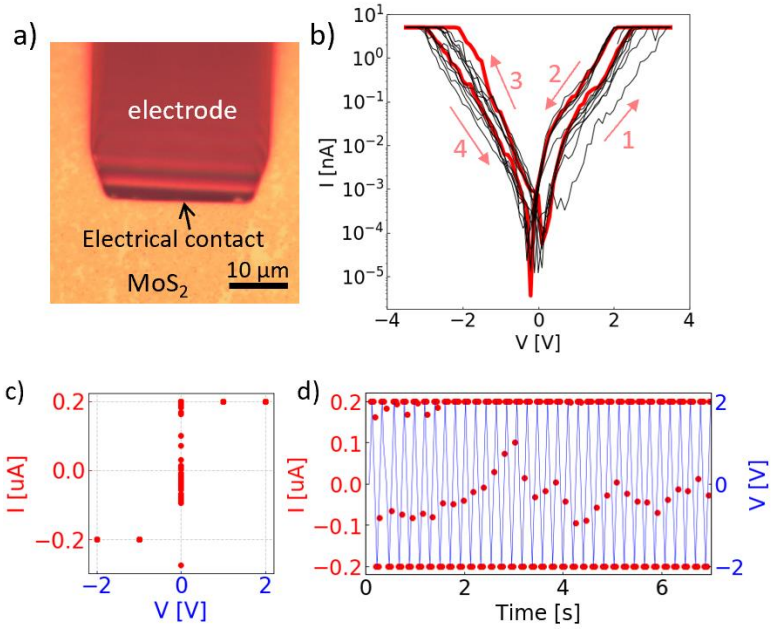

Figure S5. Electrical characteristics of MoS_2 contacted via micro-sized electrode without ligand layer. a) Microscope image of electrical contact. b) Typical *I-V* characteristics showing volatile threshold switching. c) Current response to pulses of 1 V and 2 V: for OFF state device stochastically relaxes to a random higher resistive state, as shown in d).

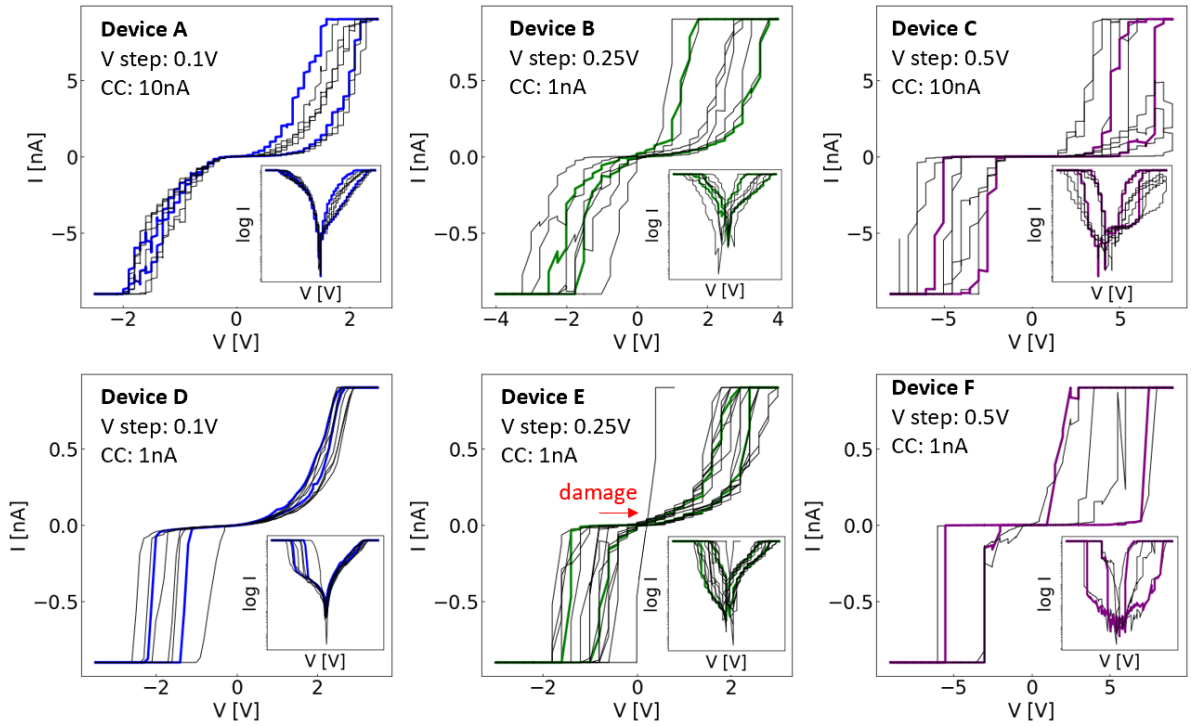

Figure S6. Statistics of *I-V* characteristics for different AuNP/MoS_2/Au nano-devices, voltage step sizes (0.1 V, 0.25 V, and 0.5 V), and current compliances (CC) (1 nA or 10 nA; higher CC destroys AuNP electrical contact). Hysteresis tends to be bigger and more stochastic for higher voltage steps. Usually, switching is sharper for V < 0 when Au atoms are not impeded by insulating citrate ligands. For **Device D** ligand layer prevents Au intercalation completely and almost no hysteresis is seen. **Device E** was shorted after 25 cycles, showing a typical device damage due to permanent Au filament shorting MoS_2.

References

[1] "High-Performance Photonic Simulation Software," can be found under https://www.lumerical.com/, **n.d.**
[2] D.-B. Grys, B. de Nijs, A. R. Salmon, J. Huang, W. Wang, W.-H. Chen, O. A. Scherman, J. J. Baumberg, *ACS Nano* **2020**, *14*, 8689.
[3] U. Bhanu, M. R. Islam, L. Tetard, S. I. Khondaker, *Sci. Rep.* **2015**, *4*, 5575.
[4] Y. Shen, W. Zheng, K. Zhu, Y. Xiao, C. Wen, Y. Liu, X. Jing, M. Lanza, *Adv. Mater.* **2021**, *33*, 2103656.
[5] X. Li, H. Zhu, *J. Materiomics* **2015**, *1*, 33.