Supporting Information

Functionalization of Transition Metal Dichalcogenides with Metallic Nanoparticles:

Implications for Doping and Gas-Sensing

Deblina Sarkar¹, Xuejun Xie¹, Jiahao Kang¹, Haojun Zhang¹, Wei Liu¹, Jose Navarrete²,

Martin Moskovits² and Kaustav Banerjee¹*

¹Department of Electrical and Computer Engineering, ²Department of Chemistry and Biochemistry,

University of California, Santa Barbara, Santa Barbara, CA 93106, USA.

* Address correspondence to: kaustav@ece.ucsb.edu

S1. STABILITY ANALYSIS OF DOPANTS

Fig. S1a shows the drain current vs. gate voltage curves of a MoS_2 FET without any NPs and after incorporation of Y NPs measured at two different times. N-type doping is observed when the device is measured immediately after Y



Fig. S1. (a) Drain current as a function of gate voltage for MoS_2 FETs without any NPs (green curves), after incorporation of Y nanoparticles and measured immediately (orange curves) and measured after 10 hrs (magenta curves). The left axis shows values in logarithmic scale while the right axis shows values in linear scale.

NP incorporation as the threshold voltage shifted towards the left and hence current increased. However, after about 10 hrs, the doping degraded as indicated by the increase in threshold voltage and decrease in current levels, which became similar to those without any NPs. Doping due to Pt NPs on the other hand, was found to be very stable as shown in **Fig. S1b**.



Fig. S1. (b) Drain current as a function of gate voltage for MoS_2 FETs without any NPs (blue curves), after incorporation of Pt nanoparticles and measured immediately (red curves) and measured after 2 days (black curves). The left axis shows values in logarithmic scale while the right axis shows values in linear scale.

S2. RAMAN SPECTROSCOPY DATA

In order to take into account the effect of variations, Raman spectroscopy measurements were done at different points on the sample. For all the measurements, in case of MoS_2 with NPs, the features are shifted towards the right (**Fig. S2**) compared to those without the nanoparticles, confirming p-type doping.



Fig. S2. The Raman spectra excited for a MoS_2 sheet before and after incorporation of Pt NPs shown by blue and red lines respectively. The red lines are shifted towards the right compared to the blue lines, indicating p-type doping by the Pt NPs.

S3. DFT SIMULATIONS OF PHONON SPECTRA

We observe a shift toward right, of the Raman peaks, upon p-doping with nanoparticles. To understand this effect, we have performed DFT simulations and calculated phonon spectra of intrinsic and p-doped MoS₂ (**Fig. S3**). Taking the example of important Raman modes A_{1g} and E_{2g}^{1} , it is shown that the energy of both A_{1g} and E_{2g}^{1} (Polar Longitudinal Optical (LO) mode) increase slightly upon p-doping, consistent with the experimental observation. Note, that the energy of Polar Transverse Optical (TO) mode decreases but this mode is not Raman active.

Physically, the shifts of Raman modes can be explained in terms of the *born effective charges* of Mo and S atoms in the MoS_2 molecule. Born effective charge is defined as the change in polarization divided by the amount an ion is displaced, so it is not zero even in the undoped cases. In intrinsic MoS_2 , it is 1.11 electrons (positive charge) for Mo atom, and it is -0.52 electrons for each S atom.

In A_{1g} mode, sulfur atoms vibrate in opposite direction, perpendicular to the basal plane. When the MoS_2 is p-doped, the negative charge on the S atom will be less and hence, the repulsive Coulomb interaction of S atoms with the adjacent S atoms in another layer will be smaller. Consequently, the binding interaction of a MoS_2 molecule in a particular layer with that in the adjacent layers will be stronger, which will make the stiffness constant of the A_{1g} mode larger, and thus, the vibration frequency will be higher according to the classical oscillator model.

For E_{2g}^{1} LO mode, the Mo and S atoms vibrate in the basal plane and the displacement of the charges is accompanied by an extra force due to the electric field, parallel to the displacement. When we p-dope the MoS₂, the polarization field will be stronger, so the restoring forces will be larger, thereby increasing the stiffness constant. Thus, the LO frequency will be higher as is observed experimentally and through simulations.



Fig. S3. (a) Phonon spectra of intrinsic and p-doped MoS₂ (molar fraction 0.1%) calculated by DFT. Inset shows Raman spectra of intrinsic and p-doped MoS₂ measured in experiments. (**b,c**) Zoom of A_{1g} mode and E_{2g}^{1} mode at Γ point. The schematic showing the direction of the atomic vibrations in A_{1g} mode and E_{2g}^{1} mode are also shown on the right of (b) and (c), respectively. In (b), doping increases the phonon energy of homopolar mode (A_{1g}), and hence, the Raman peak corresponding to the A_{1g} mode shifts to the right, as shown in the inset of (a). In (c), doping increases macroscopic polarization and thus increases the polar LO phonon energy of the E_{2g}^{-1} mode.