Piezoelectricity in single-molecular-layer transition metal dichalcogenide

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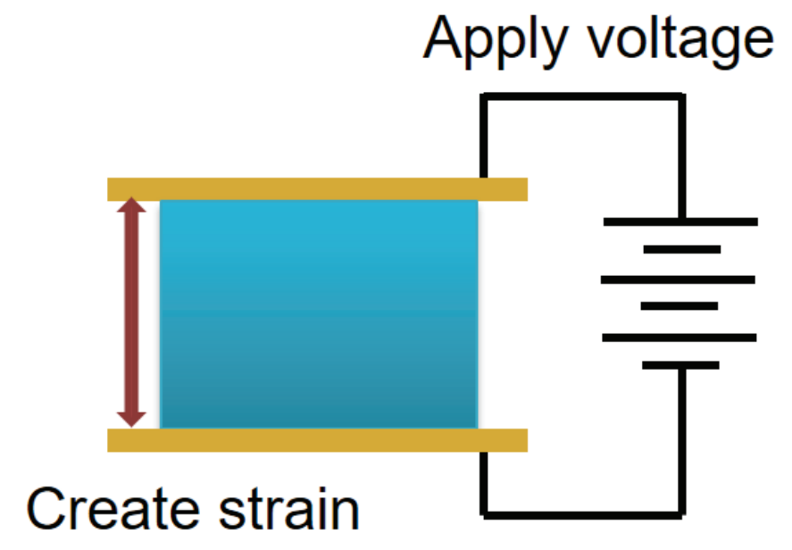
ACTUALIZATION OF THE INTERNET OF THINGS
APS physics
FIAP 2017 CONFERENCE

Background

Piezoelectricity: definition



Application:
Resonator & Motor
(electricity to strain)

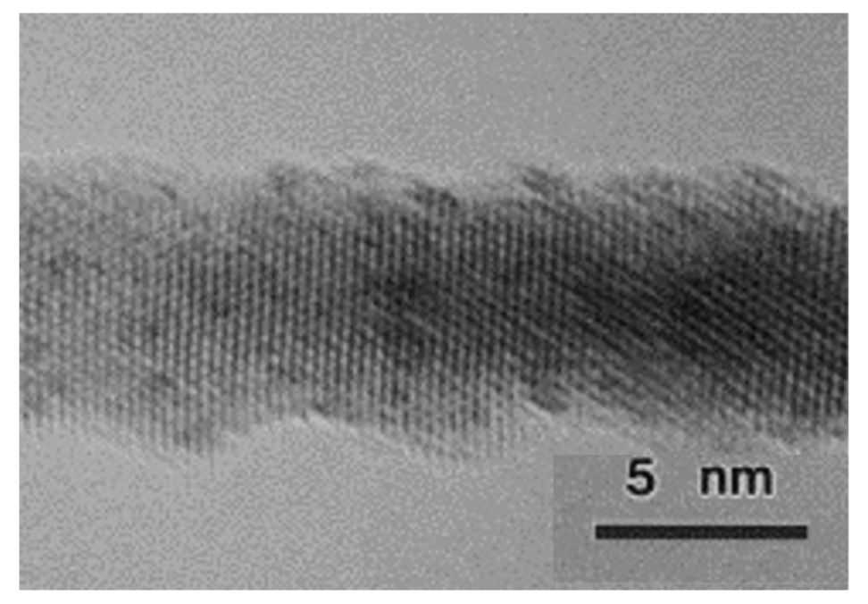
$$d_{ijk} = -\left(\frac{\partial \varepsilon_{jk}}{\partial E_i}\right)_{\sigma=0}$$

Sensor & Generator
(strain to electricity)

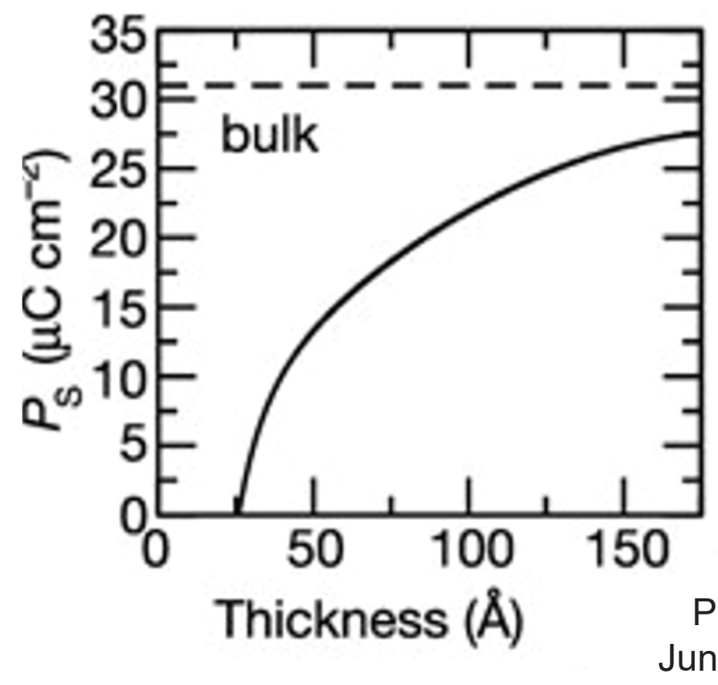
Piezoelectricity allows precise and robust conversion between electricity and mechanical force, and arises from the broken inversion symmetry in the atomic structure. It has found a wide range of applications in nano-electro-mechanical systems (NEMS).

Material challenge

Rough surface
and dangling bonds



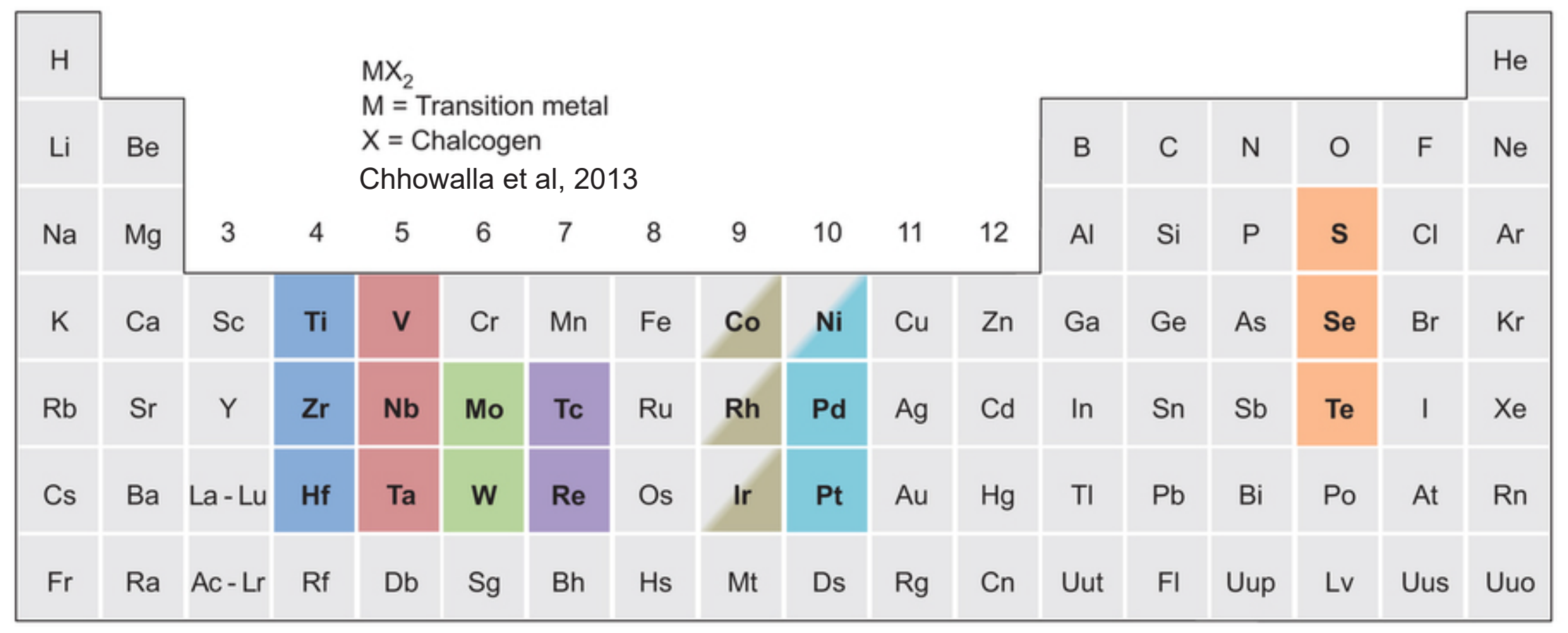
Size effect in
ferroelectric materials



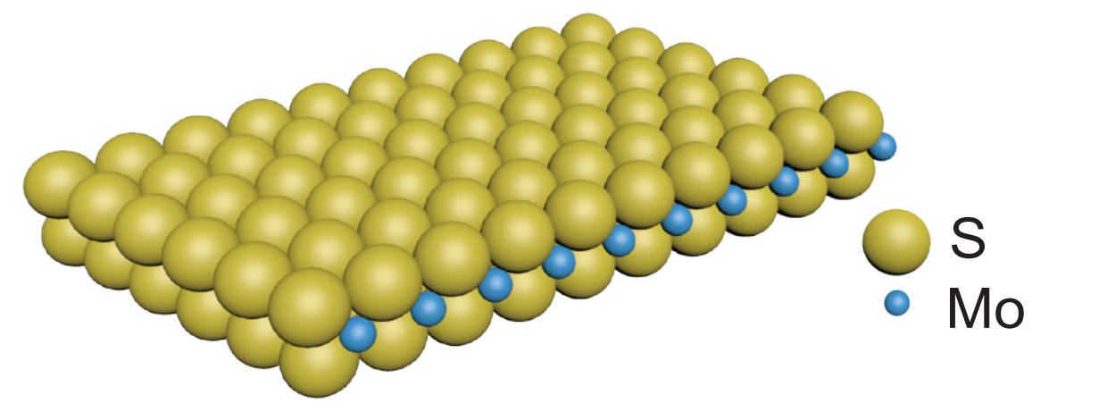
Peng et al, 2000
Junquera et al, 2003

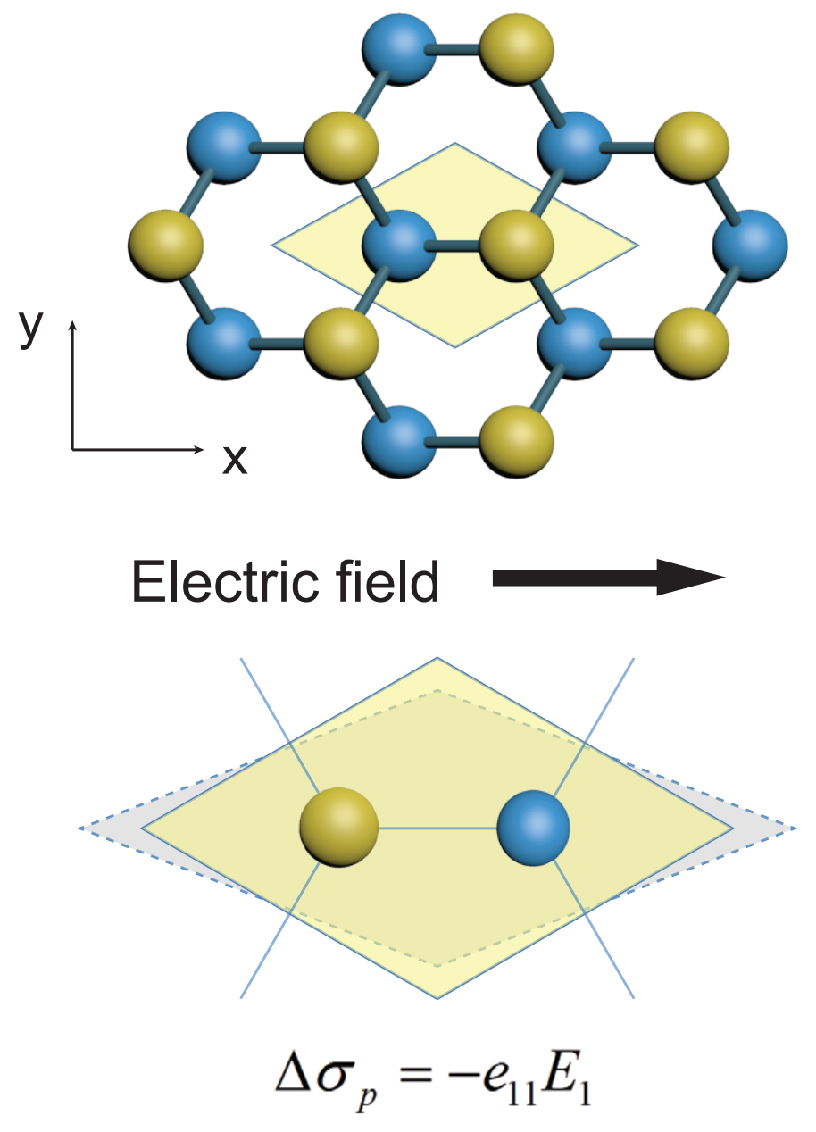
What is the ultimate scale limit of piezoelectric devices? For traditional materials it is challenging to get high-quality surface for freestanding structures. In addition, when the thickness approaches a single molecular layer, the large surface energy can cause piezoelectric structures to be thermodynamically unstable. Prior to this study, there was no experimental measurement of the intrinsic piezoelectric properties of sub-nanometer crystals.

Opportunity: layered materials



H																	He
Li	Be											B	C	N	O	F	Ne
Na	Mg	3	4	5	6	7	8	9	10	11	12	Al	Si	P	S	Cl	Ar
K	Ca	Sc	Ti	V	Cr	Mn	Fe	Co	Ni	Cu	Zn	Ga	Ge	As	Se	Br	Kr
Rb	Sr	Y	Zr	Nb	Mo	Tc	Ru	Rh	Pd	Ag	Cd	In	Sn	Sb	Te	I	Xe
Cs	Ba	La - Lu	Hf	Ta	W	Re	Os	Ir	Pt	Au	Hg	Tl	Pb	Bi	Po	At	Rn
Fr	Ra	Ac - Lr	Rf	Db	Sg	Bh	Hs	Mt	Ds	Rg	Cn	Uut	Fl	Uup	Lv	Uus	Uuo



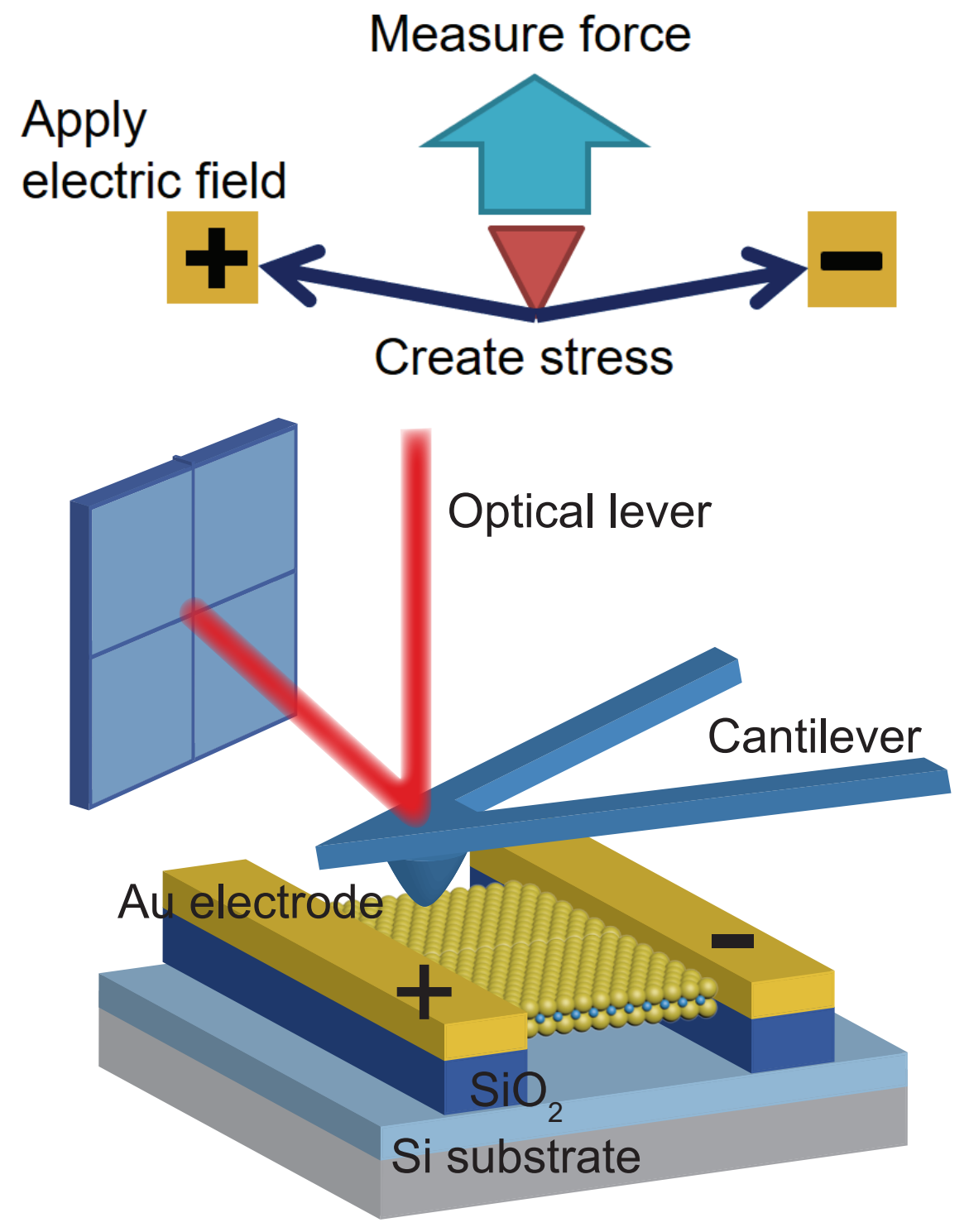


$$\Delta\sigma_p = -e_{11}E_1$$

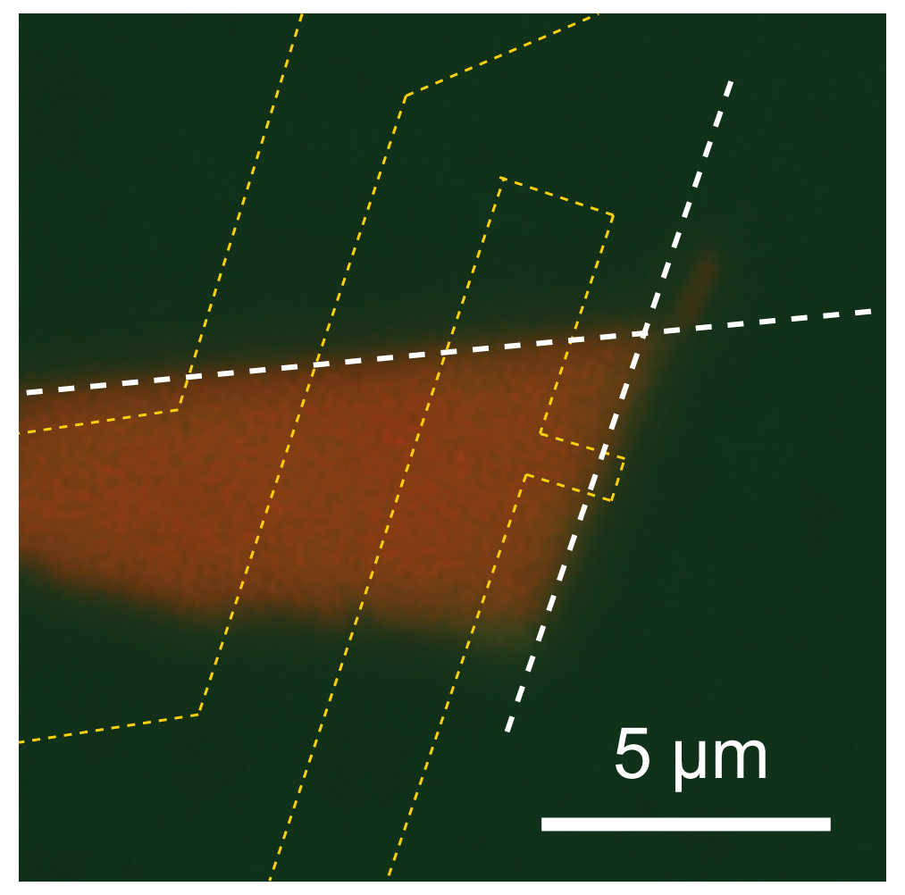
Transition-metal dichalcogenides, such as MoS_2 can retain their structural asymmetry down to the single-layer limit without lattice reconstruction under ambient condition, that enables two dimensional piezoelectricity. The membrane has a total thickness of 0.6 nm and is biocompatible for device applications.

Measure in-plane piezoelectricity

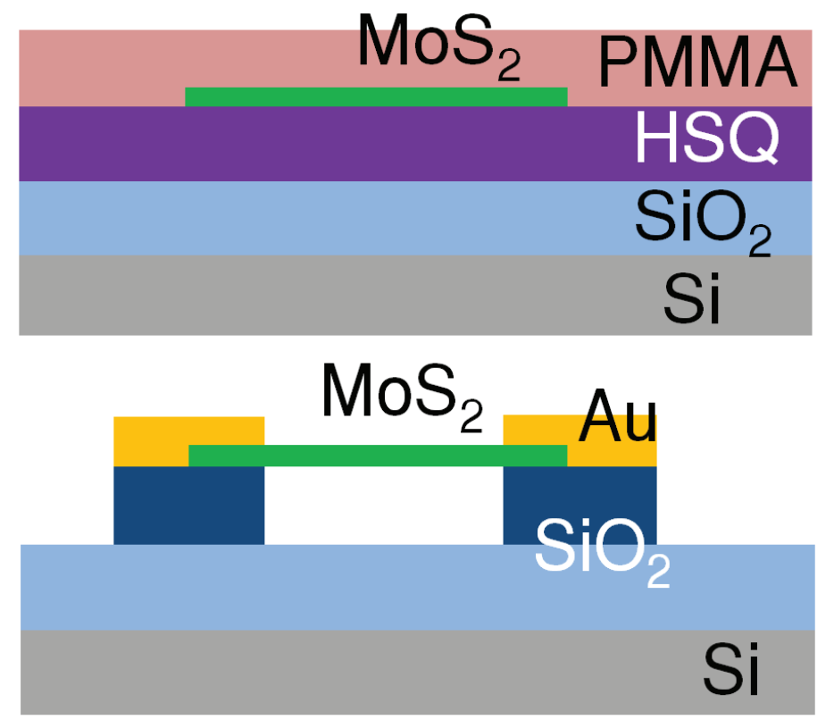
We combined a laterally applied electric field and nano-indentation in an atomic force microscope (AFM) to measure the in-plane piezoelectrically generated membrane stress. Suspending MoS_2 minimized substrate effects such as doping and parasitic charges. The two electrodes were oppositely biased relative to substrate to reduce electrostatic force. The actuation frequency was kept much lower than the mechanical resonance and quasi-static analysis is applicable.

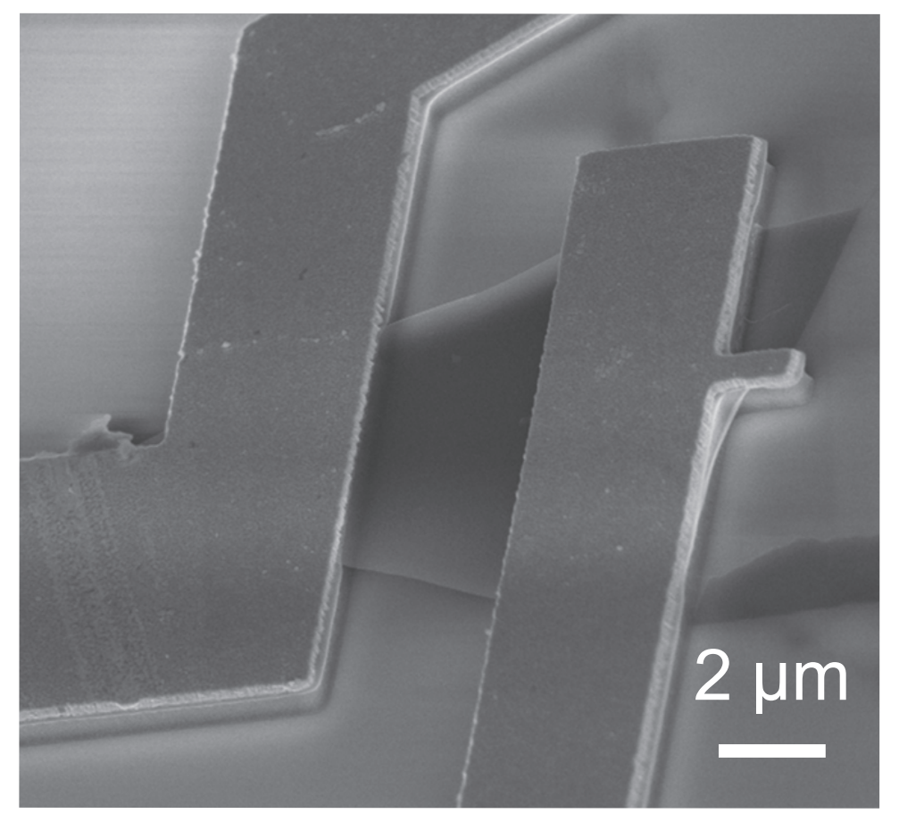


Device fabrication

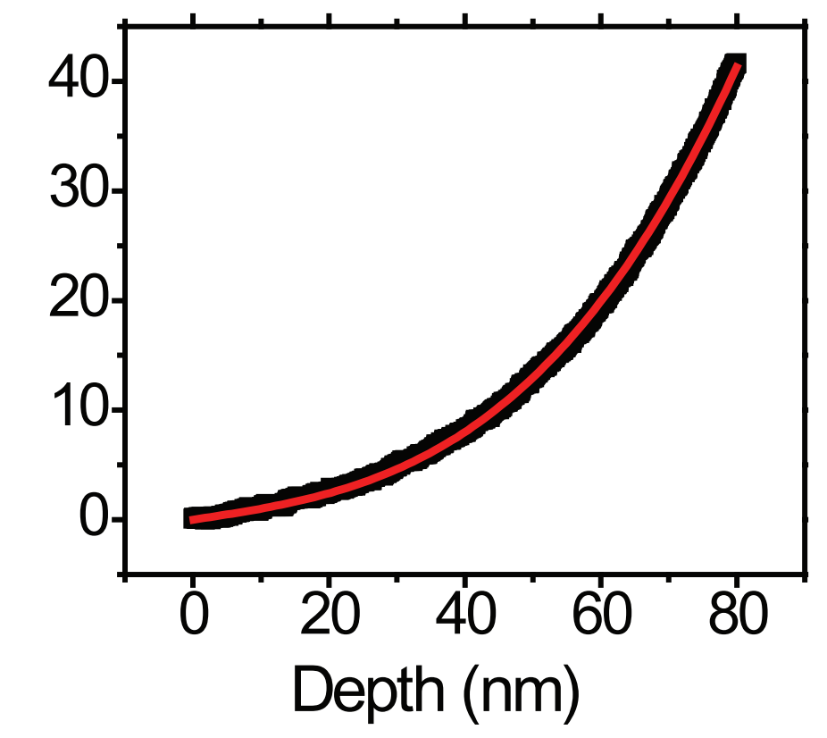


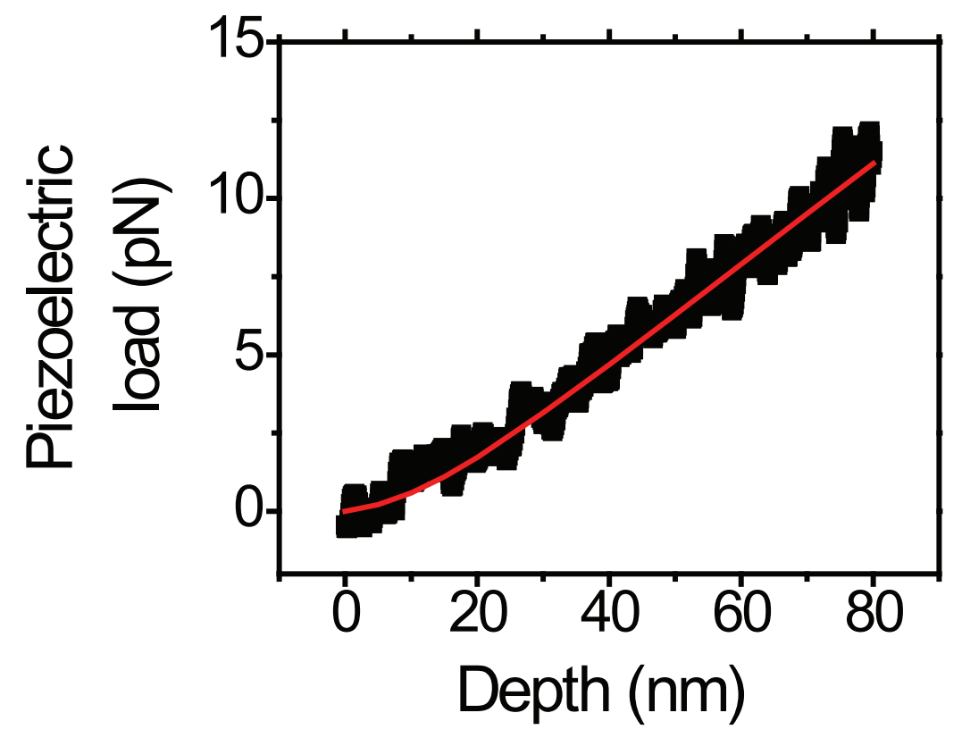
MoS_2 monolayer was produced by mechanical exfoliation on poly-methyl-methacrylate (PMMA). The electrodes were designed to be parallel to or at 60° with respect to the sharply cleaved edges. Suspension, mechanical clamping and electrical contact were simultaneously achieved by one-step electron-beam lithography (EBL). The MoS_2 flake was released by critical point drying.



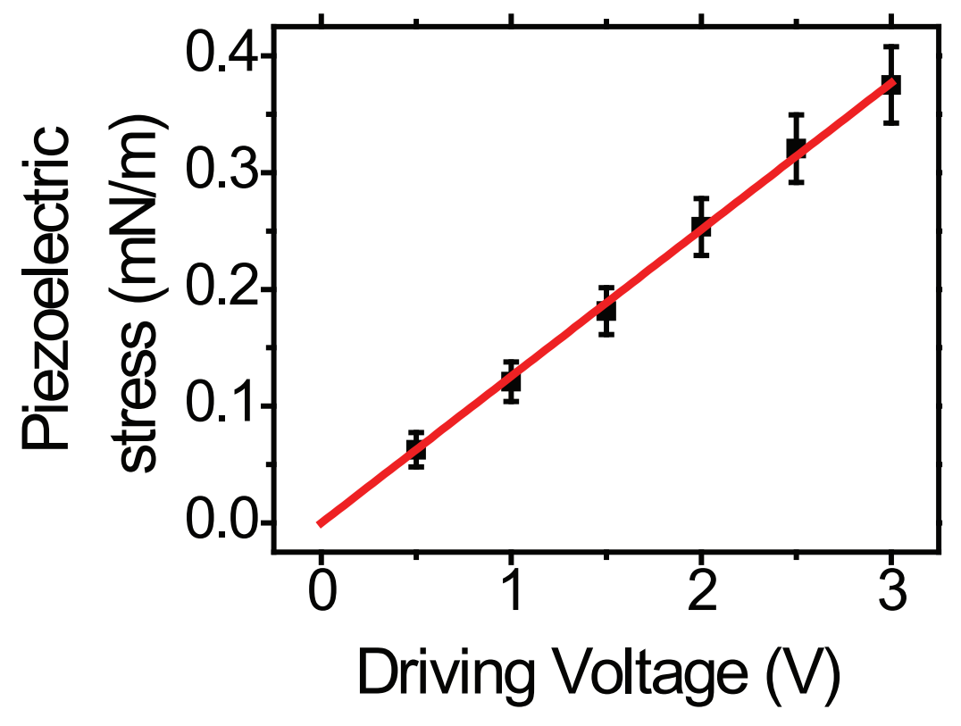


Results

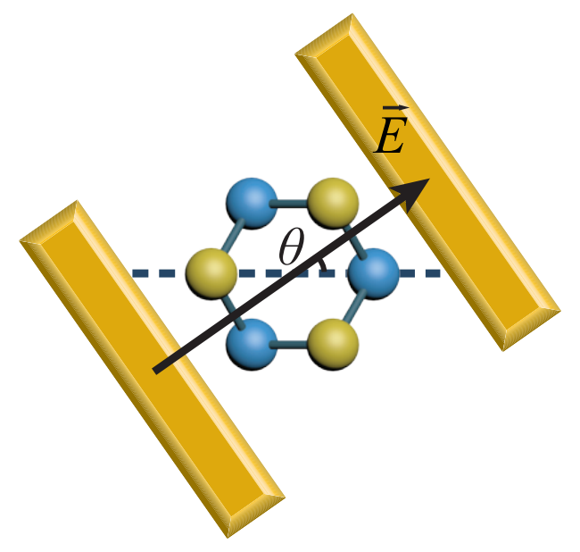




The experimental load of on a monolayer MoS_2 device (black scatter) was fit with $Y^{2D} = (1.2 \pm 0.1) \times 10^2$ N m^{-1} and $\sigma^{2D} = 45 \pm 5$ mN m^{-1} (red curve). For this device, piezoelectric stress of $\Delta\sigma_p = 0.12 \pm 0.02$ mN m^{-1} was deduced. A positive sign was assigned because the signal and the driving voltage were in phase. The piezoelectric stress increased with ramping driving voltage (black scatter). A linear fit (red curve) gives $e_{11} = (2.9 \pm 0.5) \times 10^{-10}$ C/m (or d = (2.9 ± 0.5) pm/V, The values agree well with previous ab initio calculations and experiments.



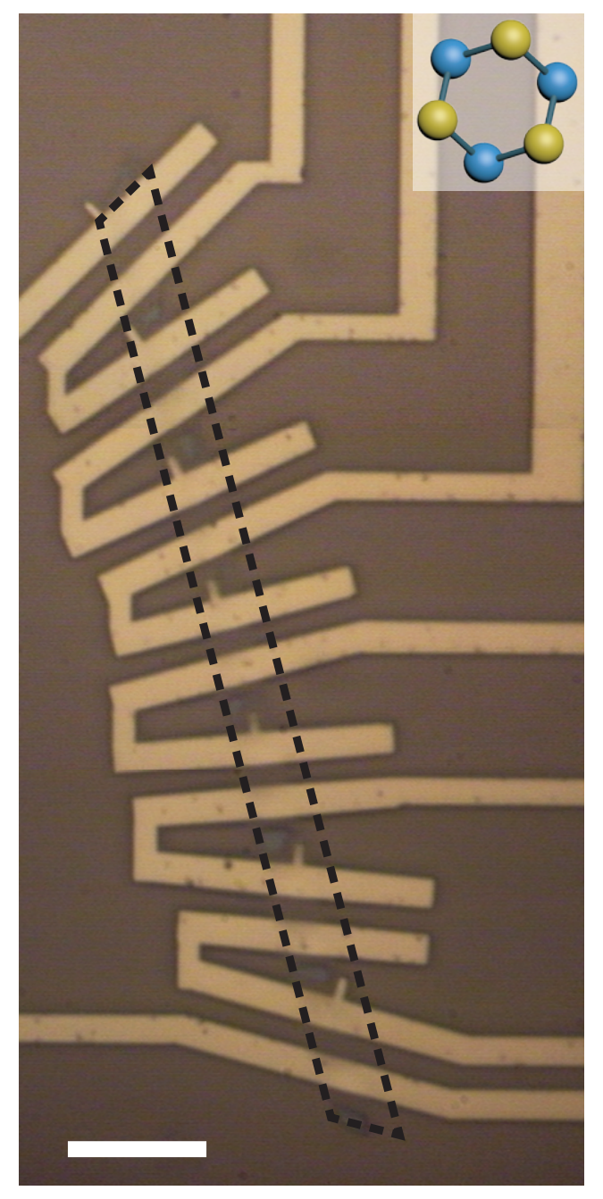
Angular & layer dependence

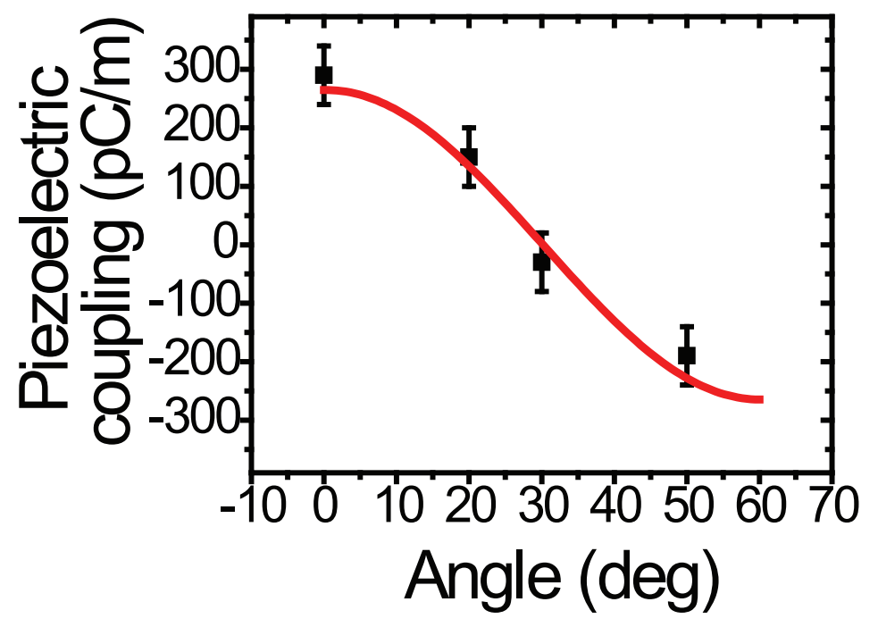


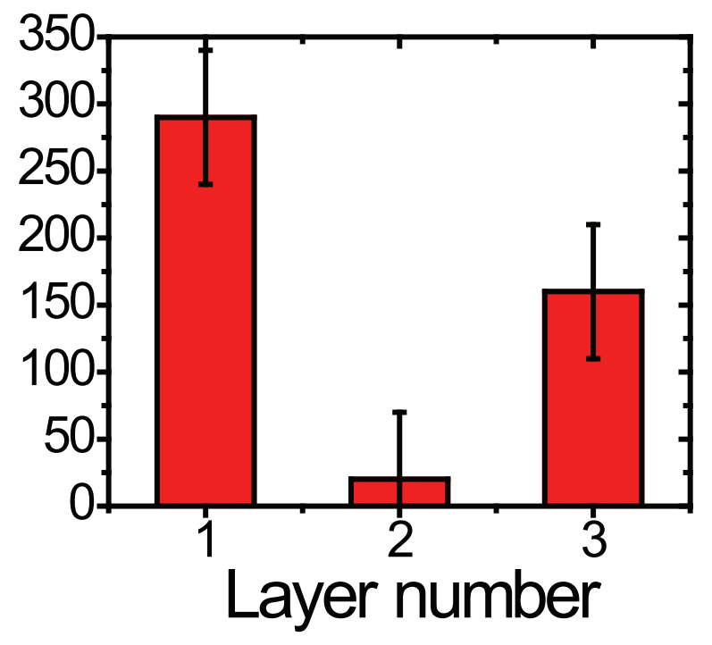
Due to its 3-fold symmetry the piezoelectric coupling of the MoS_2 monolayer is:

$$\Delta\sigma_p / E = -e_{11}\cos 3\theta$$

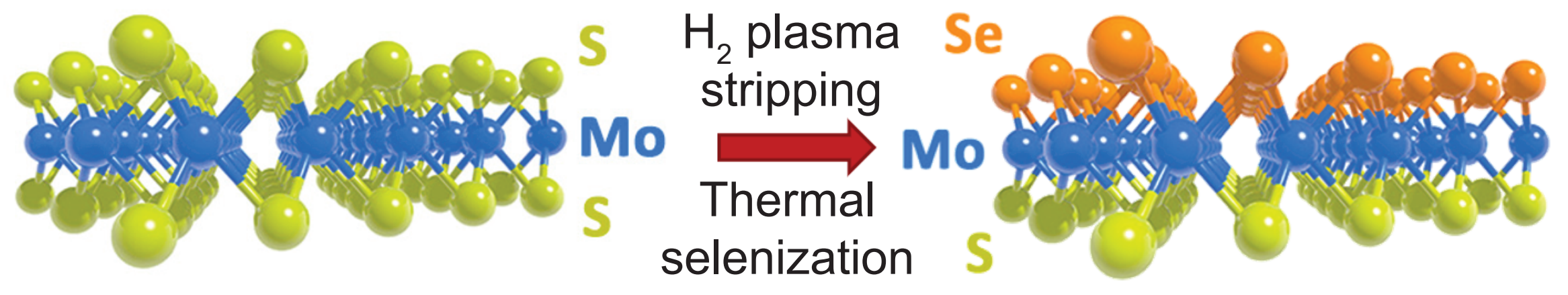
The change of sign from the upper devices to the lower ones allowed us to assign the crystal orientation, i.e. differentiating the crystal with its mirror image. We also measured the thickness dependence of the piezoelectric coefficient from natural 2H-MoS_2 crystals. For even-layer membranes, the contributions to piezoelectricity from alternating orientations of adjacent layers cancelled. That's why bulk 2H-MoS_2 is not piezoelectric.



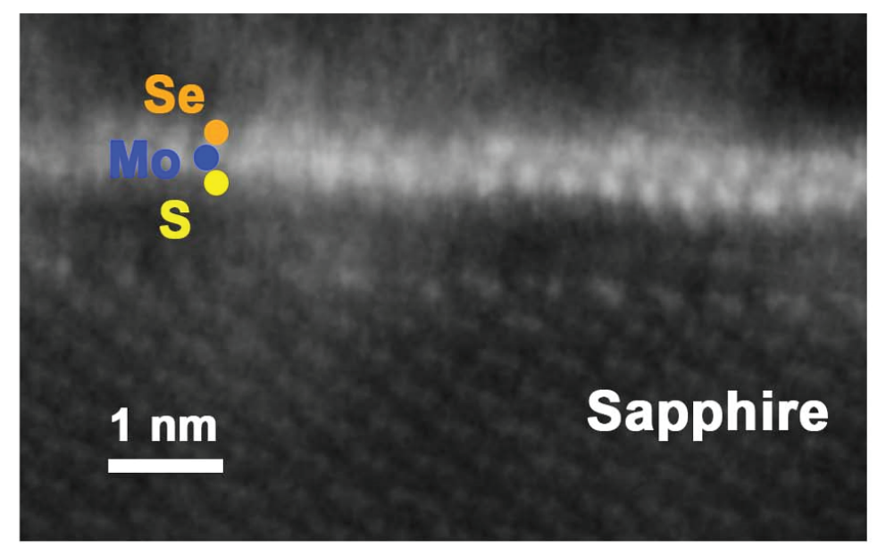


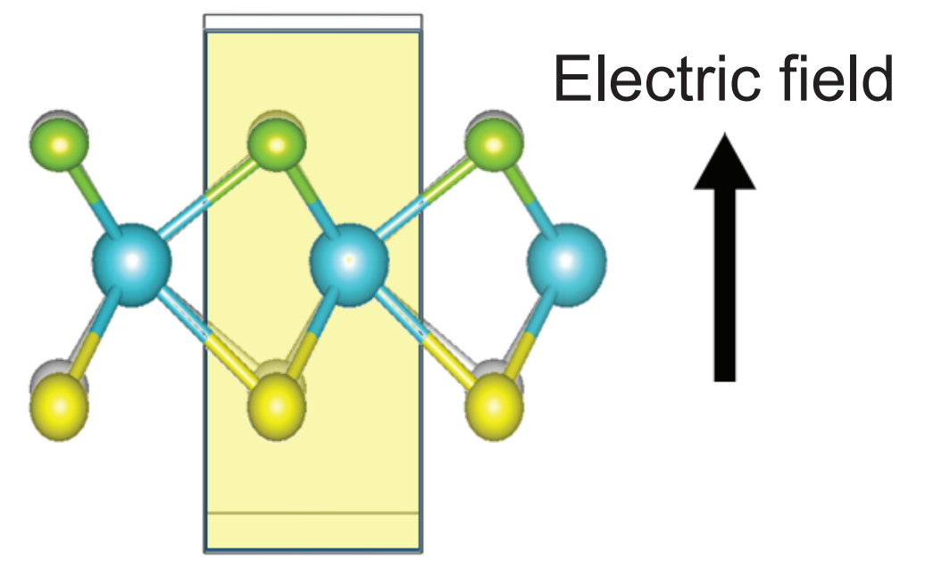


Out-of-plane piezoelectricity

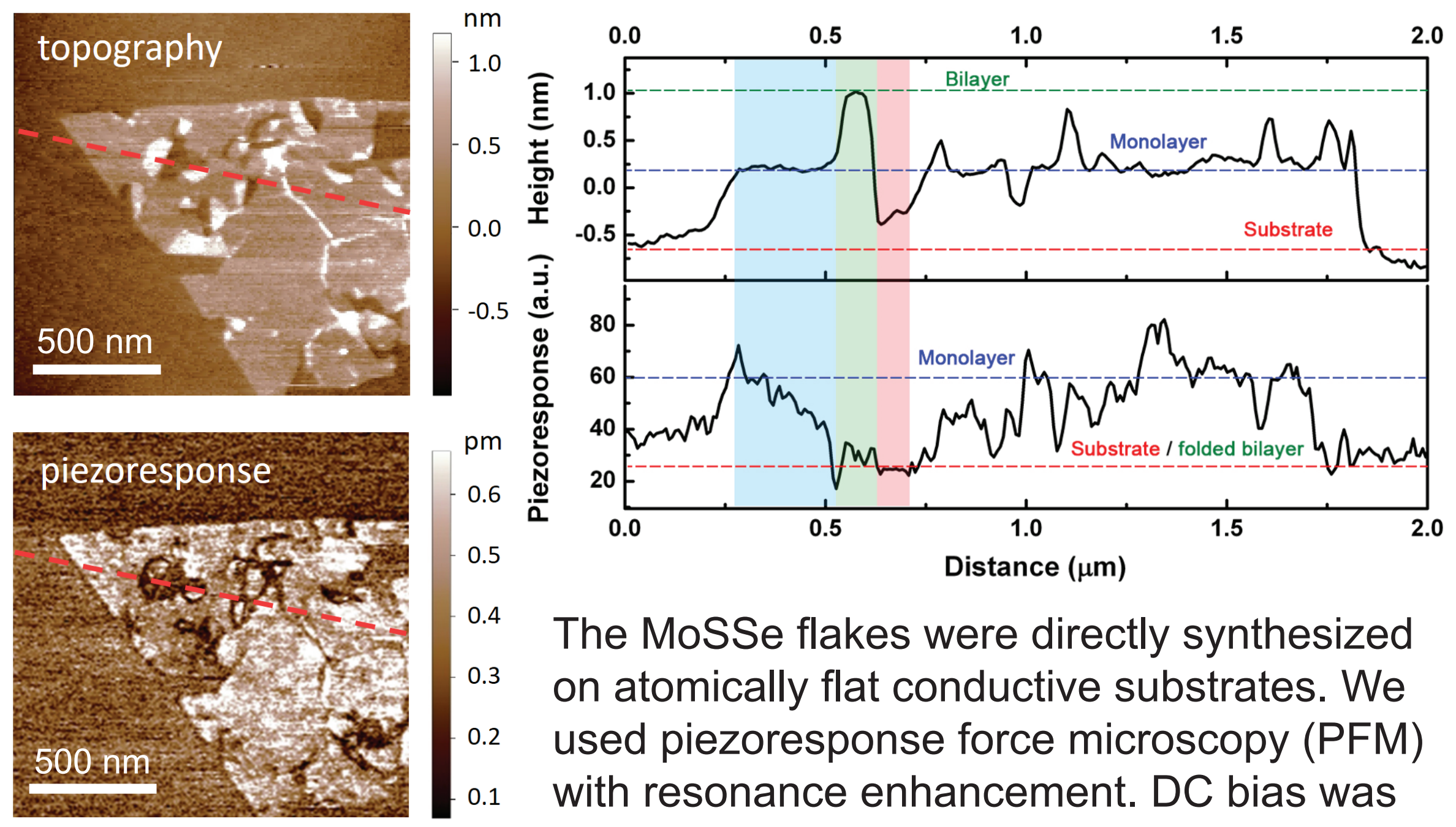


Many piezoelectric NEMS designs rely on out-of-plane electromechanical coupling. However MoS_2 has out-of-plane mirror symmetry and no piezoelectricity along z-axis. We engineered a physical-chemical process to selectively replace the sulfur atoms on one side with selenium and created structural asymmetry.





Scanning piezoresponse



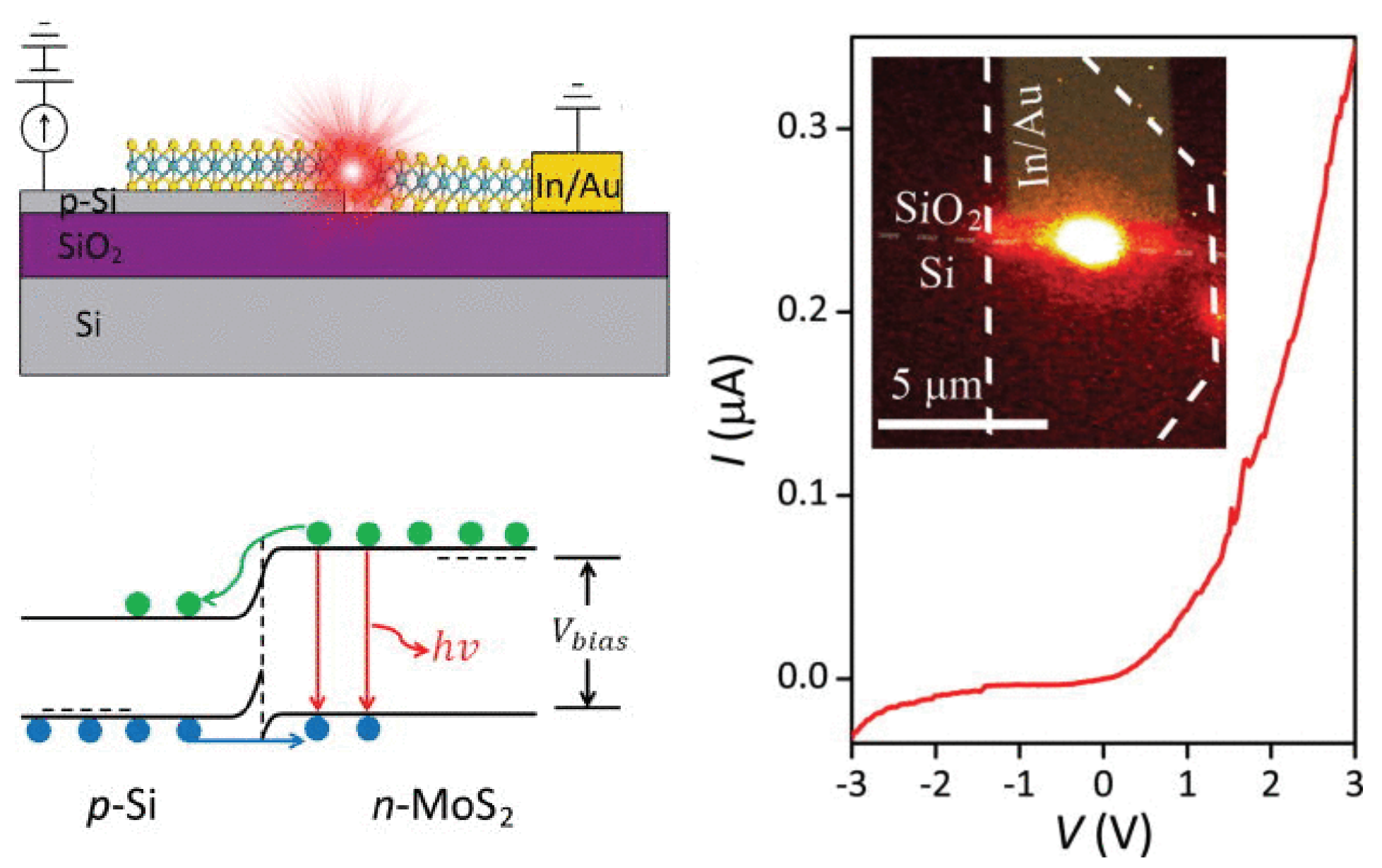
The MoSSe flakes were directly synthesized on atomically flat conductive substrates. We used piezoresponse force microscopy (PFM) with resonance enhancement. DC bias was applied to balance the potential of the tip and the substrate and minimized the electrostatic effect. There is clear piezoelectric contrast between the a MoSSe monolayer and the substrate, but no contrast for random alloy or folded bilayer. The estimated piezoelectric coefficient d_{33} is around 0.1 pm/V, and can potentially be improved by increasing the dipolar contrast.

Acknowledgement & References

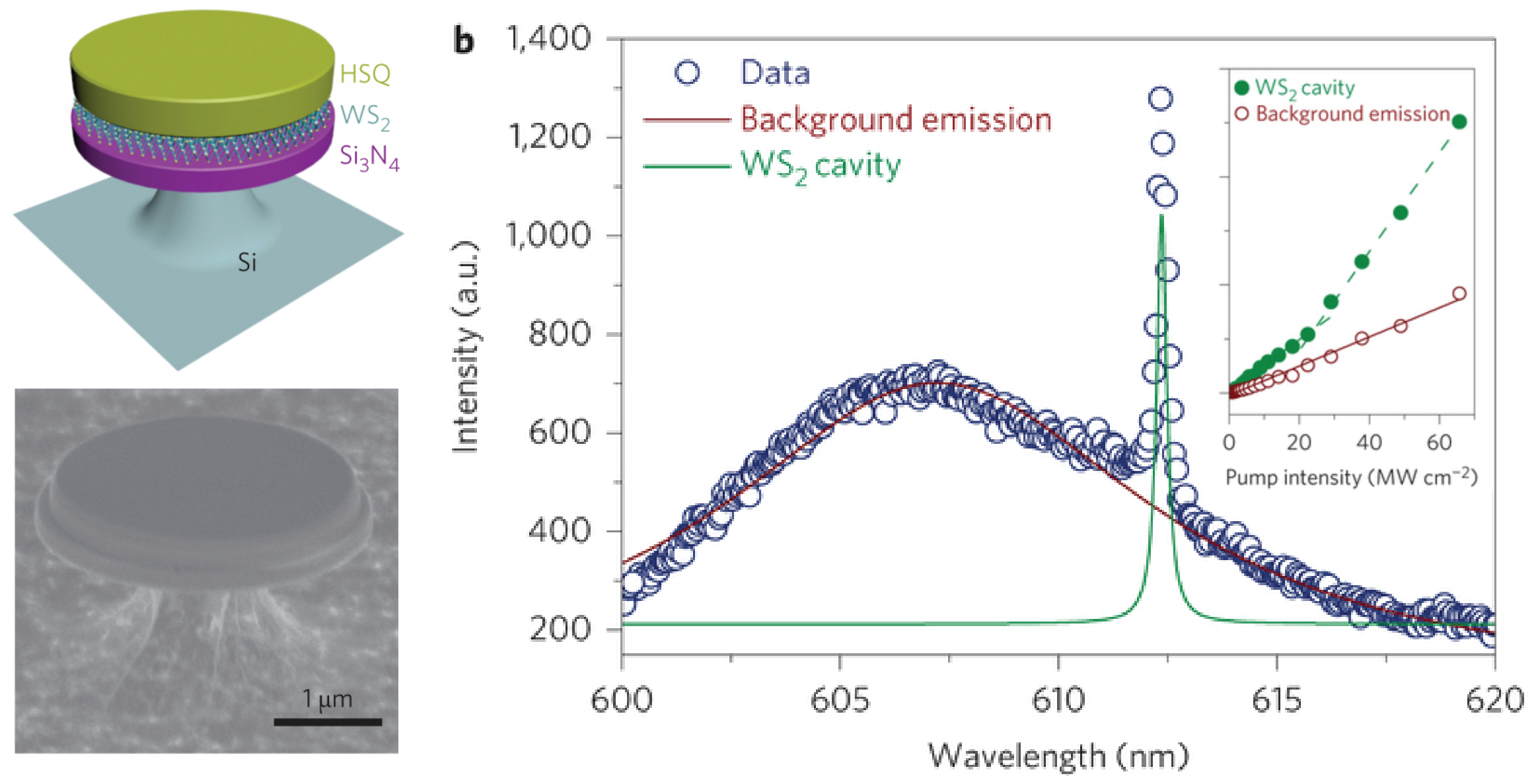
Supported by the US DOE Energy Frontier Research Center under award DOE DE-AC02-05CH11231 and NSF EFRI 2-DARE 1542741

[1] Hanyu Zhu, et al., Observation of piezoelectricity in free-standing monolayer MoS2, Nature Nanotechnology 10, 151–155 (2015).
[2] Ang-Yu Lu, et al., Janus atomic monolayers of transition metal dichalcogenides, Nature Nanotechnology, AOP 100 (2017).

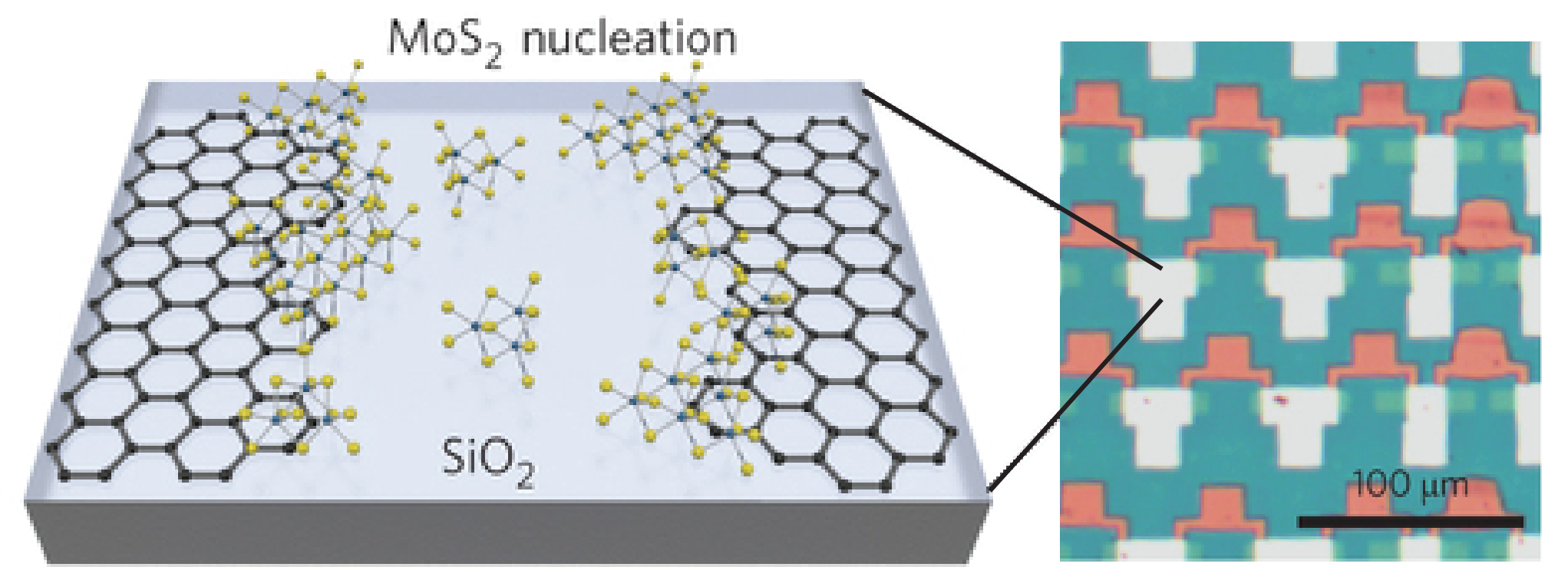
Other IoT Related Works



Light emitting diode integrated on silicon:
Efficient carrier injection and light emission was achieved in heterojunctions of monolayer MoS_2 (n-type) and heavily doped (p-type) silicon. (Ye et al., Exciton-dominant electroluminescence from a diode of monolayer MoS2, Appl. Phys. Lett. 104, 193508 (2014).)



Monolayer laser on silicon: Using a whispering gallery cavity with a high quality factor and optical confinement, we observe bright excitonic lasing from a monolayer WS_2 at visible wavelengths under optical pumping, a major step towards two-dimensional on-chip optoelectronics for optical communication and sensing. (Ye et al., Monolayer excitonic laser, Nat. Photon. 9, 727–737 (2015).)



Large-scale chemical assembly of atomically thin circuits:
Spatially controlled synthesis of heterostructures made of monolayer MoS2 and graphene enables high-performance flexible circuits. Zhao et al., Large-scale chemical assembly of atomically thin transistors and circuits, Nat. Nano. 11, 954–959 (2016).