Electronic Supplementary Material (ESI) for Nanoscale.

Supporting Information for

Layer-dependent surface potential of phosphorene and anisotropic/layer-dependent charge transfer in phosphorene-gold hybrid system

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1. Optical path length (OPL) calibration curves for mono- and few-layer phosphorene on SiO_2/Si and gold substrates

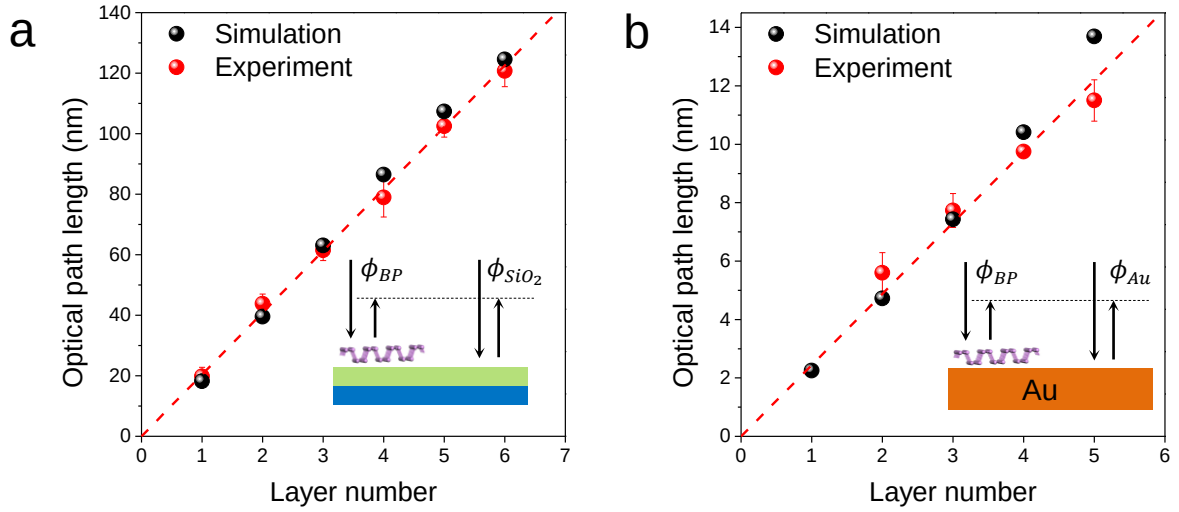

Figure S1 | OPL calibration curves for mono- and few-layer phosphorene on SiO_2/Si and gold substrates. a, OPL calibration curves (simulation and experiments) for mono- and few-layer phosphorene on SiO_2/Si (275 nm thermal oxide) substrate. For each layer number of phosphorene, at least five different samples were characterized for the statistical measurements. The red dash line is the linear trend for statistical data measured with the PSI system. Inset is the schematic plot showing the PSI measured phase shifts of the reflected light from the phosphorene flake (ϕ_{BP}) and the SiO_2/Si substrate (ϕ_{SiO_2}). **b**, OPL calibration curves (simulation and experiments) for mono- and few-layer phosphorene on gold substrate (monolayer phosphorene only has simulation result). For each layer number of phosphorene, at least two different samples were characterized for the statistical measurements. The red dash line is the linear trend for statistical data measured with the PSI system. Inset is the schematic plot showing the PSI measured phase shifts of the reflected light from the phosphorene flake (ϕ_{BP}) and the Au substrate (ϕ_{Au})

Numerical Simulation: Stanford Stratified Structure Solver (S4)[1] was used to calculate the OPL values for mono- and few-layer phosphorene on two different substrates SiO_2/Si and gold, respectively (Figure S1). The method numerically solves Maxwell's equations in multiple layers of structured materials by expanding the field in the Fourier-space. In the numerical calculation, the refractive indices used for phosphorene[2], Si, SiO_2 and Au were 3.4, 4.15 + 0.04*i*, 1.46 and 0.52 + 2.17*i*, respectively. Both the measured and calculated OPL values for these three semiconductors show a linear relationship with the layer number and they consist well with each other.

2. Phase-shifting interferometer (PSI) images for phosphorene samples

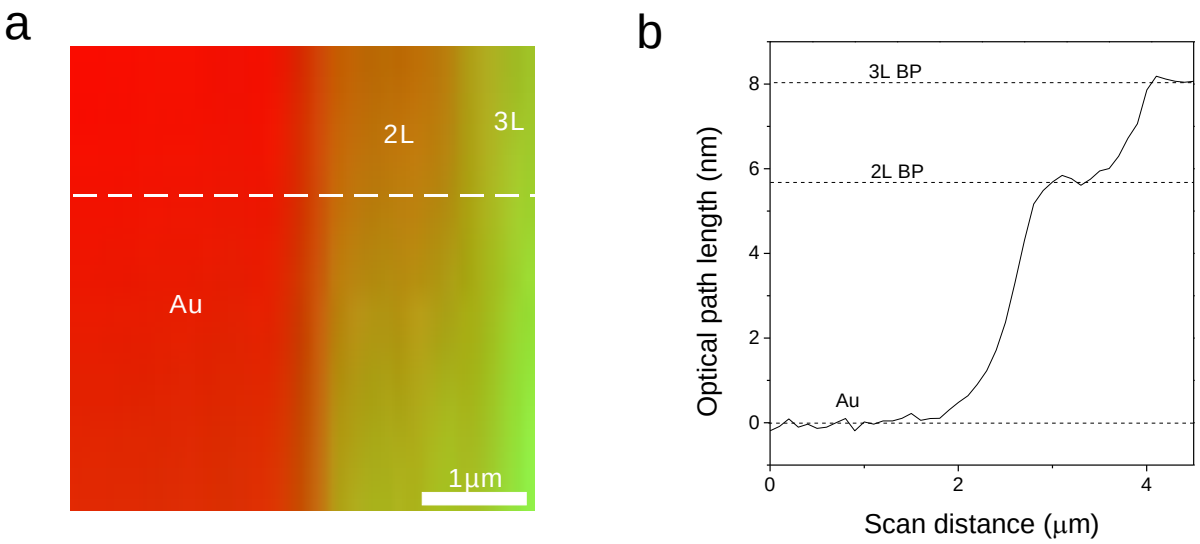

Figure S2 | PSI images of phosphorene on Au substrate. a, PSI image of phosphorene samples from the upper box on Au substrate enclosed by the dash line in Figure 2b. **b**, PSI measured OPL values versus scan position for the phosphorene along the dash line in (**a**).

3. PSI of another 2L phosphorene sample

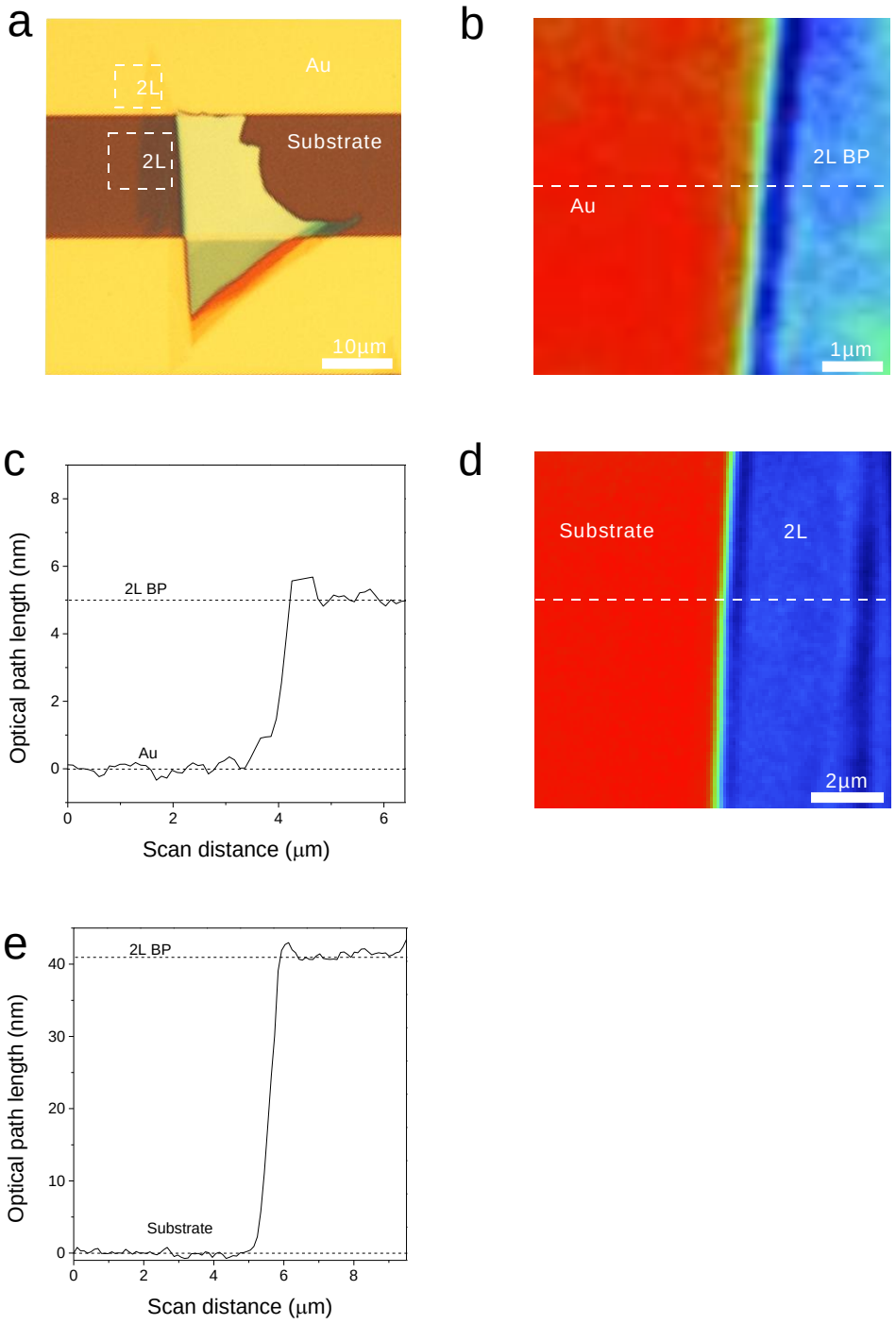

Figure S3 | PSI of another 2L phosphorene sample. a, Optical microscope image of the 2L phosphorene sample, with half on SiO_2/Si substrate and the other half on Au. **b**, PSI image of 2L phosphorene on Au from the upper box enclosed by the dash line in (**a**). **c**, PSI measured OPL values versus scan position for 2L phosphorene along the dash line in (**b**). **d**, PSI image of 2L

phosphorene on SiO_2/Si from the lower box enclosed by the dash line in (**a**). **e**, PSI measured OPL values versus scan position for 2L phosphorene along the dash line in (**d**).

4. Kelvin probe force microscope (KPFM) image for monolayer phosphorene sample

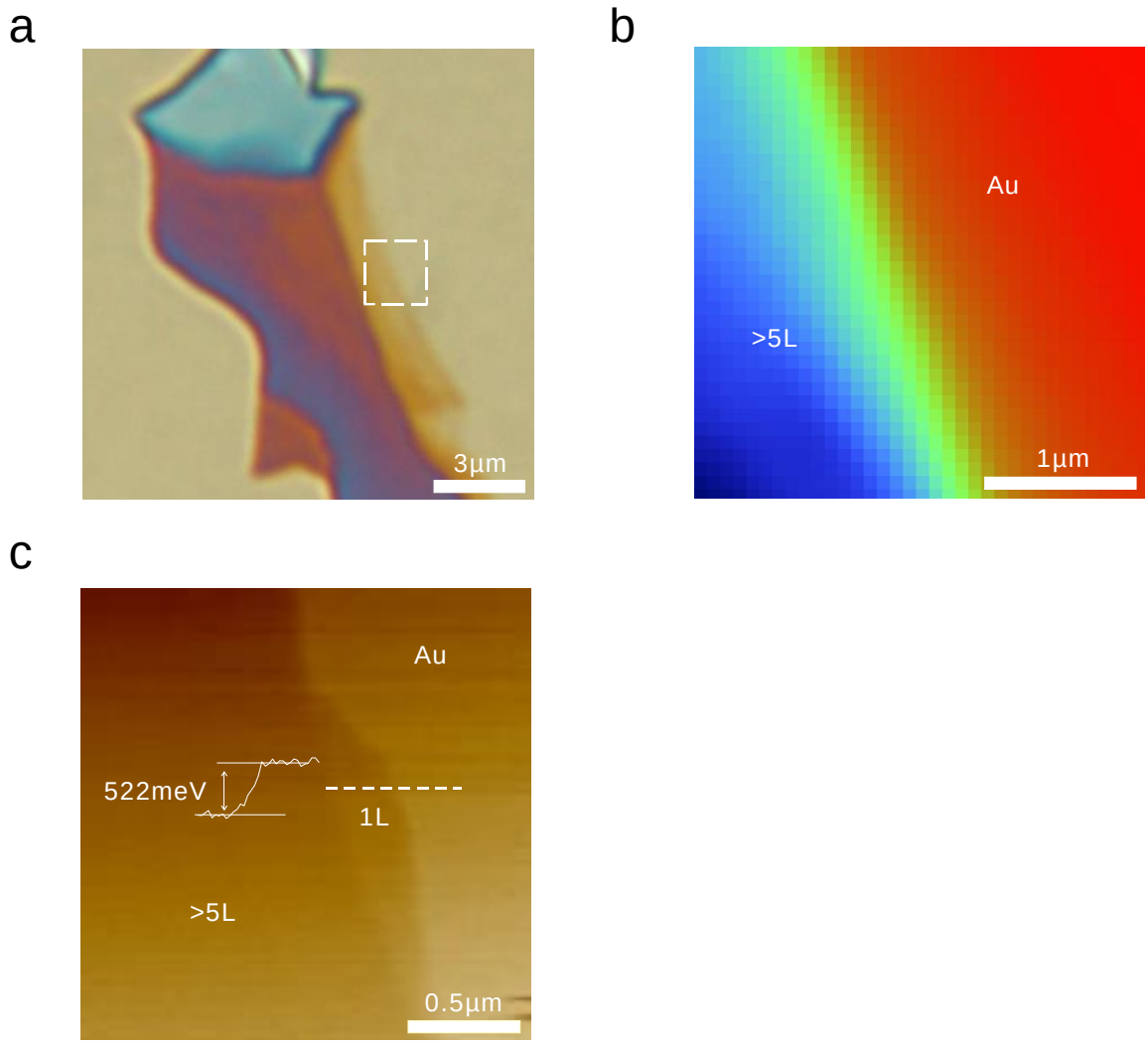

Figure S4 | KPFM for monolayer phosphorene sample. a, Optical microscope image of the monolayer phosphorene sample. **b**, PSI image of monolayer phosphorene from the box enclosed by the dash line in (**a**). KPFM image and measurement results of the monolayer phosphorene the box enclosed by the dash line in **(a).**

Here, the monolayer phosphorene is clearly observed in KPFM image as shown in Figure S4c while it is absent under the PSI image in the Figure S4b. This is because the resolution of our PSI system in lateral dimension is ~1 μm, which is limited by optical diffraction. The lateral size of the monolayer phosphorene in Figure S3c is less than 1 μm.

References

1. Liu, V.; Fan, S. S4 : A Free Electromagnetic Solver for Layered Periodic Structures. *Comput. Phys. Commun.* **2012**, 183, 2233-2244.
2. Nagahama, T.; Kobayashi, M.; Akahama, Y.; Endo, S.; Narita, S.-i. Optical Determination of Dielectric Constant in Black Phosphorus. *J. Phys. Soc. Jpn.* **1985**, 54, 2096-2099.