Electrochemically Exfoliated Large-area Phosphorene Enables Promising Flexible Nanoelectronics

Li Tao,[1,2*] Weinan Zhu,[2] and Deji Akinwande[2,*]
[1]*School of Materials Science and Engineering, Southeast University, 211189, China.*
[2]*Microelectronic Research Center, The University of Texas at Austin, TX 78758, U.S.A.*
[*] *tao@seu.edu.cn; deji@ece.utexas.edu*

Phosphorene, the phosphorus analog to graphene, has been rediscovered as a promising two-dimensional (2D) buckled atomic sheet for nanoelectronics[1-3] due to unique combined merits of graphene and transitional metal dichalcogenides. For instance, black phosphorus (BP) exhibits tunable bandgap (0.3-2 eV) and descent carrier mobility (100-1000 cm^2/Vs) with 10^3-10^5 gate modulation even on mechanically flexible polyimide substrate.[4, 5] Nevertheless, the roadblock is how to produce large-area uniform phosphorene sheets for practical use. Direct synthesis of phosphorene, e.g. layer controllable BP, remains a great challenge. Liquid phase mechanical exfoliation succeeded in volume production of few layer BP,[6, 7] but it lacks thickness control and desired electronic performance as aforementioned tape-exfoliated small flakes.

We present the first demonstration on electrochemically exfoliated (EcE) black phosphorus for flexible nanoelectronics, yielding large-area thickness-controllable high-performance phosphorene that current technique cannot afford. This new approach exfoliates large-size uniform phosphorene from bulk sources (Fig.1), depending on applied DC voltage, current and water-thinning effect. AFM indicates that EcE phosphorene sheet can reach a lateral size ~500 µm (Fig.2). typical tand 5-80 nm thickness range with uniformity evidenced by Raman mapping (Fig.3). EcE phosphorene forms suspension, which can be applied to arbitrary substrates with desired size and concentration. Bottom-gated field-effect transistors based on EcE phosphorene has been fabrication on polyimide[5] and exhibit a significantly improved symmetric ambipolar charge transport behavior on drain current versus gate voltage (I_d-V_g), compared to reported liquid phase exfoliation that usually shows p-type I_d-V_g curve[7]. Our EcE phosphorene devices observe field-effect mobility ~237 cm^2/V-s with I_{max}/I_{min} ~10^4 (Fig. 4), comparable to high-performance tape-exfoliated BP flakes. Given our recent record on tape-exfoliated BP based flexible RF transistors giving intrinsic f_T=20 GHz sustainable up to 1.5% tensile strain[5, 8], we expect such a similar high performance device on EcE phosphorene. This work employed microscopy, spectroscopy, device fabrication and characterization to investigate material and device performance of EcE phosphorene, which represent a renewed opportunity for enhanced flexible phosphorene nanoelectronics.

References:

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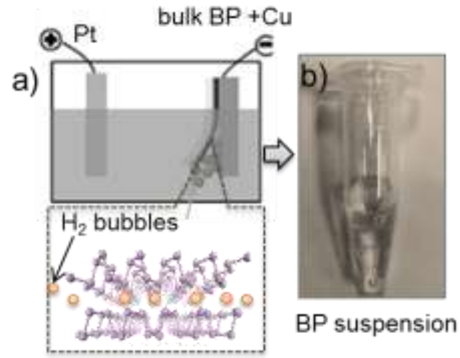

Figure 1. *Electrochemical exfoliation of black phosphorus (BP)*. **a)** Schematics of process setup and **b)** collected phosphorene suspension in a centrifuge tube.

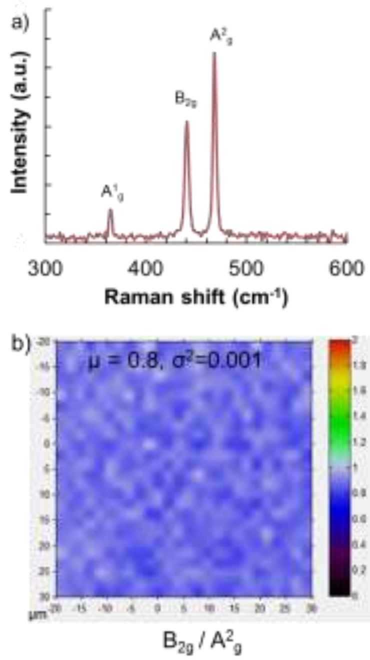

Figure 3: Raman characterization on electrochemically exfoliated phosphorene. **a**) A representative Raman spectrum with phosphorene signature peaks; **b**) $50 \times 50\,\mu m^2$ mapping data indicating uniform thickness as seen in the mean value, μ, of intensity ratio between B_{2g} and $A^2{}_g$ peaks with a small variation, $\sigma^2 < 0.001$.

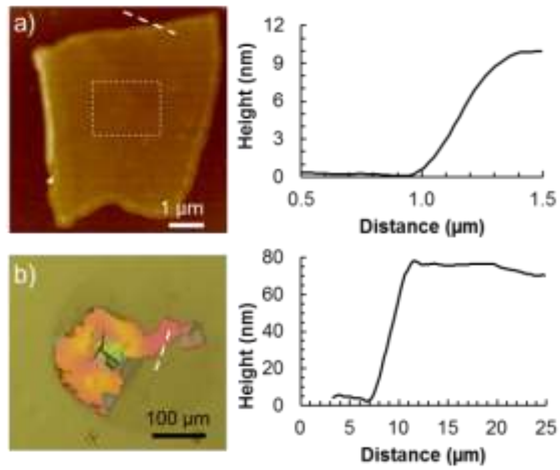

Figure 2: Atomic Force Microscope images of electrochemically exfoliated phosphorene. **a**) Thin (~10 nm) small flake and **b**) thick (~75 nm) large sheet with lateral size 500-700 µm.

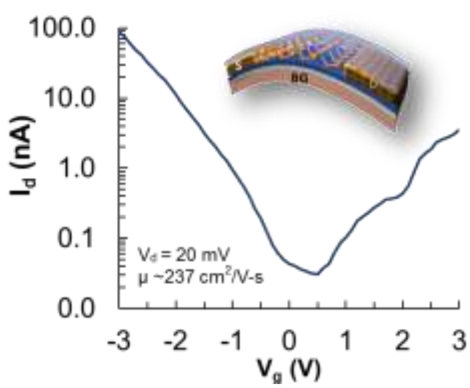

Figure 4. Electrostatic transport measurement of electrochemically exfoliated phosphorene device on polyimide. Al_2O_3 capped non-optimized device shows symmetric ambipolar I_d-V_g with estimated field-effect mobility ~237 cm^2/V-s and gate modulation (I_{max}/I_{min}) ~10^4 , which combines merits of graphene and transitional metal dichalcogenides.