Supplementary Information

Solvent Mediated Hybrid 2D Materials: Black Phosphorus - Graphene Heterostructured Building Blocks Assembled for Sodium Ion Batteries

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Experimental details

1. Co-exfoliation of graphene and black phosphorous

12 mg of black phosphorous (crystal pieces from Smart Elements) and 12 mg of graphene (Graphene X from cheaptubes) were added into 40 mL N-methyl-pyrrolidinone (NMP). The solution was sonicated in ice bath by inserting the sonicator (Sonics, VCX750, 30% amplitude) probe into the centrifuge tube sealed with PDMS and Parafilm for minimizing air exposure. The sonication process is set to be 3s pulse on and 3s pulse off to avoid excessive heating for 5 hrs. After sonication, the solution was left overnight for further use. For comparison, BP and G were individually probe sonicated in NMP solution with the same initial concentration of 0.6 mg/mL.

2. Electrode assembly by electrophoretic deposition

Electrophoretic deposition (EPD) was performed by using two identical stainless steel pieces (316 stainless steel coil from Trinity Brand Industries, 0.006 inch thick) with a size of 0.8 cm×3 cm as working and counter electrodes. Electrodes were immersed into 12 mL co-exfoliated solution in a plastic tube with an immersion depth of 2.5 cm. 200 V constant voltage was applied to the electrodes, and the corresponding current was recorded by a sourcemeter (Keithley 2400) integrated with a LabView data acquisition software.

3. Electrochemical test

Coin-cell type batteries were fabricated in an Ar-filled glovebox with O_2 level <0.5 ppm for electrochemical tests. Co-exfoliated BP/G on stainless steel by electrophoretic

deposition was cut into ~0.8 cm×0.7 cm and applied as anode materials by directly cutting the stainless steel. Whatman grade GF/F glass microfiber was used as separator. 1 M $NaPF_6$ (Sigma Aldrich, 98%) in ethylene carbonate/diethyl carbonate (EC/DEC, 1/1 v/v, Sigma-Aldrich, 99%/>99%) with 10 vol% 4-Fluoro-1,3-dioxolan-2-one (FEC) (Alfa Aesar, 98%) was used as electrolyte. Sodium metal (Strem Chemicals, 99.95%) was used as counter electrode. Electrochemical charge/discharge was performed on a MTI battery testing system with current densities of 100 mA/g_P, 200 mA/g_P, 500 mA/g_P.

4. Material characterization

The morphology of electrodes with co-exfoliated BP/G deposited on stainless steel was characterized by using a Zeiss scanning electron microscope (SEM), The zeta potential and hydrostatic sizes of different exfoliated solution was measured on a Malvern Zetasizer Nano ZS instrument. The morphology of co-exfoliated BP/G in NMP solution and after EPD on steel were further characterized by a FEI Osiris transmission electron microscope (TEM). Crystallographic analysis of bulk BP, exfoliated BP, co-exfoliated BP/G, bulk G, exfoliated G was performed by using a Scintag XGEN 4000 to obtain X-ray diffraction pattern using Cu Kα 1.542 Å.

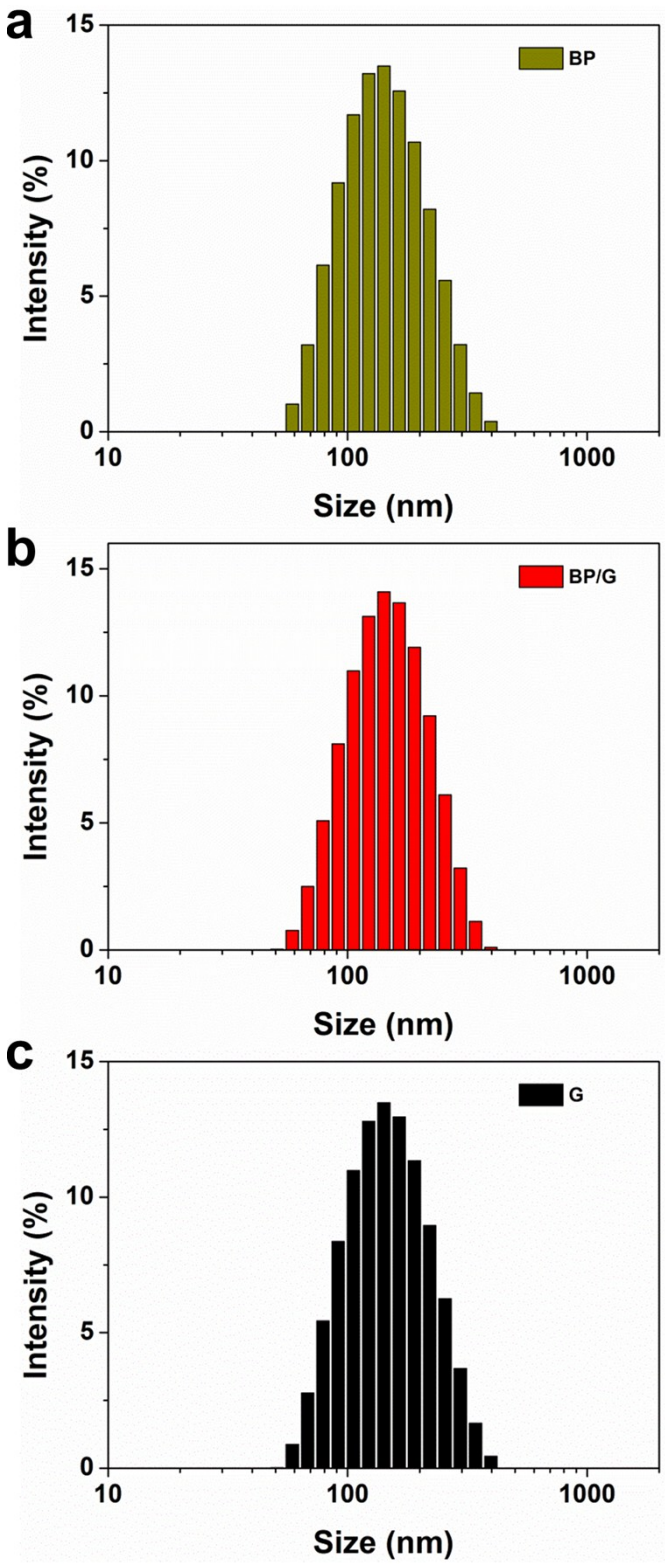

Figure S1. Hydrostatic radius distribution measured on zetasizer for (a) exfoliated BP in NMP, (b) co-exfoliated BP/G in NMP, and (c) exfoliated G in NMP.

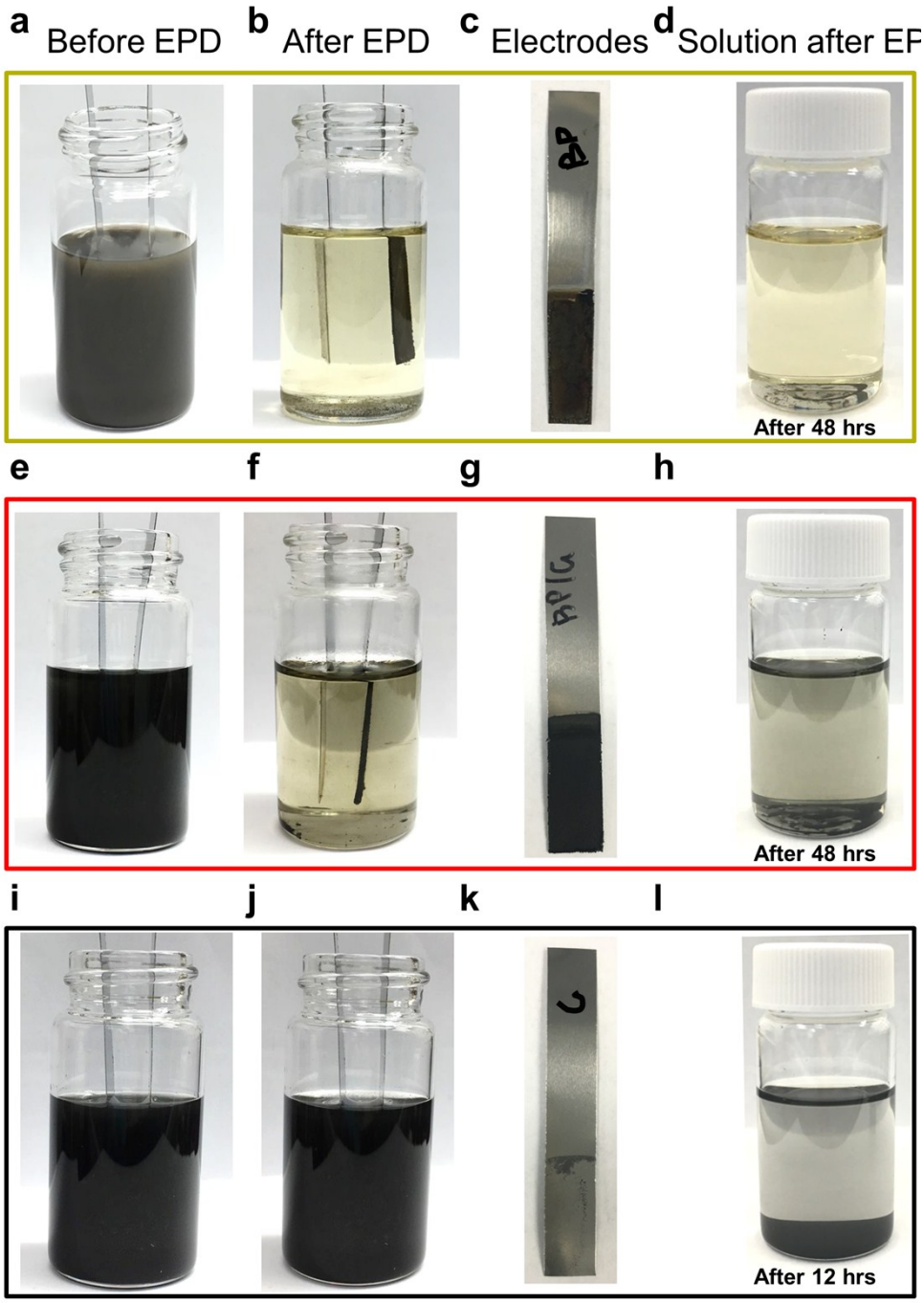

Figure S2. Exfoliated solution before and after EPD, the electrode looking and sedimentation tests for (a)-(d) BP in NMP; (e)-(h) BP/G in NMP; and (i)-(l) G in NMP.

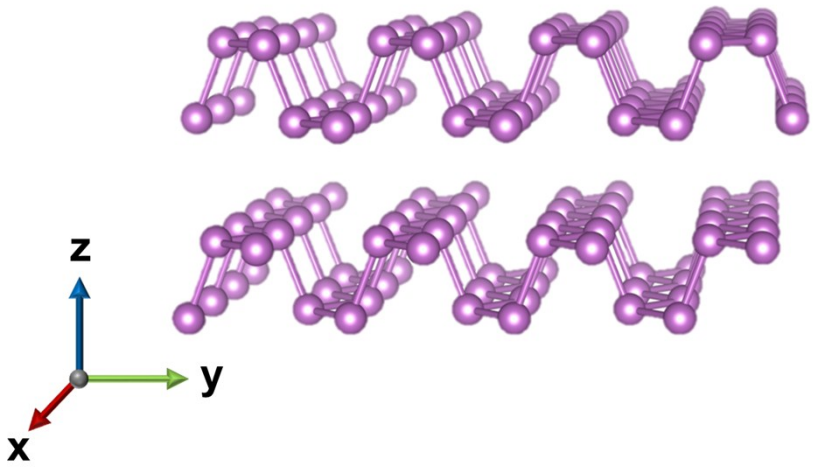

Figure S3. Coordinated of orthorhombic few-layer BP.

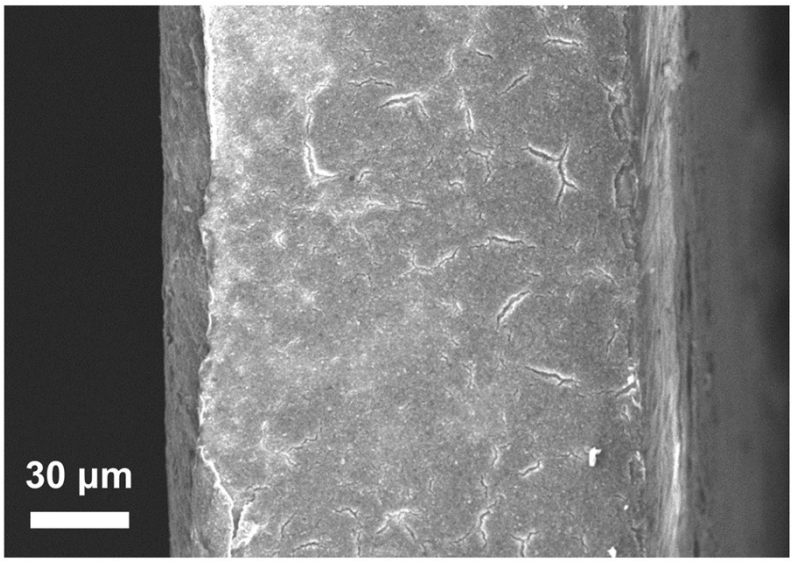

Figure S4. SEM cross-sectional view of the as-deposited materials on stainless steel electrode.

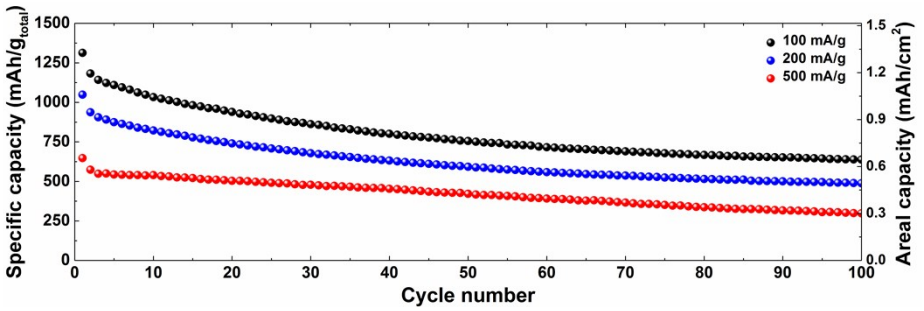

Figure S5. Specific and areal capacities upon cycling.

Table S1. Electrochemical performances comparison with other layered materials and heterostructures as sodium-ion battery anodes.

SIB Anode	1st cycle	Cycling
Graphene [Ref 31]	270 mAh/g at 200 mA/g	~118 mAh/g at 1200 mA/g for 8000 cycles
RGO paper [Ref 72]	500 mAh/g_{anode} at 100 mA/g	~100 mAh/g at 100 mA/g for 1000 cycles
MoS_2/Graphene paper [Ref 73]	943 mAh/g_{total} at 25 mA/g	214 mAh/g at 100 mA/g for 5 cycles
2D MXene/SnS_2 [Ref 74]	882 mAh/g at 100 mA/g	407 mAh/g at 100 mA/g for 200 cycles
Few layer SnS_2 on few layer RGO [Ref 75]	~850 mAh/g at 100 mA/g	649 mAh/g at 100 mA/g for 6 cycles 469 mAh/g at 800 mA/g for 1000 cycles
Porous 2D MXene [Ref 76]	641 mAh/g at 100 mA/g	180 mAh/g at 100 mA/g for 200 cycles
This work*	1183 mAh/g_{total} at 100 mA/g	648 mAh/g_{total} at 100 mA/g for 100 cycles