Multilayer Graphene Stabilized Lithium Deposition for Anode-free Lithium Metal Battery

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Graphene transfer to silicon wafer substrate

For graphene transfer to silicon wafer substrate from Cu substrate, PMMA solution was spin-coated on graphene/copper foil (500 rpm, 5 s and 3000 rpm, 30 sec) and dried in air. The copper etched with 0.5M $FeCl_{3(aq)}$ solution, and the graphene film rinsed in deionized water to remove etching solution. To remove Fe^{3+} ions residual on graphene created during etching and p-type doping caused by H_2O/O_2, the PMMA coated graphene further treated with a buffered oxide etch (BOE) solution mixture of (40% NH_4 and 49% HF with a volume ratio of 6:1) in water for 120 seconds. The silicon wafer substrate placed in a water bath that contains graphene film positioning at a tilt angle of ~45° underneath the floating film. Water was pulled out to adhere floating graphene film onto the silicon wafer substrate while positioning the film with a plastic tweezer. Thus, graphene film on silicon wafer substrate coated sequentially with PMMA and dried with air gun to improve its attachment with the substrate. Finally, the PMMA coating layer cleaned from graphene surface with acetone bath and the resulting graphene film on silicon substrate used to characterized the quality of the film, and the number of graphene layers by optical microscopy and Raman spectroscopy.

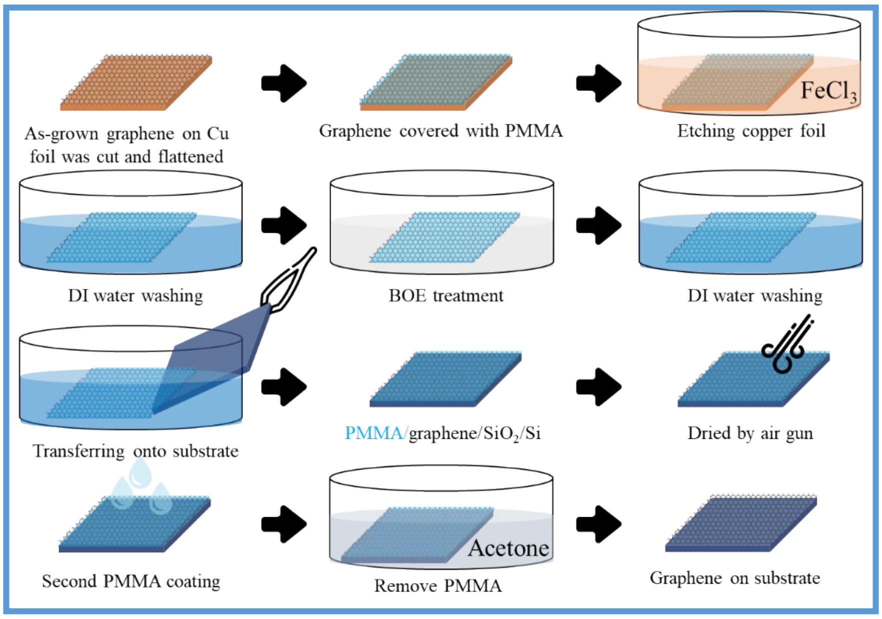

Fig. S1. Schematics showing the graphene transfer process from copper to SiO_2/Si substrate for Optical Microscopy and Raman characterization.

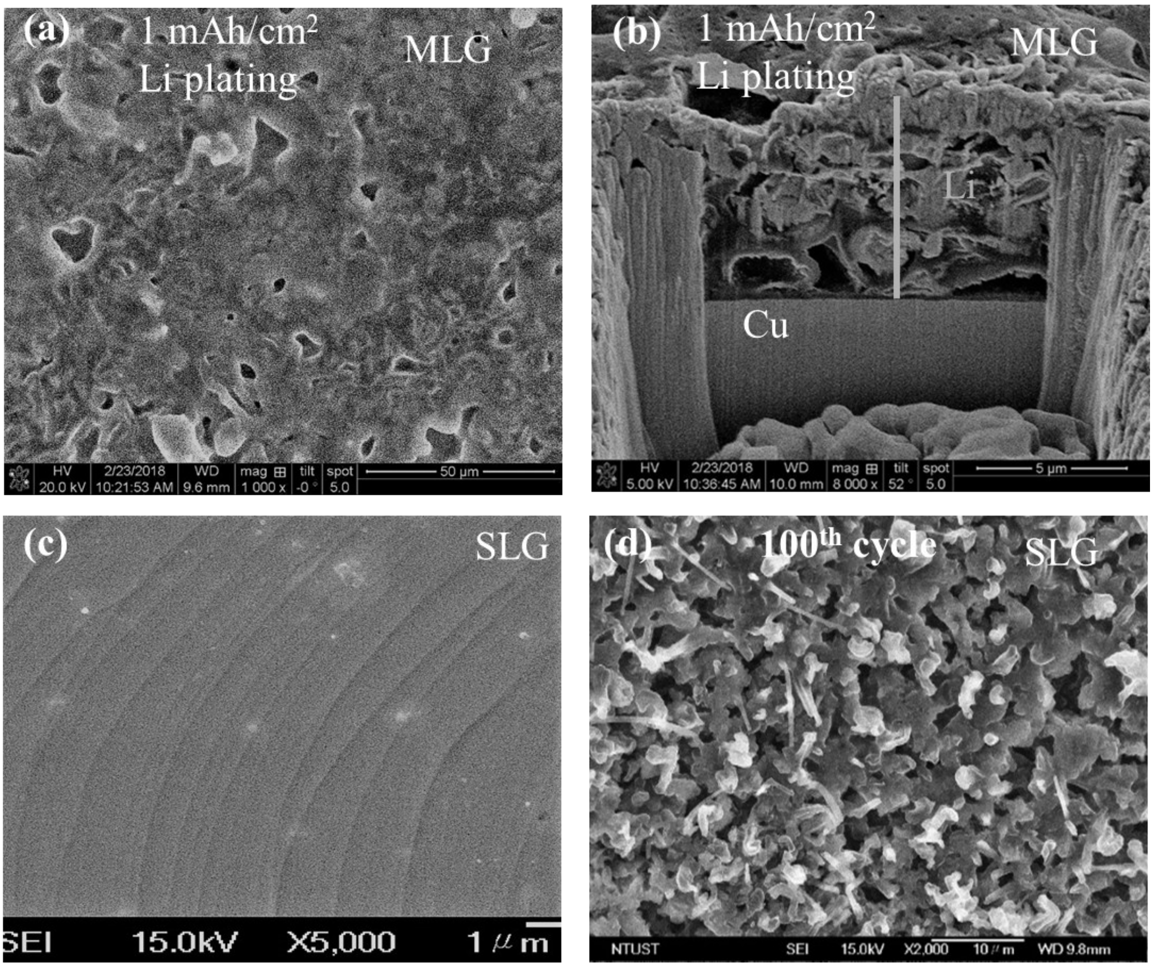

Fig. S2. Focus ion beam (FIB) image of lithium MLG protected electrode after plating 1 mAh/cm2 at current density of 1 mA/cm2 (a) top view, and (b) cross-section of deposited lithium. (c) Scanning electron micrograph of single-layer graphene on copper showing a more uniform film without patches after BOE treatment and graphene wrinkles were visible. (d) Morphology of SLG protected copper after 100^{th} Li plating/stripping cycle. Lithium morphology on anode shows compact to needle-like filaments.

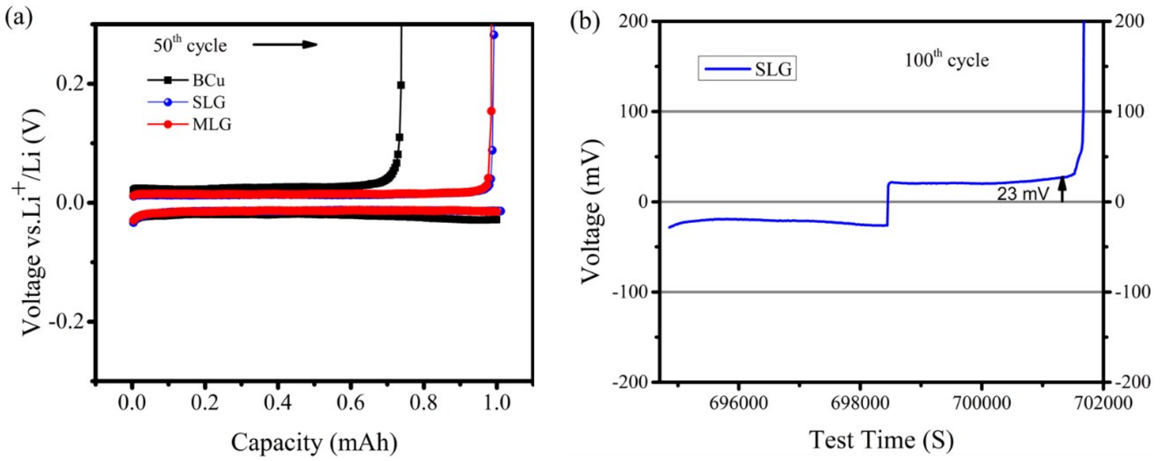

Fig. S3. (a) Selected 50th cycle voltage profile comparison of BCu, SLG and MLG and (b) 100th cycle voltage profile for single layer graphene after cycling lithium at current density of 0.5 mA cm^{-2} in 1M LiTFSI, DME/DOL, 2wt% $LiNO_3$.

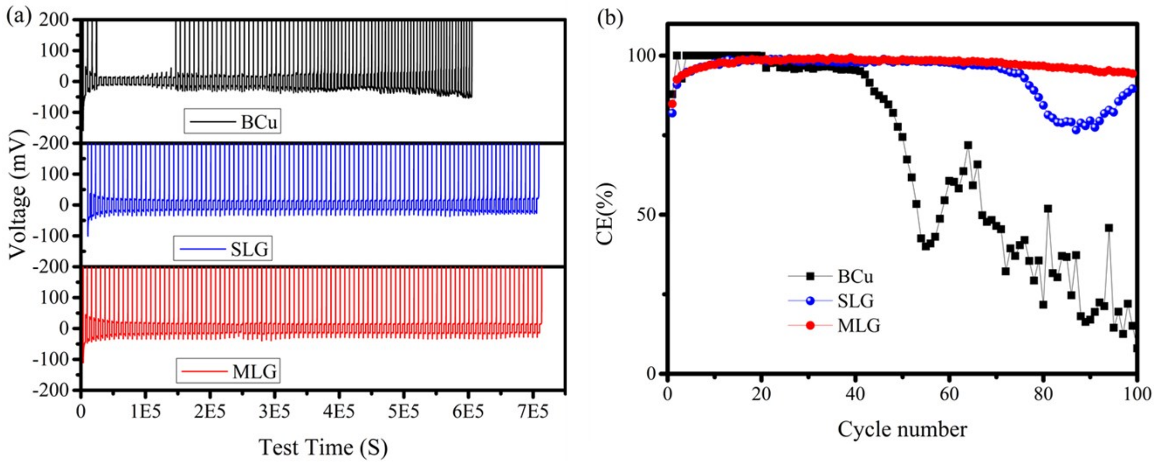

Fig. S4. Lithium cycling performance of three electrodes (BCu, SLG, and MLG). (a) voltage profile and (b) corresponding Coulombic efficiency of cells in (a) at a current density of 0.5 mA cm^{-2} and lithium deposition capacity of 0.5 mAh cm^{-2} in 1M LiTFSI, DME/DOL, 2wt% $LiNO_3$ electrolyte.

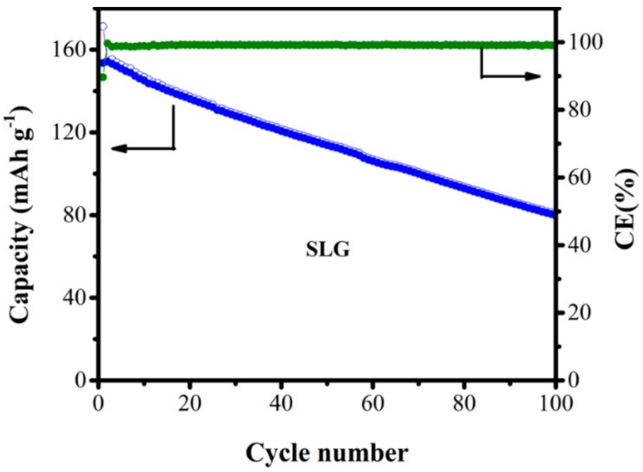

Fig. S5. Full-cell performance of SLG/LFP in 1M LiTFSI, DME/DOL, 2wt% $LiNO_3$.

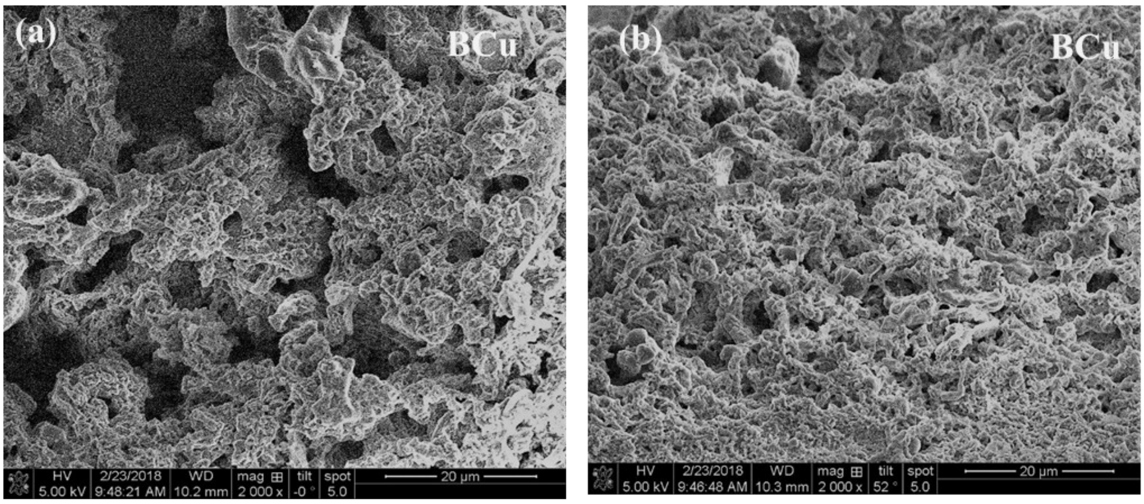

Fig. S6. FIB image of lithium morphology on bare copper (a) top view and (b) 52^{o} tilt angle side view collected after 100 cycles by pairing with $LiFePO_4$ cathode at a rate of 0.2 mA/cm^2 in 1 M LiTFSI, DME/DOL, 2wt% $LiNO_3$ electrolyte.