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Bulk graphdiyne powder applied for highly efficient lithium storage

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Methods

Synthesis of GDY powders. Copper powder was washed with 4 M HCl (100 mL), sonicated for 3 min, washed with water and EtOH, sonicated for 3 min, washed twice with acetone, and dried under N_2. Washed copper powder and pyridine (50 mL) were charged in a three-neck flask; the mixture was heated at 120 °C under N_2 for 1 h and then the temperature was decreased to 80 °C. Hexakis[(trimethylsilyl)ethynyl]benzene (200 mg) was dissolved in THF (50 mL) in an ice bath (ice and NH_4Cl) and purged with N_2 for 30 min. 1 MTBAF in THF (2.5 mL)was added under N_2 and then the mixture was stirred for 15 min at this low temperature (generally, the solution should be purple; it is related to the quality of the TBAF solution). The reaction mixture was diluted with EtOAc, washed three times with saturated NaCl, dried ($MgSO_4$), and filtered. The solvent was evaporated under vacuum while maintaining the temperature below 30 °C. (The deprotected compound should be processed in dark, rapidly, and at low temperature to avoid its decomposition).The residue was dissolved in pyridine (50 mL), transferred to a N_2-protected constant addition funnel, and added dropwise into the mixture containing pyridine (50 mL) and copper powder at 80 °C (step2); this addition process lasted for 8 h. The entire process, from deprotection to addition, should be continuous and rapid to avoid contact with oxygen. After addition of the deprotected compound, the reaction mixture was maintained at 120 °C for 3 days. Upon completion of the reaction, the pyridine was evaporated under reduced pressure. The crude products were washed sequentially with acetone and hot (80 °C) DMF. The combined crude product was washed with hot DMF to remove oligomers. The solid was heated sequentially under reflux at 100 °C for 8 h in 4 M NaOH, 6 M HCl, and 4 M NaOH to remove silicon and copper. The crude product was collected through centrifugation, washed sequentially with hot DMF (80 °C) and hot (70 °C) EtOH, and then dried.

Materials characterization.. Morphological information was obtained using field emission scanning electron microscopy (FESEM, HITACHI S-4800) and transmission electron microscope (TEM, JEOL 2010F). Raman spectra were recorded at room temperature using an Thermo Scientific DXRxi system with excitation from an Ar laser at 532 nm. The X-Ray photoelectron spectrometer (XPS) was collected on VG Scientific ESCALab220i-XL X-Ray photoelectron spectrometer, using Al Ka radiation as the excitation sources. Nitrogen adsorption/desorption measurements were performed at 77 K using a Quantachrome Autosorb gas-sorption system.

Electrochemical measurements. The electrochemical experiments were performed in 2032 coin-type cells. The electrodes were prepared by mixing 70 wt % GDY with 20 wt % Super P and 10 wt % polytetrafluoroethlyene (PTFE) binders. The obtained GDY-based electrode samples were rolled into slices and cut into square pieces of 0.5 cm × 0.5 cm (typically 2.0 mg/cm^2), then pasted on a stainless steel current-collector under a pressure of 15 MPa, followed with dried in vacuum oven at 120 °C for 4 h, used as the working electrode. Pure Li foil was used as the counter electrode, which was separated from the working electrode by a Celgard 2500 polymeric separator. The electrolyte was 1 M $LiPF_6$ in EC/DMC/DEC (1:1:1, v/v/v) containing 5% (by volume) VC. The cells were assembled in an argon-filled glovebox with the concentrations of moisture and oxygen at less than 1ppm. The galvanostatic charge/discharge cycling performance was measured using a LAND battery testing system in the voltage range from 5 mV to 3 V vs Li/Li$^+$. Cyclic voltammetry (CV) was performed using an IM6 electrochemical workstation between 5 mV and 3 V vs Li/Li$^+$ at a scan rate of 0.1 mV/s. Electrochemical impedance spectroscopy (EIS) was performed over frequencies ranging from 100 kHz to 100 mHz. The capacity was calculated based on the mass of GDY.

Results and discussion.

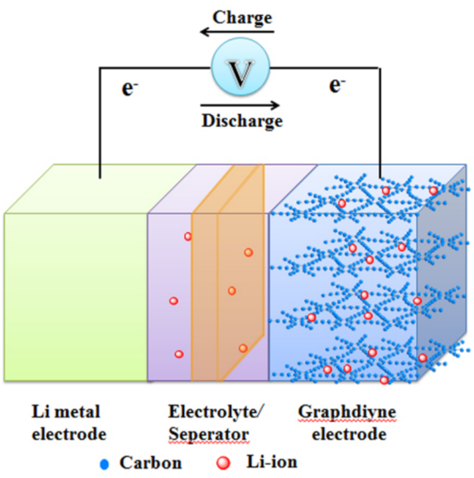

Fig. S1 Schematic representation of an assembled GDY-based battery

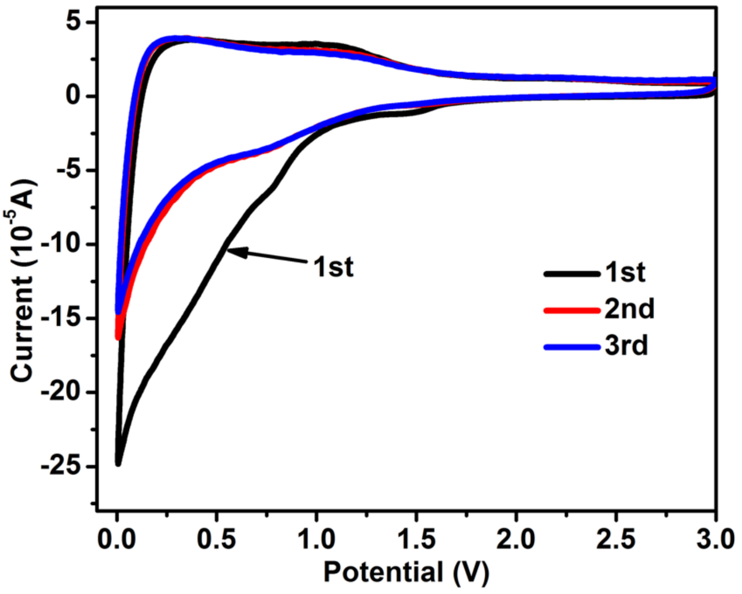

Fig. S2 Cyclic voltammogram (CV) profiles of GDY based electrode at a scan rate of 0.1 mV/s.

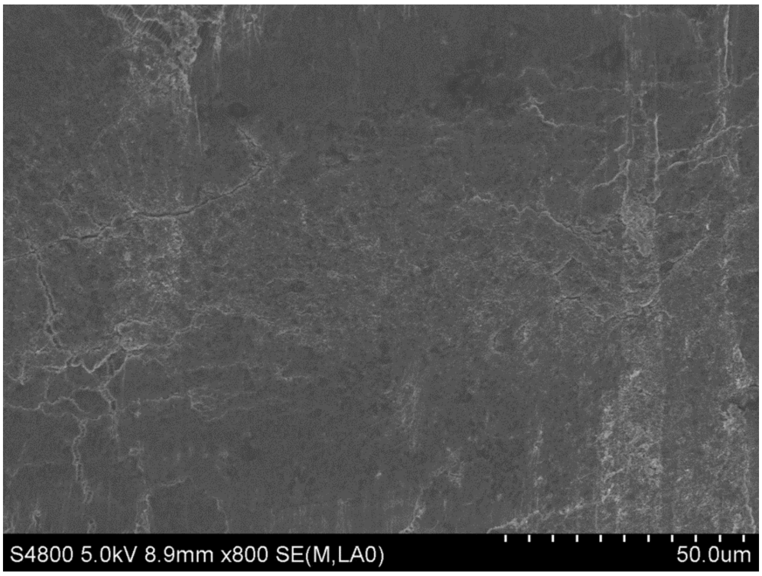

Fig. S3 The SEM images of GDY-based electrode before cycles.

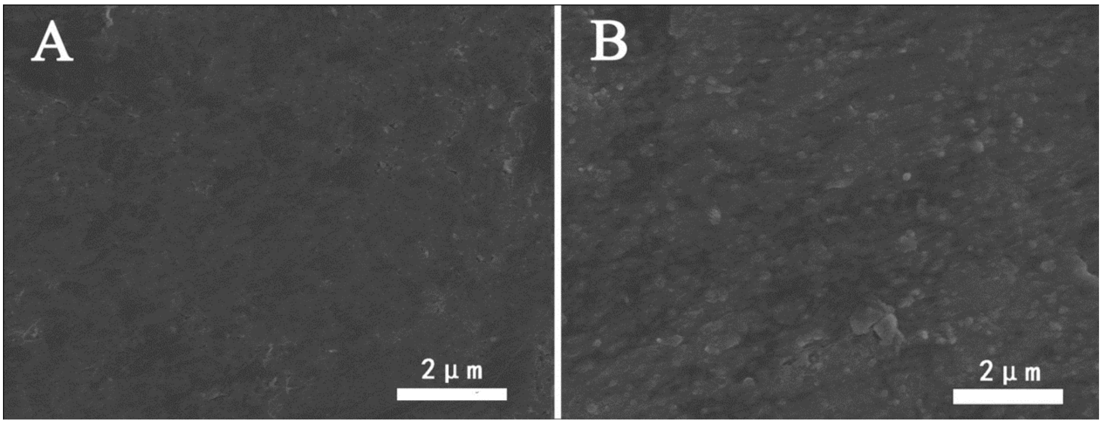

Fig. S4 The SEM images of GDY electrode before (A) and after 200 cycles (B) at a current density of 200 mA/g.

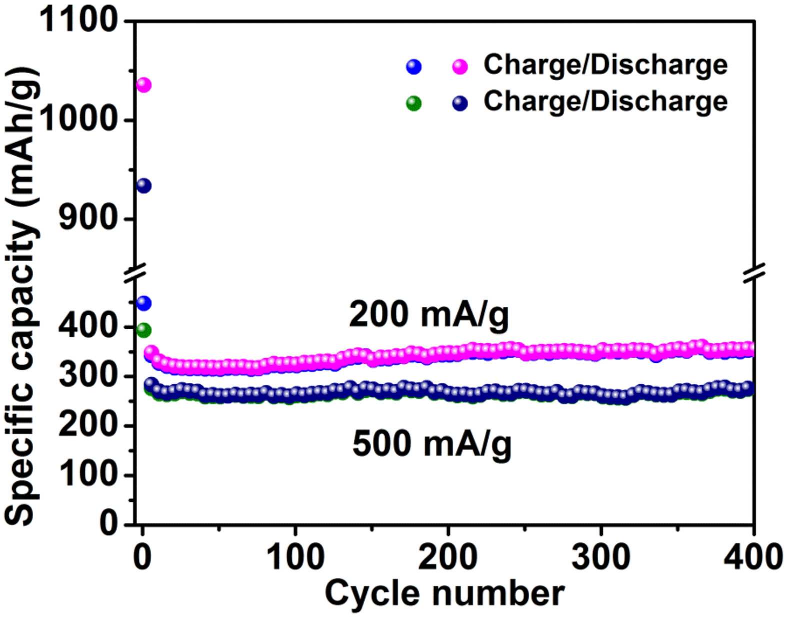

Fig. S5 Cycle performance of GDY electrodes under 200 and 500 mA/g, respectively.

Samples	Before cycles	After cycles
Re (Ω)	2.698	3.149
Rct (Ω)	44.31	81.4

Table S1 Kinetic parameters of GDY electrode before and after 200 cycles.

In the equivalent circuit, where Re represents the electrolyte resistance, R_{SEI} and CPE1 are the resistance and capacitance, respectively, of the solid electrolyte interface (SEI) formed on the electrode, Rct and CPE2 represent the charge-transfer resistance and the double layer capacitance, respectively, and Zw is the Warburg impedance related to the diffusion of lithium ions into the bulk electrode.