Abstract:
Drilling nanosized holes in the graphene basal plane can improve its capacitance and create efficient ion transport pathways. To take advantage of this effect, the holey graphene-based electrode was fabricated successfully by microwave-assisted chemical etching (MACE) and the microstructure of nanosized holes was observed by SEM. Using the cyclic voltammetry (CV), galvanostatic charge/discharge (GCD) test, it was found that the nanosized holes can improve the gravimetric capacitance from 24.35 F g⁻¹ to 48.12 F g⁻¹ in sodium sulfate solution. This positive result has a potential to open up more opportunities for mobile power supply.

Background:
According to MACE method, holey graphene can be fabricated by follow steps:
1) Pretreatment: The graphene oxide(GO) solution is pretreated by irradiating in a microwave reactor to form defected graphene oxide(dGO).
2) MACE process: The dGO is mixed with hydrogen peroxide in a reaction tube and irradiated in the microwave reactor to further etch and extend the dGO to holey graphene oxide(hGO).
3) Reduction: The hGO is reduced to hole graphene (rhGO), which can provide abundant ion transport channels and achieve charge transfer.

Results:
The surface morphology of rhGO was investigated using SEM at different magnification as shown in figure 1. It can be clearly seen wrinkled surfaces and which are smooth with folding and wrinkles at edges(Fig. 1a, b). As shown in Fig. 1b, the 10~20 nanosized holes were found like nearly spherical on the smooth surface, but they are not well dispersed.

Figure 1 | Structural characterization of rhGOS by SEM (a) SEM image of interior microstructures of rhGO. Scale bar, 500nm. (b) SEM image of nanosized holes on rhGO. Scale bar, 100nm.

Figure 2 | Electrochemical characteristic of rGO-EC and rhGO-EC in 1 M Na₂SO₄. (a) CV curves of rGO-EC and rhGO-EC at a scan rate of 100 mV s⁻¹. (b) Galvanostatic charge/discharge curves of rGO-EC and rhGO-EC at a current density of 5 A g⁻¹. (c) Comparison of specific capacitances versus different current densities for rGO-EC and rhGO-EC.

- The CV(Fig. 2a) and GCD(Fig. 2b) indicate that rhGO-ECs shows a significantly improved electrochemical performance beyond the rGO-ECs. The approximate rectangular part of CV curves and the triangular GCD curves reveal an almost electrical-double-layer capacitive behavior as well as efficient electrolyte ion transport throughout the rhGO-EC.
- The GCD curves also can derive the specific capacitance values(Fig 2c). A good gravimetric capacitance of 48.12 F g⁻¹ at a current density of 1 A g⁻¹ is exhibited by rhGO-ECs. On the contrary, the gravimetric capacitance of rGO(24.35 F g⁻¹) electrodes is about half of the rhGO.
- Increasing the current density up to 100 A/g, the rhGO displayed a 66.73% capacitance retention (32.11 F g⁻¹), the GO only retained about 55.77% of its initial capacitance (13.58 F g⁻¹).

Conclusion:
The holey graphene fabricated successfully via MACE method exhibits a better electrochemical performance when in comparison with graphene. Moreover, through SEM, the diameter of spherical nanoholes are found in a range of 10nm to 20nm, but the distribution and quantity of nanoholes are not ideal. From electrochemical measurements, the nanoholes on graphene create efficient ion transport pathway and minimize the impact of graphene re-stacking significantly. In the future, more work should focus on the population and distribution of nanosized holes.

References:

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