Supplementary Information

Comparison of Reduction Products from Graphite Oxide with that from Graphene Oxide for Anode Application in Lithium-ion Batteries and Sodium-ion Batteries

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1. Results and discussion:



3.1 Structural characterization and morphology

Figure S1 Scanning electron microscopy (SEM) images of a),b) graphite flake, c)graphite oxide, d)graphene oxide. Transmission electron microscope (TEM) image of e)parallel-orientated graphene, f)randomly oriented graphene.

The Figure S1 shows the schematic comparisons of the formation and the SEM and TEM images of the samples. The graphite flake as the beginning of both the red line and the blue line in Figure 1 is the starting raw material, as shown in the Figure S1a and S1b, providing a seed point for the oxidation process since the flake graphite would have numerous localized defects in the π -structure [1]. After

oxidation through modified Hummers method, the graphite oxide formed with a well-organized layered structure is shown in Figure S1c. After exfoliation, similar to Ref. [2], thin and crumpled graphene oxide formed (Figure S1d). Compared with graphene oxide, graphite oxide retains a stacked structure similar the raw material graphite. On the contrary, graphene oxide was exfoliated into few-layered stacks. After reduction, parallel- orientated graphene (POG in Figure 2a and 2c) and randomly oriented graphene (ROG in figure 2b and 2d) kept the structure of their parents respectively.



Figure S2 X-ray photoelectron spectroscopy (XPS) C_{1s} spectra of a) graphite oxide and graphene oxide, b) parallel oriented graphene (POG) and randomly oriented graphene (ROG).

Sample	C_{1s}	O _{1s}	C/O
Graphite flake	95.7%	4.3%	22.26
Graphite oxide	64.9%	33.7%	1.93
POG	68.2%	21.9%	3.11
Graphene oxide	61.8%	35.6%	1.73
ROG	85.1%	10.1%	8.43

Table S1 O/C ratio analysis data obtained from XPS

As shown in Figure S2, the C_{1s} spectrum of the samples can be deconviluted into several sub-peaks. The carbon combined with O in the POG and ROG have much lower peaks than that in graphite oxide and graphene oxide respectively, indicating the removal of oxygen-containing groups in graphite oxide and graphene oxide. The result can be again confirmed by the C and O contents listed in Table S1. The C/O ratio of ROG is up to 8.43, which is much higher than that of POG (3.11). This result indicates less degree of reduction for the POG than ROG.



Figure S3 Nitrogen sorption isotherms of graphite.

Figures S3 is the N₂ vapor pressure isotherms obtained on the graphite as a reference. The specific surface areas of graphite is only 81 m²g⁻¹, which is much smaller than that of POG (523 m²g⁻¹) and that of ROG (713 m²g⁻¹), as shown in Figure 3.



Figure S4 X -ray diffraction (XRD) patterns of Graphite, graphite oxide and graphene oxide.

Figure S4 shows the X-ray powder diffraction patterns. The d_{002} has greatly increased from 0.335 nm (graphite) to 0.85 nm (graphite oxide) due to water intercalation through Hummers method [1]. Note that after fully exfoliation, graphene oxide exhibits a larger d_{002} (1.42 nm) than graphite oxide (0.85 nm), which was the result of weakened interaction between graphene platelets through exfoliation. The increased d_{002} promoted the reduction process and lead to complete reduction degree for ROG, as shown in Figure 3. It is believed that due to this high-degreed reduction, functional groups on ROG was less than POG. The less of functional groups caused restacking and smaller d_{002} of ROG (compared with POG) as shown in Figure 6.

3.4 Electrochemical performance in lithium-ion batteries



Figure S5 X -ray diffraction (XRD) patterns and lattice parameters for the graphite before and after intercalation.

Samples	a (Å)	c(Å)
Graphite before intercalation	2.4587	6.6954
Graphite after intercalation	2.4694	6.7263

Table S2 Lattice parameters for the graphite before and after Li⁺ intercalation and de-intercalation

After lithium intercalation, all XRD absolute intensities of (002) face for POG (Figure 6 (c)), ROG (Figure 6 (d)) and graphite (Figure S5) have decreased. This result suggests lower degrees of periodicity on (002) face, which is the result of even randomly arranged structure after the lithium intercalation. Meanwhile, after lithium-intercalation, the intensity of the (002) diffraction peak decrease and peak position shifts towards a lower angle, suggesting that lithium intercalation causes expansion to the inter graphene sheets and introduce additional disorder to the morphology of graphene sheet assembly. After lithium intercalation, the d₀₀₂ for graphite has expanded about 10%, which is similar to previous study [3]. Besides, the lattice parameters for the graphite has increased as shown in Table S2. This might be caused by the lithium intercalation and the repulsion force between the intercalated lithium ions.



Figure S6 Schematic image of parallel oriented graphene and randomly oriented graphene: a) before lithium intercalation, b) after lithium intercalation. X -ray diffraction (XRD) patterns of electrode material after lithium intercalaion: c) parallel oriented graphene and d) randomly oriented graphene.

There are two peaks after lithium intercalation as shown in Figure S6d, indicating two larger d_{002} : 0.415 nm and 0.508 nm respectively for ROG. The expansion ratio is up to 23% and 49% respectively (only 16% for POG in Figure 6c). This large expansion ratio for ROG might be the result of repulsion force Van der Waals forces together in Figure S6b. The repulsion force between the intercalated lithium ions would expand the inter layer space for ROG. While the Van der Waals forces for ROG itself was weakened due to exfoliation as discussed. These two forces work together lead to the instability of lithium intercalation and de-intercalation channel and poor electrochemical performance of ROG as anode in LIB.



Figure S7 a) Cyclic voltammograms at a potential scan rate of 0.1 mV s⁻¹, b) galvanostatic chargedischarge curves at 50 mA g⁻¹, c)cycling performance at current density of 50mA g⁻¹, d) Coulombic efficiency, e) rate performance and f) lithium intercalation schematic image of graphite anode (LiC₆).

Figure 7 shows the electrochemical performance of graphite as anode in lithium-ion batteries. For graphite electrode, the plateaus in Figure S7 (b) suggest the staging phenomenon, corresponding to the cathodic peaks for graphite in Figure S7 (a). Figure S7 (c) shows the cycling performance of graphite,

which capacity is only 200 mAh g⁻¹. The rate performance of graphite has been shown in Figure S7

(e). The capacity drop dramatically with the increase of current density.

Reference:

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