Supporting Information

Exploiting Anti-T-shaped Graphenes Architecture to Form Low Tortuosity, Sieve-like Interfaces for High-performance Anodes for Li-Based Cells

Dong Wang,¹ Wei Zhang,*¹,²,³ Nicholas E. Drewett,² Xiaofei Liu,¹ Seung Jo Yoo,³ Sang-Gil Lee,³ Jin-Gyu Kim,³ Ting Deng,¹ Xiaoyu Zhang,¹ Xiaoyuan Shi,¹ and Weitao Zheng*¹

¹ State Key Laboratory of Automotive Simulation and Control, and Department of Materials Science, and International Center of Future Science, and Electron Microscopy Center, Jilin University, Changchun 130012, China

² CIC Energigune, Albert Einstein 48, Miñano 01510, Spain

³ Electron Microscopy Research Center, Korea Basic Science Institute, Daejeon 34133, South Korea

⁴ Ikerbasque, Basque Foundation for Science, Bilbao 48013, Spain

*E-mail: weizhang@jlu.edu.cn / wzhang@cicenergigune.com ; wtzheng@jlu.edu.cn

Experimental Section

Synthesis of multilayer-graphene nanowalls anchored on carbon paper: The carbon paper used was commercialized Toray carbon paper (CP). Every CP was tailored to be a wafer of 16mm in diameter. Subsequently, the multilayer-graphene nanowalls would be grown on this CP substrate using RF-PECVD. The parameters were 200W (power), 890°C (temperature), 30min (time) and 1000Pa (pressure), and the gas employed was CH₄:Ar =20sccm:80sccm. Each side of CPs was treated for 30min. Every cut CP was weighed using an electron balance (Sartorius BT125D), with the weight of the cut CP in the 15.5 - 15.8mg range and the weight of the CPVG approximately 0.02 - 0.04 mg more after coating.

Synthesis of Li₂S@CPVG cathode: CPVG was firstly prepared as host and current collector of Li₂S by PECVD. Then 0.5M lithium sulfide ethanol solution was prepared in glove box, and 30µL
configured solution was taken and dropped onto the CPVG, and then Li2S@CPVG cathode was harvested after dry at 80°C. The weight difference of Li2S@CPVG cathode after dry was measured by electronic balance, which reflects the weight of Li2S.

**Electrochemical Measurements:** Electrochemical experiments were performed on CR2032 coin cells assembled, using an MSK-110 coin cell crimper, in an argon-filled glove box with lithium foil(14mm) as the counter and reference electrodes. The prepared multilayer-graphene nanowalls anchored on CP(CPVG) were used as the cathode (working) electrodes. The membrane selected was Celgard 2325, and two electrolytes was used, 1MLiPF6 in EC/ DMC/DEC =1:1:1 (simply named ECe in this paper) and 1M LiTFSI and 3% LiNO3 in DOL/DME=1:1(simply named DOLe in this work). Electrochemical characterization was carried out on a Neware battery testing system. The electrochemical impedance spectroscopic (EIS) data of the cells was characterized by PARSTAT 2273, and the parameters for EIS at the high frequency was1 MHz and at the low frequency 1 mHz. The applied voltage was the open circuit voltage of battery. Every EIS was tested after wetting for more than 30min. Cyclic Voltammetry (CV) was performed using a CHI660e electrochemical analyzer. The experiments were carried out on 2032 coin cells consisting of CP and CPVG working electrodes, Li foil reference/counter electrodes and the DOLe electrolyte. The ECe and DOLe electrolytes were commercial electrolytes purchased from DoDoChem ([http://www.dodochem.cn/products/pid_14.html](http://www.dodochem.cn/products/pid_14.html))

**Materials Characterization:** A Raman spectrometer equipped with a 514.5nm laser (JY T64000, Horiba Jobin Yvon Corp.) was used to characterize the surface carbon bonding in CP and CPVG. The surface structure and elemental mapping of CP and CPVG was performed by FESEM (Field emission scanning electron microscopy, HITACHI, SU-8010 & S-4800) equipped with EDS. To obtain the interfacial information in the fibers of CP and CPVG, the samples were randomly cracked. The surface chemical element and chemical bonding for SEI film characterization was taken by X-ray photoelectron spectroscopy (VG (R3) scienta R3000). For the microstructural characterization, HRTEM, STEM and EELS analyses were carried out using TEM (FEI, ThemisZ & Carl Zeiss, Libra 200 HT Mc Cs). The materials after cycling in battery testing were separated using the MSK-110D decrimper, and the samples cleaned using DME solution and ethanol solution in succession.
Supporting information for Li-ion sulfur Battery

It is possible to calculate the theoretical energy density of a Li-S battery with a graphite anode, by using the equation:

\[ C_{\text{battery}} = \frac{C_{\text{anode}} \times C_{\text{cathode}}}{C_{\text{anode}} + C_{\text{cathode}}} \]  \hspace{1cm} (1)

where \( C (\text{Li}_2\text{S}) = 1166 \text{ mAh/g} \) and \( C (\text{carbon}) = 372 \text{ mAh/g} \), the voltage \( V \) of S and C in Li-based battery is \( \sim 2.1 \text{ V} \) (V).

\[ E_{\text{battery}} = C_{\text{battery}} \times V_{\text{battery}} \]  \hspace{1cm} (2)

The energy density of Li-S battery using carbon-based anode is \( E \),

\[ E = C \times V = 1166 \times 372 \times 2.1/1166+372 = \sim 588 \text{ (Wh/kg)} \]  \hspace{1cm} (3)

where \( C \) represents capacity, \( V \) represents voltage, and \( m \) represents the relative mass of S and C.

Clearly, by using carbon materials as the anode or host for Li-S battery, theoretical energy densities between588 and 2600 Wh/kg may be obtained (depending on the mass ratio of C and Li metal). Thus, developing a full understanding of the properties of an intercalation anode (including graphite) in ether based electrolytes is critical for high energy density batteries.

Although emerging Li-S batteries (with Li metal anodes and sulfur cathodes) exhibit a higher energy density (that can achieve up to 2600 Wh/kg),\(^1\),\(^2\) the problems of Li metal anode, such as the notorious dendrite issue and low Columbic efficiency (CE),\(^3\) have become the main bottleneck for large-scale commercial applications. To solve such problems, replacing Li metal with a lithium source (i.e. a lithium containing material) to create a Li\(^+\)-S battery consisting of graphite anodes and sulfur cathodes would seem to be a feasible option, as it yields a theoretical energy density of 600 Wh/kg.

Unfortunately, EC-based electrolytes are incompatible with poly-sulfides or sulfur radicals, and thus are unsuitable for working Li–S batteries.\(^4\) Consequently, carbon based materials are rarely used as active anodes for Li-S batteries. Given their potential utility, however, two main routes towards solving these issues in Li-S batteries have been proposed.

Firstly, it is possible to functionalize the surface of a carefully structured carbon so that its microspores (~0.5 nm) can restrict the contact of the electrolyte with sulfur directly, and thus enable the use of EC-based electrolytes.\(^5\) This is an important property, as it is generally accepted
that an EC electrolyte enables formation of a stable SEI film which prevents co-intercalation. However, although the type of electrolyte used in Li-S batteries has only has minor changes, the continuous consumption of electrolyte and further growth of SEI layers on the electrode surface leads to degraded battery life and performance.

Alternatively, tuning graphite enables its use in ether-based electrolytes, and an effective SEI film can result from the usage of the concentrated electrolytes.\(^6\) In this way, it is possible to develop a graphite electrode with a stable SEI film and thus obtain long-term cycling life. The co-intercalation issue, however, can still occur as the disordered defects induce irregular electric fields, and may fail to facilitate this protection mechanism.

It should be noted that if pristine CP is used not only as a current collector, but also as the active material, it may provide an energy density of \(~40\) mAh/g. It is worth noting, therefore, that a modified CP yields an energy density up to \(160\) mAh/g, based on the mass of the whole anode and at a current of \(~100\) mA/g. After cycling for 80 cycles at a current density of \(125\) mA/g, VGCPs show a reversible energy density of \(125\) mAh/g with a very high cumbic efficiency (CE) of over \(99.95\%\). Previous research has demonstrated that graphene may provide a maximum capacity of \(1700\) mAh/g for Li ion storage.\(^7\) Given the mass loading of graphene is 0.02–0.04 mg for these materials, the Li ion capacity of the graphene layer is subsequently far below 0.068 mAh — a relatively negligible value in comparison to the \(~2.6\) mAh of CP and CPVG (at \(50\) mA/g) observed in this study.

The harvested high rate performance and high CE indicate the structured interface enables size and charge selectivity. Moreover, various carbon surfaces may lead to the formation of different SEI films, which significantly influence rate capabilities.

In summary, these results demonstrate not on an improved material, but also provide a roadmap to future design strategies which protect the intercalation material, and improve its interfacial properties, for a wide range of battery systems.
Figure S1.  (a) The photographs of CPVG and CP, (b) The top view of CPVG by using SEM, (c) The cross-section view of CPVG by using SEM

The initial CP is gray and the CPVG is dark from observation by eye. As the CP thickness is ~200 μm, the graphene layers were coated through a double-side growth mode (~ 30 min for every side). Consequently, the carbon fibers of CP were fully covered. Figure S1c further confirms that the internal carbon fibers of CP were coated with graphene layers.
Figure S2. (a) HRTEM image of CPVG, (b) HRTEM image of CPVG for identifying the anti-T-shaped graphene coating layer
Figure S3. The fitting data of Raman spectra for both CP and CPVG.

The lower, fitted data shown in Figure S3 is the Raman spectra of CP, and the upper is the fitted Raman data for CPVG. The Tuinstra–Koenig relation can be used to evaluate the average in-plane crystalline size ($L_a$) of the un-irradiated glassy carbon and the size $L_a$ of the carbon materials, and it is given by the formula: $L_a=C\lambda^*/I_D/I_G$.

Studies have previously shown that the Tuinstra-Koenig relationship is applicable to a wide range of carbon materials with sp$^2$ bonds. $^8$ $C_\lambda$ represents the laser wavelength dependent constant, calculable from the fact that a 514.5 nm wavelength excitation laser was used. The data in Figure S3 was analyzed using Gaussian fitting (as shown in Table S1), and it was found that that the $I_D/I_G$ increased, indicating that the surface of CPVG exhibited a smaller graphite crystallite size. The spectrum also showed an additional peak at 1620 cm$^{-1}$ (i.e. the D’ peak). The increasing intensity of the D’ peak implies the sp$^2$ carbon material possessed a small crystallite size, which was commonly found in these vertically aligned carbon materials. $^9$-$^{12}$ The T peak is often found in
UV-Vis Raman, and indicates a C-C sp$^3$ signal. The D+G peak represents the increasing disorder from the fragments of graphene.

**Figure S4.** The Raman spectra of CP and CP2

The Raman spectra in **Figure S3** demonstrate that the CP remained unchanged at 890 °C, as shown by the constant $I_D/I_G$. CP refers to the state before the PECVD coating, and the CP2 refers to the side of the covered CP upon which vertical multilayer-graphene nanowalls were not grown after the PECVD process (as a result of the contact with the substrate).
Figure S5. The cycle performance of CP and CPVG at a current density of 1 mA/cm² in the electrolyte of DOLe: (a) and (b) are the charge–discharge curves of the capacity corresponding to voltage profiles at 1st and 5th cycle; (c) is the charge–discharge curves of the time corresponding voltage profiles during 40th to 50th cycle; and (d) is the charge-discharge capacity and columbic efficiency plots over 80 cycles at 1 mA/cm².
Figure S6. The X-ray energy dispersive spectroscopy (EDS) elemental mapping of CP and CPVG after several cycles in DOLe electrolyte. (a), (d) the SEM of mapping area in CP and CPVG, respectively; (b) and (c) C, F mapping of CP after cycles, respectively; (e) and (f) the C, F mapping of CP after cycles; (g) and (h) the CVs of CP and CPVG for 1st, 2nd and 5th cycle at 10 mV/s.

The EDS elemental mapping of CP and CPVG, after cycles, has demonstrated that the interfacial F element distribution on the surface is different for the CP and CPVG materials. For CP, the F content in interface area is higher than that on the surface. For CPVG, the F content in interface area is lower than that on the surface area. By contrast, C is uniformly distributed in two samples. This suggests that the anti-T-shaped graphene interface in CPVG highly effective at suppressing the intercalation of non-Li elements. No SEI film on the CP and CPVG was observed.
due to the low spatial resolution in Figures S6a/d; However, the EIS (see Figures 3e/f) and the CV (see Figures S6g/h) demonstrate the SEI film was indeed generated on the surface of CP and CPVG, which is expressed as the redox peak observed at ~1V in the first discharge.
Figure S7. The EDS of the cracked cross-section of the fibers found in the cycled CP (a) and cycled CPVG (b)

The EDS elemental ratio of the cross-section cleavage of fibers for CP and CPVG is shown in Figure S7. Every sample was prepared by washing with DME and ethly alcohol. The fibers of CP after cycling had been intercalated with other non-Li elements, whereas the CPVG shows astable intercalation/deintercalation. Moreover, examination of the CPVG in DOLe confirmed the existence of fibers free of S or F.
As the Li intercalated into the graphite anode, the $I_D/I_G$ of CP anode increased, consistent with the report from Kostecki et al.$^{13}$ however, the decreased $I_D/I_G$ of CPVG demonstrates that the surface nanocrystalline carbon became ordered after the Li ion intercalation/deintercalation into/out of the nanowalls (thus acting partially as the SEI film). The Raman spectroscopic analysis indicates the CPVG was stable after 50 cycles, due to the higher $I_D/I_G$ and ordering carbon surface (the value 1.46 is still larger than the CP, in contrast with the initial 2.1 in Figure S3).
Figure S9. The equivalent circuit model of CP (a) and CPVG (b) during an initial state, charge state and discharge state.
Figure S10. The XPS of CP, CPVG, CP50 and CPVG50.
Figure S11. The O1s fitting data of (a), (b), (c), and (d) CP, CPVG, CP after 50 cycles and CPVG after 50 cycles, respectively.
Figure S12. The XPS of Li 1s of CPVG and CP after cycles.
Figure S13.  (a) The discharge data of a full cell (Li$_2$S@CPVG cathode coupled with Li or CP or CPVG) at 1 C, (b) The cyclic performance of Li-S full cell at 0.5C (CPVG) and the Li foil at 0.03/0.05C

In this study, we chose a Li$_2$S@CPVG as cathode (the CPVG acts as current collector in cathode, details in Experimental Section), in comparison that the Li$_2$S@CPVG coupled with Li...
foil can harvest 230 mAh/g at 1C. Here, the CP/CPVG was taken as anode for Li-S battery after 40 cycles (To fully activate Li$_2$S), the discharge capacity of the CP could provide ~70 mAh/g (there is theoretical capacity of 1166 mAh/g for Li$_2$S); in contrast, a ~200 mAh/g at 1 C between 1~3 V can be reached for the CPVG.

It is well known that the performance of a full cell depends on the performance of both cathode and anode. The cell based on Li metal anode shows higher discharge/charge plateau due to the redox potential. There is an obvious plateau at ~1.3 V in CPVG during discharge process, whereas it cannot be found in CP after several cycles.

Figure S13b shows the cyclic performance of a full cell based on CPVG, and in contrast with the cell of Li foil as anode. The CPVG full cell shows that there is a high rate performance and stability of cyclic performance. At 0.5C, there is ~230 mAh/g for CPVG and there is almost no degeneration after 80 cycles. Contrastively, the CPVG@Li$_2$S/Li foil shows that there is ~450 mAh/g of activated S in CPVG@Li$_2$S cathode. Therefore, it can harvest higher performance Li$_2$S/CPVG full cell to couple with higher performance Li$_2$S.
Table S1.  The details of Raman fitting data.

| CP sample | Position (cm$^{-1}$) | Area (a.u.) | $I_D/I_G$ |
|-----------|----------------------|-------------|-----------|
| D peak    | 1354                 | 6636        | 0.26      |
| G peak    | 1584                 | 13850       |           |
| D' peak   | 1617                 | 1917        |           |
| T peak    | 1045                 | 2397        |           |
| 2D peak   | 2710                 | 13020       |           |
| CPVG sample |                   |             |           |
| D peak    | 1354                 | 43810       | 2.1       |
| G peak    | 1587                 | 8065        |           |
| D' peak   | 1622                 | 6904        |           |
| T peak    | 1095                 | 8628        |           |
| 2D peak   | 2701                 | 19490       |           |
| D+G peak  | 2949                 | 5058        |           |
### Table S2. The fitting data of EIS for CP, CPVG before and after charge and discharge cycles

|       | $R_s$ | $R_f$ | $R_{f2}$ | $CPE_{T1}$ | $CPE_{P1}$ | $CPE_{T2}$ | $CPE_{P2}$ | $CPE_{T3}$ | $CPE_{P3}$ |
|-------|-------|-------|----------|------------|------------|------------|------------|------------|------------|
| CP    | 3.8   | 52.0  | 1.8E-5   | 0.76       |            |            |            |            |            |
| CPV49C| 3.1   | 49.6  | 1043     | 3.9E-5     | 0.72       | 6.2E-4     | 0.78       |            |            |
| CPV50D| 3.0   | 53.1  | 986.3    | 7.1E-5     | 0.65       | 5.4E-4     | 0.81       |            |            |
| CPV50C| 3.3   | 55.1  | 977.2    | 3.9E-5     | 0.72       | 5.6E-4     | 0.81       |            |            |
| CPVG  | 4.0   | 62.6  | 7.4E-6   | 0.85       |            |            |            |            |            |
| CPV49C| 2.3   | 6.0   | 26.3     | 4.5E-6     | 0.95       | 0.3E-3     | 0.70       | 0.014      | 0.81       |
| CPV50D| 7.5   | 3.34  | 4.8      | 5.1E-4     | 0.63       |            | 0.27       | 0.89       |            |
| CPV50C| 2.6   | 6.20  | 15.0     | 6.9E-6     | 0.91       | 0.3E-3     | 0.70       | 0.026      | 0.96       |
Table S3. The details of C1s fitting data for CP, CPVG, CP50 and CPVG50. Every peak is described by the peak position (eV), the content ratio (%) and the bonding groups.

| C1s     | Peak I   | Peak II  | Peak III | Peak IV | Peak V  | Peak VI  |
|---------|----------|----------|----------|---------|---------|----------|
| CP      | 284.5(eV)| 285.5    | 286.6    | 288     | 290.3   |          |
|         | 44.1%    | 32.6%    | 11.1%    | 6.6%    | 5.6%    |          |
| Csp2    | Csp3     | C-O-H    |          |         |         |          |
| CPVG    | 284.5    | 285.5    |          |         |         |          |
|         | 78.0%    | 22%      |          |         |         |          |
| Csp2    | Csp3     |          |          |         |         |          |
| CP-50   | 284.5    | 285.1    | 286.7    | 289     | 290.2   | 293.1    |
|         | 25.1%    | 19%      | 13.4%    | 3.5%    | 7.9%    | 30.1%    |
| Csp2    | Csp3     | C-O/C-N  | C=O      | -COO-   | -CF3    |          |
| CPVG-50 | 284.5    | 285.5    | 286.5    | 288     | 289.6   | 292.7    |
|         | 6.9%     | 54.6%    | 19.3%    | 2.8%    | 1.4%    | 15.0%    |
| Csp2    | C-sp3/Li,C| C-O/C-N  | C=O      | -COO-   | -CF3    |          |
Table S4. The details of O1s fitting data for CP, CPVG, CP50 and CPVG50. Every peak is described by the peak position (eV) and the bonding groups.

| O1s   | Peak 1 | Peak 2 | Peak 3 | Peak 4 |
|-------|--------|--------|--------|--------|
| CP    | 530.3  | 531.7  | 533    |        |
|       | O=COH  | C=O/CO₂| C-OH/H₂O |        |
| CPVG  | 531.8  | 533.1  |        |        |
|       | CO₂    | H₂O    |        |        |
| CP-50 | 531.8  | 532.6  | 533.2  | 533.8  |
|       | C-OH/Li₂O₂ | Li₂CO₃ | LiN(SO₂CF₃)₂, -OH, H₂O, CO₂ |        |
| CPVG-50 | 530.4  | 532.2  | 532.9  | 533.6  |
|       | R-O-Li | Li₂CO₃ | LiN(SO₂CF₃)₂, -OH, H₂O, CO₂ |        |
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