Supporting Information

Graphene oxide-wrapped dipotassium terephthalate hollow microrods for enhanced potassium storage

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Experimental

Synthesis of hollow microrod K$_2$TP and bulk K$_2$TP

The K$_2$TP was feasibly synthesized with a reflux condensation process referring to literature. In detail, firstly, 22 mmol KOH (AR, 99%) was dissolved in 40 ml deionized water in 20% mass excess, and 10 mmol terephthalic acid (PTA) (Alfa, 98%) was added under the temperature of 50 °C under stirring and then standing the aqueous solution for 8~12 h. Secondly, 100 ml absolute ethanol was added followed by a refluxing process at 90 °C for 12 h. Utilizing ethanol is to precipitate the product and control grain size via decreasing its solubility. Thirdly, the as-obtained precipitate was centrifuged and filtered with ethanol to get rid of surplus alkali. Lastly, hollow microrod K$_2$TP was obtained by vacuum-drying at 110 °C overnight. The procedure for the synthesis of bulk K$_2$TP is similar to the synthesis of hollow microrod K$_2$TP as above. The difference is that 100 ml absolute ethanol was added into the aqueous solution of KOH and PTA after stirring under 50 °C directly without static process.

Synthesis of K$_2$TP@GO

The K$_2$TP@GO was simply synthesized as follows: 0.2 g K$_2$TP was dispersed in 20 ml (10 wt% relative to K$_2$TP) graphene oxide (GO) aqueous solution (0.5 mg ml$^{-1}$) under stirring uniformly. The product was obtained by freezing-dry for at least 48 h. We prepared hollow microrods of K$_2$TP using the neutralization reaction between terephthalic acid and KOH in 50 °C aqueous solution under stirring, and refluxing at 90 °C overnight. Then, K$_2$TP was added into graphene oxide aqueous solution.
Finally, K$_2$TP@GO was obtained by freeze-drying the homogeneous solution of graphene oxide and K$_2$TP.

**Characterization**

The crystalline structure of the materials was characterized by X-ray diffraction (XRD, D8-Advance, Bruker, Cu K$_\alpha$ radiation, $\lambda=1.542$ Å) at a scan rate of 40° min$^{-1}$ in the range of 10°–80°. Thermal gravimetric analysis (TGA) was taken on a thermal analyzer (STA 409 PC) from 100 to 800 °C at the heating rate of 10 °C min$^{-1}$ in air. Fourier transform infrared spectrometer (FTIR, Shimadzu, IR Prestige-21) test was operated within the wavenumber range of 1000–3500 cm$^{-1}$. The morphologies of the materials were conducted by field-emission scanning electron microscopy (FE-SEM, SU8010, 97HITACHI).

*In-situ* XRD experiment during electrochemical testing of battery was performed on a Bruker D8 Discover X-ray diffractometer with a non-monochromated Cu K$_\alpha$ X-ray source scanned at 20 ranges of 18 – 33°. For *in-situ* XRD measurement, the electrode was placed right behind an X-ray-transparent beryllium window which also acted as a current collector. The *in-situ* XRD signals were collected using the planar detector in a still mode during the charge/discharge processes, and each pattern took 120 s to acquire.

The electrochemical measurements were carried out by assembling 2016 coin cells, which were assembled in a glove box filled with pure argon gas, using potassium metal (99.5%, Sigma-Aldrich) as both the counter electrode and the reference electrode, a 0.8 M KPF$_6$ in ethylene glycol dimethyl ether (DME) as electrolyte and a whatman glass microfiber filter (Grade GF/F) as the separator. Anodes were obtained by mixing 60% the as-synthesized active materials (K$_2$TP@GO or K$_2$TP), 30% acetylene black, and 10% PVDF (using N-methyl-2-pyrrolidone as solvent). The homogeneous slurry was casted onto Cu foil and dried under a vacuum oven at 60 °C overnight. The anodes were punched into circle slice with an area of ~0.785 cm$^2$ and the average electrodes mass loading obtained was about 1.5 - 2.0 mg/cm$^2$. The electrochemical performance of the cells was tested by a Land Battery Test System with a cut-off voltage range from 0.1 to 2.0 V (vs. K/K$^+$). Cyclic voltammetry (CV)
were performed from 0.1 to 2.0 V at a scan rate of 0.1 mV s\(^{-1}\) and impedance spectroscopy (EIS) with the amplitude of 10 mV in the frequency range from 100 kHz to 0.01 Hz were measured with a Biologic VMP-3 electrochemical workstation.

**Diffusion coefficients of K\(_2\)TP@GO and K\(_2\)TP**

Diffusion coefficients of K\(_2\)TP@GO and K\(_2\)TP are calculated based on the Randles–Sevcik equation, where \(I_p\) is the peak current, \(n\) is the number of electrons transferred per molecule during the electrochemical reaction, \(A\) is the active surface area of the electrode, \(C\) is the concentration of potassium ions in the anode, \(D\) is the apparent K\(^+\) diffusion coefficient of the whole electrode involving the diffusion of both potassium ions and electrons, and \(v\) is the scanning rate.

\[
I_p = \frac{N F v D}{0.4463 n F A C (\frac{RT}{n^2})^{1/2}} = 2.69 \times 10^5 \times n^{3/2} AD^{1/2} C v^{1/2}
\]

![TGA analysis of as-synthesis K\(_2\)TP](image)

**Fig. S1** TGA analysis of as-synthesis K\(_2\)TP.
**Fig. S2** SEM images bulk $K_2TP$.

**Fig. S3** The storage potassium performance of GO in half cell at current density of 200 mA g$^{-1}$. The GO electrode exhibits a discharge capacity of $\sim$14.0 mAh g$^{-1}$ at a current density of 200 mA g$^{-1}$. In addition, due to the low content of GO in the $K_2TP@GO$ composite, the GO contributes to the negligible capacity of the $K_2TP@GO$ composite.
Fig. S4 CV curves of K$_2$TP in the electrochemical window between 0.1 and 2.0 V at a scan rate of 0.1 mV s$^{-1}$ in the first four cycles.

Fig. S5 Charge and discharge curves of K$_2$TP@GO at the current density of 200 mA g$^{-1}$. 
Fig. S6 Rate performance of $\text{K}_2\text{TP}$ at different rates ranging from 20 to 1000 and back to 50 mA g$^{-1}$. The rate performance of bulk $\text{K}_2\text{TP}$ is quite poor as its capacity decreases to almost zero when the current is increased to 1000 mA g$^{-1}$.

Fig. S7 Charge and discharge curves of $\text{K}_2\text{TP}@\text{GO}$ (A) and $\text{K}_2\text{TP}$ (B) at different rates ranging from 50 to 1000 and back to 50 mA g$^{-1}$. 
Fig. S8 Cycling measurements of tested at 500 mA g\(^{-1}\).

Fig. S9 Coulombic efficiency of K\(_2\)TP@GO electrode at the current density of 500 and 1000 mA g\(^{-1}\).
Fig. S10 CV curves of K₂TP@GO (A) and K₂TP (B) at diversity scan rates, and (C) the corresponding relationship between the peak current (Ip) and the square root of scan rate \( v^{1/2} \). (D) EIS plots of two electrodes.

To verify the diffusion coefficients of K\(^+\) of K₂TP@GO and bulk K₂TP electrode, CVs tests were conducted at variable scan rates (Fig. S10 A and B). The diffusion coefficients of K\(^+\) are calculated based on the Randles–Sevcik Equation. From the slope of the fitting line collected from the anodic peak A and peak B, the diffusion coefficient of the K₂TP@GO is estimated to be 1.56× 10\(^{-11}\) cm\(^2\) s\(^{-1}\), which is 8.45 times higher than that of the bulk K₂TP (1.84× 10\(^{-12}\) cm\(^2\) s\(^{-1}\)) (Fig. S10C and D).
Fig. S11 EIS plots of K\textsubscript{2}TP@GO and K\textsubscript{2}TP electrodes at different rates ranging after 100 cycles at the current density of 100 mA g\textsuperscript{-1}.

To provide further insights, electrochemical impedance-spectroscopy (EIS) was applied to quantify the resistance at the electrode/electrolyte interface. The results demonstrate a much smaller charge transfer resistance (R\textsubscript{ct}) of the K\textsubscript{2}TP@GO (164.1 Ω) compared to that of bulk K\textsubscript{2}TP (544.5 Ω) before cycling, manifesting a superior electron transfer. Apparently, the R\textsubscript{ct} value of K\textsubscript{2}TP@GO still remains much lower than that of bulk K\textsubscript{2}TP after 100 cycles at 100 mAh g\textsuperscript{-1}. (Fig. S11). This is because graphene wrapped layer restrains the dissolution as well as accommodates the volume expansion during repeated potassiation/depotassiation processes.

Fig. S12 I–V measurement of K\textsubscript{2}TP@GO (A) and K\textsubscript{2}TP (B). The I–V measurement shows that the electric conductivity of K\textsubscript{2}TP@GO is much more
superior to $K_2TP$.

**Fig. S13** In-situ XRD patterns of $K_2TP@GO$ electrode during galvanostatic depotassiation/potassiation process at 100 mA g$^{-1}$. The image plot of the diffraction patterns at $25 – 29.5^\circ$ during the first three cycles.

**Fig. S14** Schematic illustration of the $K^+$ insertion/extraction in $K_2TP@GO$ electrode.
<table>
<thead>
<tr>
<th>Active materials</th>
<th>Current density (mA g⁻¹)</th>
<th>Reversible capacity (mAh g⁻¹)</th>
<th>Cycle numbers</th>
<th>Capacity retention</th>
<th>Voltage ranges (V)</th>
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<tbody>
<tr>
<td>K₂TP@GO (This Work)</td>
<td>200</td>
<td>212</td>
<td>100</td>
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<td>K₂TP⁸¹</td>
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<td>400</td>
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<td>181</td>
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<td>170</td>
<td>100</td>
<td>91%</td>
<td>0.1 – 2.5</td>
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<tr>
<td>K₂SBDC@GO⁸²</td>
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<td>124</td>
<td>100</td>
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<tr>
<td>K₂C₆O₆⁸³</td>
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<td>150</td>
<td>100</td>
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<td>Sn-C⁸⁶</td>
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<td>105</td>
<td>30</td>
<td>64%</td>
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References