Supporting Information

3D Organic Na$_4$C$_6$O$_6$/Graphene Architecture for Fast Sodium Storage with Ultralong Cycle Life

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Experimental

The preparation of Na$_4$C$_6$O$_6$ and graphene oxide (GO):

Na$_4$C$_6$O$_6$ was fabricated by annealing of disodium rhodizonate (Na$_2$C$_6$O$_6$) at 400°C for 2h under Ar atmosphere. Graphene oxide nanosheets were synthesized from natural graphite flakes by a modified Hummers method, the details of which are described elsewhere.

The fabrication of 3D Na$_4$C$_6$O$_6$-graphene architectures:

The 3D architectures were fabricated by a simultaneous hydrothermal and assembly procedure. In a typical procedure, a 10 mL of GO (2 mg mL$^{-1}$) aqueous dispersion were mixed with amounts of Na$_4$C$_6$O$_6$ powder at a certain ratio, and the resulting mixture was then hydrothermally treated at 180 oC for 12h. Finally, the as-prepared samples were freeze-dried to preserve the 3D architectures formed during the synthesis process.

Morphological and Structural Characterization:
The morphology and microstructure of the samples were systematically investigated by SEM (JEOL-7500), TEM (Tecnai G2 F20 U-YWIN), XPS (ESCALAB 250), and XRD (Rigaku D/max2500PC) was carried out using Gu Kα radiation over the rage of 5~90° measurement. Fourier transform infrared (FTIR) spectra were recorded on a Nicolet iS50 spectrometer by using the KBr pellets in the frequency range 4000-400 cm⁻¹ to characterize and confirm the chemical structure of polyimide. Raman spectra of as-prepared samples were recorded on a Horiba JY LaRAM ARAMIS Raman microscopy. X-ray photoelectron spectra were recorded by a Thermo Electron Corporation ESCALAB 250 XPS spectrometer using a monochromatized Al Kα radiation with 200 eV pass energy with 30 eV step over the sample(500 μm × 500 μm).

**Electrochemical Measurements:**

Electrochemical experiments were carried out in 2032 coin-type cells. The working electrodes were prepared by mixing active materials, carbon black, and poly (vinyl difluoride) (PVDF) at a weight ratio of 7:2:1 and pasted on pure copper foil. And then dried at 120 °C under vacuum for 12 h. The loading of the active materials is about 0.5 mg cm⁻². Pure sodium foil was used as the counter electrode. The electrolyte consisted of a solution of 1 M NaClO₄ in EC/DEC and a glass fiber film as the separator. The cells were assembled in an argon-filled glove box with the concentration of moisture and oxygen below 0.1 ppm. The charge and discharge measurements were operated on Land CT2001A system at various current density (74.4-3720 mA g⁻¹). Electrochemical impedance spectroscopy (EIS) measurements were executed on Autolab electrochemical workstation (PGSTAT302N). The electrochemical performance was tested at various current densities in the voltage range of 0.01-3.00 V. The impedance spectra were recorded by applying a sine wave with amplitude of 5.0 mV over the frequency range from 100 kHz to 0.01 Hz. Fitting of the impedance spectra to the proposed equivalent circuit was performed by the code Zview.
Scheme S1. The synthesis route of Na₄C₆O₆. Na₄C₆O₆ was obtained by annealing of disodium rhodizonate at 400°C for 2h under Ar with by-product carbon monoxide.

Figure S1. The XRD patterns of Na₂C₆O₆, Na₂C₆O₆ annealed at 300°C and Na₄C₆O₆ (Na₂C₆O₆ annealed at 400°C); The XRD peaks of as-prepared Na₄C₆O₆ are mainly presented at 13, 23,
29, 33 and 40°, similar to the case of Li₄C₆O₆, indicating that they have the similar crystalline and chemical structure.

**Figure S2.** The FTIR spectra of Na₄C₆O₆ and Na₂C₆O₆. In case of Na₄C₆O₆, the peaks show at 1456 and 3425 cm⁻¹ are assigned to the quinone and O-Na, respectively, and the peak at 1723 cm⁻¹ disappears, revealing that there is only one kind of C=O retained after the annealing treatment at 400°C in Ar.
Figure S3. The EDX analysis pattern of Na$_4$C$_6$O$_6$. The atomic ratio of Na, C and O is about 2:3:3, in accordance with the elemental ratio of Na$_4$C$_6$O$_6$, clearly demonstrating that Na$_4$C$_6$O$_6$ is obtained successfully during our fabrication process.

Figure S4. High resolution C1s spectra of Na$_4$C$_6$O$_6$ and Na$_2$C$_6$O$_6$. The C=O show a obviously decrease from Na$_2$C$_6$O$_6$ to Na$_4$C$_6$O$_6$. In the meanwhile, the content of C-O-Na increased from 15.3% to 31.9% (based on the total C content) when Na$_2$C$_6$O$_6$ changed to Na$_4$C$_6$O$_6$. 
**Figure S5.** a) Typical SEM image of disodium rhodizonate; b) Typical SEM image of Na₄C₆O₆; the morphology of Na₄C₆O₆ obviously changed compared with Na₂C₆O₆.

**Figure S6.** Typical TEM images of Na₄C₆O₆-graphene nanocomposites.
Figure S7. TG curves of pure Na₄C₆O₆ and Na₄C₆O₆-graphene hybrid, the content of Na₄C₆O₆ was calculated 94.8% based on the follow equation: the content of Na₄C₆O₆ = residue ratio of Na₄C₆O₆-graphene sample/residue ratio of pure Na₄C₆O₆.

Figure S8. The XRD patterns of Na₄C₆O₆ extracted from Na₄C₆O₆-graphene composite and the dissolved and dried Na₄C₆O₆; both of them have similar characteristic peaks, demonstrating that the grain size of Na₄C₆O₆ can be changed by recrystallization treatment.
Figure S9. The FTIR spectra of Na₄C₆O₆-bulk and Na₄C₆O₆ extracted from Na₄C₆O₆-graphene composite. The spectrum of extracted Na₄C₆O₆ exhibits all the same characteristic peaks to those of bulk.

Figure S10. CV curves of Na₄C₆O₆-graphene nanocomposites for the first two cycles.
**Figure S11.** CV curves of pure graphene for the first cycle tested under 0.1 mA s\(^{-1}\).

**Figure S12.** CV curves of pure Na\(_4\)C\(_6\)O\(_6\) for the first cycle tested under 0.1 mA s\(^{-1}\).

**Figure S13.** Nitrogen adsorption-desorption isotherms of Na\(_4\)C\(_6\)O\(_6\)-graphene nanocomposites, the specific surface areas is 33 m\(^2\) g\(^{-1}\).
Figure S14. The first two discharge-charge curves for graphene at 74.4 mA g\(^{-1}\).

Figure S15. The charge-discharge curves for Na\(_4\)C\(_6\)O\(_6\)-Graphene at various rate.

Figure S16. Nyquist plots of 3D Na\(_4\)C\(_6\)O\(_6\)-graphene architecture, pure Na\(_4\)C\(_6\)O\(_6\), and graphene.
Figure S17. AC impedance spectra of 3D, Na$_4$C$_6$O$_6$-graphene architecture, graphene, and pure Na$_4$C$_6$O$_6$ measured after 90 cycles. R$_1$ is the electrolyte resistance, and C$_1$ and R$_2$ are the capacitance and resistance of the surface film formed on the electrodes, respectively. C$_2$ and R$_3$ are the double-layer capacitance and charge-transfer resistance, respectively, W$_1$ is the Warburg impedance related to the diffusion of sodium ions into the bulk electrodes.

Table S1. IPC measurement of Na$_4$C$_6$O$_6$ and Na$_2$C$_6$O$_6$ samples

<table>
<thead>
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<th>samples</th>
<th>Theroy numerical value (wt. %)</th>
<th>measured numerical value (wt. %)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Na$_4$C$_6$O$_6$</td>
<td>35.4</td>
<td>36.6</td>
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<td>Na$_2$C$_6$O$_6$</td>
<td>21.5</td>
<td>20.6</td>
</tr>
</tbody>
</table>

Table S2. XPS measurement of Na$_4$C$_6$O$_6$ and Na$_2$C$_6$O$_6$ samples
samples | measured numerical value (wt. %)
--- | ---
Na₄C₆O₆ | 17.66
Na₂C₆O₆ | 8.55

**Table S3.** Fitting results of AC impedance spectra of Na₄C₆O₆-graphene, Na₄C₆O₆, and graphene.

<table>
<thead>
<tr>
<th>Samples</th>
<th>R₁(Ω)</th>
<th>R₂(Ω)</th>
<th>R₃(Ω)</th>
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<tbody>
<tr>
<td>Na₄C₆O₆-graphene</td>
<td>6.8</td>
<td>15.8</td>
<td>162.3</td>
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<tr>
<td>Na₄C₆O₆</td>
<td>95.1</td>
<td>214.2</td>
<td>511.4</td>
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<tr>
<td>graphene</td>
<td>6.0</td>
<td>9.9</td>
<td>25.8</td>
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