Supplementary Information (SI)

A Method for Synthesis of Zeolitic Imidazolate Framework-Derived LiCoO₂/CNTs@AlF₃ with Enhanced Lithium Storage Capacity

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**Experimental Section**

1. **Synthesis of ZIF-67**

Briefly, Co(NO$_3$)$_2$·6H$_2$O (2.4 g) and 2-methylimidazole (2.7 g) were dispersed in 30 mL of methanol by sonication. The reaction mixture was subsequently heated to 50°C for 5 min in a microwave oven. Then the resultant product was collected by centrifugation (6000 rpm, 3 min) and washed with methanol for three times. The purple powder was dried at 60°C overnight in vacuum to obtain ZIF-67 nanoparticles.

2. **Synthesis of LiCoO$_2$, LiCoO$_2$@AlF$_3$, LiCoO$_2$/CNTs and LiCoO$_2$/CNTs@AlF$_3$**

The as-prepared ZIF-67 and Li$_2$CO$_3$ (0.16g) were mixed and grounded in a mortar, then calcined at 800°C for 3h in air with a heating rate of 2°C min$^{-1}$ to get brown LiCoO$_2$ sample. Later, LiCoO$_2$ was immersed into 10 ml Al(NO$_3$)$_3$·9H$_2$O solution, and 10 ml NH$_4$F solution was added to it drop by drop. The molar ratio of Al and F is 1:3. After stirring at 80 °C for 5h, the mixture was collected by centrifugation (6000 rpm, 3 min) and dried in vacuum. After that, the powders were mixed with a certain amount of carbon nanotubes (CNTs) in an ethanol solution reacted at 50 °C for 800 mins under solvothermal method to obtain LiCoO$_2$/CNTs@AlF$_3$.

Similarly, to prepare LiCoO$_2$, LiCoO$_2$/CNTs and LiCoO$_2$@AlF$_3$, we repeated the above steps without CNTs addition or AlF$_3$ coating.

3. **Characterization**

PXRD patterns were measured on a Bruker D8 Advance diffractometer with a Cu target tube and a graphite monochromator. Raman spectra were obtained on a Renishaw inVia confocal Raman microscope equipped with an argon ion laser beam. Sorption isotherms were measured at 77 K with a Belsorp max gas sorption analyzer. The surface morphology and architecture were characterized using FESEM (TESCAN Maia 3, Czech) operating at 5 kV and TEM (FEI Talos F200X) at an acceleration voltage of 200 kV. In addition, XPS was recorded on an K-Alpha+ XPS spectrometer using Al Kα radiation.

4. **Electrochemical measurement**

To assess the electrochemical behavior of fabricated nanomaterials, the working electrode consisted of active materials, Super P and PVDF were mixed in a weight ratio of 8:1:1. Then, the obtained mixture was dispersed in N-methyl-2-pyrrolidone and stirred overnight. The slurry was subsequently coated onto a piece of aluminum foil and dried at 55 °C for 12 h then 100 °C for 8 h.
Electrochemical measurements were carried out using CR 2032 coin-type cells, using with a lithium foil as the counter electrode, a Celgard 2400 membrane as the separator, and 1 M LiPF₆ dissolved in ethylene carbonate and diethyl carbonate (1:1 ratio) as the electrolyte. After that, coin cells were assembled in an Ar-filled glove box. The galvanostatic charge/discharge tests were carried out at different current densities via a multichannel LAND CT2001 testing system (China) from 3 to 4.2 V (vs Li⁺/Li). Cyclic voltammetry curves were measured using a CHI660E electrochemical workstation with different scanning rate. EIS of the various electrodes was performed on the same workstation at 25 °C over a frequency range of 100 kHz to 0.01 Hz. Commercial lithium cobaltate for comparison is produced from Alfa Aesar.

![Figure S1 TEM images of the ZIF-derived bare LiCoO₂.](image1)

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![Figure S2 PXRD patterns of the simulated and as-prepared ZIF-67 analogues.](image2)

Figure S2 PXRD patterns of the simulated and as-prepared ZIF-67 analogues.
Figure S3 High-resolution XPS spectrum of C1s, Co 2p, Al 2p and F 1s.

Figure S4 Pore size distribution curve of LiCoO$_2$/CNTs@AlF$_3$ sample.
Figure S5 PXRD patterns of other fabricated lithium cobaltate samples.

Figure S6 Raman spectra of the compared samples.

Figure S7 (a) Discharge capacity and coulombic efficiency of LiCoO$_2$/CNTs@AlF$_3$ at the temperature of 50 °C at 0.5 C. (b) Rate capabilities of LiCoO$_2$/CNTs@AlF$_3$ and commercial LiCoO$_2$. 
Table S1. Comparison of the electrochemical properties of LiCoO$_2$/CNTs@AlF$_3$ and other coated LiCoO$_2$ materials previously reported.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Voltage range (vs Li/Li$^+$)</th>
<th>Cycle number</th>
<th>Current density</th>
<th>Specific capacity (mAh g$^{-1}$)</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>Al$_2$O$_3$ coated LiCoO$_2$</td>
<td>3.3 - 4.5 V</td>
<td>200</td>
<td>2.8 C</td>
<td>145</td>
<td>S1</td>
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<tr>
<td>TiO$_2$-coated LiCoO$_2$</td>
<td>3.0 - 4.5 V</td>
<td>100</td>
<td>1 C</td>
<td>160 (RT) 160 (50 °C)</td>
<td>S2</td>
</tr>
<tr>
<td>ZnO-coated LiCoO$_2$</td>
<td>3.0 - 4.5 V</td>
<td>200</td>
<td>0.2 C</td>
<td>155</td>
<td>S3</td>
</tr>
<tr>
<td>LiAlO$_2$/Al$_2$O$_3$-coated LiCoO$_2$</td>
<td>2.8 - 4.3 V</td>
<td>425</td>
<td>3 C</td>
<td>128</td>
<td>S4</td>
</tr>
<tr>
<td>Al-Ti-oxide coated LCO</td>
<td>3.0 - 4.5 V</td>
<td>100</td>
<td>1 C</td>
<td>180</td>
<td>S5</td>
</tr>
<tr>
<td>phosphate coated LCO</td>
<td>3.0 - 4.5 V</td>
<td>500</td>
<td>1 C</td>
<td>142 (RT) 130 (45 °C)</td>
<td>S6</td>
</tr>
<tr>
<td>LCO@BT</td>
<td>3.0 - 4.5 V</td>
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<td>0.2 C</td>
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<td>S7</td>
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<td>MgF$_2$@LCO</td>
<td>3.0 - 4.4 V</td>
<td>160</td>
<td>1 C</td>
<td>142 (45 °C)</td>
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<td>LCO-TiO$_2$ (90)</td>
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<tr>
<td>LiCoO$_2$/CNTs@AlF$_3$</td>
<td>3.0 - 4.2 V</td>
<td>500</td>
<td>1 C (174 mA g$^{-1}$)</td>
<td>120</td>
<td>This work</td>
</tr>
</tbody>
</table>

References


