Supplementary information

Cobalt Vacancies Assisted Ions Diffusion in Co$_2$AlO$_4$/Carbon Nanofibers for Enhancing Lithium Battery Performance

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SEM and TEM images of Co$_2$AlO$_4$/C NFs and Co$_2$AlO$_4$ NFs: By observing the SEM images of Co$_2$AlO$_4$/C NFs and Co$_2$AlO$_4$ NFs through Fig. S1a and Fig. S1b, they are all continuous nanofibers with different diameters. Many Co$_2$AlO$_4$ nanoparticles embedded in carbon nanofibers were observed by the TEM image in Fig. S1c. The HRTEM image shows the excellent graphitization of carbon nanofibers with an interplanar spacing of 0.33 nm corresponding to (002) surface and the nanoparticles are encased in graphite with interplanar spacing of 0.28 nm and 0.24 nm corresponding (220) and (311) surface of Co$_2$AlO$_4$ in Fig. S1e. Nanofibers are composed of Co$_2$AlO$_4$ nanoparticles shown in Fig. S1d. The HRTEM image shows regular crystal faces of 0.47nm and 0.28nm correspond to (111) and (220) surface of Co$_2$AlO$_4$ in Fig. S1f.

Composition ratio in Co$_2$AlO$_4$/C NFs @ Co$_2$AlO$_4$ NS and Co$_2$AlO$_4$/C NFs respectively: To clearly investigate the degree of graphitization and the thermal behavior of carbon in Co$_2$AlO$_4$/C NFs @ Co$_2$AlO$_4$ NS. The Raman spectrum of the material is shown in the Fig. S2a. The spectrum of Co$_2$AlO$_4$/C NFs @ Co$_2$AlO$_4$ NS composites clearly exhibited a pair of peaks at 1323.8 and 1597.5 cm$^{-1}$, corresponding to a defect or disorder evoked D band and a crystalline G band of graphitic materials, respectively. The large intensity of D band implied that there are numerous sp3 structures in the carbon nanofibers, which were probably introduced during calcinations. These amorphous carbons should partially decompose less than 300°C, which has been reported in previous works$^{1-2}$. The proportion of carbon and Co$_2$AlO$_4$ in Co$_2$AlO$_4$/C NFs
@ Co$_2$AlO$_4$ NS and Co$_2$AlO$_4$/C NFs can be understood in Fig. S2b, which ~30% carbon and 
~70% Co$_2$AlO$_4$ are in Co$_2$AlO$_4$/C NFs @ Co$_2$AlO$_4$ NS and ~34% carbon and ~66% Co$_2$AlO$_4$
are in Co$_2$AlO$_4$/C NFs.

**Rate performance of Co$_2$AlO$_4$/C NFs:** The Co$_2$AlO$_4$/C NFs electrode shows poor cyclic
stability at a current density of 100mA g$^{-1}$. The specific discharge capacity of Co$_2$AlO$_4$/C NFs
only remains at 482.3 mAh g$^{-1}$ after 10 cycles. The rate performance of the Co$_2$AlO$_4$/C NFs
electrode is much lower than Co$_2$AlO$_4$/C NFs @ Co$_2$AlO$_4$ NS electrode.
Fig. S1. SEM images of (a) Co$_2$AlO$_4$/C NFs and (b) Co$_2$AlO$_4$ NFs, TEM images of (c)Co$_2$AlO$_4$/C NFs and (d) Co$_2$AlO$_4$ NFs, HRTEM images of (e) Co$_2$AlO$_4$/C NFs and (f)Co$_2$AlO$_4$ NFs
Fig. S2. (a) Raman spectrum of Co$_2$AlO$_4$/C NFs @ Co$_2$AlO$_4$ NS, (a) TGA curves of different samples.

Fig. S3. High resolution XPS spectra of the (a) O1s, (b) Al 2p of Co$_2$AlO$_4$/C NFs @ Co$_2$AlO$_4$ NS and Co$_2$AlO$_4$/C NFs.

Fig. S4. Rate performance of Co$_2$AlO$_4$/C NFs at various current density.
Fig. S5. Li distribution site. (a) site 1 for Li atom distribution without Co vacancy. (b) site 2 for Li atom distribution without Co vacancy. (c) Li at site 1 will spontaneously migrate to the vacancy site once Co vacancy forms.

Fig. S6. Density of state (DOS) of Co, Li and O atoms. (a) DOS of Co and O atom in Co\textsubscript{2}AlO\textsubscript{4} without vacancy. (b) DOS of Li and O atom in Co\textsubscript{2}AlO\textsubscript{4} with Co at the tetrahedral site being replaced by Li. From DOS, it can be seen that the bonds between Co and O are stronger than those between Li and O. It means that once Co at the tetrahedral site is located by Li atoms, Li atom is much easy displacement during Li migration process between tetrahedral interstice, explaining the energy barrier decrease.
Fig. S7. (a) and (b) are TEM images at different regions, and (c) is the SAED pattern of Co$_2$AlO$_4$/C NFs @ Co$_2$AlO$_4$ NS at a current density of 500 mA g$^{-1}$ after 500 cycles.

Fig. S8. High-resolution XPS spectra of the Co 2p of Co$_2$AlO$_4$/C NFs @ Co$_2$AlO$_4$ NS in initial state and after 500 cycles.
Table S1  
Summary of the electrochemical performance of various anode materials with similar morphologies.

<table>
<thead>
<tr>
<th>Active substance</th>
<th>Cyclic stability</th>
<th>Refs</th>
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<tbody>
<tr>
<td>MoS$_2$ nanoplates embedded in Carbon nanofibers</td>
<td>after 100 cycles, 1007 mAh g$^{-1}$ at 100 mAg$^{-1}$</td>
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<td>SnO$_2$ nanoflowers on N-doped carbon nanofibers</td>
<td>after 100 cycles, 750 mAh g$^{-1}$ at 100 mAg$^{-1}$</td>
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<td>carbonaceous backbones supported MoSe$_2$ nanosheets</td>
<td>after 100 cycles, 610.8 mAh g$^{-1}$ at 100 mAg$^{-1}$</td>
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<td>Porous carbon nanofiber @MoS$_2$ core/sheath fiber</td>
<td>after 50 cycles, 736 mAh g$^{-1}$ at 50 mAg$^{-1}$</td>
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<td>N-doped carbon encapsulated FeS nanosheets with amorphous TiO$_2$</td>
<td>after 500 cycles, 402.5 mAh g$^{-1}$ at 1000 mAg$^{-1}$</td>
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<tr>
<td>Co$_2$AlO$_4$/carbon nanofibers @Co$_2$AlO$_4$ nanosheets</td>
<td>after 100 cycles, 810 mAh g$^{-1}$ at 100 mAg$^{-1}$ after 400 cycles, 688.5 mAh g$^{-1}$ at 500 mAg$^{-1}$</td>
<td>This work</td>
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References:


