

## Electronic Supplementary Information

### **Multidimensional and hierarchical carbon-confined cobalt phosphide nanocomposite as advanced anodes for lithium and sodium storage**

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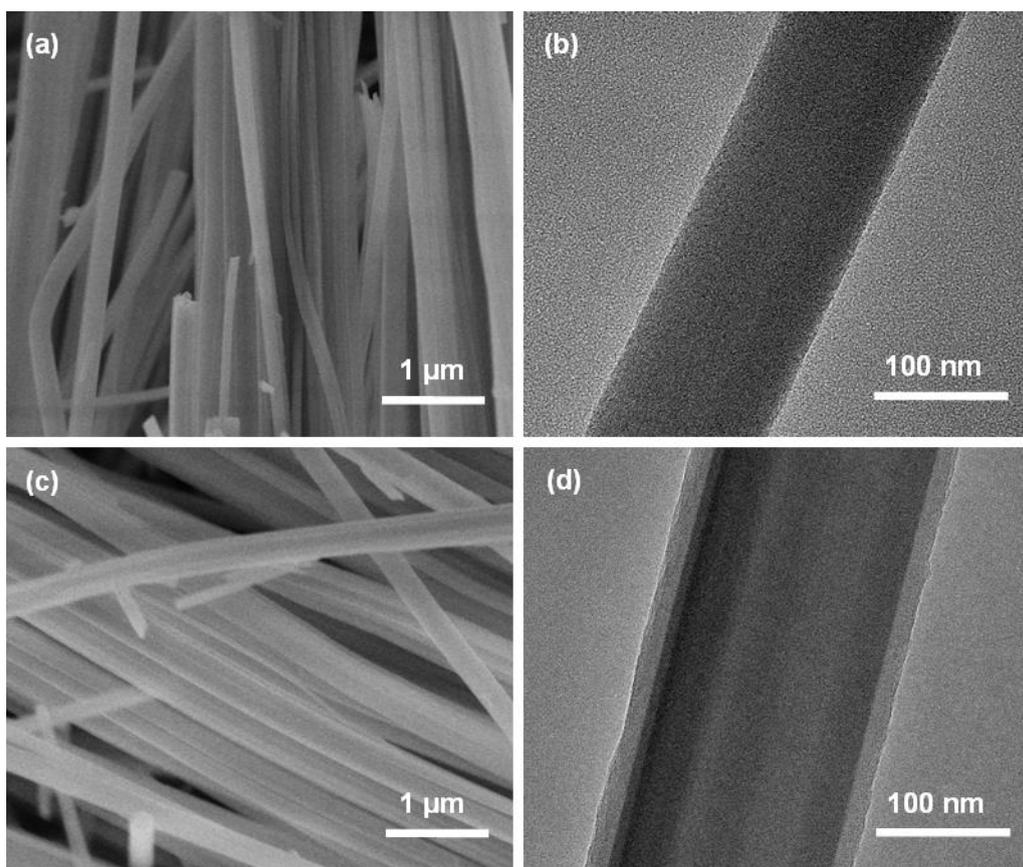
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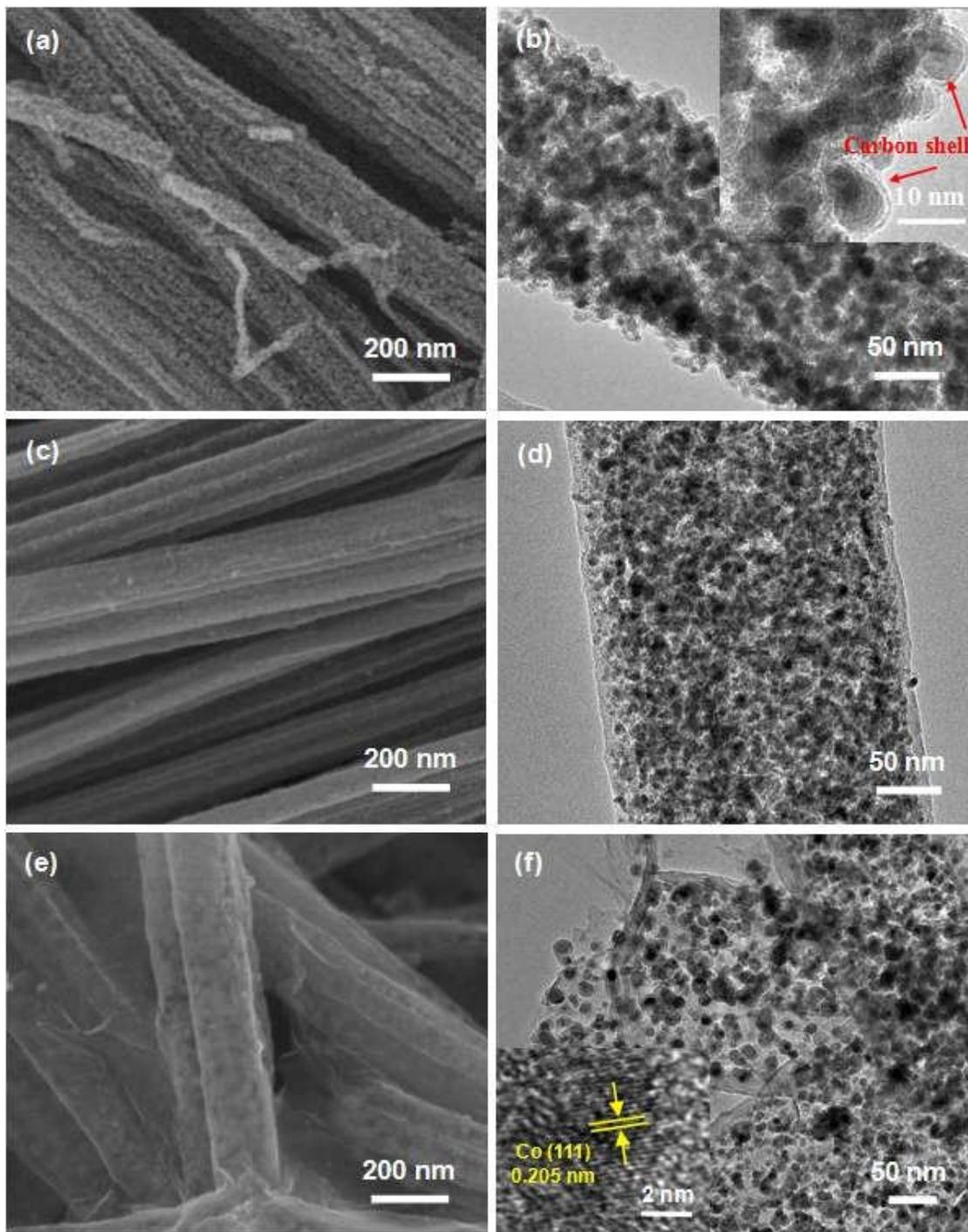
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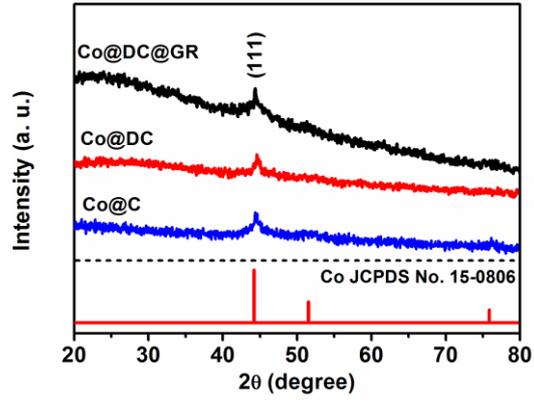
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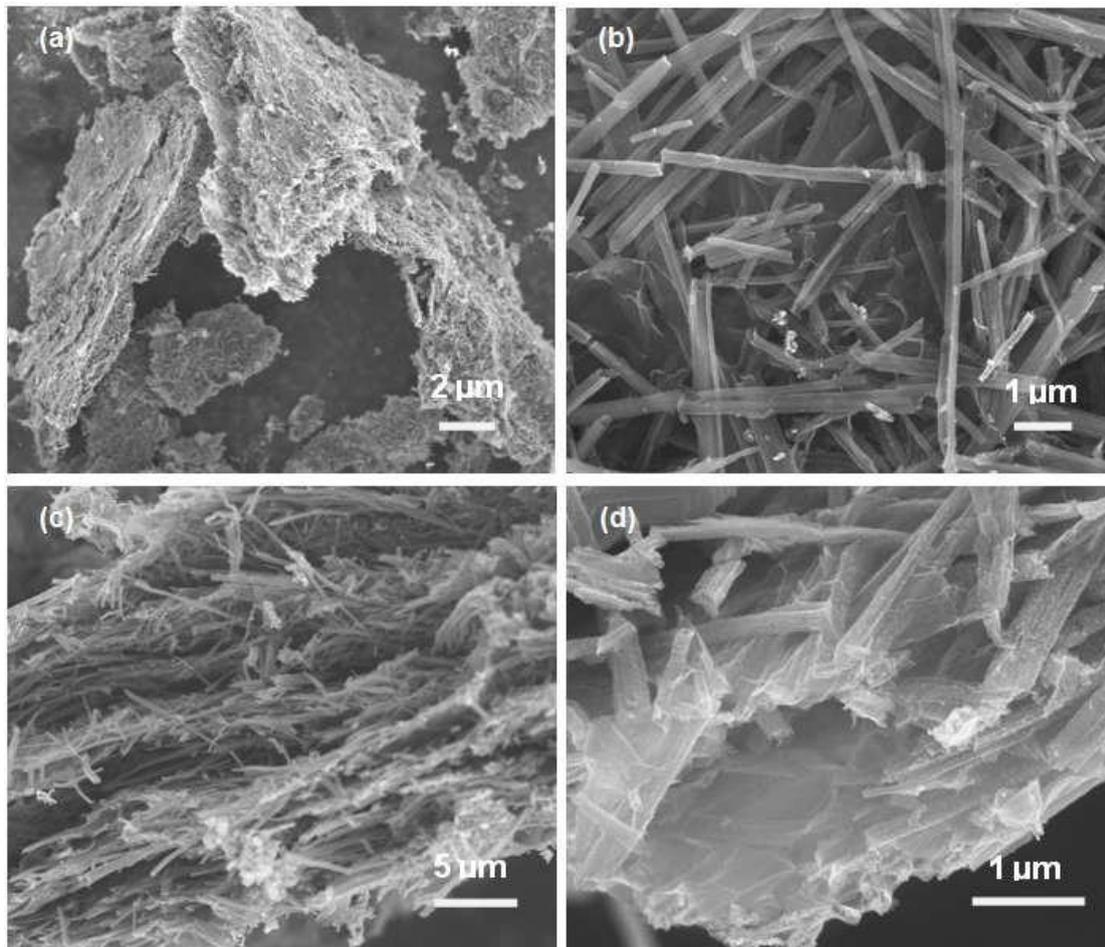
**Figure S1** (a and b) SEM and TEM images of (a and b) Co-NAT precursor and (c and d) Co-NTA@hydrotherm carbon nanofibers.



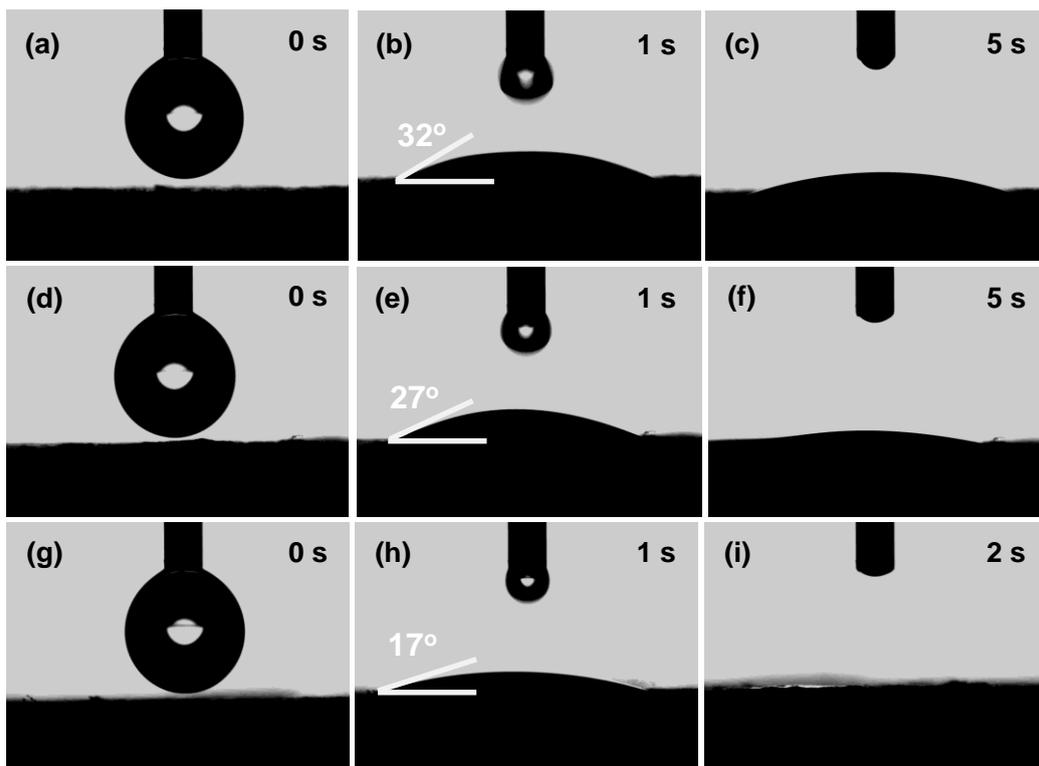
**Figure S2** SEM and TEM images of (a and b) Co@C, (c and d) Co@DC and (e and f) Co@DC@GR.



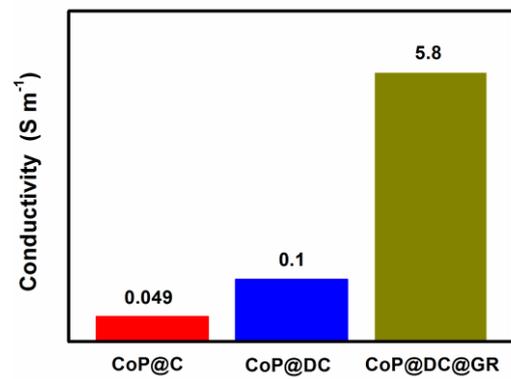
**Figure S3** XRD patterns of Co@C, Co@DC and Co@DC@GR.



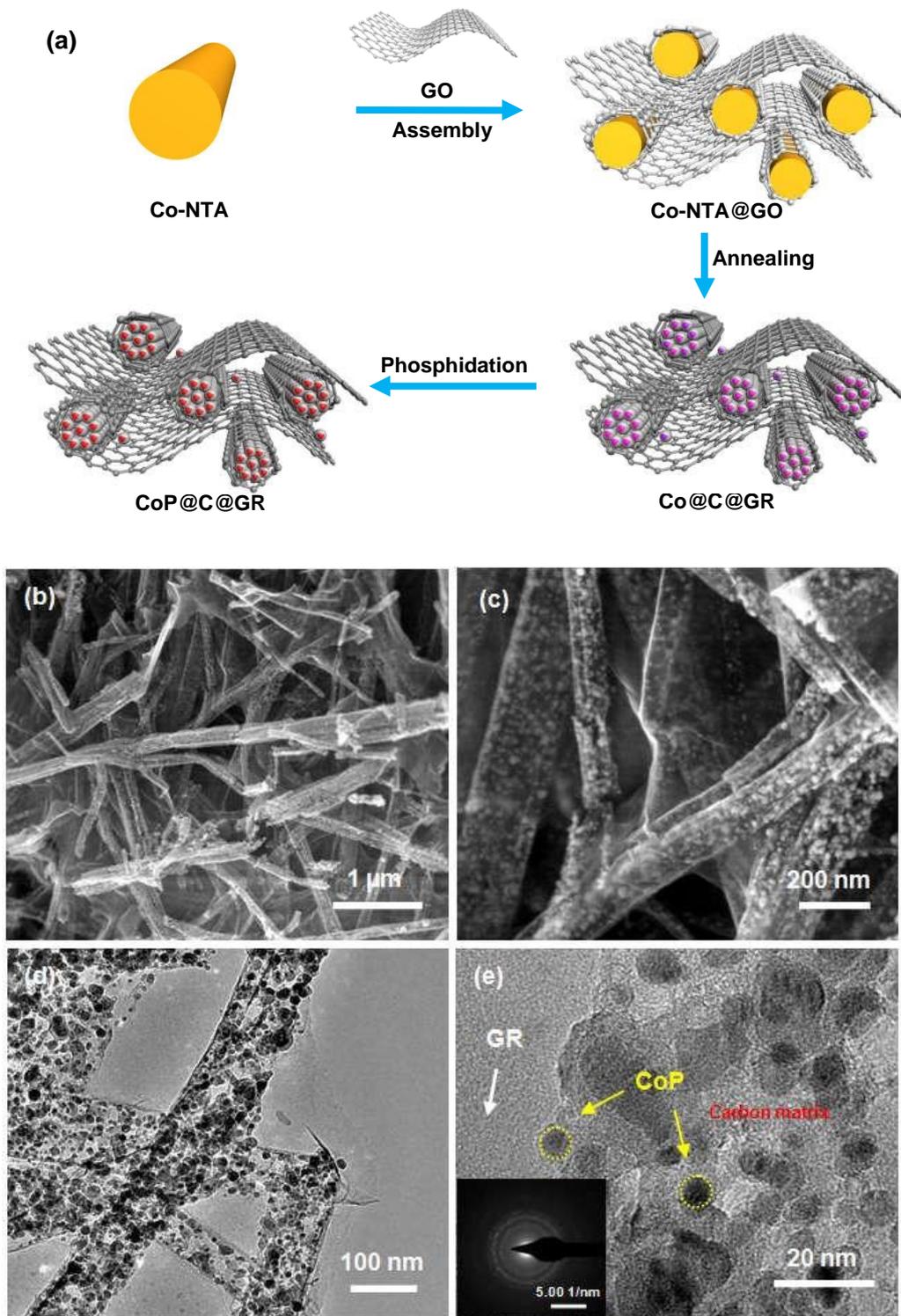
**Figure S4** (a and b) low magnification and (c and d) cross-section images of CoP@DC@GR.



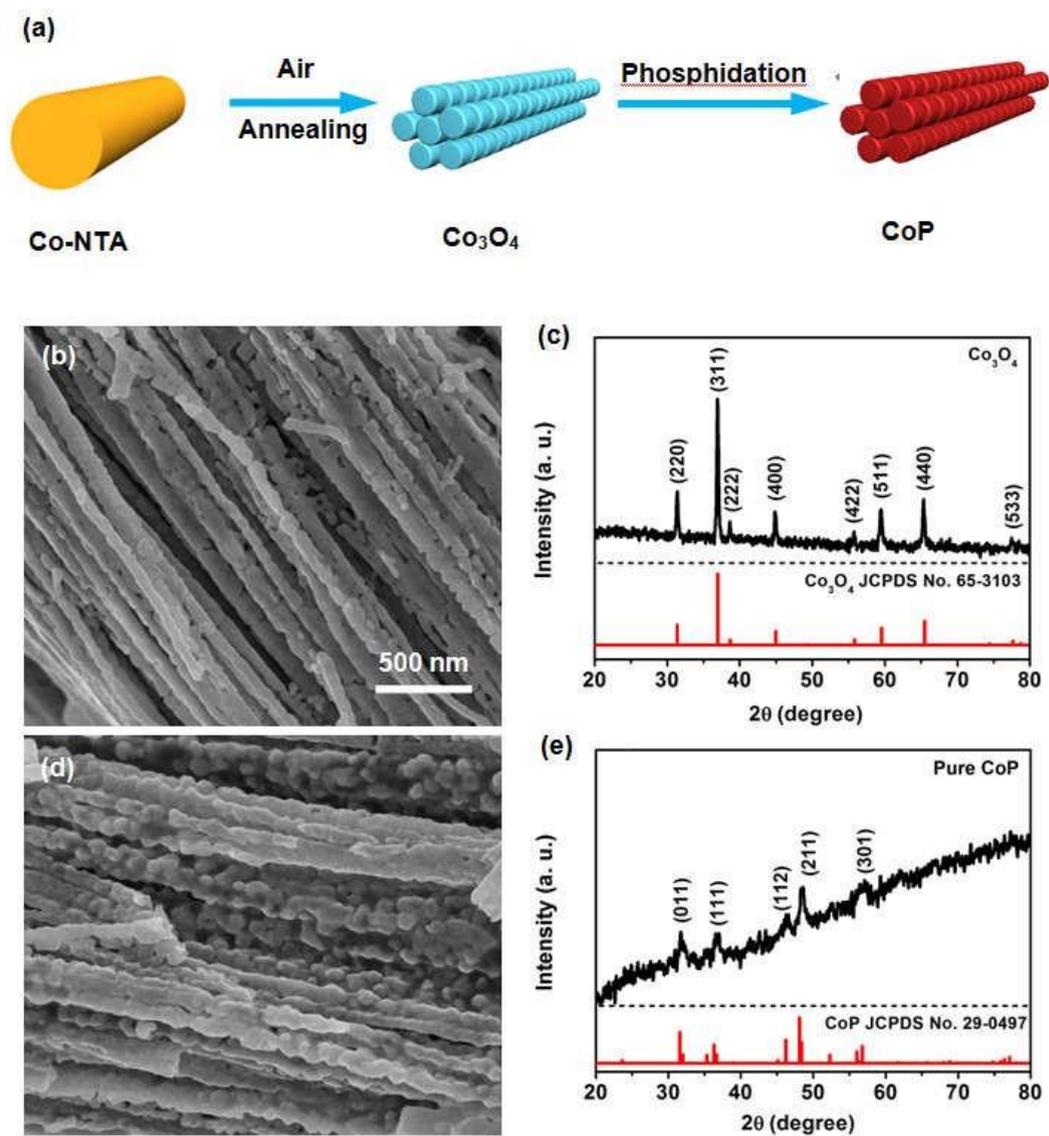
**Figure S5.** Surface wetting of LiPF<sub>6</sub> electrolyte droplet on (a-c) CoP@C, (d-f) CoP@DC and (g-i) CoP@DC @GR.



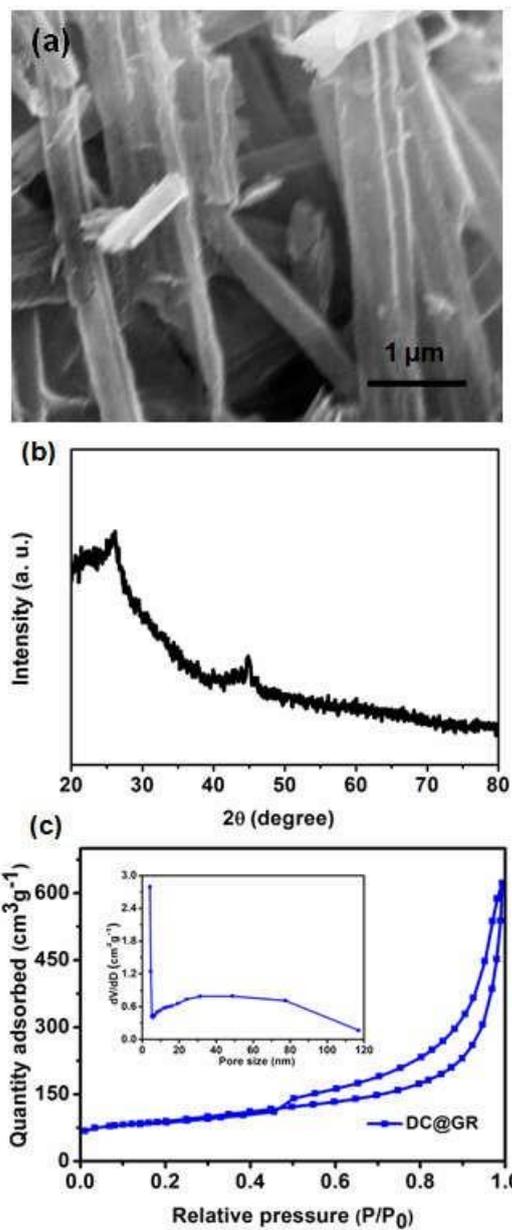
**Figure S6** Electrical conductivities of the pressed pellets of CoP@C, CoP@DC and CoP@DC@GR.



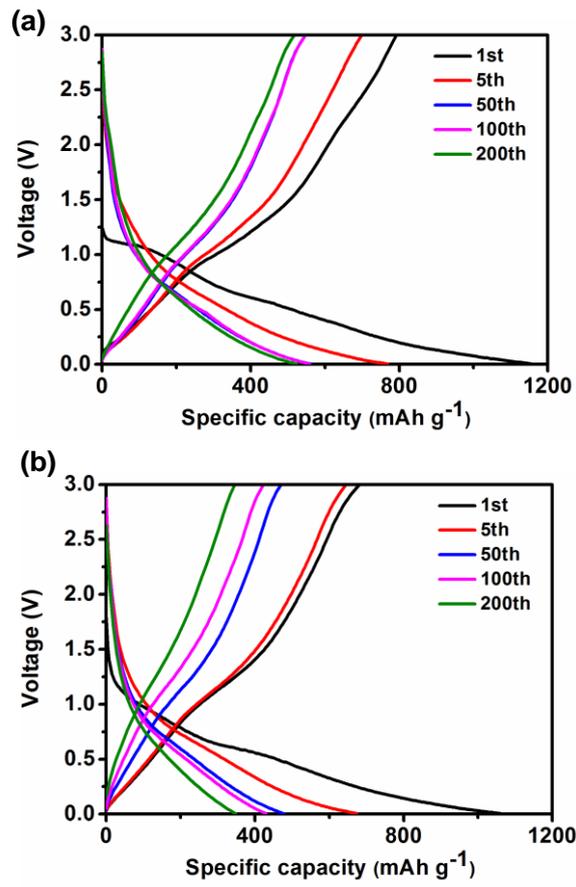
**Figure S7** (a) Schematic illustration of the synthesis of CoP@C@GR nanocomposite; (b and c) SEM and (d and e) TEM images of CoP@C@GR nanocomposite.



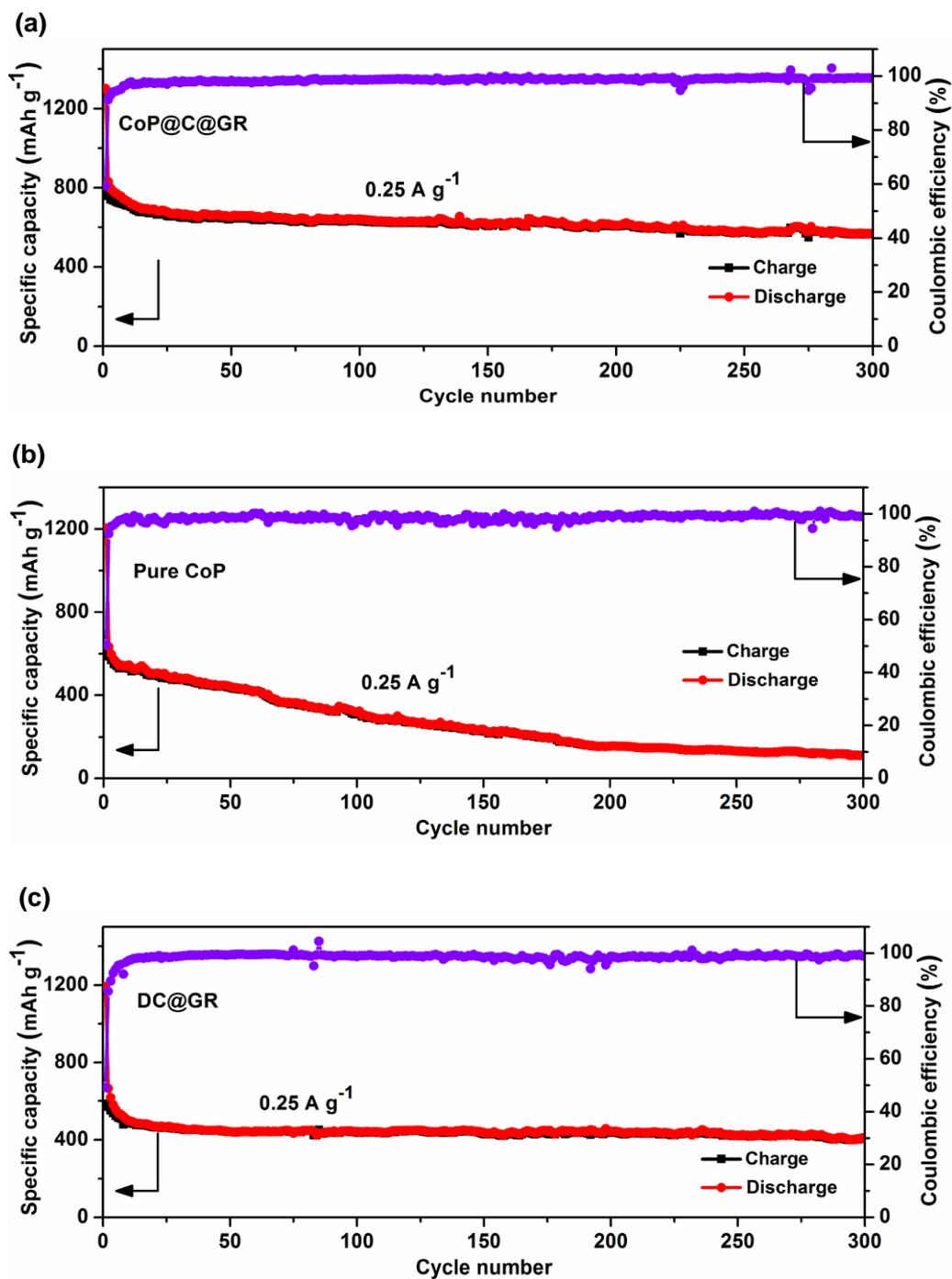
**Figure S8** (a) Schematic illustration of the synthesis of pure CoP nanofibers; SEM images of (b)  $\text{Co}_3\text{O}_4$  nanofibers and (d) pure CoP nanofibers; XRD patterns of (c)  $\text{Co}_3\text{O}_4$  nanofibers and (e) pure CoP nanofibers.



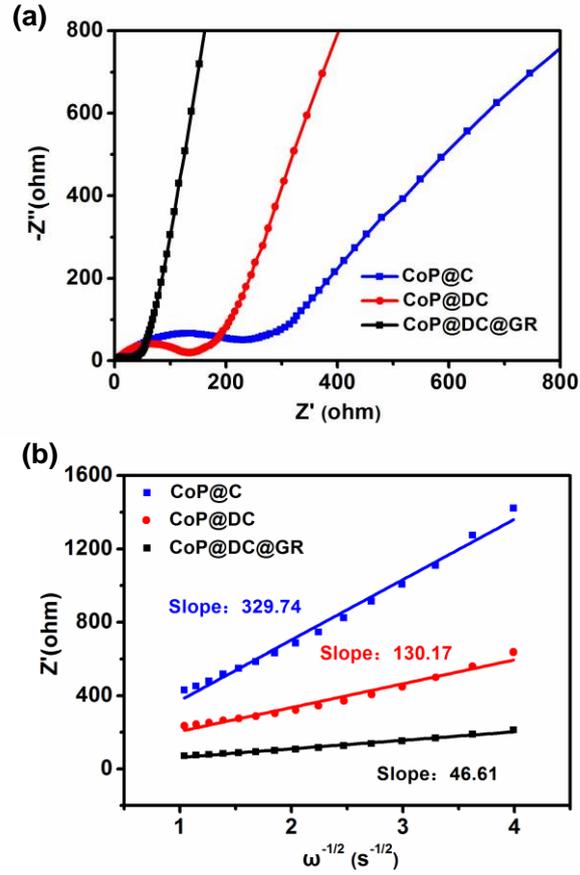
**Figure S9** (a) SEM image, (b) XRD pattern and (c) Nitrogen adsorption/desorption isotherms of DC@GR nanocomposite.



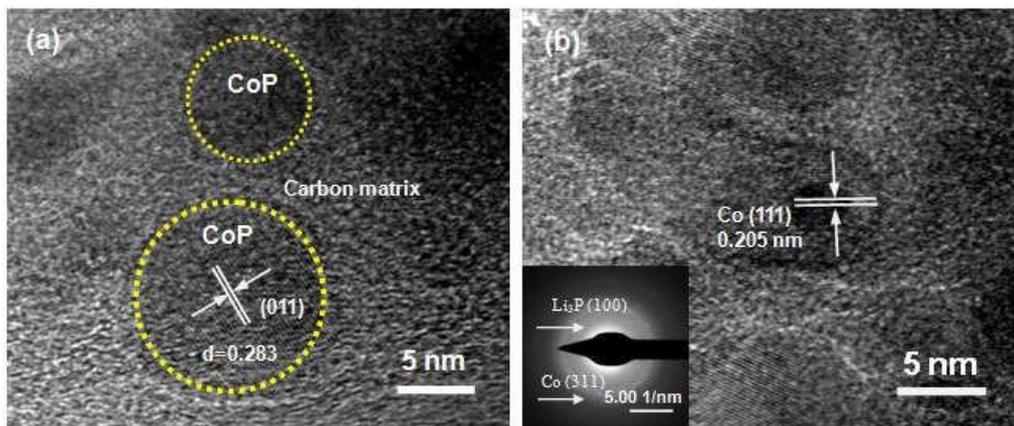
**Figure S10** Discharge and charge profiles of (a) CoP@DC and (b) CoP@C electrodes.



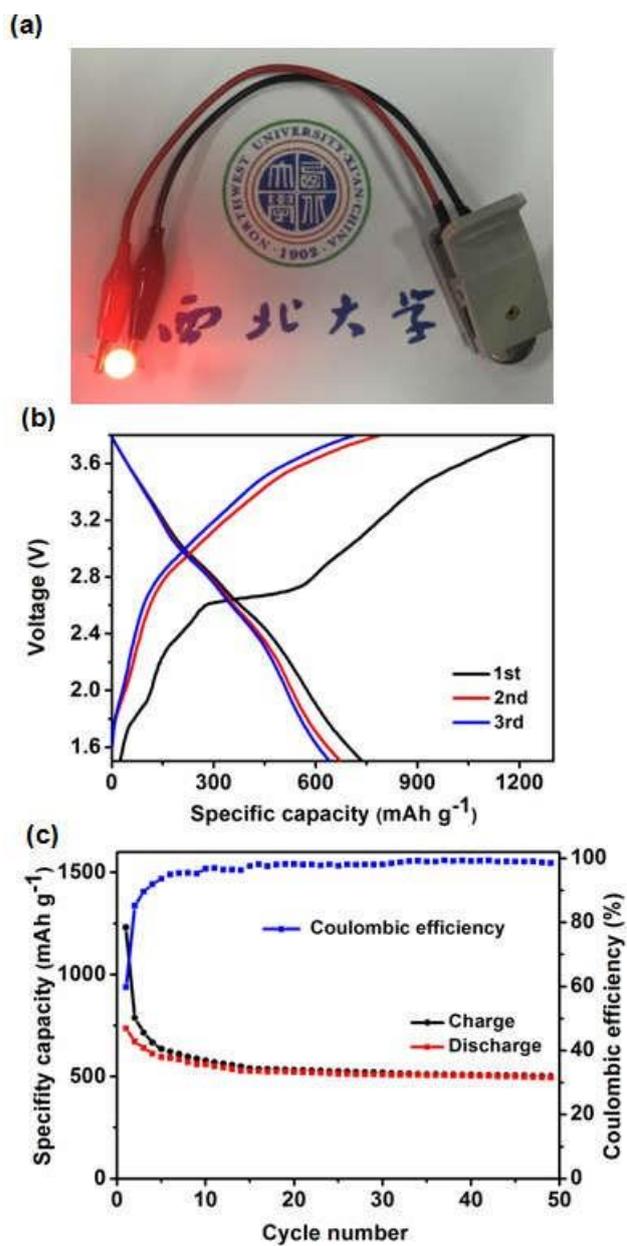
**Figure S11** Cycling performance and Coulombic efficiencies of CoP@C@GR, pure CoP and DC@GR at a current density of  $0.25 \text{ A g}^{-1}$ .



**Figure S12** (a) Nyquist plots for the electrodes made of CoP@C, CoP@DC and CoP@DC@GR after 70 cycles at a current density of  $0.25 \text{ A g}^{-1}$ ; (b) Linear fits (relationship between  $Z'$  and  $\omega^{-1/2}$ ) in low-frequency region of CoP@C, CoP@DC and CoP@DC@GR electrodes.



**Figure S13** (a) HRTEM image of the fully charged electrode in LIBs; (b) TEM image of the fully discharged electrode in LIBs.



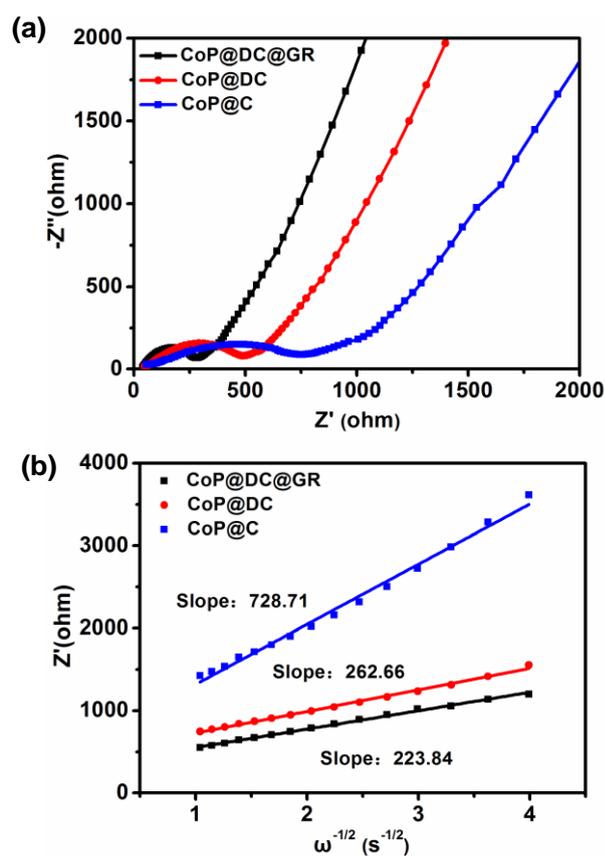
**Figure S14** (a) Schematic representation of the CoP@DC@GR//LiCoO<sub>2</sub> full-cell; (b) Charge and discharge profiles of the CoP@DC@GR//LiCoO<sub>2</sub> full-cell; (c) Cycle performance the CoP@DC@GR//LiCoO<sub>2</sub> full-cell.

**Table S1 A comparison study of the CoP@DC@GR hybrid nanofibers with other typical phosphide anode materials for SIBs.**

<b>Materials</b>	<b>Current density</b>	<b>Specific capacity, cycle number</b>	<b>Ref.</b>
<b>CoP@DC@GR</b>	<b>0.1 A g<sup>-1</sup></b>	<b>650 mAh g<sup>-1</sup>,100 cycles</b>	<b>This work</b>
	<b>0.5 A g<sup>-1</sup></b>	<b>398 mAh g<sup>-1</sup>,300 cycles</b>	
<b>CoP@C-RGO</b>	<b>0.1 A g<sup>-1</sup></b>	<b>473 mAh g<sup>-1</sup>, 100 cycles</b>	<b>49</b>
<b>CoP</b>	<b>0.1 A g<sup>-1</sup></b>	<b>315 mAh g<sup>-1</sup>, 25 cycles</b>	<b>50</b>
<b>Ni<sub>2</sub>P@pGN</b>	<b>0.2 A g<sup>-1</sup></b>	<b>161 mAh g<sup>-1</sup>, 100 cycles</b>	<b>29</b>
<b>H-FeP@C@GR</b>	<b>0.1 A g<sup>-1</sup></b>	<b>400 mAh g<sup>-1</sup>, 250 cycles</b>	<b>16</b>
<b>Sn<sub>4</sub>P<sub>3</sub>@C</b>	<b>0.1 A g<sup>-1</sup></b>	<b>580 mAh g<sup>-1</sup>, 120 cycles</b>	<b>51</b>
<b>CuP<sub>2</sub>/C</b>	<b>0.15 A g<sup>-1</sup></b>	<b>430 mAh g<sup>-1</sup>, 30 cycles</b>	<b>52</b>
<b>Ni<sub>2</sub>P@C/GA</b>	<b>0.15 A g<sup>-1</sup></b>	<b>254 mAh g<sup>-1</sup>, 100 cycles</b>	<b>13</b>

**Table S2 The comparison study of lithium and sodium storage for the CoP@DC@GR nanocomposite.**

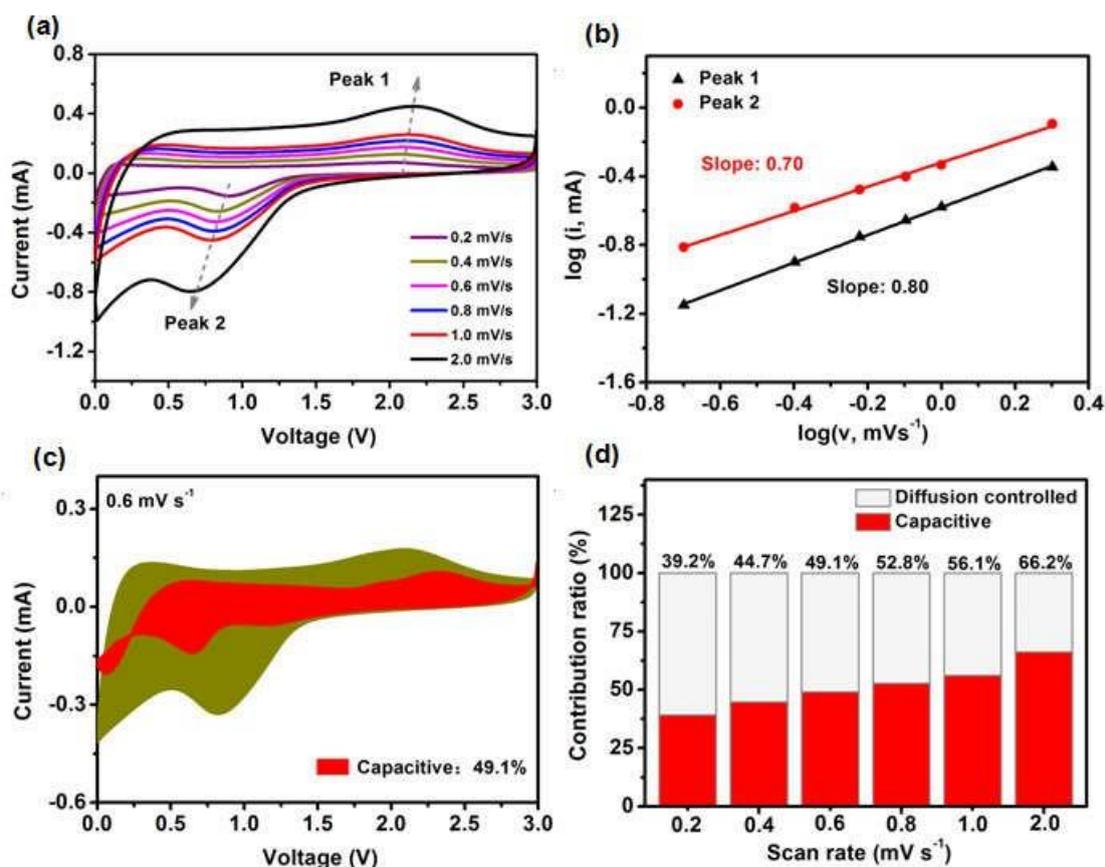
	<b>Lithium storage (0.25 A g<sup>-1</sup>)</b>	<b>Sodium storage (0.1 A g<sup>-1</sup>)</b>
<b>Initial reversible capacity</b>	<b>855 mAh g<sup>-1</sup></b>	<b>801 mAh g<sup>-1</sup></b>
<b>Initial Coulombic efficiency</b>	<b>73%</b>	<b>64%</b>
<b>Reversible capacity</b>	<b>754 mAh g<sup>-1</sup> after 300 cycles</b>	<b>650 mAh g<sup>-1</sup> after 100 cycles</b>
<b>Capacity retention</b>	<b>88%</b>	<b>81%</b>



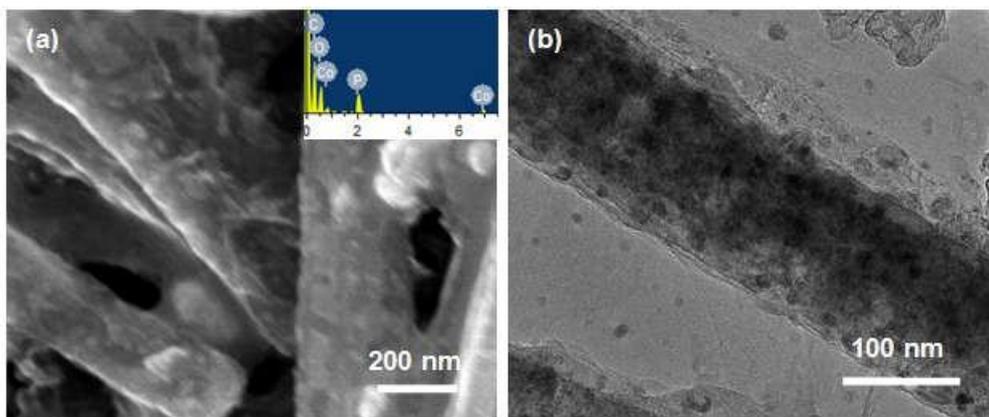
**Figure S15** (a) Nyquist plots for the electrodes made of CoP@C, CoP@DC and CoP@DC@GR after 3 cycles for SIBs; (b) Liner fits (relationship between  $Z'$  and  $\omega^{-1/2}$ ) in low-frequency region of CoP@C, CoP@DC and CoP@DC@GR electrodes.

**Table S3** The comparison study of  $R_{ct}$  for CoP@C, CoP@DC and CoP@DC@GR electrodes.

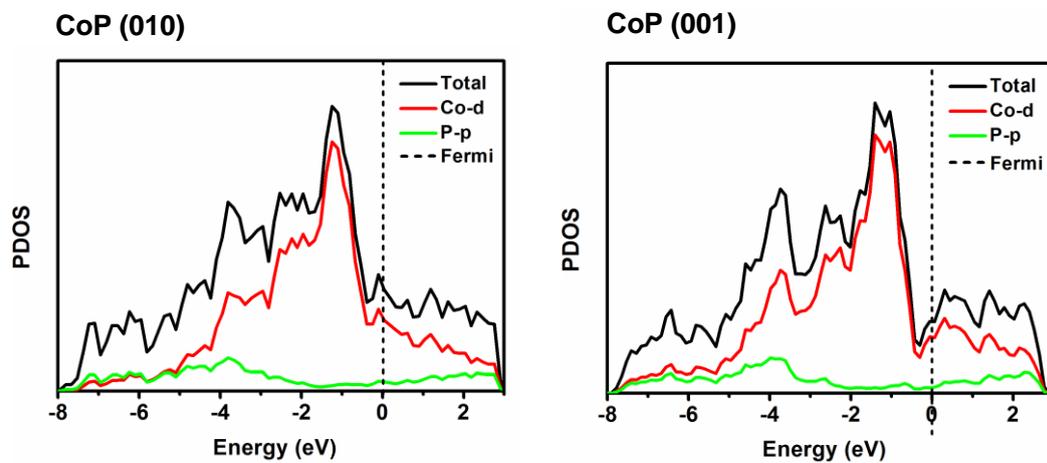
	Electrode	For LIBs	For SIBs
<b>Rct</b>	CoP@C	217 $\Omega$	740 $\Omega$
	CoP@DC	127 $\Omega$	498 $\Omega$
	CoP@DC@GR	45 $\Omega$	257 $\Omega$



**Figure S16.** (a) CV curves at different scan rates from 0.2 to 2.0 mV s<sup>-1</sup> for SIBs; (b) Log  $i$  vs.  $\log v$  plots at oxidation and reduction state; (c) Capacitive- and diffusion-controlled contribution to charge storage at 0.6 mV s<sup>-1</sup>; (d) Normalized contribution ratio of capacitive- and diffusion-controlled capacities at different scan rates.



**Figure S17** SEM and TEM images of CoP@DC@GR electrode after 100 cycles for SIBs.



**Figure S18** Projected density of states (PDOS) of the CoP surfaces. The Fermi level (dashed line) is set as zero.