

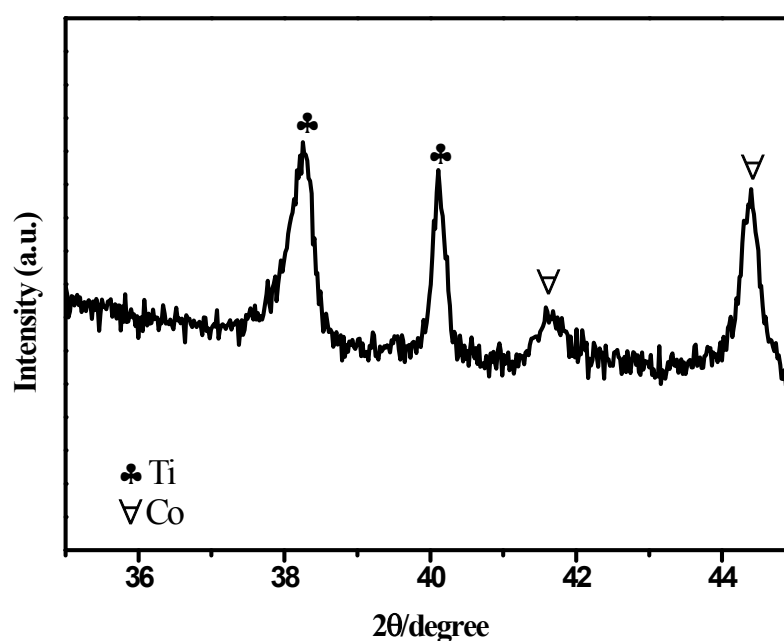
## Supporting Information

### Binder-free Co-CoO<sub>x</sub> nanowire array for lithium ion battery with excellent rate capability and ultra-long cycle life

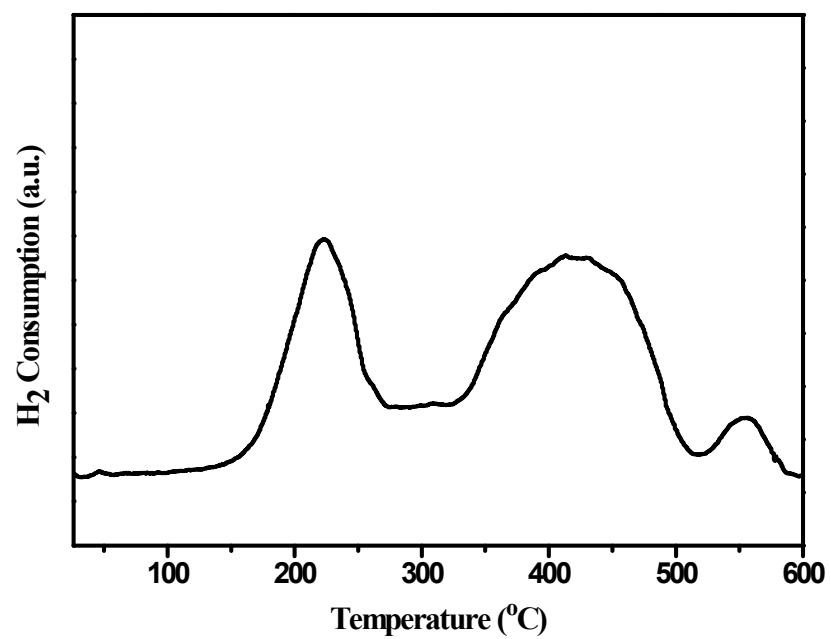
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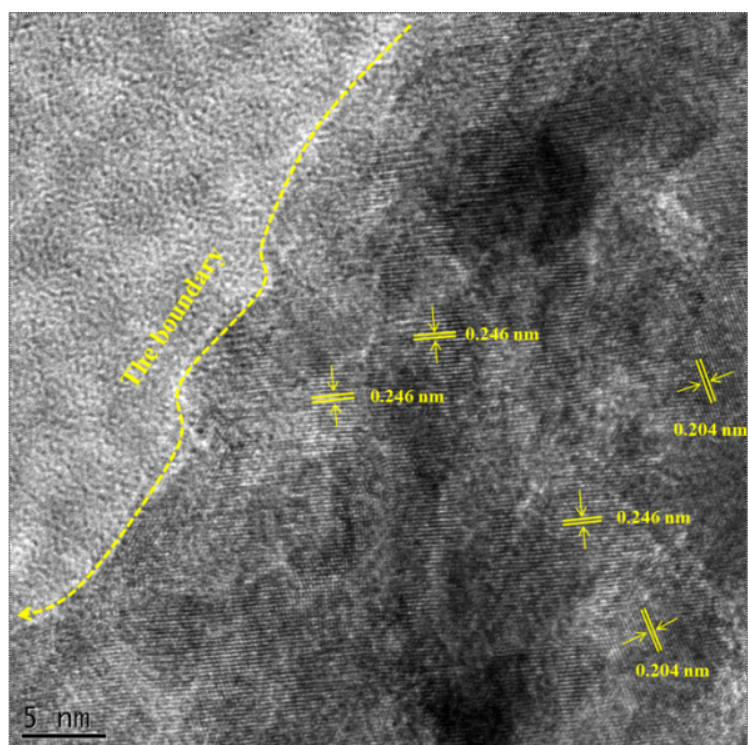
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**Fig. S1** XRD patterns of the as-prepared Co-CoO<sub>x</sub> NWAs with Ti foil with the scan rate of 0.01 s<sup>-1</sup>. Metallic Co has two peaks at 41.6 ° and 44.5°. Diffraction peaks of CoO and Co<sub>3</sub>O<sub>4</sub> are not observed.



**Fig. S2** H<sub>2</sub>-TPR profile of the obtained Co-CoO<sub>x</sub> NWAs. Two main reduction peaks were observed, which belongs to CoO<sub>x</sub>.<sup>1,2</sup>



**Fig. S3** HRTEM image of the Co-CoO<sub>x</sub> NWAs.

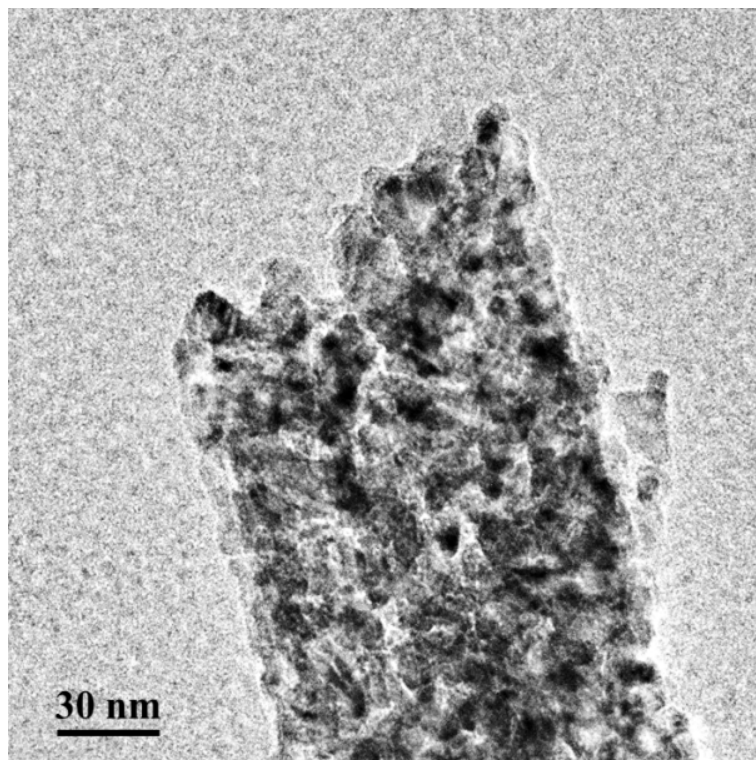
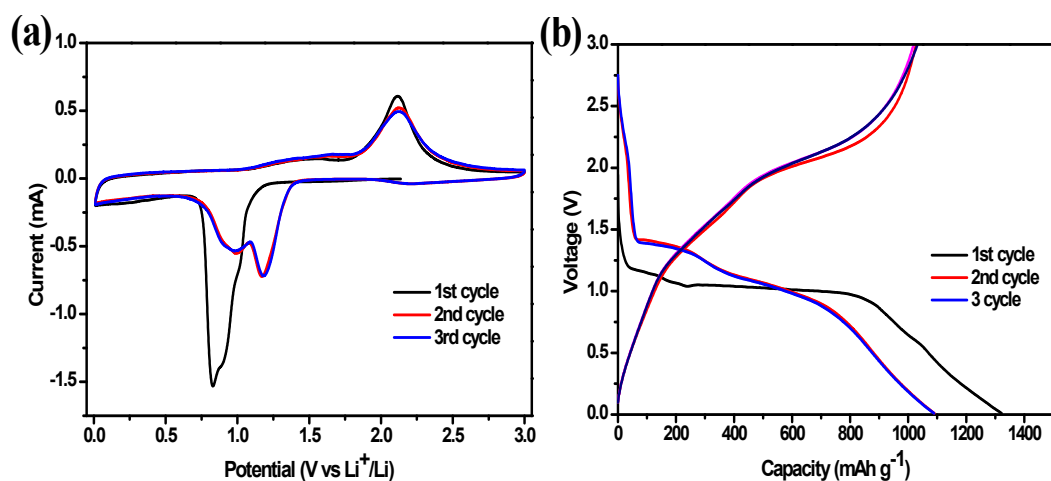
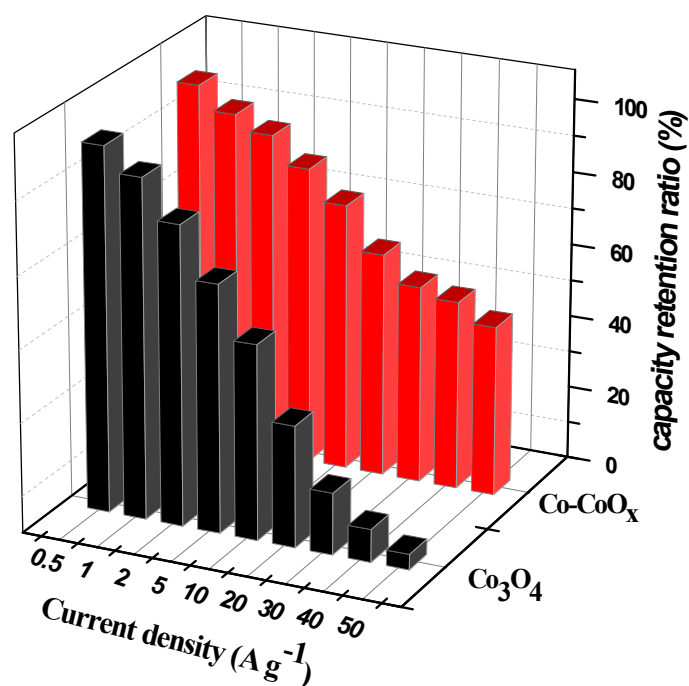


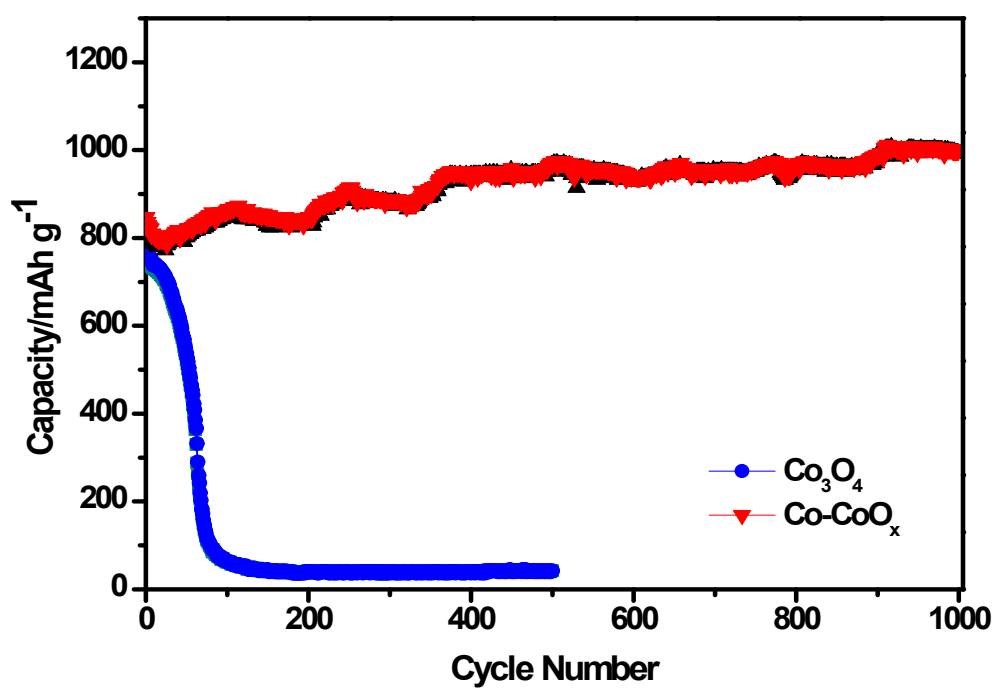
Fig. S4 TEM image of the Co-CoO<sub>x</sub> nanowire.



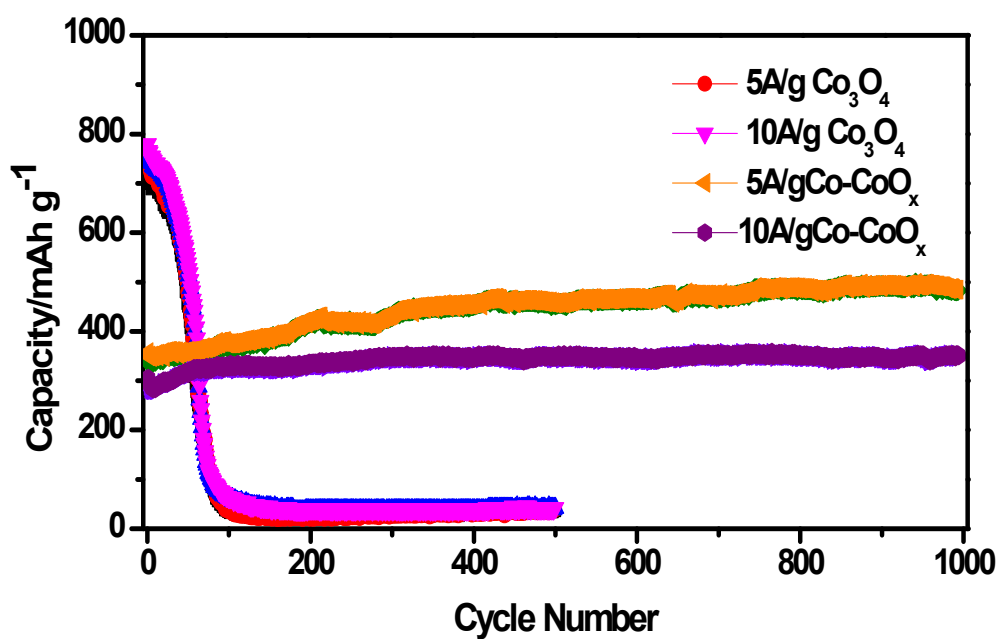
**Fig. S5** (a) The first three cyclic voltammograms of the  $\text{Co}_3\text{O}_4$  NWAs electrode, (b) Typical charge and discharge curves of first three cycles at a current density of  $0.5 \text{ A g}^{-1}$  of  $\text{Co}_3\text{O}_4$  NWAs. These data are in accord with the performance of grass-like  $\text{Co}_3\text{O}_4$  NWAs in our previous work.<sup>3</sup>



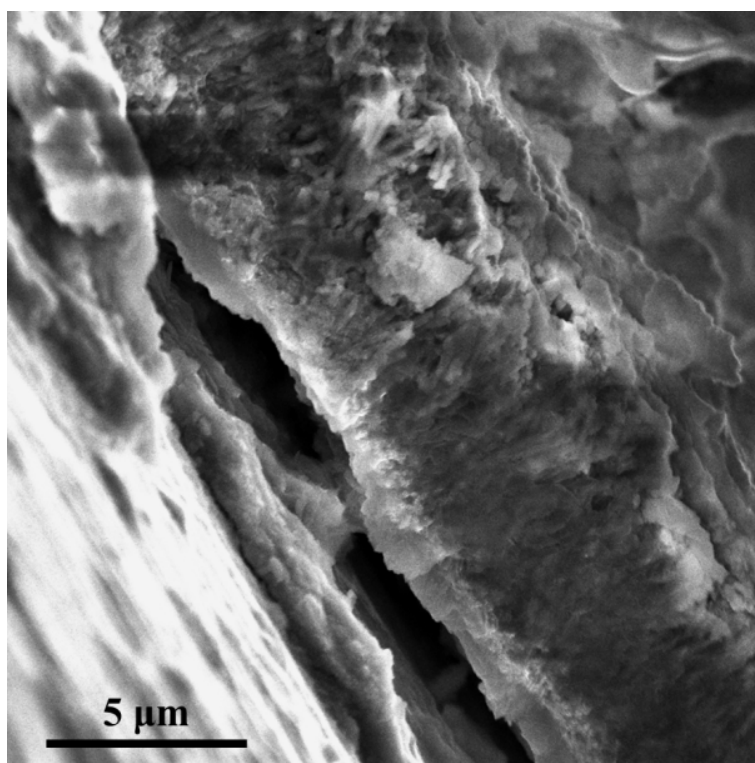
**Fig. S6** Capacity retention ratios of Co<sub>3</sub>O<sub>4</sub> and Co-CoO<sub>x</sub> NWAs at various current densities. Capacity retention ratio is the ratio of the discharge capacity at an assigned rate to the discharge capacity at 0.5A g<sup>-1</sup>. Obviously, Co-CoO<sub>x</sub> NWAs maintain higher capacity retention ratio than Co<sub>3</sub>O<sub>4</sub> NWAs at the same rate. Along with the increasing of the rate, the gap between Co-CoO<sub>x</sub> NWAs and Co<sub>3</sub>O<sub>4</sub> NWAs is widened. Even at 50 A g<sup>-1</sup>, the capacity retention ratio of Co-CoO<sub>x</sub> NWAs also keep at 46.6%, while that of Co<sub>3</sub>O<sub>4</sub> NWAs is only 4.2%.



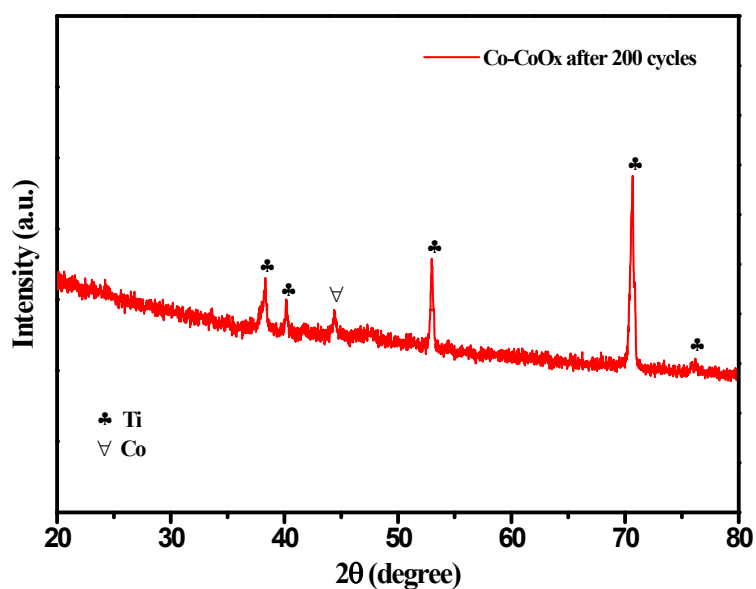
**Fig. S7** Cycling performance of  $\text{Co}_3\text{O}_4$  and  $\text{Co-CoO}_x$  at a current density of  $10 \text{ A g}^{-1}$ . The capacity data are based on the mass of  $\text{CoO}_x$ .  $\text{Co-CoO}_x$  NWAs show a high reversible capacity of  $990 \text{ mAh g}^{-1}$  at  $10 \text{ A g}^{-1}$  after 1000 cycles, while  $\text{Co}_3\text{O}_4$  NWAs exhibit a rapid capacity fading in the first 100 cycles at  $10 \text{ A g}^{-1}$ .



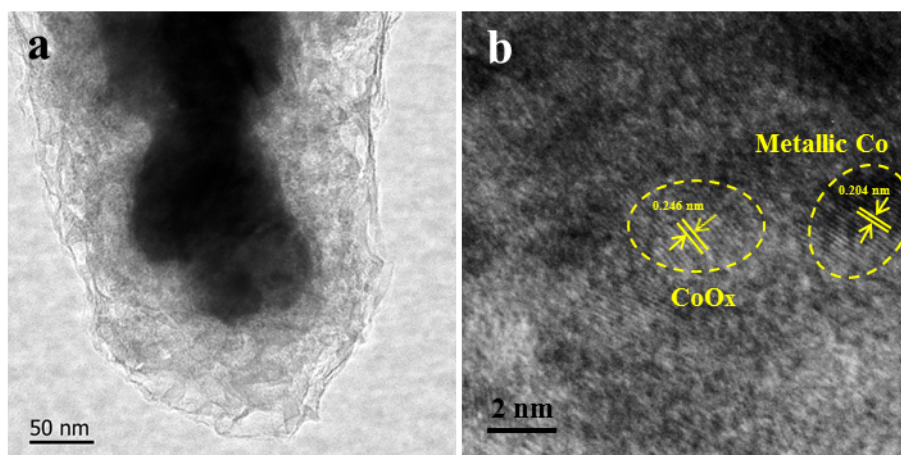
**Fig. S8** Cycling performance of Co<sub>3</sub>O<sub>4</sub> and Co-CoO<sub>x</sub> at current densities of 5 A g<sup>-1</sup> and 10 A g<sup>-1</sup>. These capacity data are based on the total mass of Co and CoO<sub>x</sub>. It is obvious that Co-CoO<sub>x</sub> NWAs have a better cycle performance than Co<sub>3</sub>O<sub>4</sub> NWAs even when metallic Co is include in active materials.



**Fig S9** SEM image of Co-CoO<sub>x</sub> NWAs from the side view after 200 cycles at 20 A g<sup>-1</sup>. After 200 cycles, the thickness of Co-CoO<sub>x</sub> array changes to 6 μm. The change of electrode thickness is related to the large volume change of Co-CoO<sub>x</sub> array during cycling, and the formation of solid electrolyte interphase (SEI) film.



**Fig. S10** XRD patterns of Co-CoO<sub>x</sub> array after 200 cycles at 20 A g<sup>-1</sup>



**Fig. S11** TEM images of Co-CoOx array electrode after 200 cycles at 20 A g<sup>-1</sup>.

### References

1. Y. Ren, P. G. Bruce and Z. Ma, *J. Mater. Chem.*, **2011**, 21, 9312.
2. B. Wang, Z. Qin, G. Wang, Z. Wu, W. Fan, H. Zhu, S. Li, Y. Zhang, Z. Li and J. Wang, *Catalysis Lett.*, **2013**, 143, 411-417.
3. L. Zhan, S. Wang, L. Ding, Z. Li and H. Wang, *Electrochim. Acta*, **2014**, 135, 35-41.