

## Support Information

# **Co<sub>3</sub>O<sub>4</sub> functionalized Porous Carbon nanotube Oxygen-Cathode to Promote Li<sub>2</sub>O<sub>2</sub> Surface Growth for Improved Cycling Stability in Li-O<sub>2</sub> Batteries**

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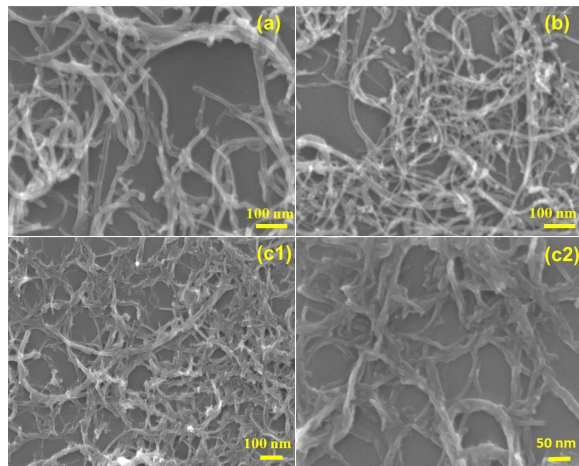


Figure S1. SEM images of (a): o-CNT; (b): p-CNT; (c1) and (c2): p-CNT/Co<sub>3</sub>O<sub>4</sub>[M].

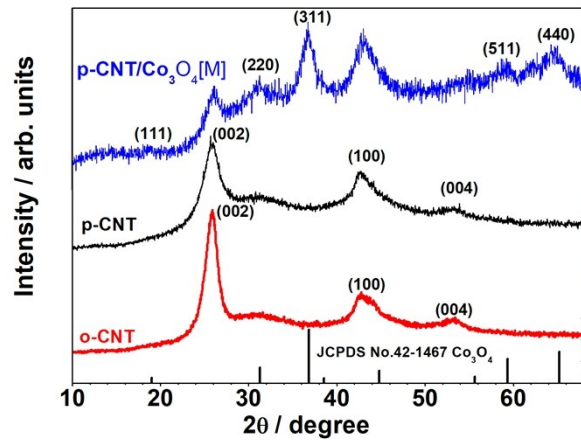


Figure S2. XRD patterns of (e): o-CNT; (f): p-CNT; (g): p-CNT/Co<sub>3</sub>O<sub>4</sub>[M].

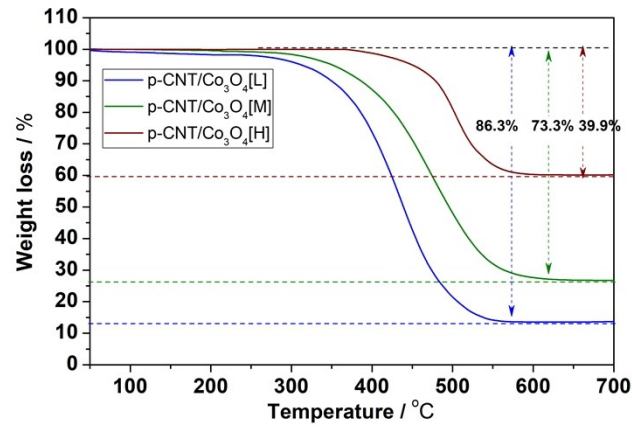


Figure S3. TG curve of p-CNT/Co<sub>3</sub>O<sub>4</sub>[L], p-CNT/Co<sub>3</sub>O<sub>4</sub>[M] and p-CNT/Co<sub>3</sub>O<sub>4</sub>[H].

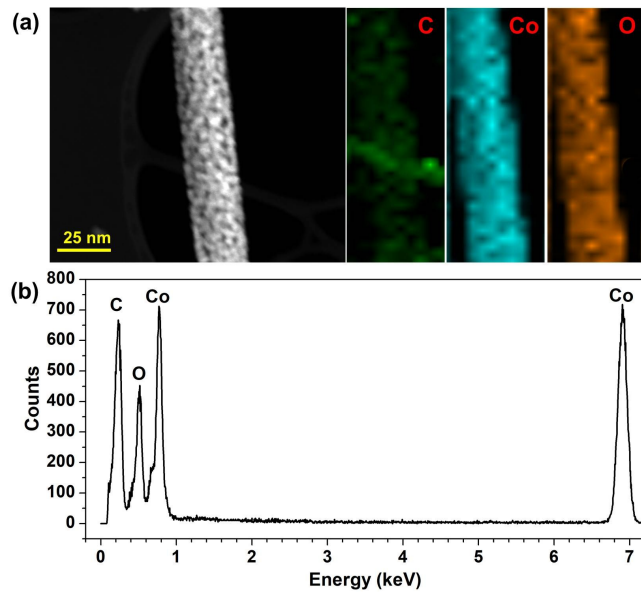


Figure S4 (a): HAADF-STEM image and EDX maps (of the C, Co, and O elements and of all three elements in the composite) of the p-CNT@Co<sub>3</sub>O<sub>4</sub>[M] sample; (b) EDX analysis of the p-CNT/Co<sub>3</sub>O<sub>4</sub>[M].

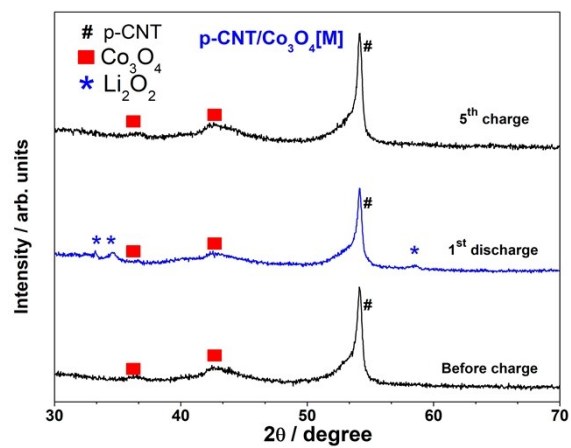


Figure S5. XRD patterns of the p-CNT/Co<sub>3</sub>O<sub>4</sub>[M] before discharge, after 1<sup>st</sup> discharge, and after 5<sup>th</sup> charge.

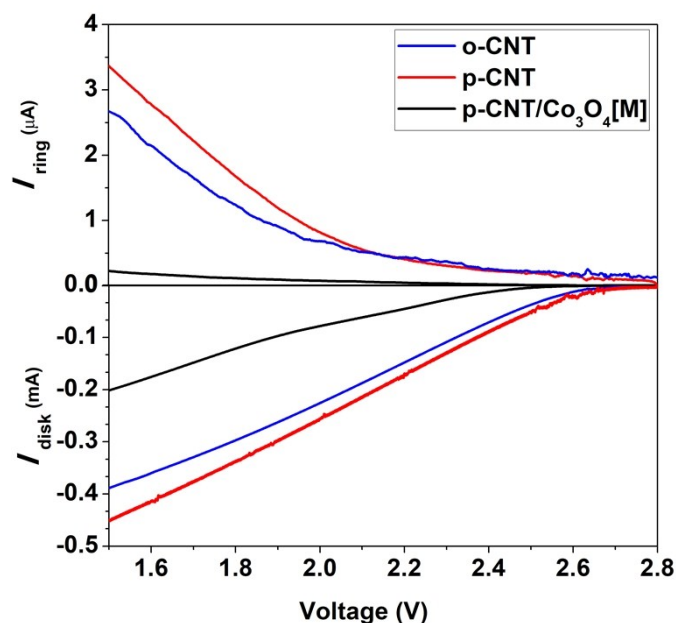


Figure S6. RRDE curves of the o-CNT, p-CNT and p-CNT/Co<sub>3</sub>O<sub>4</sub>[M] catalysts.

We do the rotating ring disk electrode (RRDE) to evaluate the role of Co<sub>3</sub>O<sub>4</sub> on the formation of Li<sub>2</sub>O<sub>2</sub>, in particularly the oxygen adsorption strength on different cathode catalysts. The RRDE of o-CNT, p-CNT and p-CNT/Co<sub>3</sub>O<sub>4</sub>[M] were tested to determine the concentration of O<sub>2</sub><sup>-</sup> adsorbed on the surface of disk or dissolved in solution. In the RRDE studies, O<sub>2</sub> is firstly reduced at the disk and then dissolved O<sub>2</sub><sup>-</sup> in electrolyte is oxidized and detected at the ring. The low ring current of p-CNT/Co<sub>3</sub>O<sub>4</sub>[M] demonstrated a very small concentration of O<sub>2</sub><sup>-</sup> in the electrolyte solution, suggesting that O<sub>2</sub><sup>-</sup> is mainly adsorbed on the p-CNT/Co<sub>3</sub>O<sub>4</sub>[M], leading to surface thin film growth mode. In contrast, the higher ring current of o-CNT and p-CNT indicated that O<sub>2</sub><sup>-</sup> is dissolved in solution, resulting in solution growth mode. The RRDE results show that the decorated Co<sub>3</sub>O<sub>4</sub> surface layer possesses stronger oxygen adsorption strength, and hence lead to the transformation of the discharge product from the toroid-type Li<sub>2</sub>O<sub>2</sub> via the solution growth mechanism to the thin film-type Li<sub>2</sub>O<sub>2</sub> via the surface growth mechanism.

Table S1. BET surface area and pore volume of o-CNT, p-CNT, p-CNT/Co<sub>3</sub>O<sub>4</sub>[L], p-CNT/Co<sub>3</sub>O<sub>4</sub>[M] and p-CNT/Co<sub>3</sub>O<sub>4</sub>[H].

Sample	S <sub>BET</sub> (m <sup>2</sup> g <sup>-1</sup> )	S <sub>pore</sub> (cm <sup>3</sup> g <sup>-1</sup> )
o-CNT	131.8	0.26
p-CNT	551.7	0.90
p-CNT/Co <sub>3</sub> O <sub>4</sub> [L]	402.9	0.80
p-CNT/Co <sub>3</sub> O <sub>4</sub> [M]	355.7	0.64
p-CNT/Co <sub>3</sub> O <sub>4</sub> [H]	167.0	0.33



Table S2. Fitted values for equivalent circuit elements by simulation of EIS data in Figure 7.

Samples	$R_o$ ( $\Omega$ )		$R_{ct}$ ( $\Omega$ )	
	Initial	5 <sup>th</sup> charge	Initial	5 <sup>th</sup> charge
o-CNT	47.0	77.9	96.2	229.4
p-CNT	44.7	71.4	55.5	194.1
p-CNT/Co <sub>3</sub> O <sub>4</sub> [M]	41.7	56.1	74.3	100.5