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An ultra-high-performance anode material for supercapacitors: self-assembled long Co₃O₄ hollow tubes network with multiple heteroatoms (C-, N- and S-) doping

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Fig. S1 SEM images of the surface morphology and structure of ESM at different angles and magnifications.

Fig. S1 shows the SEM images of original ESM at different angles and magnifications. As shown in Fig. S1a, the surface morphology of ESM exhibits that the thick fibers connect with each other to form a network, and are arranged irregularly. These fibers are observed at a higher magnification, and the diameter of fibers ranges from 1 to 3 um (Fig. S1b).



Fig. S2 TG-DSC curves of CESM-1 (a), CESM-3 (b) and CESM-6 (c). XRD patterns of these obtained samples (e). Nitrogen adsorption-desorption isotherm (f) and pore size distribution (g) of

activated carbon.

Fig. S2(a-c) shows the TG-DSC curves of CESM-1, CESM-3 and CESM-6 at heating rate of 10 °C min⁻¹ from 30 to 800 °C in air. For the TG curves, It can be clearly observed that all the samples

experience shows a great weight loss in the range of 300-450 °C, which is caused by the removal of the ESM and the decomposition of Co(OH)(CO₃)_{0.5}. According to the TG curves, the loading amounts of Co(OH)(CO₃)_{0.5} on the ESM was increased with the increased hydrothermal time. From the DSC curves, an exothermic peak was observed to be at about 350 °C, which corresponds to the crystallization of Co₃O₄ from the decomposition of Co(OH)(CO₃)_{0.5}.¹ When the temperature is up to 450 °C, the weight losses of these samples moves to equilibrium completely. Fig. S2d shows the XRD patterns of CESM-1, CESM-3 and CESM-6. It can be clearly observed that all of the products show the same diffraction peaks, which is indexed to the face centered cubic phases of Co(OH)(CO₃)_{0.5} (JCPDS card No. 48-0083). The N₂ isotherm and pore size distribution of the activated carbon are shown in Fig. S2(e and f). As depicted in Fig. S2e, the activated carbon shows a type I isotherm, which is indicative of the microporous character.² The pore size distribution of the activated carbon ranges from 1.5 to 5 nm (Figure S2f). The measured BET specific surface area of activated carbon is 2167 m² g⁻¹, and the pore volume is 1.08 cm³ g⁻¹.



Fig. S3 SEM images of CESM-1 (a), CESM-3 (b), CESM-6 (c), Co₃O₄-p (d), Co₃O₄-n (e) and

Co₃O₄-s (f), respectively.

	EDX (wt %)			XPS (atom %)						
	Co	0	С	Ν	S	Co	0	С	Ν	S
Co ₃ O ₄ -p	55.41	32.23	3.47	1.08	7.8	22.73	53.83	16.18	1.45	5.81
Co ₃ O ₄ -n	64.13	28.85	4.57	1.04	1.41	29.53	50.95	16.14	0.88	2.51
Co ₃ O ₄ -s	61.33	32.65	3.27	1.32	1.43	29.67	50.14	15.99	0.99	3.21

Table S1 Elements (atomic %) of the samples determined by EDS and XPS.



Fig. S4 The XPS patterns of the fabricated samples at the wide scan.



Fig. S5 The electrochemical performances of the obtained products and activated carbon are

investigated in 6 M KOH in a three-electrode system. The CV curves (a-c, g) and GCD curves (d-f, h)

of Co₃O₄-p, Co₃O₄-n, Co₃O₄-s and activated carbon, respectively. Nyquist impedance curves (i) of the



Fig. S6 The specific capacitance values of activated carbon at different current density.

References:

- 1. S. Xiong, J. S. Chen, X. W. Lou and H. C. Zeng, Adv Funct Mater, 2012, 22, 861-871.
- 2. X. Jin, M. Zhang, Y. Wu, J. Zhang and J. Mu, *Ind Crop Prod*, 2013, 43, 617-622.