## Supporting Information

## Formation of Co-Mn mixed oxide double-shelled hollow spheres as advanced electrodes for

## hybrid supercapacitors

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Fig. S1 FESEM and TEM images of Co-glycerate solid spheres.



Fig. S2 XRD pattern of Co-glycerate solid spheres.



**Fig. S3** Low-magnification FESEM image of Co-Mn mixed oxide hollow spheres precursor after hydrothermal process in KMnO<sub>4</sub> solution for 1 h.



**Fig. S4** XRD patterns of double-shelled Co-Mn mixed oxide hollow spheres after hydrothermal process in KMnO<sub>4</sub> solution for 1 h and the corresponding crystalline Co-Mn-DHS product after calcination treatment in air at 350 °C.



Fig. S5 EDX spectrum of crystalline Co-Mn-DHS sample.



Fig. S6 (a) HAADF-STEM image and (b-d) elemental mapping data of Co-Mn-DHSs.



Fig. S7 XPS spectra of (a) Co 2p and (b) Mn 2p for crystalline Co-Mn-DHS sample.

The Co 2p spectrum could be fitted into two spin-orbit doublets and two shakeup satellites by using a Gaussian fitting method. The fitting peaks at around 779.8 and 795.3 eV belong to Co<sup>3+</sup>, while the other two peaks at 781.2 and 797.1 eV can be ascribed to Co<sup>2+</sup>. As for the Mn 2p spectrum, there are two main spin-orbit peaks located at 642.1 eV  $(2p_{3/2})$  and 653.8 eV  $(2p_{1/2})$ , revealing the presence of both Mn<sup>2+</sup> and Mn<sup>3+</sup>.



Fig. S8 N<sub>2</sub> adsorption-desorption isotherm at 77 K of crystalline Co-Mn-DHS sample.



**Fig. S9** XRD pattern of Co-Mn mixed oxide hollow spheres after hydrothermal process in KMnO<sub>4</sub> solution for 10 min.



**Fig. S10** FTIR spectra of Co-glycerate and Co-Mn mixed oxide samples obtained after hydrothermal process in KMnO<sub>4</sub> solution for 10 min and 60min.



Fig. S11 FESEM and TEM images of Mn-glycerate solid spheres.



**Fig. S12** (a) CV curve at the sweep rate of 10 mV s<sup>-1</sup> and the red region corresponding to the capacitive contribution to the total current; (b) capacitive contribution at different sweep rates for the Co-Mn-DHS electrode.



**Fig. S13** (a) TEM image of Co-Mn-SHS sample. Electrochemical evaluations of the Co-Mn-SHS electrode: (b) CV curves; (c) discharge voltage profiles at different current densities; (d) specific capacitance as a function of current density.



**Fig. S14** (a) FESEM image, (b-c) TEM images, (d) N<sub>2</sub> adsorption-desorption isotherm, and (e) the corresponding pore size distribution of CMK-3 sample.



**Fig. S15** (a) CV curve and (b) charge/discharge voltage profile of CMK-3 at a current density of 2 A  $g^{-1}$  in KOH solution (2.0 M).



**Fig. S16** Charge/discharge voltage profiles of Co-Mn-DHS//CMK-3 HSC at various current densities.



Fig. S17 Ragone plot of Co-Mn-DHS//CMK-3 HSC device.

HSC device	Working potential (V)	Energy density (Wh kg <sup>-1</sup> )	Power density (W kg <sup>-1</sup> )	Reference
Co-Mn-DHS//CMK-3	1.6	33.8 20.5	1602 16020	This work
NiCo <sub>2</sub> O <sub>4</sub> /NiO/Co <sub>3</sub> O <sub>4</sub> // active carbon (AC)	1.6	43.02	820.29	<i>Chem. Eng. J.</i> , 2019, <b>368</b> , 51-60.
RGO/Mn <sub>3</sub> O <sub>4</sub> //RGO	1.6	14.3	21300	<i>Adv. Funct.</i> <i>Mater.</i> , 2018, <b>28</b> , 1707247
NiCo <sub>2</sub> O <sub>4</sub> @CNT/CNT/ /treated carbon cloth	1.6	27.6 7.11	550 2860	<i>Adv. Funct.</i> <i>Mater.</i> , 2017, <b>27</b> , 1702160
NiCo <sub>2</sub> O <sub>4</sub> //AC	1.4	24.5 15.78	175 1385	<i>Electrochim. Acta</i> , 2019, <b>299</b> , 509- 517
NiCo <sub>2</sub> O <sub>4</sub> - CNT@DNA//AC	1.5	69.7 52.2	373.9 12046.2	<i>Nano Energy</i> , 2019, <b>56</b> , 751-758
Mn-Co//AC	1.8	45.8	300	<i>Electrochim. Acta</i> , 2018, <b>289</b> , 72-81
MnCo- LDH@Ni(OH) <sub>2</sub> //AC	1.5	47.9	750	<i>J. Mater. Chem.</i> <i>A,</i> 2017, <b>5</b> , 1043- 1049.
NiCo <sub>2</sub> S <sub>4</sub> @Ni <sub>3</sub> V <sub>2</sub> O <sub>8</sub> //A C	1.6	42.7	200	<i>J. Mater. Chem.</i> <i>A</i> , 2016, <b>4</b> , 5669- 5677

 Table S1 Comparison of electrochemical performance of various Mn/Co-based HSC devices.