Electronic Supplementary Material (ESI) for Journal of Materials Chemistry A.

Supporting Information

Hierarchical walnut-like $Ni_{0.5}Co_{0.5}O$ hollow nanospheres comprised of ultrathin nanosheets for advanced energy storage devices

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The volumetric energy density (E_{vol}, Wh L^{-1}) were evaluated according to the following equation

$$E_{vol} = E \times \rho$$

$$\rho = \frac{m}{V}$$

where E (Wh kg^{-1}) is the specific energy density based on total mass of active electrode material including $Ni_{0.5}Co_{0.5}O$ and active carbon. ρ (g cm^{-3}) is the packing density of active materials verse volume of total materials including active material, carbon black and binder. m (g) is a certain mass of active electrode material, and V (cm^3) is the volume of total electrode material. We calculated the volume of total electrode material by measuring the radius (r) and thickness (h) of the compressed total electrode material under the pressure of 10 MPa. ($V = h \times \pi \times r^2$)

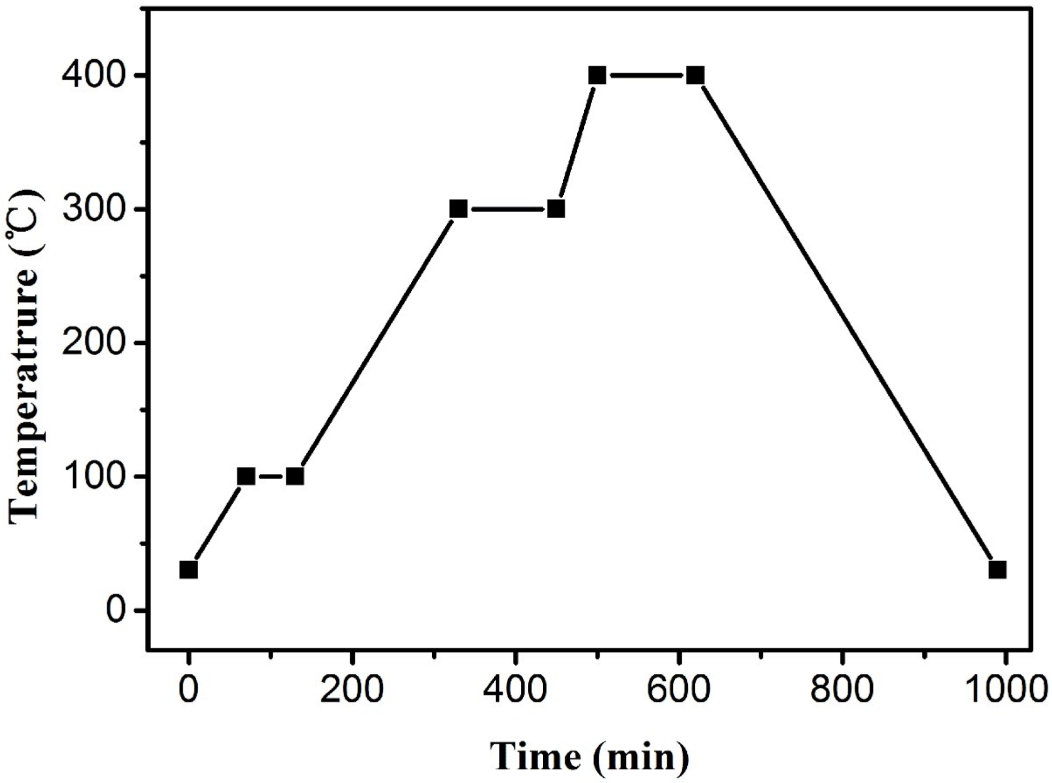

Figure S1. *Anneal program of* $Ni_{0.5}Co_{0.5}O$ *precursor nanospheres.*

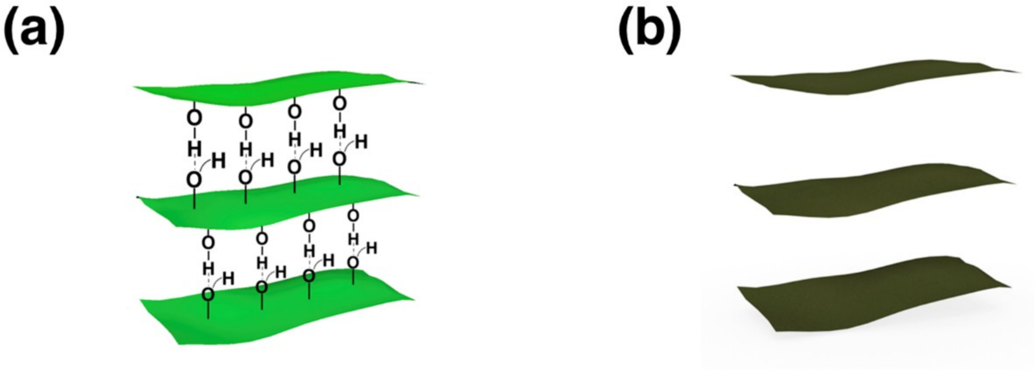

Figure S2. *Schematic illustration of (a) the overlapped* $Ni_{0.5}Co_{0.5}O$ *precursor and (b) the layered* $Ni_{0.5}Co_{0.5}O$ *sheets structure.*

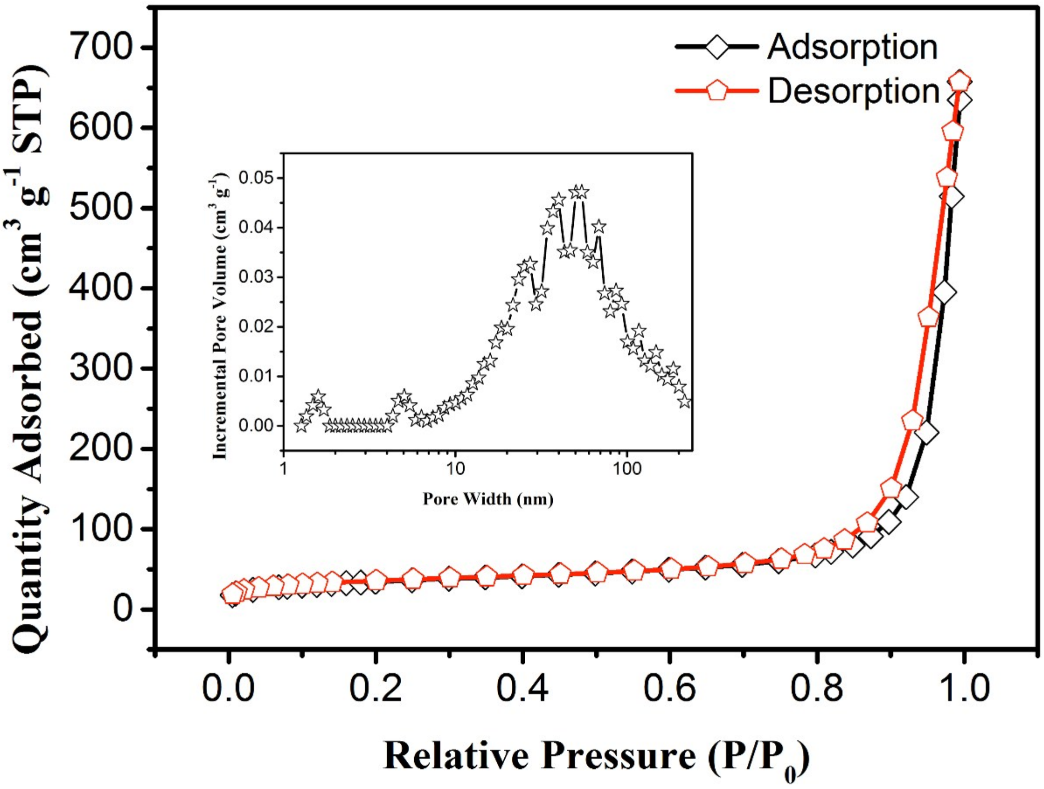

Figure S3. *Nitrogen adsorption/desorption isotherm of the walnut-like* $Ni_{0.5}Co_{0.5}O$ *hollow nanospheres and the inset is the pore size distribution calculated by the NLDFT method.*

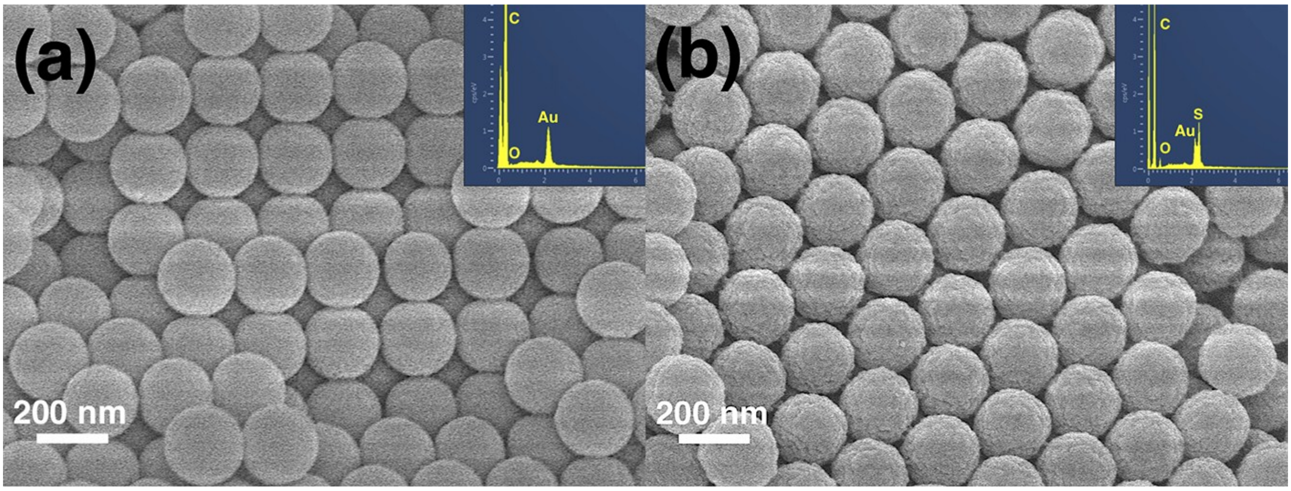

Figure S4. *SEM images of (a) polystyrene (PS) nanospheres and (b) sulfonated polystyrene (sPS) nanospheres and the insets are the energy dispersive spectrometry (EDS), respectively.*

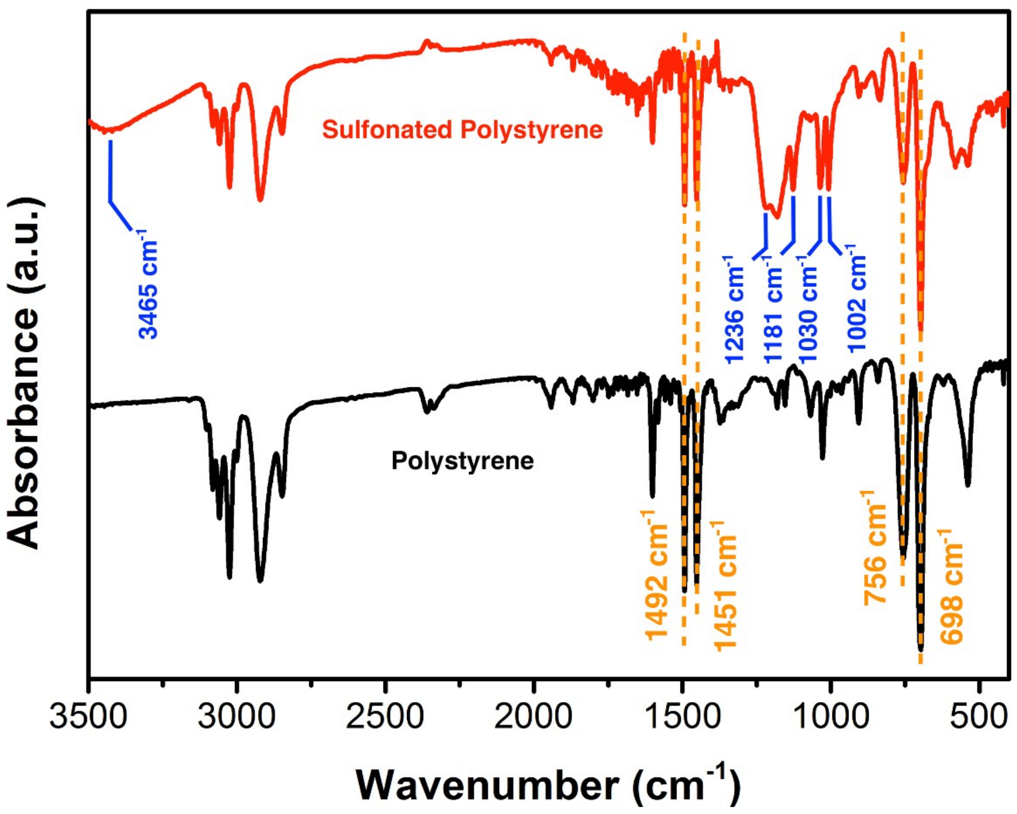

Figure S5. *FT-IR spectra of polystyrene nanospheres (PS, black line) and sulfonated polystyrene nanospheres (sPS, red line).*

The absorbance of polystyrene could be observed clearly at 1492, 1451, 756 and 698 cm^{-1} not only from the PS nanospheres, but also from the sPS nanospheres, indicating the main composition was well reserved under the sulfonated process and the sulfonated was occurred only on the surface of the nanospheres. The absorbance at 1236 and 1181 cm^{-1} may derived from the antisymmetric stretching vibration of S=O and the split absorption peak at 1030 and 1002 cm^{-1} may attributed to the S=O symmetric stretching vibration generated. The absorbance at 3465 cm^{-1} may due to the oxhydryl produced by the R-SO_3H.

Table S1 Comparison of electrochemical performance of our proposed NCO-HNS with other published Ni-Co-O materials.

Electrode materials	**Morphology**	**Electrolyte**	**Specific capacitance/capacity***	**Working potential (V vs. SCE, Hg/HgO or Ag/AgCl)**	**Stability**	**Rate performance**	**Ref.**
NRGO-$NiCoO_2$	Nanoparticle	3 M KOH	508 F g^{-1} (0.5 A g^{-1})	0 - 0.5	93% (2000)	30.7% (20 A g^{-1})	[1]
$CoNiO_2$	Nanoparticle	1 M KOH	184 F g^{-1} (1 A g^{-1})	0 - 0.45	-	79.9% (5 A g^{-1})	[2]
$NiCo_2O_4$	Tetragonal microtube	2 M KOH	1387.9 F g^{-1} (2 A g^{-1})	0 - 0.55	-	72.8% (20 A g^{-1})	[3]
$NiCo_2O_4$	Nanoplates	2 M KOH	332 F g^{-1} (0.375 A g^{-1})	0 - 0.7	86% (2000)	61% (5 A g^{-1})	[4]
$NiCo_2O_4$/3D GF	Flower-like	6 M KOH	1402 F g^{-1} (1 A g^{-1})	0 - 0.45	76.6% (5000)	77.03% (20 A g^{-1})	[5]
$NiCo_2O_4$	Nanobelts	6 M KOH	1072.9 F g^{-1} (1 A g^{-1})	0 - 0.55	78.09% (3000)	62.19% (10 A g^{-1})	[6]
$NiCo_2O_4$	Nanoplatelet	2 M KOH	1362 F g-1 (1 A g^{-1})	0 - 0.4	-	70.8% (16 A g^{-1})	[7]
$NiCo_2O_4$/Ni foam	Nanograss	6 M KOH	1230 F g^{-1} (1 A g^{-1})	0 - 0.5	46.9% (2000)	74% (30 mA cm^{-2})	[8]
$NiCo_2O_4$/Ni	Nanosheets	6 M KOH	1.1 F cm^{-2} (1 mA cm^{-2})	0 - 0.5	99.1% (1000)	81% (10 mA cm^{-2})	[9]
$NiCo_2O_4$/CNT	Nanoparticles	2 M KOH	828 F g^{-1} (1 A g^{-1})	0 - 0.37	81% (3000)	71% (20 A g^{-1})	[10]
$NiCo_2O_4$	Porous microspheres	2 M KOH	774 F g^{-1} (2 mV s^{-1})	-0.1 - 0.5	-	52.3% (100mV s^{-1})	[11]
$NiCo_2O_4$/rGO	Hollow nanoparticle	2 M KOH	1238 F g^{-1} (1 A g^{-1})	0 – 0.4	-	36% (10 A g^{-1})	
NCO-HNS	Hollow nanospheres	2 M KOH	221.8 mAhg^{-1} /1452 F g^{-1} (1 A g^{-1})	0 - 0.55	99.4% (3000)	79% (20 A g^{-1})	This work

*In our work, we use the specific capacity to evaluate the ability of storing the electric charge for our battery-type materials.[12] In order to compare the electrochemical properties of our work with other Ni-Co-O electrode materials in literatures, we also use specific capacitance here which calculated from the GCD curves according to the following equation.[13]

$$C_s = \frac{I \times \Delta t}{m \times \Delta V}$$

where C_s (F g^{-1}) is the specific capacitance, I (A) is the current intensity, Δt (s) is the discharge time, m (g) is the mass of the active materials （NCO-HNS） and ΔV is the potential window of the electrodes.

Table S2 Comparison of electrochemical performance of our assembled NCO-HNS//AC with other published Ni-Co-O devices.

Electrode materials	**Morphology**	**Electrolyte**	**Specific capacitance/capacity**	**Working potential (V)**	**Specific energy density (Wh kg^{-1})**	**Power density (W kg^{-1})**	**Ref.**
NRGO-$NiCoO_2$// NRGO-$NiCoO_2$	Nanoparticle	3 M KOH	58 F g^{-1} (0.5 A g^{-1})	0 - 0.8	-	-	1
$CoNiO_2$//AC	Nanoparticle	1 M KOH	76.8 F g^{-1} (1 mA cm^{-2})	0 - 1.7	24	415.4	2
$NiCo_2O_4$/CC//PGP	Nanosheets	PVA–LiOH gel	71.32 F g^{-1} (5 mA cm^{-2})	0 - 1.8	60.9	568.2	14
$NiCo_2O_4$/CNT	Nanoparticles	2 M KOH	105 F g^{-1} (1 mA g^{-1})	0 - 1.4	28.58	700	10
CNG//RGO	Nanorods	1 M KOH	111.1 F g^{-1} (1 A g^{-1})	0 – 1.5	28	3613	15
NCO-HNS//AC	Hollow nanospheres	2 M KOH	53.8 mAh g^{-1} / 133.6 F g^{-1} (0.5 A g^{-1})	0 – 1.45	38.3&19.3	743.5&7604.9	This work

*In the two-electrode experiment of this work, the current density is based on the total mass (NCO-HNS and active carbon) of the two electrodes.

References

1 Y. Xu, J. Wei, L. Tan, J. Yu and Y. Chen, *J. Mater. Chem. A*, 2015, **3**, 7121–7131.

2 W. Du, Y. Gao, Q. Tian, D. Li, Z. Zhang, J. Guo and X. Qian, *J. Nanopart. Res.*, 2015, **17**, 368–12.

3 F. Ma, L. Yu, C. Xu and X. W. D. Lou, *Energy Environ. Sci.*, 2016, **9**, 862–866.

4 T. Kim, A. Ramadoss, B. Saravanakumar, G. K. Veerasubramani and S. J. Kim, *Appl. Surf. Sci.*, 2016, **370**, 452–458.

5 C. Zhang, T. Kuila, N. H. Kim, S. H. Lee and J. H. Lee, *Carbon*, 2015, 1–28.

6 J. Xu, L. Li, P. Gao, L. Yu, Y. Chen, P. Yang, S. Gai and P. Yang, *Electrochim. Acta*, 2015, **166**, 206–214.

7 S. Jiang, Y. Sun, H. Dai, P. Ni, W. Lu, Y. Wang, Z. li and Z. Li, *Electrochim. Acta*, 2016, **191**, 364–374.

8 D. S. Sun, Y. H. Li, Z. Y. Wang, X. P. Cheng, S. Jaffer and Y. F. Zhang, *J. Mater. Chem. A*, 2016, **4**, 5198–5204.

9 T. Wang, Y. Guo, B. Zhao, S. Yu, H. Yang, D. Lu, X. Fu, R. Sun and C. Wong, *J. Power Sources*, 2015, **286**, 1–34.

10 S. Xu, D. Yang, F. Zhang, J. Liu, A. Guo and F. Hou, *RSC Advances*, 2015, **5**, 74032–74039.

11 S. Khalid, C. Cao, L. Wang and Y. Zhu, *Sci. Rep.*, 2016, **6**, 22699.

12 T. Brousse, D. Belanger and J. W. Long, *J. Electrochem. Soc.*, 2015, **162**, A5185–A5189.

13 S. Zhang and N. Pan, *Adv. Energy Mater.*, 2014, **5**, 14011401.

14 Z. Gao, W. Yang, J. Wang, N. Song and X. Li, *Nano Energy*, 2015, **13**, 306–317.

15 J. Xiao and S. Yang, *J. Mater. Chem.*, 2012, **22**, 12253–10.