

# Composition controlled nickel cobalt sulfides core-shell structure as high capacity and good rate-capability electrodes for hybrid supercapacitors

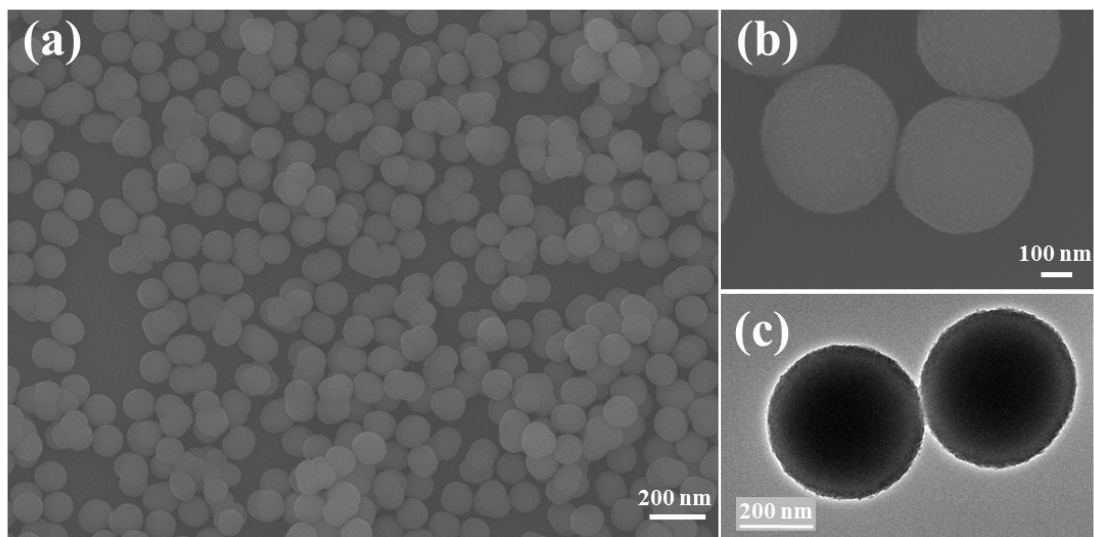
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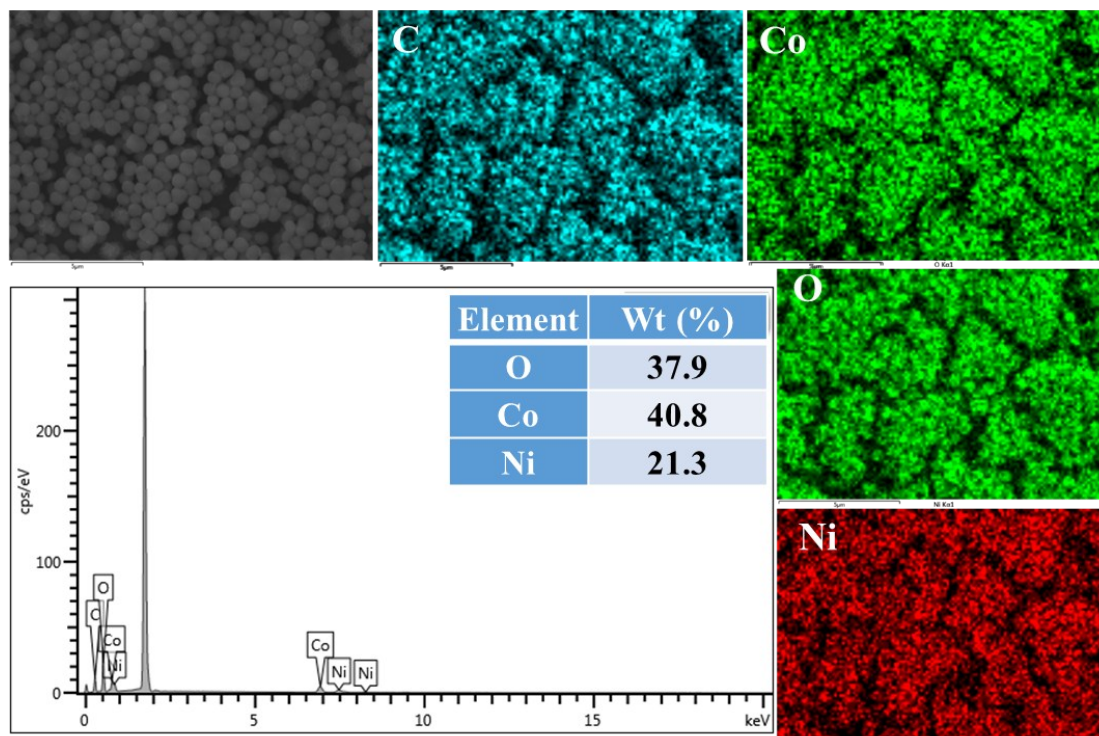
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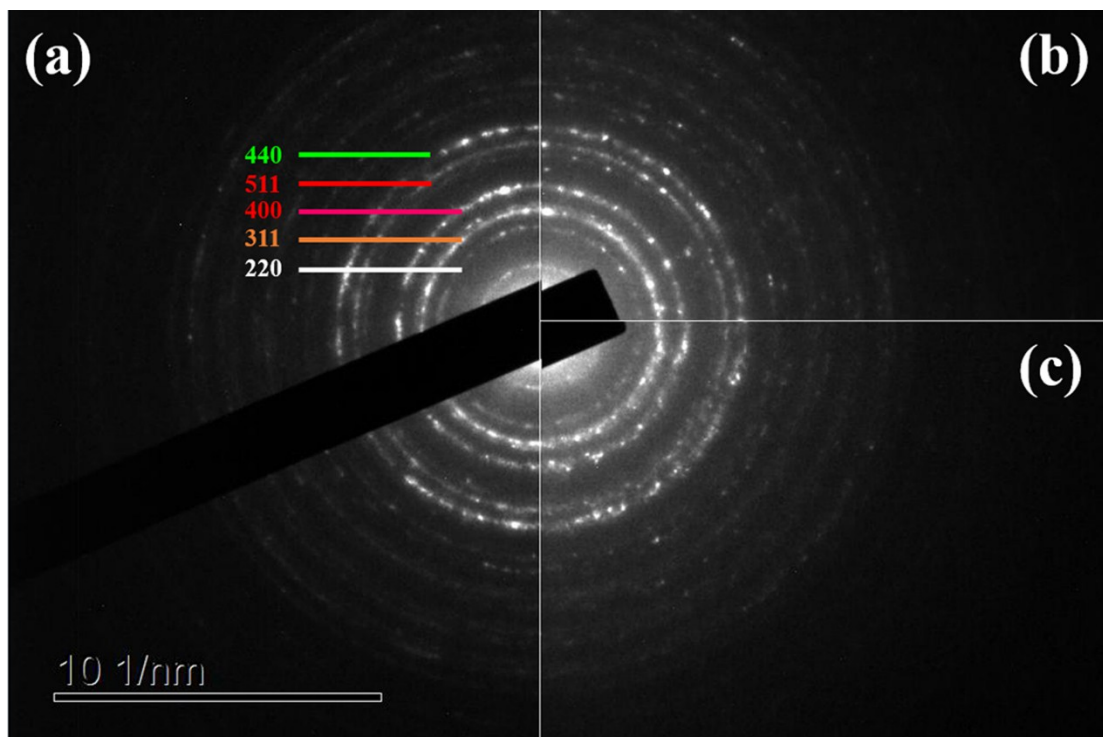
[+] These authors contributed equally to this work.



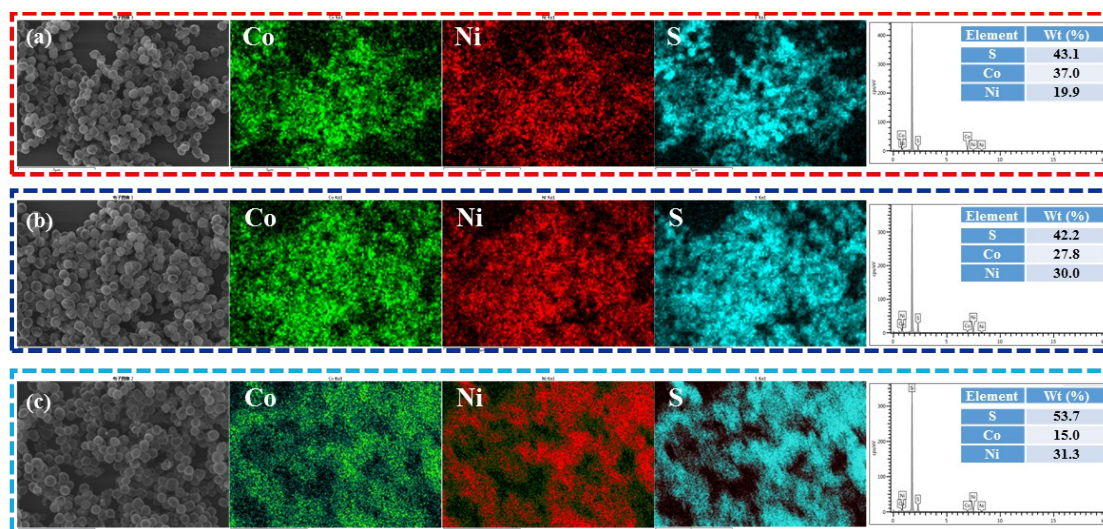
**Figure S1.** The morphology of the precursors NiCo-glycerate spheres corresponding to the  $\text{NiCo}_2\text{S}_4$  sample. (a, b) FESEM image. (c) TEM image.



**Figure S2.** SEM image and EDS-elemental mapping images of NiCo-glycerate spheres corresponding to the  $\text{NiCo}_2\text{S}_4$  sample.



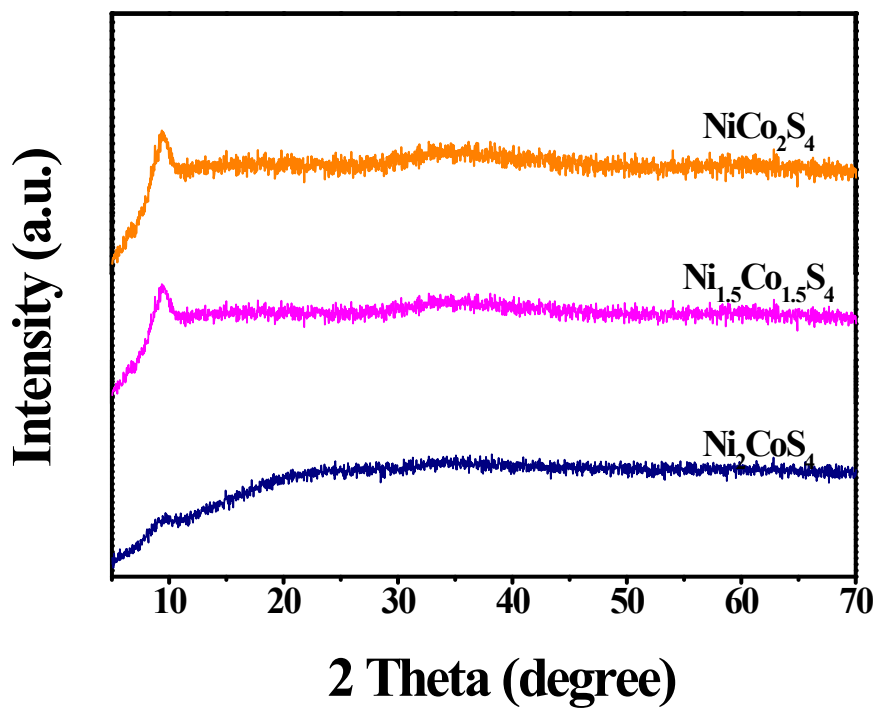
**Figure S3.** The SAED patterns of the Ni–Co sulfides: (a)  $\text{NiCo}_2\text{S}_4$ , (b)  $\text{Ni}_{1.5}\text{Co}_{1.5}\text{S}_4$ , and (c)  $\text{Ni}_2\text{CoS}_4$ , respectively.



**Figure S4.** SEM-EDS elemental mapping images and its corresponding EDS spectra: (a)  $\text{NiCo}_2\text{S}_4$ , (b)  $\text{Ni}_{1.5}\text{Co}_{1.5}\text{S}_4$ , and (c)  $\text{Ni}_2\text{CoS}_4$ .

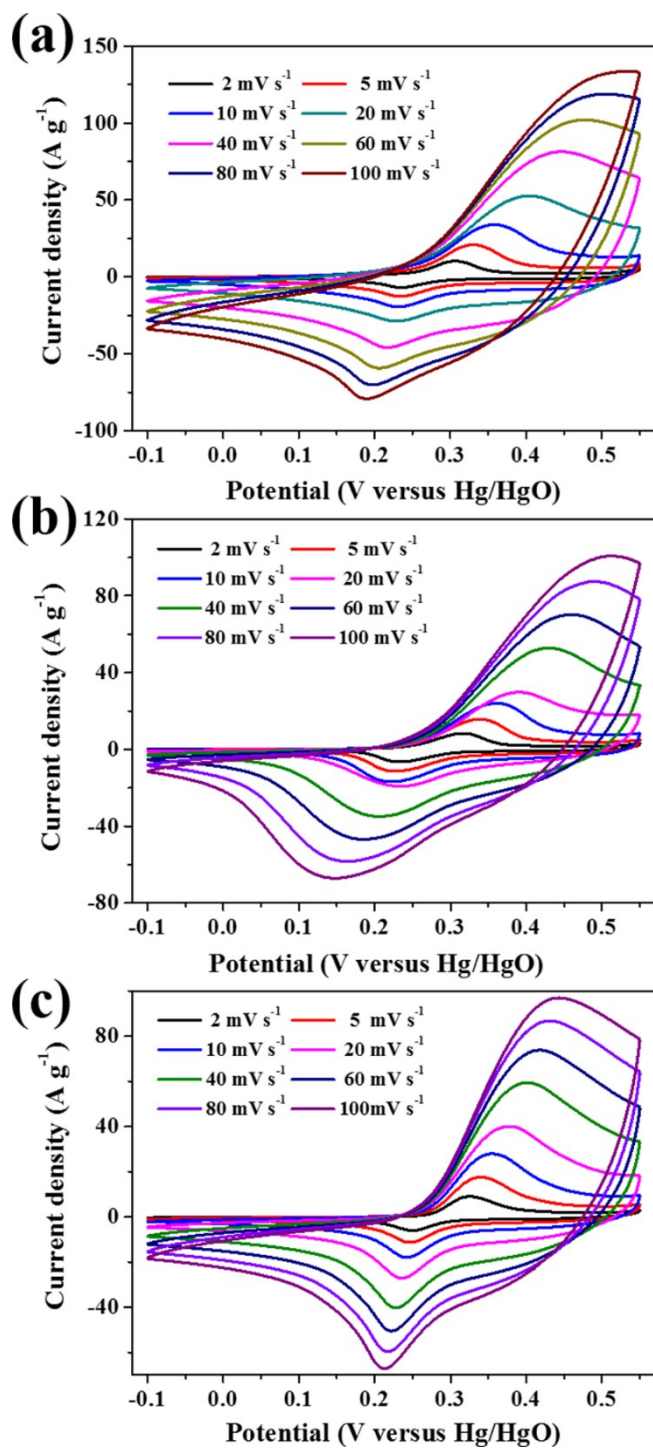
**Table S1.** The ratio of nickel and cobalt according to their XPS data.

<i>Element</i>	<i>Ni At (%)</i>	<i>Co At (%)</i>	<i>R<sub>Ni/Co</sub></i>
<i>NiCo<sub>2</sub>S<sub>4</sub></i>	<b>35.1</b>	<b>64.9</b>	<b>1/1.9</b>
<i>Ni<sub>1.5</sub>Co<sub>1.5</sub>S<sub>4</sub></i>	<b>47.2</b>	<b>52.8</b>	<b>1/1.1</b>
<i>Ni<sub>2</sub>CoS<sub>4</sub></i>	<b>65.4</b>	<b>34.6</b>	<b>1.9/1</b>

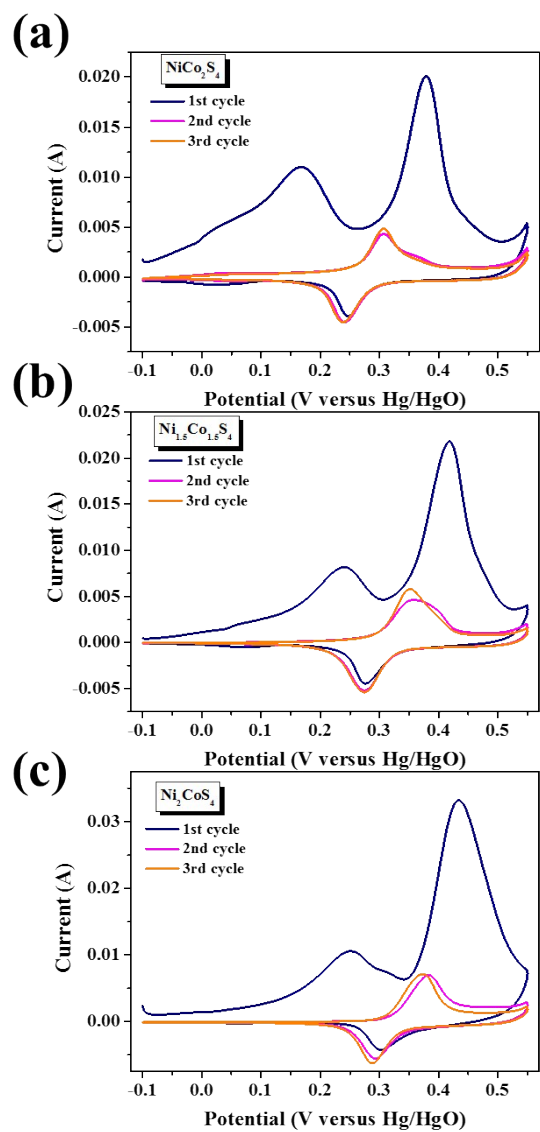


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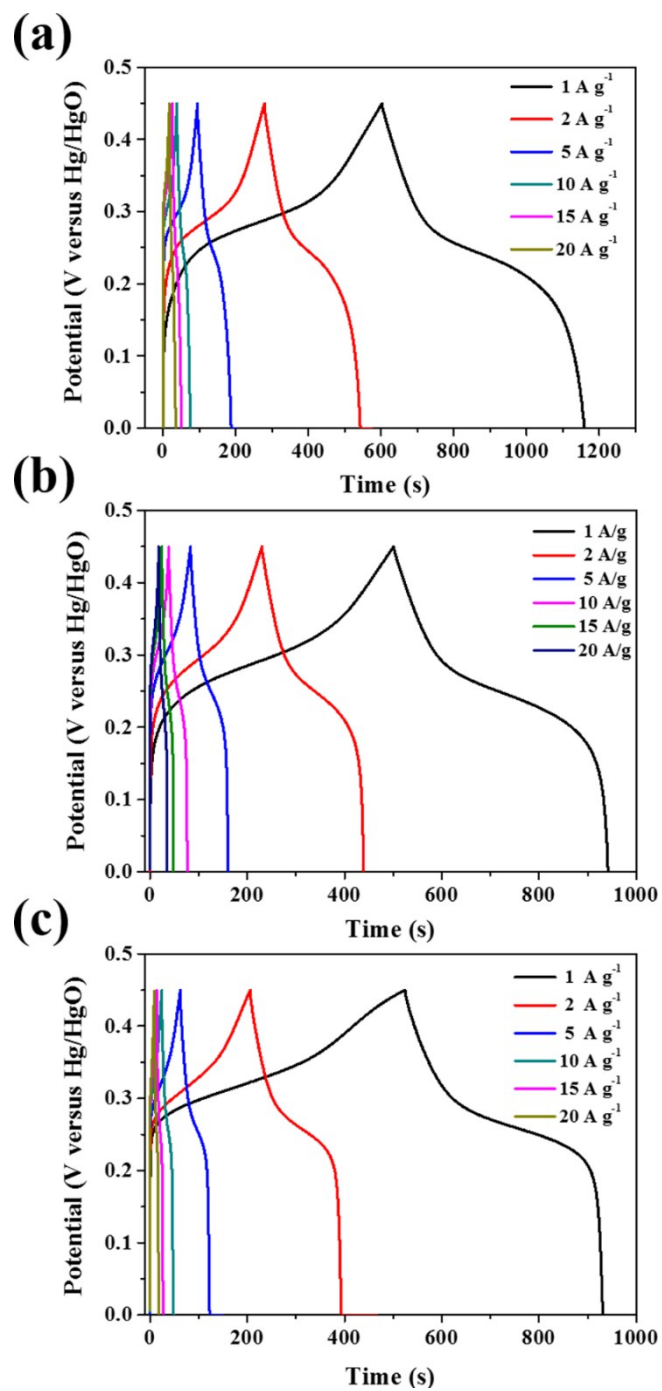
**Figure S5.** XRD patterns of the NiCo-glycerate precursor of NiCo<sub>2</sub>S<sub>4</sub>, Ni<sub>1.5</sub>Co<sub>1.5</sub>S<sub>4</sub>, and Ni<sub>2</sub>CoS<sub>4</sub>.



**Figure S6.** The cyclic voltammety curves with the scan rate ranging from 2 to 100  $\text{mV s}^{-1}$  of (a)  $\text{NiCo}_2\text{S}_4$ , (b)  $\text{Ni}_{1.5}\text{Co}_{1.5}\text{S}_4$ , and (c)  $\text{Ni}_2\text{CoS}_4$ .



**Figure S7.** The first three CV curves at  $0.5 \text{ mV s}^{-1}$  of (a)  $\text{NiCo}_2\text{S}_4$ , (b)  $\text{Ni}_{1.5}\text{Co}_{1.5}\text{S}_4$  and (c)  $\text{Ni}_2\text{CoS}_4$ . Both of the samples are full immersed into 6M KOH solution overnight and tested with a fresh electrode.

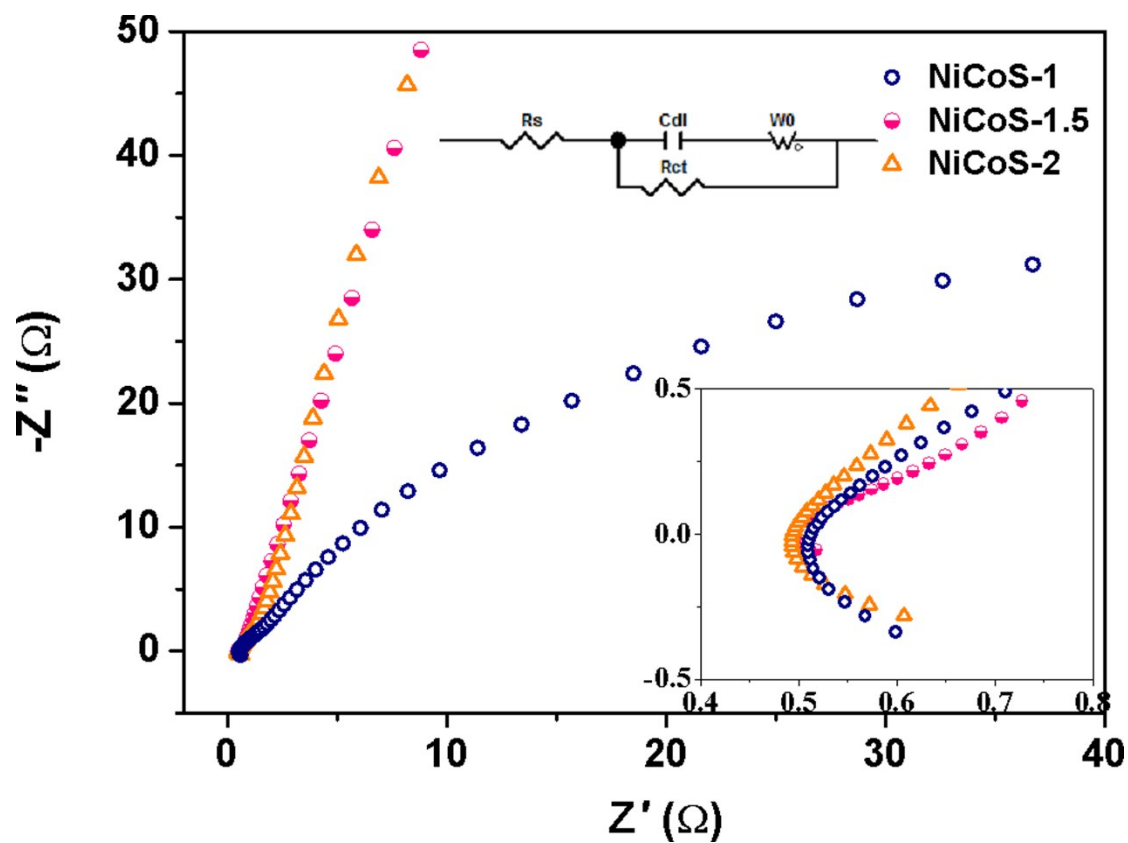


**Figure S8.** The galvanostatic charging/discharging voltage profiles with the current density ranging from 1 to 20 A g<sup>-1</sup> of (a) NiCo<sub>2</sub>S<sub>4</sub>, (b) Ni<sub>1.5</sub>Co<sub>1.5</sub>S<sub>4</sub>, and (c) Ni<sub>2</sub>CoS<sub>4</sub>.

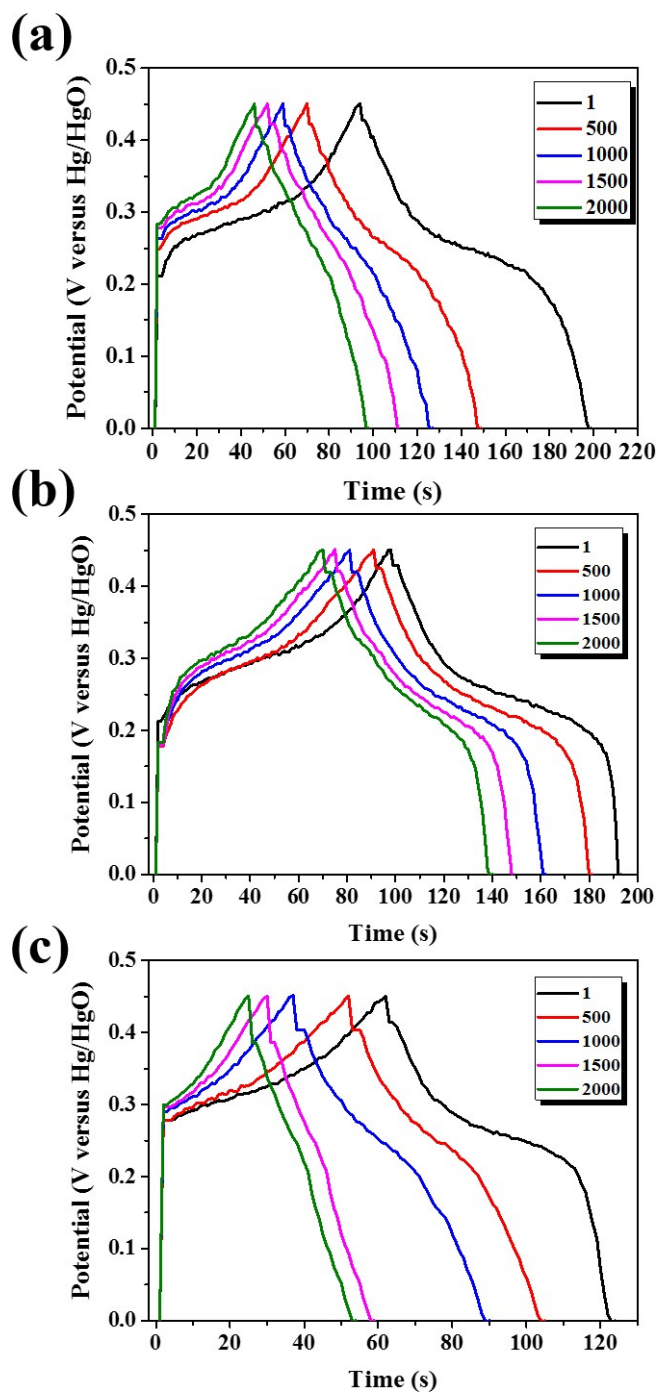
**Table S2.** Rate capacity of Ni–Co sulfide with different micro/nano structure from recent reports in three electrode configuration.

Reference	Micro/nano structure	Capacity	Specific capacity	Capacity retention
This work	Core-shell sphere (Ni <sub>1.5</sub> Co <sub>1.5</sub> S <sub>4</sub> )	122 mAh g <sup>-1</sup> (1 A g <sup>-1</sup> )	98 mAh g <sup>-1</sup> (20 Ag <sup>-1</sup> )	<b>80%</b> from 1 to 20 A g <sup>-1</sup>
1	Mesoporous nanosheet	124 mAh g <sup>-1</sup> (1 A g <sup>-1</sup> )	103 mAh g <sup>-1</sup> (20 Ag <sup>-1</sup> )	<b>83.3%</b> from 1 to 20 A g <sup>-1</sup>
2	Nanosheet	173 mAh g <sup>-1</sup> (1 A g <sup>-1</sup> )	705 mAh g <sup>-1</sup> (20 Ag <sup>-1</sup> )	<b>68%</b> from 1 to 20 A g <sup>-1</sup>
3	Hollow tubular syructure	159 mAh g <sup>-1</sup> (2 A g <sup>-1</sup> )	108 mAh g <sup>-1</sup> (20 Ag <sup>-1</sup> )	<b>68%</b> from 2 to 20 A g <sup>-1</sup>
4	Hollow nanoneedle arrays on carbon fiber paper	208 mAh g <sup>-1</sup> (1 A g <sup>-1</sup> )	129 mAh g <sup>-1</sup> (20 A g <sup>-1</sup> )	<b>62%</b> from 1 to 20 A g <sup>-1</sup>
5	Hollow nanoprism	136 mAh g <sup>-1</sup> (1 A g <sup>-1</sup> )	89 mAh g <sup>-1</sup> (20 Ag <sup>-1</sup> )	<b>65%</b> from 1 to 20 A g <sup>-1</sup>
6	NiCo <sub>2</sub> S <sub>4</sub> /Ni(OH) <sub>2</sub> core- shell heterostructured nanotube arrays on carbon-fabric	450 mAh g <sup>-1</sup> (1 mA cm <sup>-2</sup> )	266 mAh g <sup>-1</sup> (20 mA cm <sup>-2</sup> )	<b>59%</b> from 1 to 20 mA cm <sup>-2</sup>
7	Nanotube array	302 mAh g <sup>-1</sup> (3 A g <sup>-1</sup> )	158 mAh g <sup>-1</sup> (20 Ag <sup>-1</sup> )	<b>52%</b> from 3 to 20 A g <sup>-1</sup>
8	Hollow hexagonal	48 mAh g <sup>-1</sup> (1 A g <sup>-1</sup> )	25 mAh g <sup>-1</sup> (20 Ag <sup>-1</sup> )	<b>53%</b> from 1 to 20 A g <sup>-1</sup>
9	Nanosheet on graphene	129 mAh g <sup>-1</sup> (1 A g <sup>-1</sup> )	76 mAh g <sup>-1</sup> (20 Ag <sup>-1</sup> )	<b>50%</b> from 1 to 20 A g <sup>-1</sup>

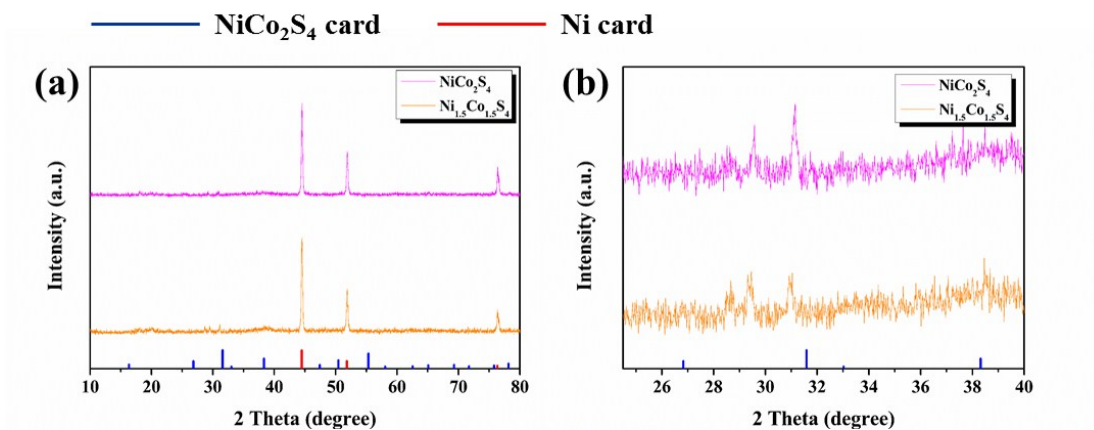




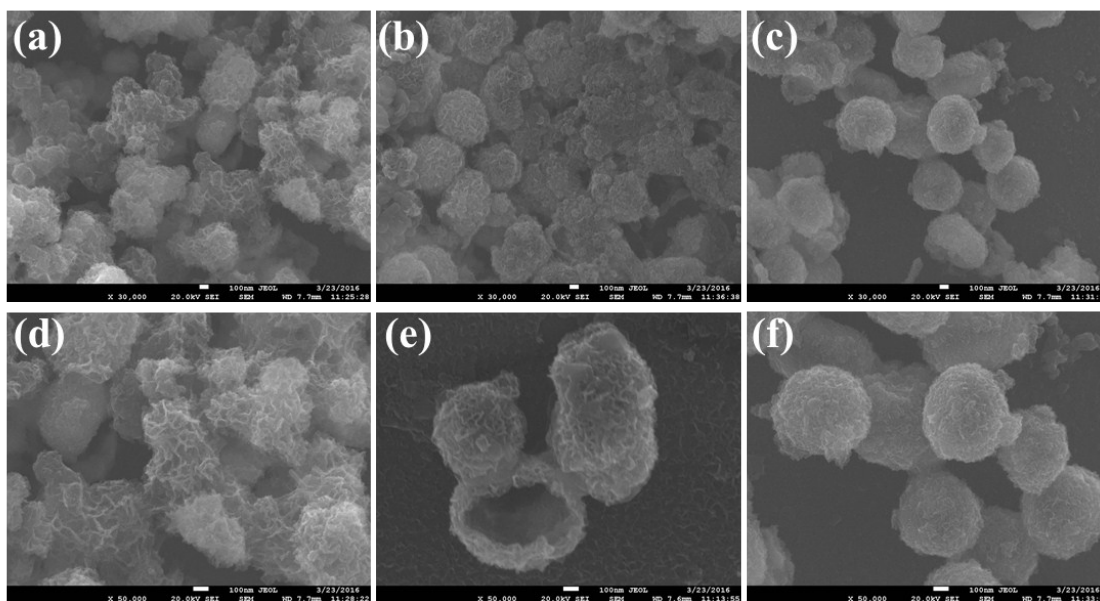
**Figure S9.** The electrochemical impedance spectra of (a)  $\text{NiCo}_2\text{S}_4$ , (b)  $\text{Ni}_{1.5}\text{Co}_{1.5}\text{S}_4$ , and (c)  $\text{Ni}_2\text{CoS}_4$ .



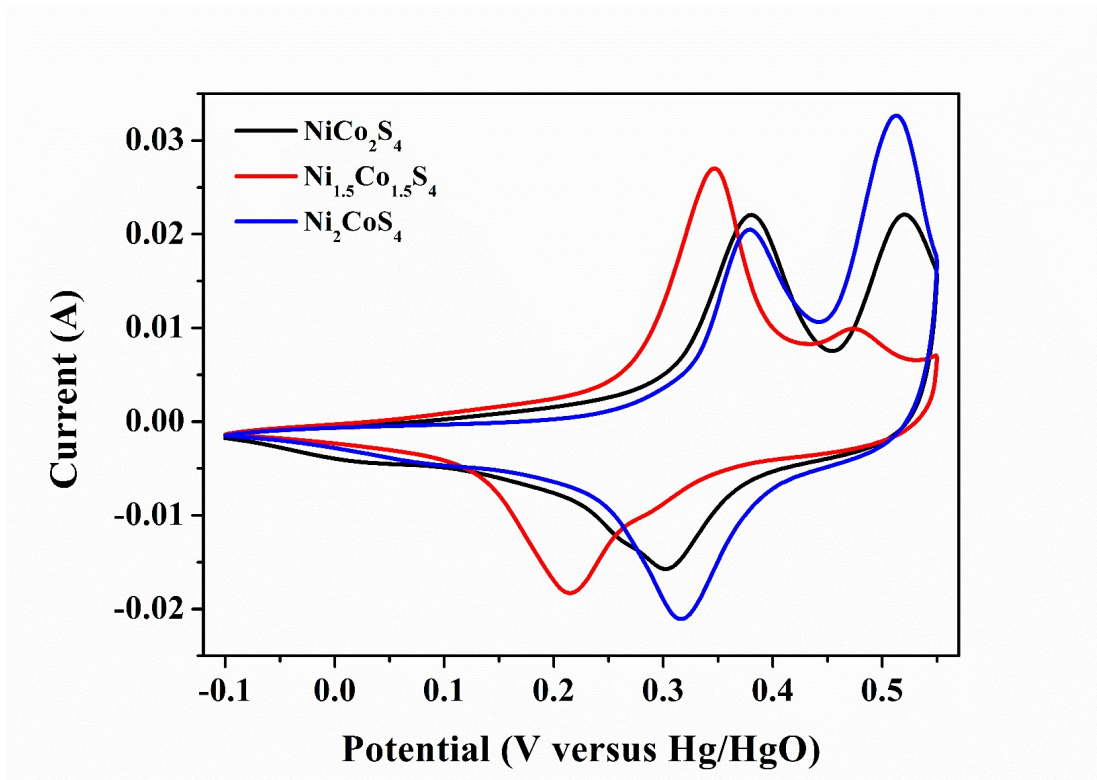
**Figure S10.** The 1<sup>st</sup>, 500<sup>th</sup>, 1000<sup>th</sup>, 1500<sup>th</sup>, 2000<sup>th</sup> charge and discharge cycles of (a)  $\text{NiCo}_2\text{S}_4$ , (b)  $\text{Ni}_{1.5}\text{Co}_{1.5}\text{S}_4$ , and (c)  $\text{Ni}_2\text{CoS}_4$  during 2000 cycles long-term cycling test.



**Figure S11.** XRD pattern of the nickel cobalt sulfides samples with nickel foam were characterized after 2000 cycles test ranging from (a)  $10^\circ$  -  $80^\circ$ , and (b)  $24.5^\circ$  -  $40^\circ$ .



**Figure S12.** FESEM images of the Ni–Co sulfides: (a, d).  $\text{NiCo}_2\text{S}_4$ , (b, e)  $\text{Ni}_{1.5}\text{Co}_{1.5}\text{S}_4$ , and (c, f)  $\text{Ni}_2\text{CoS}_4$  after cycling for 2000 cycles at a current density of  $5 \text{ A g}^{-1}$ , respectively.



**Figure S13.** CV curves the nickel cobalt sulfides measured after 2000 charge and discharge cycles.

## Supplementary Reference

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