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

Supporting Information

Electrochemical Oxidation to Construct Nickel Sulfides/Oxides Heterostructure with Improvement of Capacitance

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1. Experimental Section

1.1 Materials

Nickel sulfate (Fisher Scientific, 99.8%), thiourea (Oakwood Chemical), potassium hydroxide (Fisher Scientific, 88.5%), potassium chloride (Fisher Scientfic 99.7%) and commercial nickel foam (MTI, purity> 99.99%) were all purchased from commercial vendors and used as received. Water was deionized (18 MΩ/cm) with a Barnstead E-Pure system.

1.2 Electrochemical methods

Electrochemical deposition was performed using a Gamry Interface 1000 potentiostat. Nickel foam was cut into a size of 0.5 × 3 cm as the substrate for electrodeposition. Aqueous Ag/AgCl (saturated KCl) reference electrode was purchased from CH Instruments. The reference electrode in aqueous media was calibrated with ferrocenecarboxylic acid ($E_{Fc\text{-}COOH}{}^{+/0}$ = 0.28 V vs Ag/AgCl) in pH 7 phosphate buffer.

1.3 Physical methods

Scanning electron microscopy (SEM) images were collected on a FEI QUANTA FEG 650 (FEI, USA). X-ray diffraction (XRD) patterns were recorded on a Rigaku MinifexII Desktop X-ray diffractometer. Nickel and sulfur analyses were carried out on a Thermo Electron iCAP inductively coupled plasma spectrophotometer. The X-ray photoelectron spectroscopy was conducted using a Kratos Axis Ultra instrument (Chestnut Ridge, NY). The X-ray photoelectron spectra were collected using the monochromatic Al Kα source (1486.7 eV) at a 300 × 700 μm spot size. Low resolution survey and high resolution region scans at the binding energy of energy of interest were collected for each sample. XPS data were analyzed using the CASA XPS software, and energy corrections on high resolution scans were calibrated by referencing the C 1s peak of adventitious carbon to 284.5 eV.

1.4 Preparation of Ni_3S_2/NF

Before electrodeposition, the nickel foam was sonicated in ethanol for 10 min, washed with deionized water and dried under nitrogen. 0.25 cm^2 of the nickel foam was exposed to the electrolyte (0.5 M thiourea and 5 mM $NiSO_4{\cdot}6H_2O$ in water). A Ag/AgCl electrode as the reference electrode, a platinum wire as the counter electrode together with the nickel foam as the working electrode constituted a three electrodes system. Electrolyte was deaearated with nitrogen bubbling for more than 20 min before deposition and kept under a nitrogen atmosphere throughout the deposition process. The deposition was carried out with cyclic consecutive linear scans between -1.2 and 0.1 V vs. Ag/AgCl at a scan rate of 5 mV/s under stirring at 500 rpm. After deposition, the working electrode (Ni_3S_2/NF) was rinsed with water and ethanol gently and dried under vacuum overnight at room temperature. Ni_3S_2/NF was annealed at 300 ℃ for 2 hours under argon to enhance the physical attachment of electrodeposited Ni_3S_2 on the nickel foam. The Ni_3S_2/NF was stored under vacuum at room temperature before electrochemical experiments.

1.5 Preparation of ECO-Ni_3S_2/NF

The in situ electrochemical oxidation was conducted in 1.0 M deaerated KOH by a continuous potential cycling at a scan rate of 15 mV/s between 0.6 and 1.2 V vs. Ag/AgCl for ~10 cycles, reaching stable cyclic voltammograms.

1.6 Electrochemical Measurement

The electrochemical properties of the prepared samples were investigated with a CHI 760E electrochemical workstation in fresh 1.0 M KOH using cyclic voltammetry and galvanostatic charge-discharge methods in a conventional three-electrode cell between 0 and 0.55 V, respectively, at various scan rates and current densities. The resulting materials were directly used as working electrodes. The Ag/AgCl and Pt wire were used as the reference and counter electrode, respectively.

2. Figures

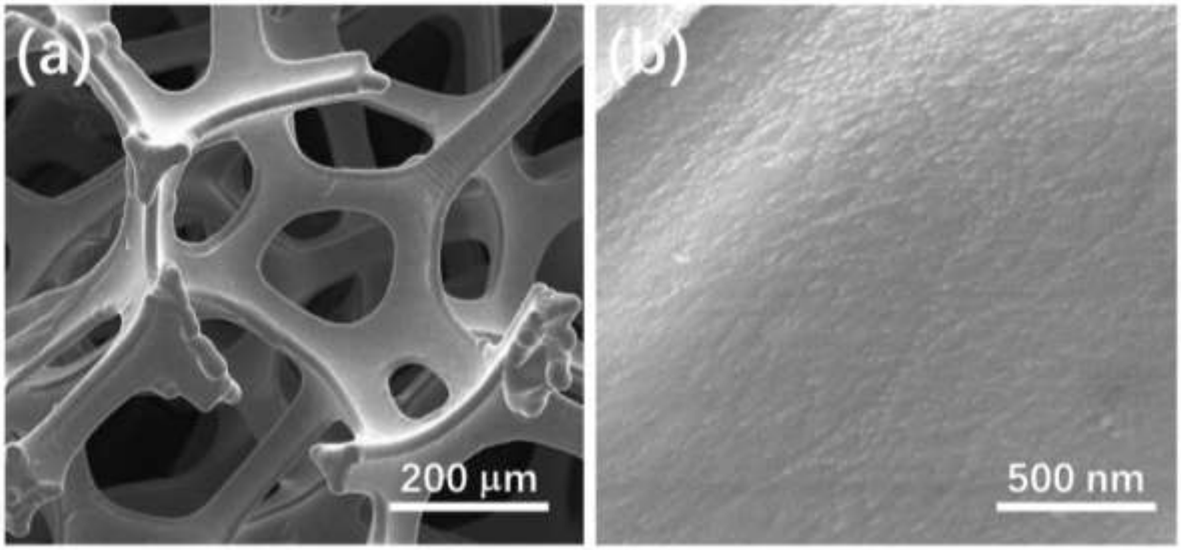

Figure S1. SEM images of a fresh nickel foam.

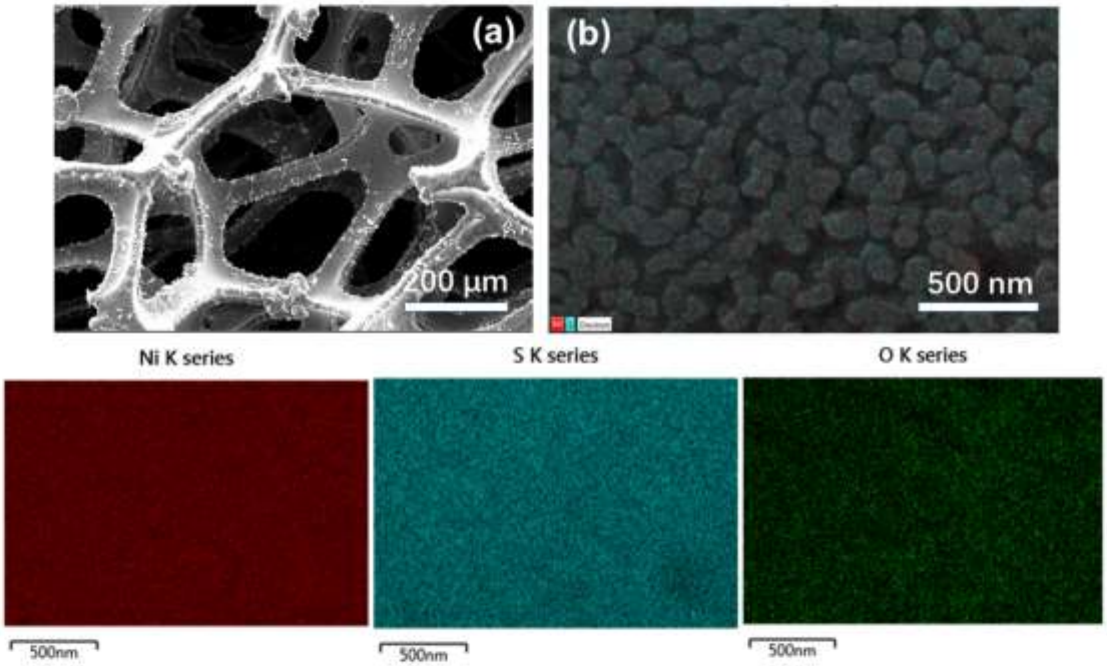

Figure S2. (a) SEM image and (b) elemental mapping images of Ni, S, and O in an as-prepared Ni_3S_2/NF.

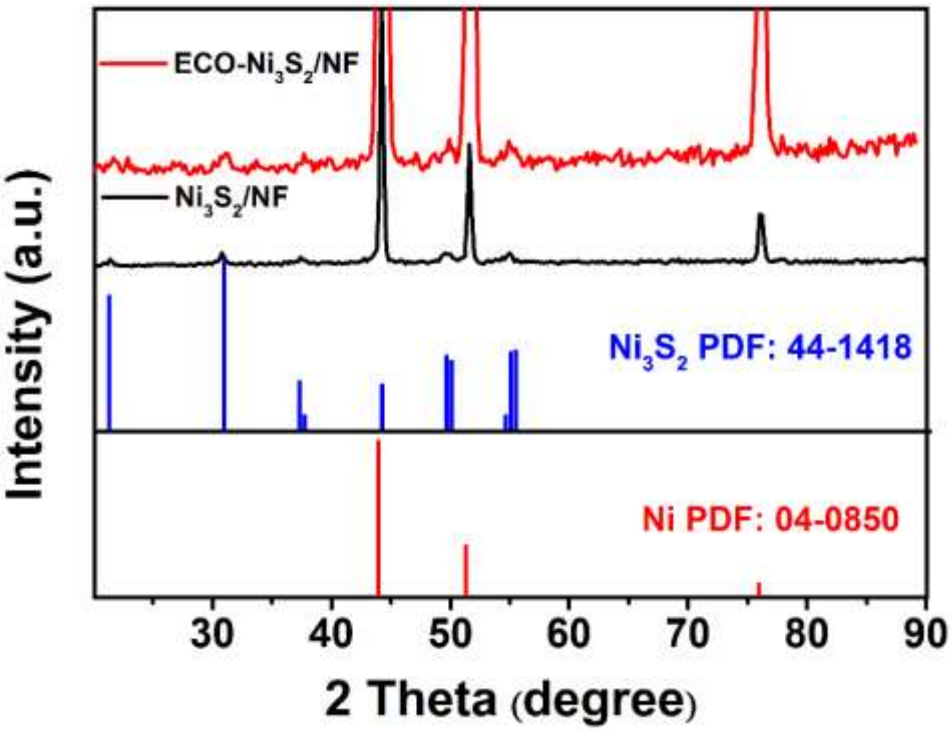

Figure S3. XRD patterns of Ni_3S_2/NF and ECO-Ni_3S_2/NF with the standard patterns of Ni_3S_2 and Ni.

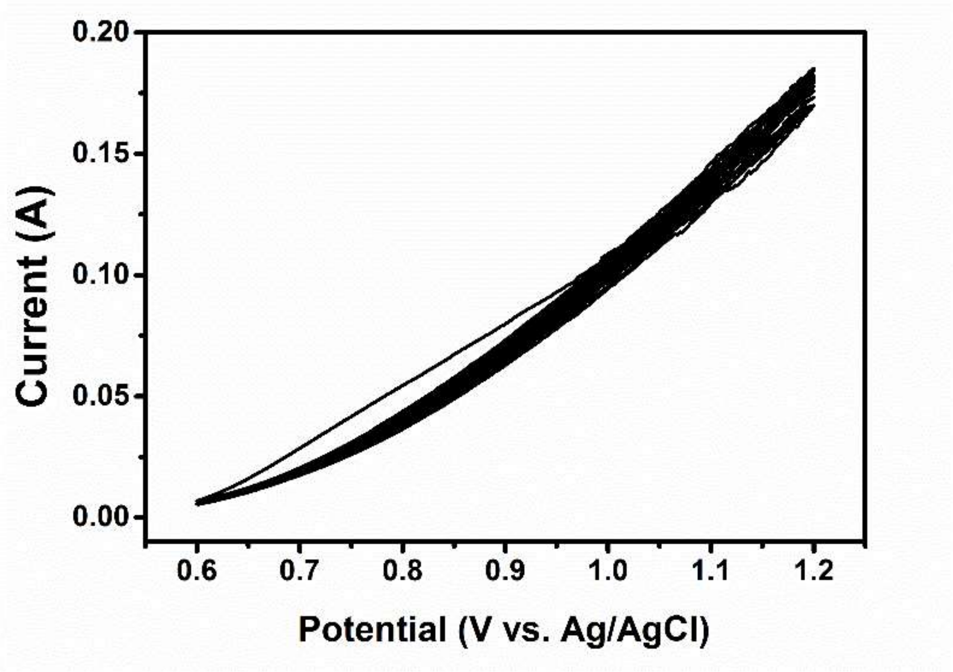

Figure S4. Cyclic voltammograms of electrochemical oxidation for the preparation of ECO-Ni_3S_2/NF at a scan rate of 15 mV/s in 1.0 M KOH.

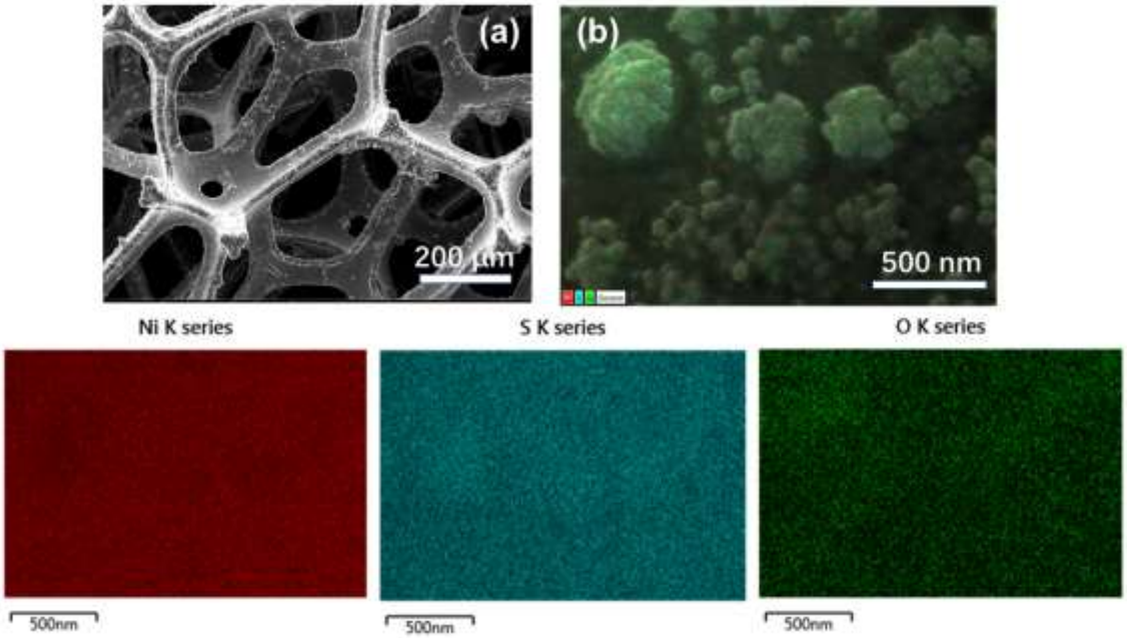

Figure S5. (a) SEM image and (b) elemental mapping images of Ni, S, and O in ECO-Ni_3S_2/NF.

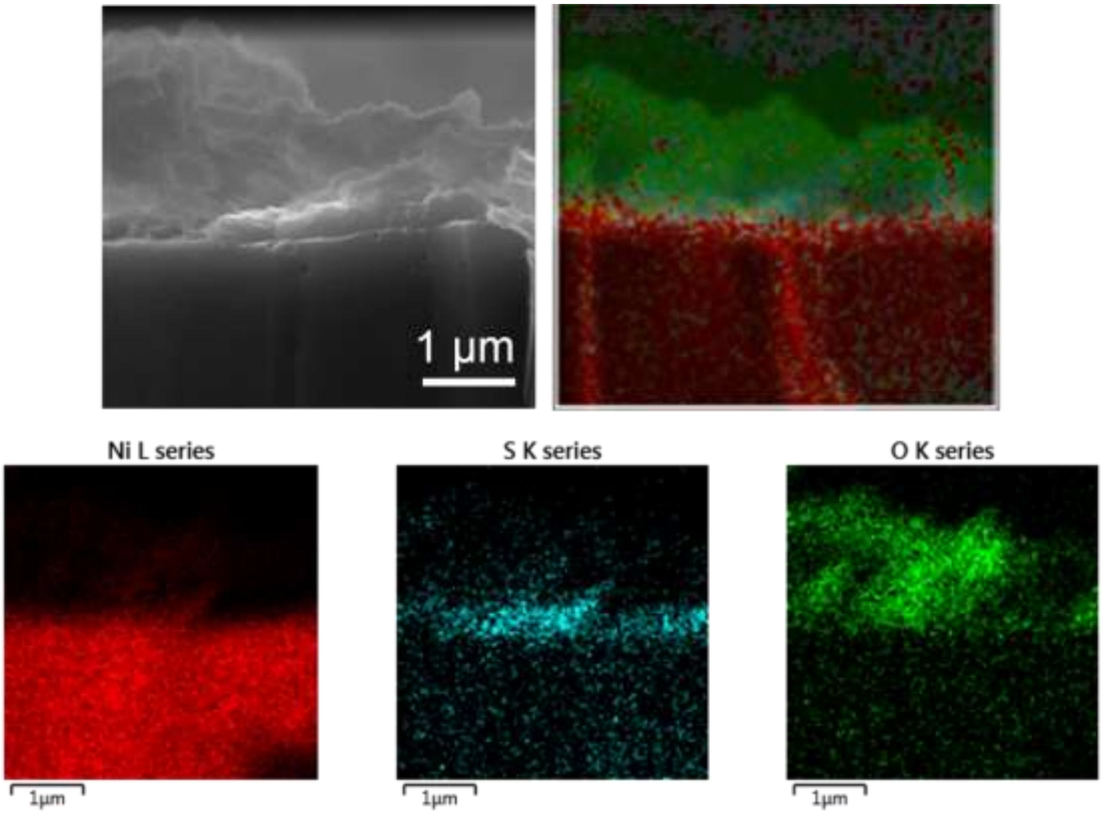

Figure S6. Cross-section elemental mapping images of Ni, S, and O in ECO-Ni_3S_2/NF.

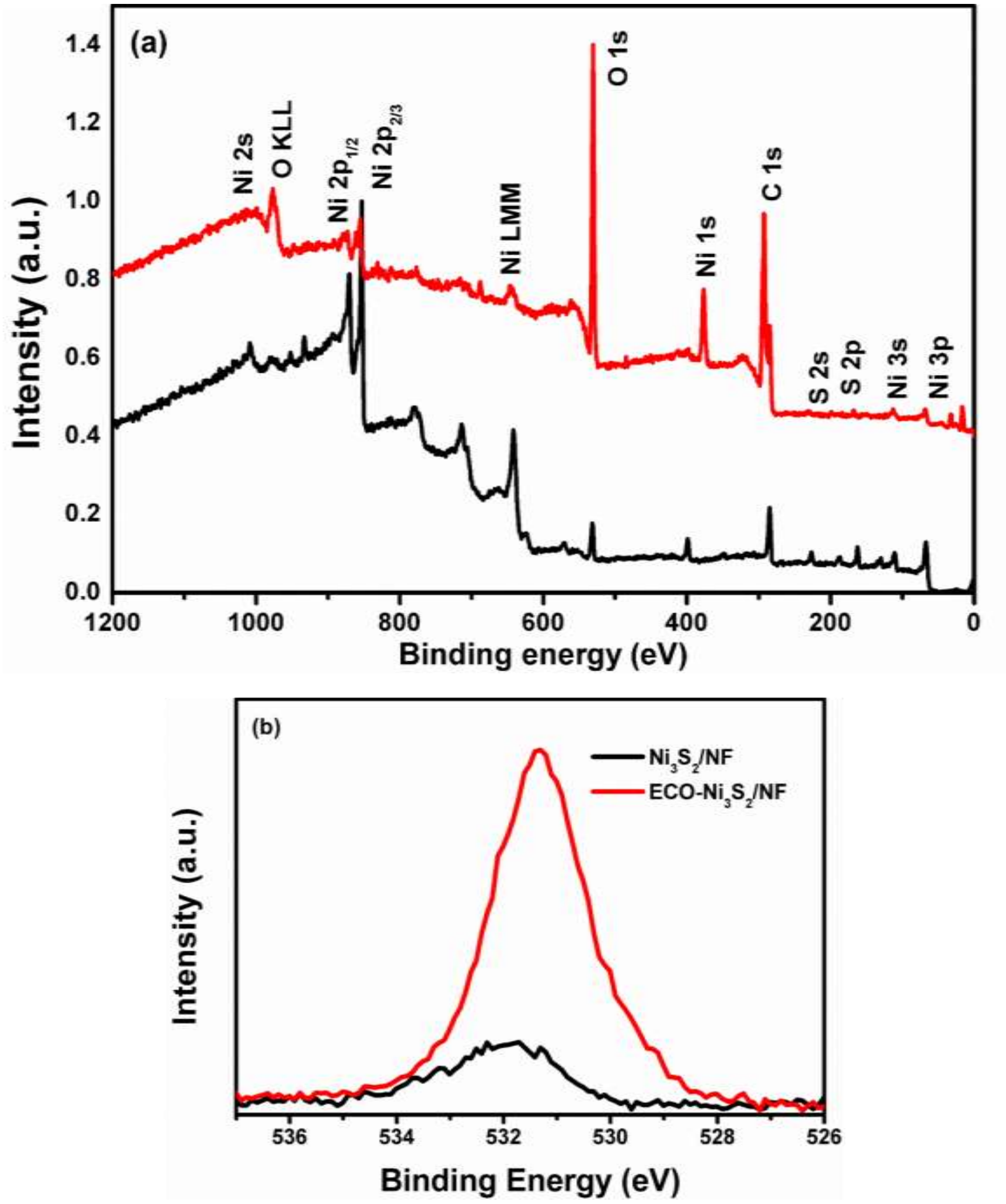

Figure S7. (a) XPS survey spectra and (b) the corresponding high-resolution O 1s XPS spectra of Ni_3S_2/NF (black) and ECO-Ni_3S_2/NF (red)

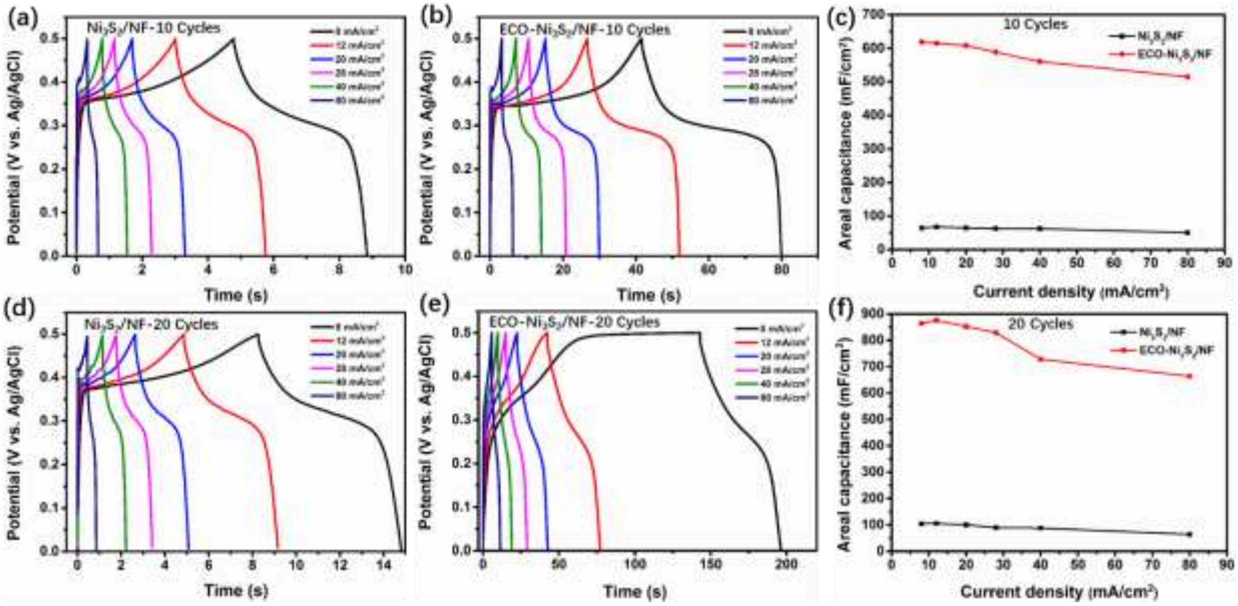

Figure S8. Galvanostatic charge-discharge curves of (a) Ni_3S_2/NF-10, (b) ECO-Ni_3S_2/NF-10, (d) Ni_3S_2/NF-20, (e) ECO-Ni_3S_2/NF-20, and (c, f) areal capacitance comparison curves of Ni_3S_2/NF-x before and after ECO in 1.0 M KOH.

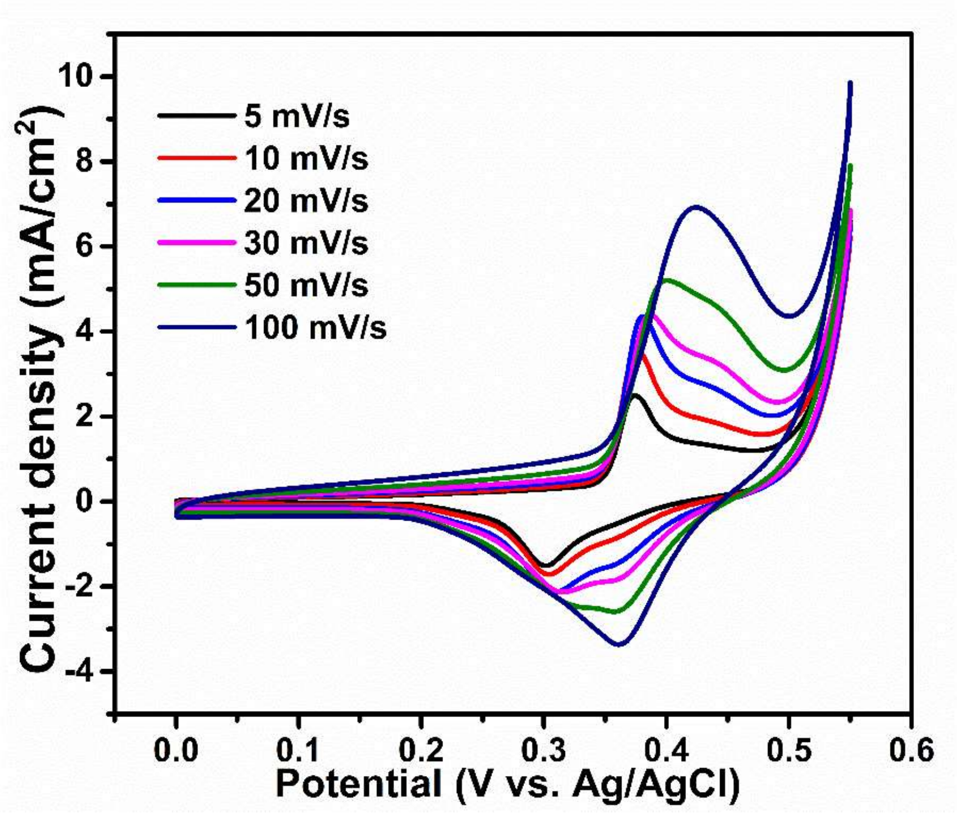

Figure S9. Cyclic voltammograms of Ni_3S_2/NF at different scan rates in 1.0 M KOH.

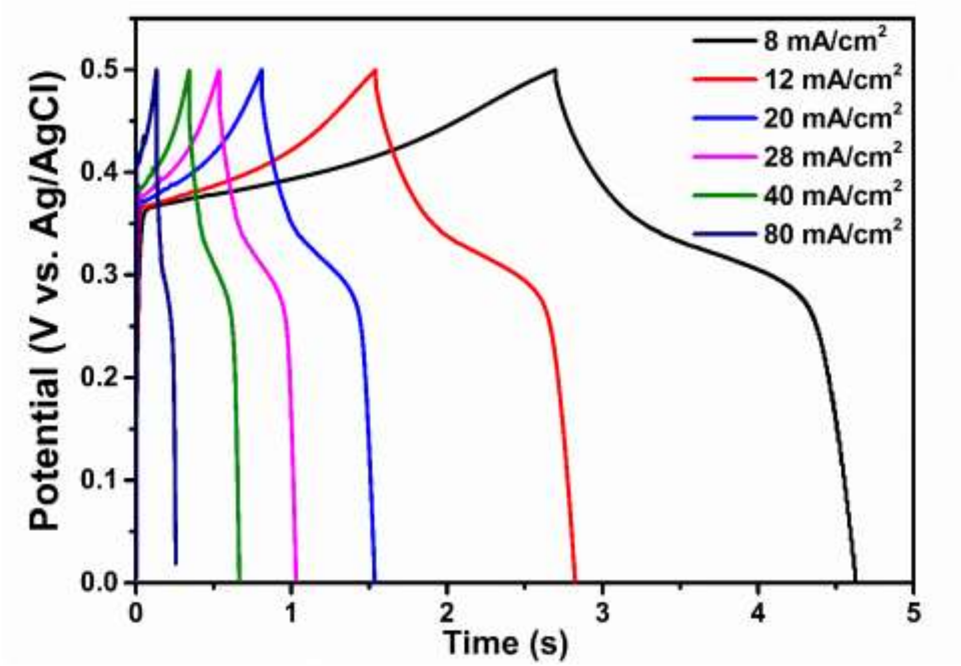

Figure S10. Galvanostatic charge-discharge curves of Ni_3S_2/NF at various current densities in 1.0 M KOH.

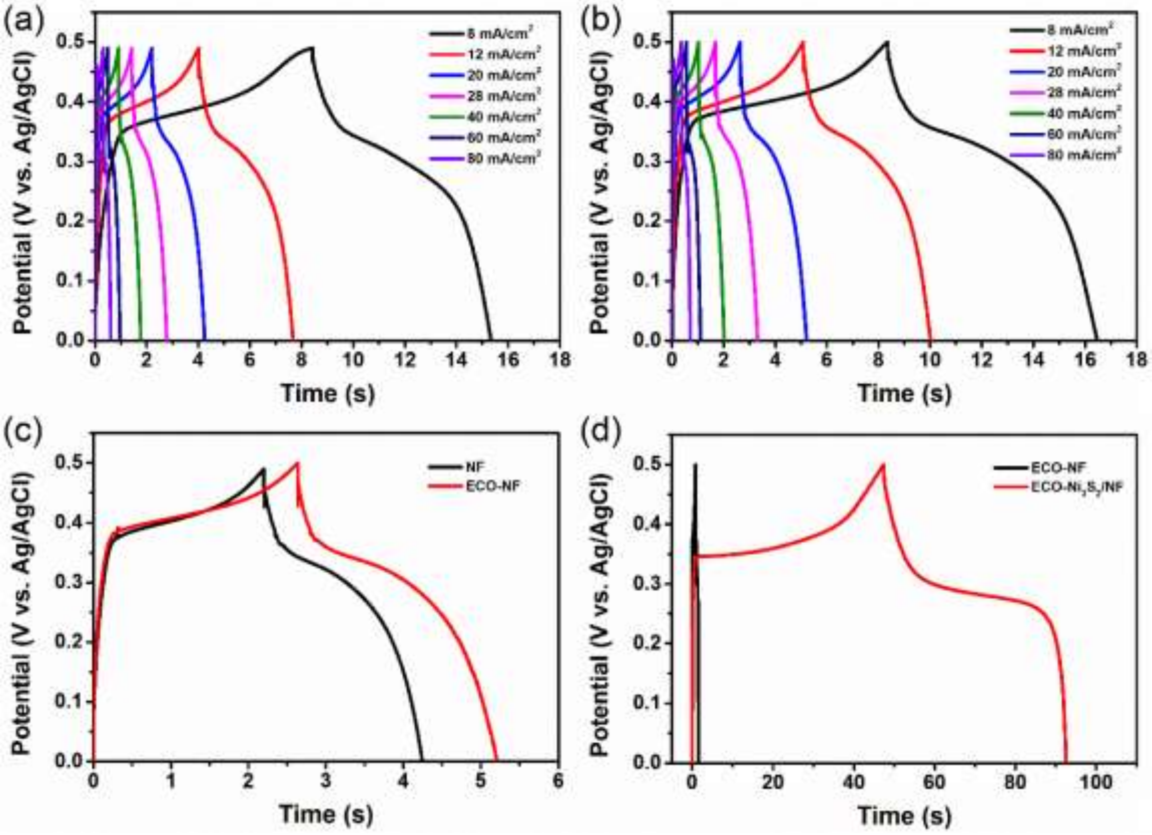

Figure S11. Galvanostatic charge-discharge curves of (a) NF at different current densities, (b) ECO-NF at different current densities, (c) NF and ECO-NF at a current density of 20 mA/cm^2, (d) ECO-NF and ECO-Ni$_3$S$_2$/NF at a current density of 20 mA/cm^2 in 1.0 M KOH.

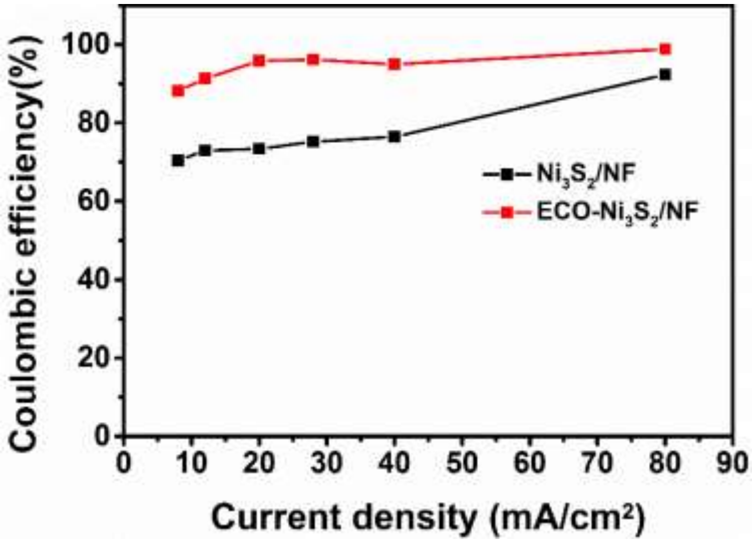

Figure S12. Coulombic efficiencies of Ni$_3$S$_2$/NF and ECO-Ni$_3$S$_2$/NF at different current densities.

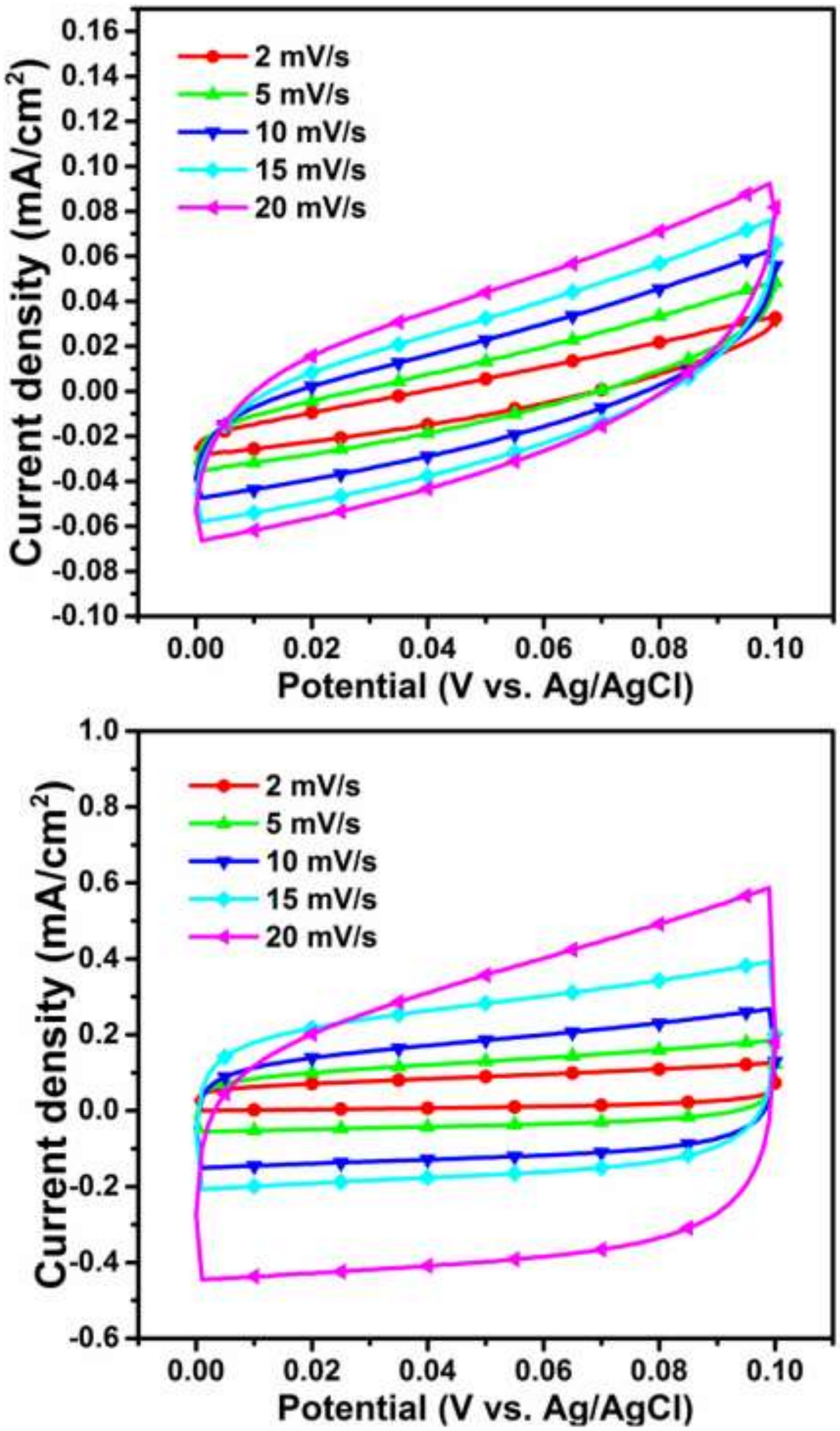

Figure S13. Cyclic voltammograms of Ni_3S_2/NF (top) and ECO-Ni_3S_2/NF (bottom) in a non-Faradaic region (0 – 0.1 V vs Ag/AgCl) at different scan rates in 1.0 M KOH.

3. Tables

Table S1. Capacitance comparison between as-prepared Ni_3S_2/NF and ECO-Ni_3S_2/NF at different current densities.

Current density (mA/cm^2)	**Capacitance of as-prepared Ni_3S_2/NF (mF/cm^2)**	**Capacitance of ECO-Ni_3S_2/NF (mF/cm^2)**	**Enhancement**
8	31.4	2035.2	64.8
12	31.2	1996.1	64.0
20	29.6	1828.5	61.8
28	28.6	1744.4	61.0
40	26.4	1634.7	61.9
80	20.8	1216.1	58.5

Table S2. Comparison of ECO-Ni_3S_2/NF with other reported supercapacitors.

Electrodes	**Electrolyte**	**Current density (mA/cm^2)**	**Capacitance (mF/cm^2)**	**ECSA (cm^2)[a]**	**References**
Ni_3S_2/NF	**1 M KOH**	**12**	**31**	**6.5**	**This work**
ECO-Ni_3S_2/NF	**1 M KOH**	**12**	**1996**	**46.8**	**This work**
Ni_3S_2/Carbon Nanotube	2 M KOH	9.6	544	N/A	*ACS Appl. Mater. Interfaces*, 2013, **5**, 12168
NiS/NiSe	2 M KOH	7.5	720	N/A	*Chem. Mater.* 2014, **26**, 3418
Ni_3S_2/ Carbon Cloth	6 M KOH	4	1230	N/A	*J. Mater. Chem. A*, 2016, **4** , 1319
Ni_3S_2 @MoS_2/Carbon Cloth	6 M KOH	4	1500	N/A	*J. Mater. Chem. A*, 2016, **4** , 1319
Ni_3S_2/oxidized NF	3 M KOH	10	2370	N/A	*J. Mater. Chem. A*, DOI:10.1039/C6TA01547F
Ni@NiO	6.0 M KOH	8	2000	N/A	*NPG Asia Mater.* **2014**, 6, 129.
NiS	2 M KOH	2	*718*	N/A	*Mater. Lett.* 2014, **124**,133.
NiO/NF	6.0 M KOH	15	600	N/A	*Nano Lett.* **2014**, *14*, 731.
WO_{3-x}/MoO_{3-x}	0.5 M Na_2SO_4	5	303	N/A	*Adv. Energy Mater.* ***2012***, *2, 1328.*
$NiCo_2O_4$	PVA-KOH	1	*161*	N/A	*J. Mater. Chem. A* **2013**, *1*, 2468.

[a] ECSA was calculated according to the reported method (McCrory, C. C. L.; Jung, S.; Peters, J. C.; Jaramillo, T. F. *J. Am. Chem. Soc.* **2013**, *135*, 16977-16987). 40 $\mu F/cm^2$ was used as the double layer capacitance of a flat electrode.