Electronic Supplementary Material (ESI) for Chemical Science.

Edge Overgrowth of Spiral Bimetallic Hydroxides Ultrathin-Nanosheets for Water Oxidation

*Bing Ni, and Xun Wang**
Department of Chemistry, Tsinghua University, Beijing, 100084, China
E-mail: wangxun@mail.tsinghua.edu.cn

Experiment Section

Synthesis of spiral ultrathin-nanosheets with overgrew edge (SUNOE): For NiFe SUNOE, 0.114g $NiCl_24H_2O$ and 0.060g $(NH_4)_2Fe(SO_4)_26H_2O$ were weighed and transferred into a 40mL- polytetrafluoroethene autoclave. Then 8 mL ethanol were added to dissolve the salts by sonication. Though the sulfate seemed not fully dissolved, 2mL oleylamine (OAm) was injected into the autoclave, some precipitate appeared immediately. The solution became transparent again as 30mL hexane was adding into the system. For NiCo SUNOE, 0.024g $NiCl_24H_2O$ and 0.014g $CoSO_47H_2O$ were added into an 11mL- polytetrafluoroethene autoclave. Then 2mL ethanol was injected to dissolve salts. While the $CoSO_47H_2O$ was not fully dissolved, the solution showed a blue color. The color went darker when 0.5mL OAm was added. Then 8mL hexane was transferred into the autoclave. For CoFe SUNOE, 0.014g $CoCl_24H_2O$ and 0.009g $(NH_4)_2Fe(SO_4)_26H_2O$ were added into an 11mL- polytetrafluoroethene autoclave. Then 0.5mL octylamine and 8mL hexane were added in sequence. The sulfates could not fully dissolve in ethanol, but they didn't affect the formation of SUNOE with both cations, since the amine would help to further dissolve the salts. After all these steps were done, seal the autoclave and put it into oven set temperature at 140°C and 8 hours to react. After cooling down, the products were washed 3 times by using ethanol and centrifugating at 10000 rpm for 5 minutes. Then samples were dispersed in 10mL cyclohexane for NiFe SUNOE and 2mL cyclohexane for NiCo and CoFe SUNOE. Dilute the solution and drop a drop on TEM grid for morphology test. All the chemicals except OAm were purchased from Sinopharm Chemical Reagent Co., Ltd, OAm was obtained from Acros.

The ratio of salts, amine and solvent are optimized to get pure SUNOE. Slightly changing them could also result in similar SUNOE, but less purities. Substituting the chloride salts with nitrate salts would also synthesize SUNOE, but less purities, while changing the amount of sulfate would dramatically change the morphology, this means it's not the chloride but sulfate are vital to form SUNOE.

Sample preparation for oxygen evolution reaction (OER) test: In a typical sample preparation, after washing and dispersing in certain amount of solvent as decribled before, 1mL cyclohexane solution was transferred into PE tube, then 0.05mL nafion was injected, and sonicate for 30mins. The samples with carbon were prepared by adding another 1mg Vulcan XC-72 carbon before sonicate. The mass load was dertermined by inductively coupled plasma optical emission spectrometer. Then 6μL solution were dropped on the glassy carbon electrode with a surface area of 0.196cm^2.

Sample preparing method could influence the performance of catalyst. When drying the as-prepared products first and then re-dispersing in solvent (no matter in polar or nonpolar solvent) to prepare sample for OER test, the performances were not as good as directly using solution right after products were washed. This could be ascribed to difficulty in re-dispersion. Also, introducing carbon into the sample would help to reach high activities.

The OER performance were test in KOH (1mol/L) and conducted with Princeton P4000 electrochemical workstation using a three electrode cell where Pt foil served as the counter electrode. Cyclic voltammetry (CV) were used to stabilize the materials. After the CV curves were stable, set the rotation speed of electrode at 1600 rpm and measure the linear sweep voltammetry (LSV) at scan rate of 10mV/s. After LSV test, tafel plots were got by the tafel test function of Princeton P4000. The chronopotential test were used to study the stabilities of products, set the current at 1.96mA or 3.92mA, correspond to 10mA/cm^2 and 20mA/cm^2, and test for 2 hours.

Super capacitor test: For super capacitor test, products were dried first, the 16mg products, 2mg acetylene black and 2mg polyvinylidene fluoride (PVDF) were mixed. After dropping 2 drops of N-Methyl pyrrolidone (NMP) and grinding, the black product were smeared on 1*1 cm foam nickel which had already weighed, and pressed under 10MPa for about 10 seconds. The mass loading is around 2mg. Electrochemical measurements were conducted in an aqueous KOH electrolyte (1mol/L) using a three electrode cell with Pt foil as the counter electrode. The specific capacitances were calculated based on equation (1):

$$C=\frac{It}{\Delta E} \quad (1)$$

Where C, I, t and ΔE are the specific capacitance (F/g) of the electroactive materirals, discharging current density (A/g), the discharging time (s) and the discharging potential range (V). The charge-discharge efficiencies were calculated based on equation (2):

$$\eta=\frac{t_{\text{charge}}}{t_{\text{discharge}}}\times 100\% \quad (2)$$

Where η,t_{charge} and $t_{\text{discharge}}$ are charge-discharge efficiency, charging time (s) and discharging time [1](s).

The charge-discharge windows are narrow since higher voltage would cause the evolution of oxygen. The percentages of oxidized cation were calculated based on equation (3):

$$p=\frac{C\times\Delta E}{F\times n} \quad (3)$$

Where p, C, ΔE, F and n are percentage of oxidized cations, specific capacitance (F/g), discharging potential range (V), Faraday constant (96480 C/mol) and amount of electrical active element, respectively.

Sample Characterization:

X-ray diffraction (XRD):

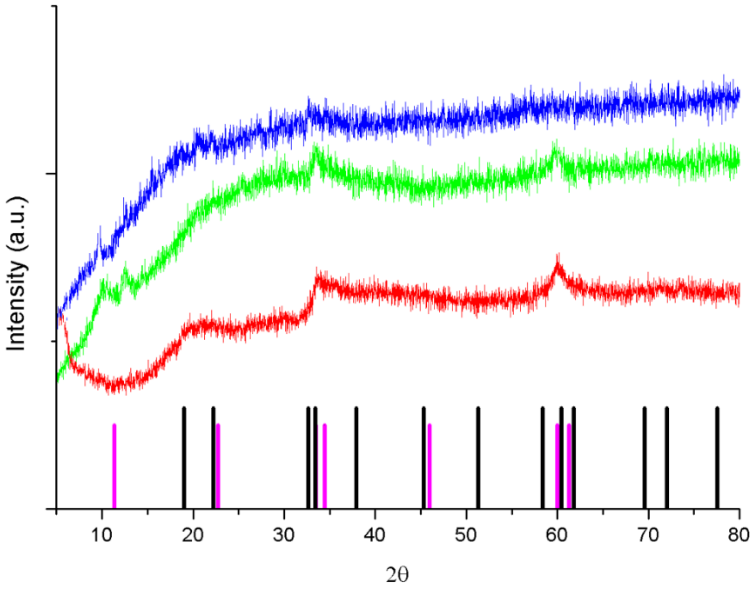

Figure S1: XRD data of different products, red line for NiFe SUNOE, blue line for CoFe SUNOE and green line for CoNi SUNOE. The pink vertical line is peak for α-$Ni(OH)_2$ (JCDPS: 38715), black line is α-$Co(OH)_2$ (JCPDS: 020925). The reaction happened here could be dehydration of precursors, thus form hydroxides or oxides, by comparing the broaden peaks, it would be more reasonable to infer the SUNOE are bimetallic hydroxides. While in some other researches, the XRD data for ultrathin hydroxides adopt similar peaks[2, 3], this could further support our conclusion for a layered alpha phase structure.

Transform Infrared Spectrometer (FT-IR Spectrometer):

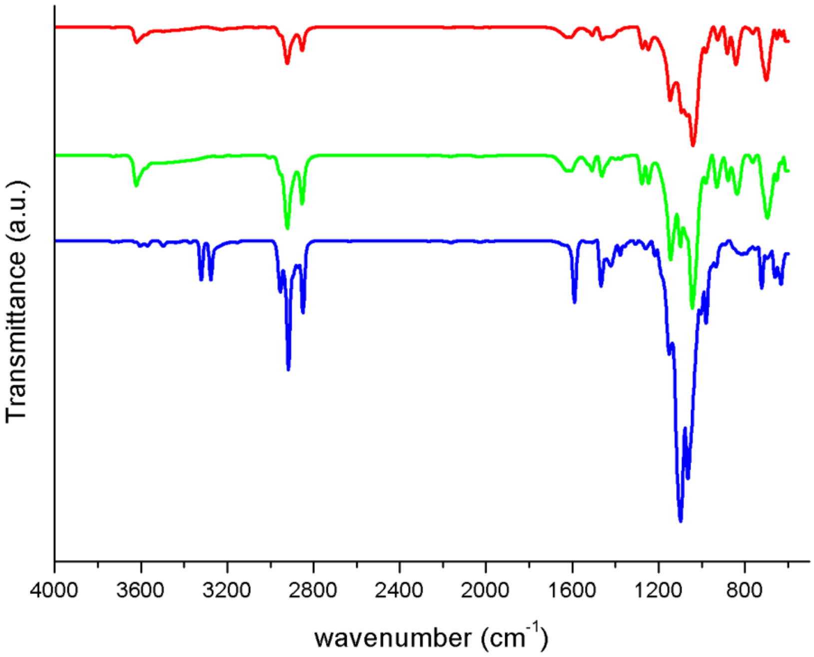

Figure S2: FT-IR data, red line for NiFe SUNOE, green line for CoNi SUNOE, blue line for CoFe SUNOE. The strong absorption at 1040-1210 cm^{-1} could owe to SO_4^{2-}. The peaks (2931 cm^{-1} and 2848 cm^{-1}) correspond to the CH2 and CH3 stretching vibrations and the peaks at 1510 and 1465 cm^{-1} correspond to the N−H mode, suggesting that amine molecules adsorb on SUNOE because of the existance in the synthesis.

X-ray photoelectron spectroscopy (XPS):

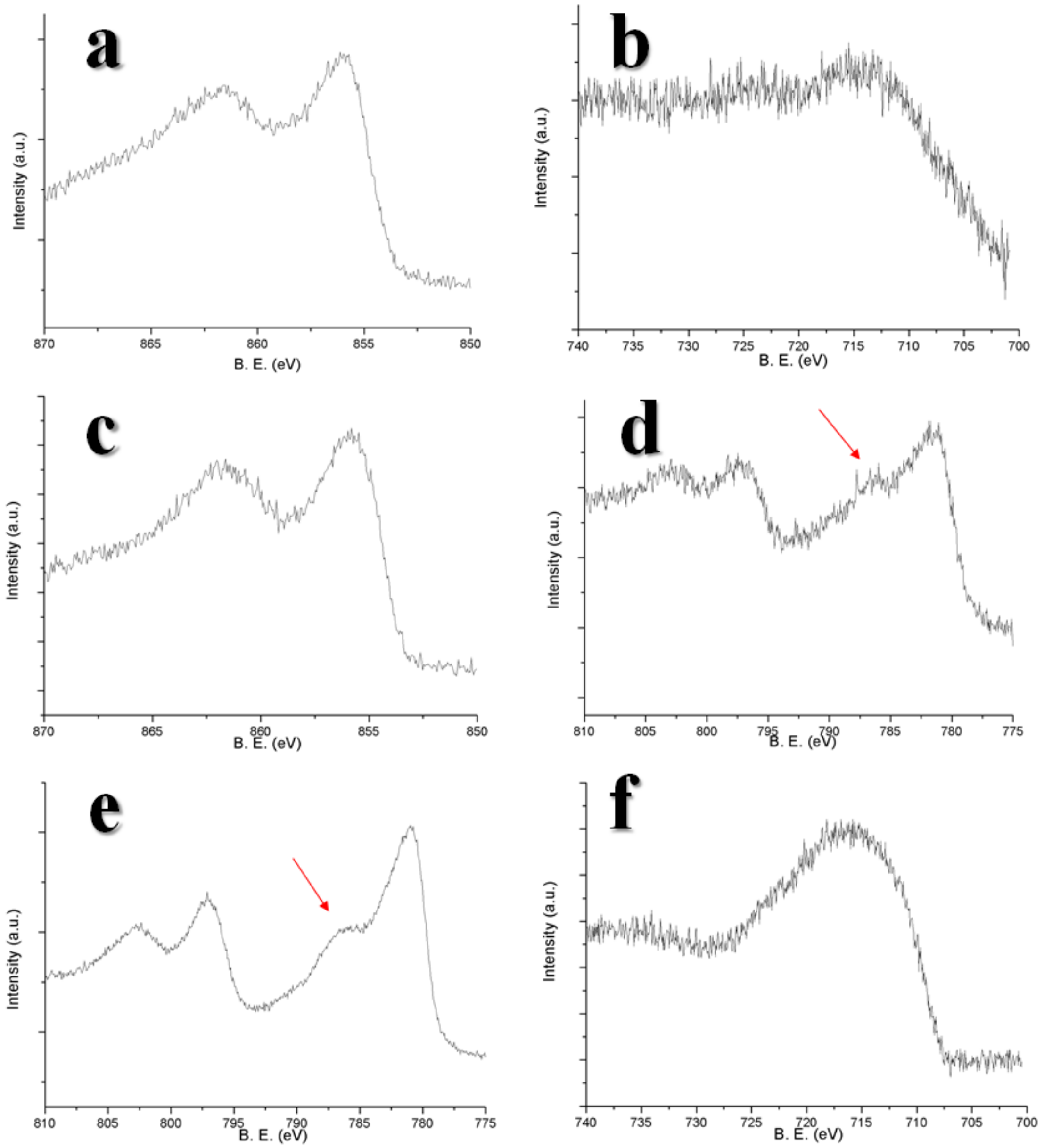

Figure S3: XPS data. (a,b) are results of NiFe SUNOE, (a) for Ni and (b) for Fe; (c,d) are results for CoNi SUNOE, (c) for Ni and (d)for Co; (e,f) are results for CoFe SUNOE, (e) for Co and (f) for Fe. There is almost no need to further do peak differential. The Ni in (a) and (c) are almost same with the Ni(OH)$_2$[4], the red arrow in (d) and (e) indicate +2 valence of Co[5]. For Fe, the peaks are broaden and hard to do peak differential. However in such reductive reaction environment, it would be more reasonable to infer valence of Fe stays same in reaction, which is +2.

Inductively Coupled Plasma Optical Emission Spectrometer (ICP-OES)

Considering XRD, FT-IR and XPS data, the products are hybrid hydroxides, the compostion of metals and sulfer in each sample were determined via ICP-OES. Then total compositon of each product was achieved by calculating the balance of charge.

Table S1: ICP-OES data for these three SUNOE

	NiFe SUNOE		CoNi SUNOE		CoFe SUNOE	
	Weight %	Atom Ratio	Weight %	Atom Ratio	Weight %	Atom Ratio
Co			7.347	0.1247	18.68	0.3169
Fe	4.974	0.08906			1.956	0.03503
Ni	20.44	0.3483	20.68	0.3523		
S	6.919	0.2157	6.035	0.1882	9.004	0.2808
	$Ni_{0.348}Fe_{0.089}(OH)_{0.442}(SO_4)_{0.216}$		$Ni_{0.352}Co_{0.125}(OH)_{0.578}(SO_4)_{0.188}$		$Co_{0.317}Fe_{0.035}(OH)_{0.142}(SO_4)_{0.281}$	

TEM image at Lower Magnification:

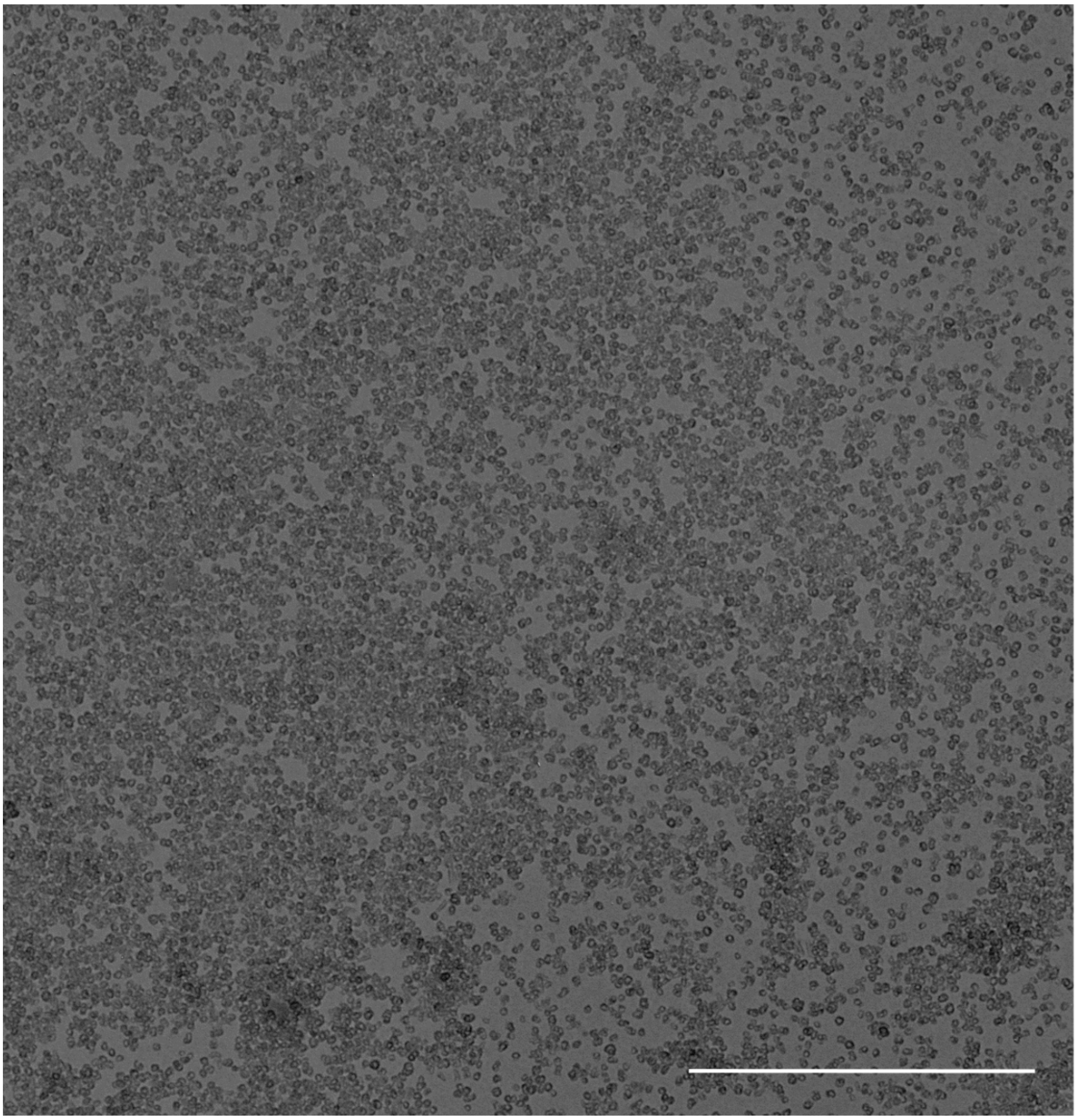

Figure S4: TEM images at lower magnification shows high purity of NiFe SUNOE. Scale bar: 2μm.

Energy Dispersive Spectroscopy Line Scan:

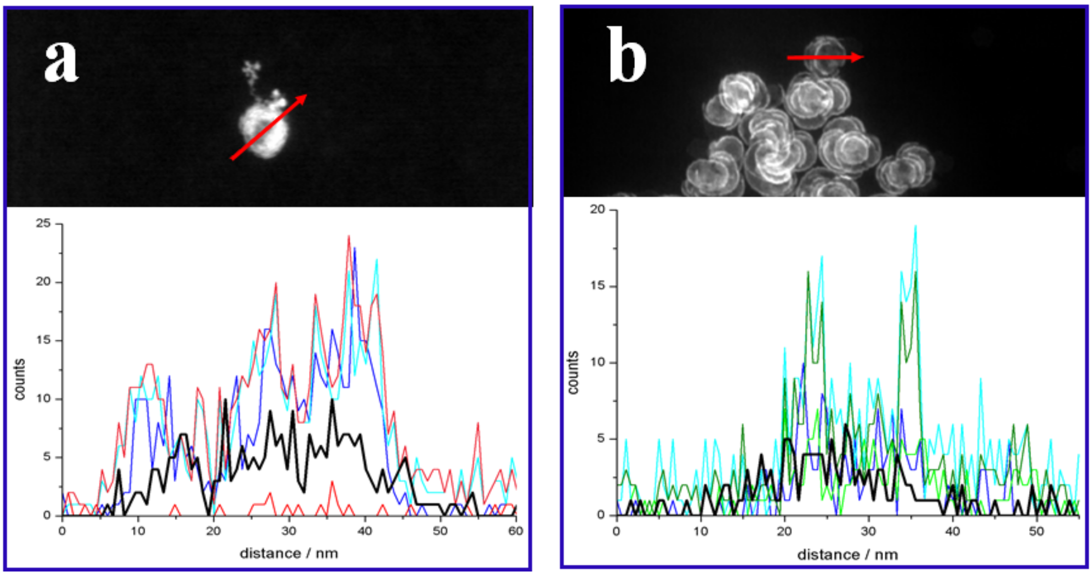

Figure S5: Energy dispersive spectroscopy line scan for CoFe (a) and CoNi (b) SUNOE, black line indicate S, green line is Ni-K, olive line is Ni-L, red line is Fe-K, pink line is Fe-L, blue line is Co-K, cyan line is Co-L. Red arrows in STEM image show scan directions. Only representative data of these three products are shown in main text and supporting infomation, other experimental results are not shown

Mechanism Study:

Amount of SO_4^{2-}:

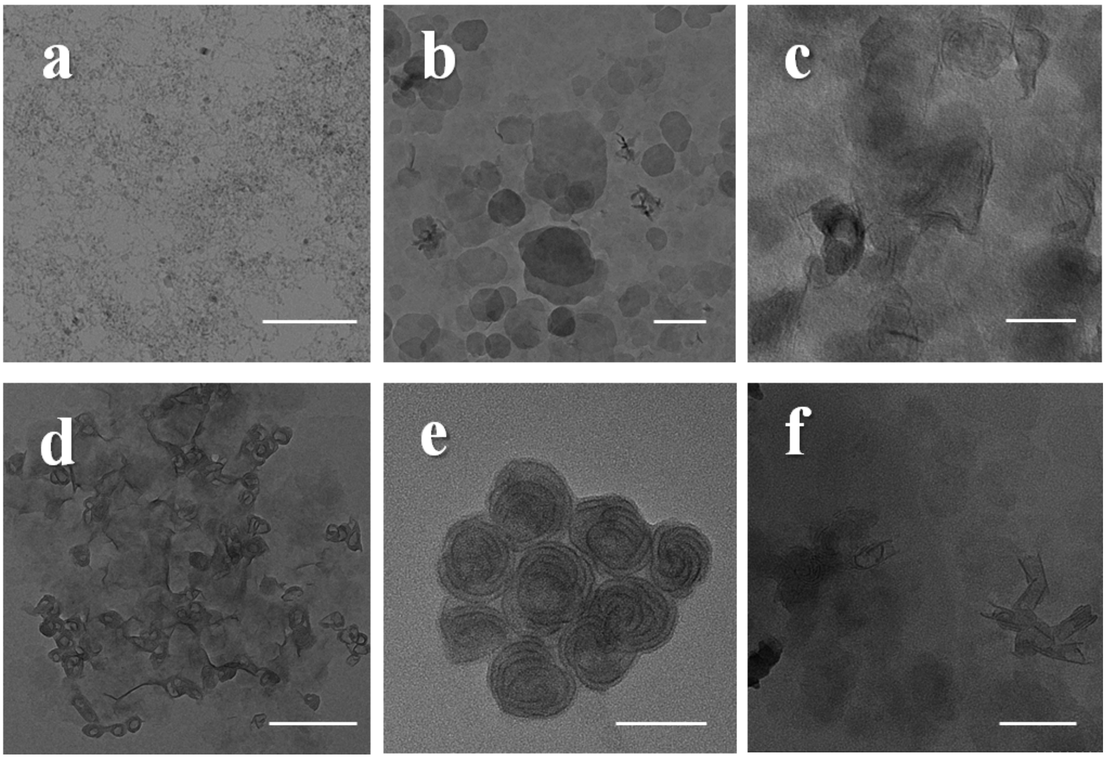

Figure S6: (a,b) products without SO_4^{2-}, the precursors in (a) are $Co(NO_3)_2$ and $FeCl_2$, precursors in (b) are $Co(NO_3)_2$ and $Ni(NO_3)_2$, the ratios of metals are the same with pure SUNOE. Then keeping the ratio of Co:Ni = 1:2, and changing the ratio of SO_4^{2-} by using combination of $Co(NO_3)_2$, $Ni(NO_3)_2$, $CoSO_4$ and $NiSO_4$, the final morphologies are different. The ratio of metal to SO_2^{2-} in (c) is 6:1, (d) is 4:1, (e) is 3:2 and (f) is 1:1. Scale bar: a,100nm; b,200nm; c, 50nm; d,200nm; e, 50nm; f, 100nm.

Ratio of metal:

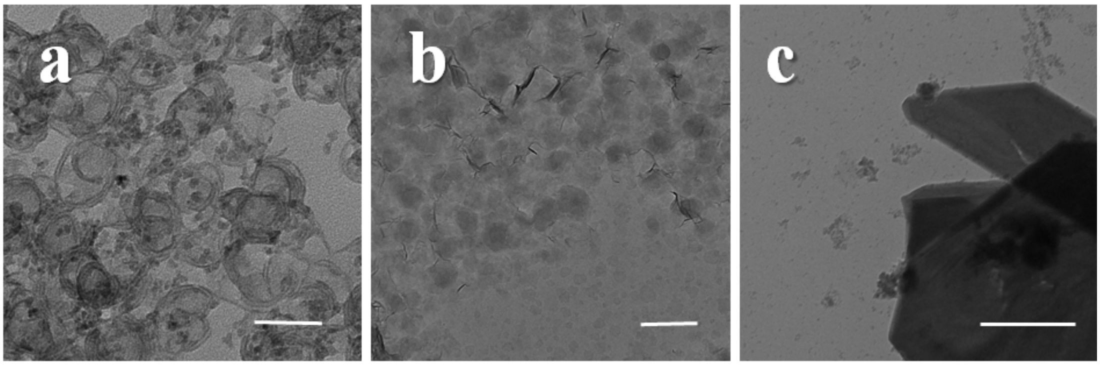

Figure S7: Without the second metal, it's difficult to form SUNOE. With only $CoSO_4$ as metal precursor (a), some SUNOE may be formed but not pure. This may be due to the oxidization of Co-amine complex, Co atoms with different valences may help the growth of SUNOE. With only $NiSO_4$ (b) or $(NH_4)_2Fe(SO_4)_2$ (c) as metal precursor, no SUNOE could form. Scale bar: a, 50nm; b, c, 200nm.

Solvent Ratio:

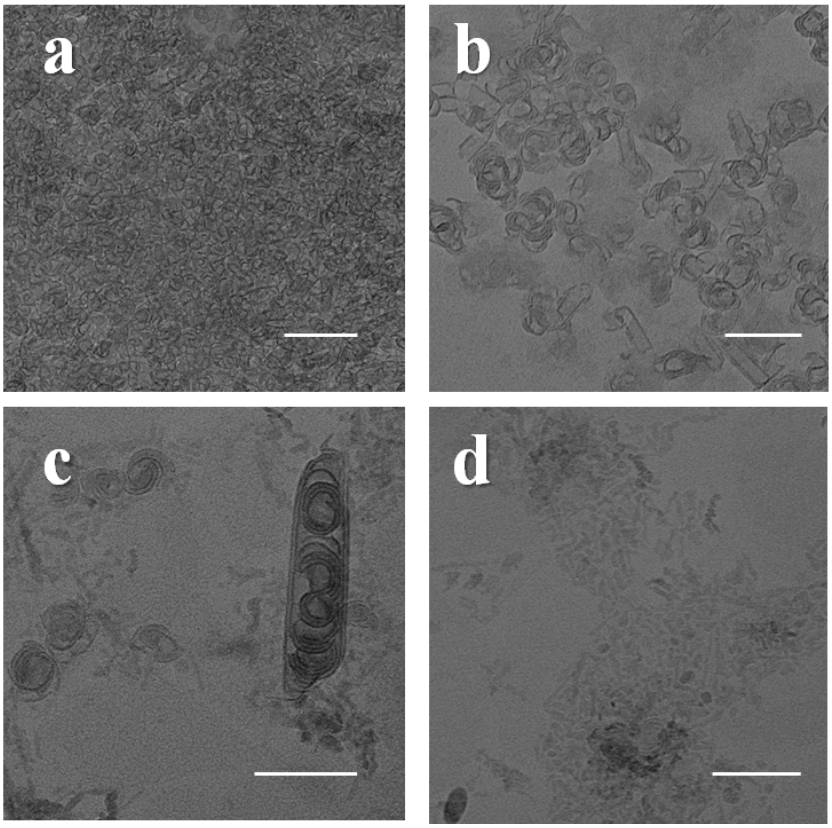

Figure S8: the ratio of hexane to ethanol would greatly change the morphology. Using $CoSO_4$ system as an example for consideration of simplified parameters, when hexane to ethanol is 9:1 (a), SUNOE would form, decreasing the ratio to 8:2 (b), the products are not pure. Further decreasing the ratio to 7:3 (c), spiral structure with more complexity could be observed. When the ratio decrease to 6:4 (d), no SUNOE could be seen. Scale bar: a, 200nm; b, c ,d, 100nm.

Temperature:

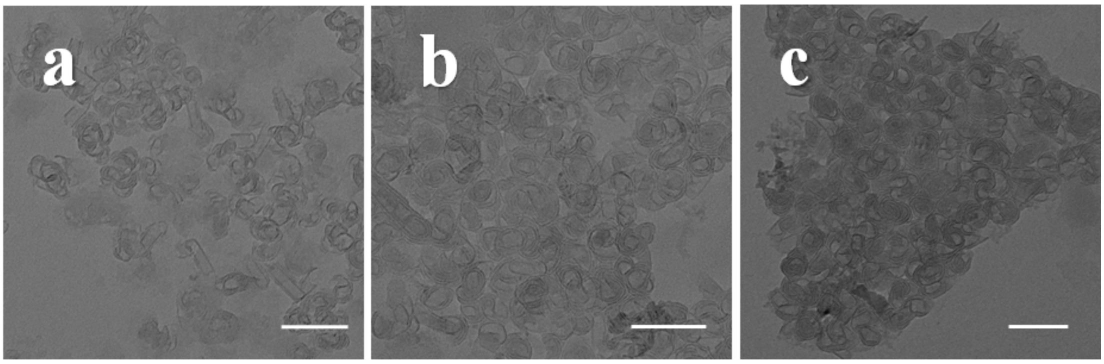

Figure S9: temperature is not essential to this reaction. Taking $CoSO_4$ system as an example for consideration of simplified parameters, when set temperature at 140 (a), 120 (b), 100 ^oC (c), the morphology didn't change a lot. Scale bar: 100nm.

Reaction time:

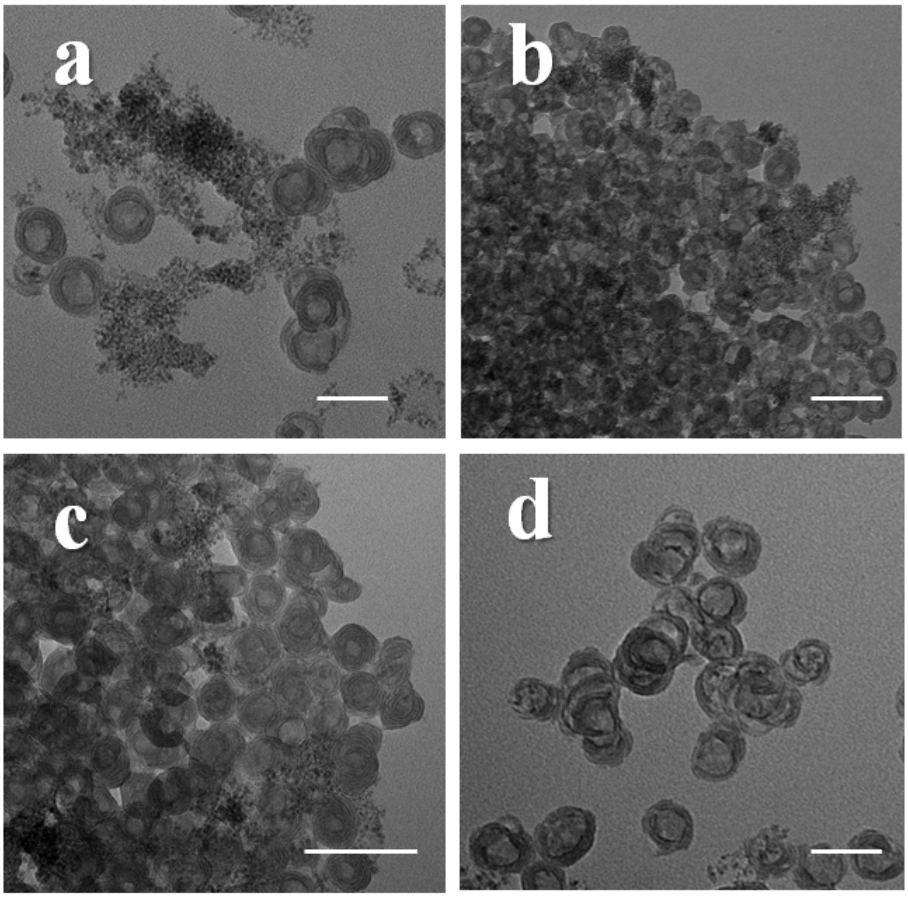

Figure S10: the influence of reaction time seems not essential for produce SUNOE, for 2(a), 4(b), 6(c) and 8(d) hours, SUNOE in all experiments are main products. Scale bar: a, d, 50nm; b, d, 100nm.

TEM Image after Electrochemical Test

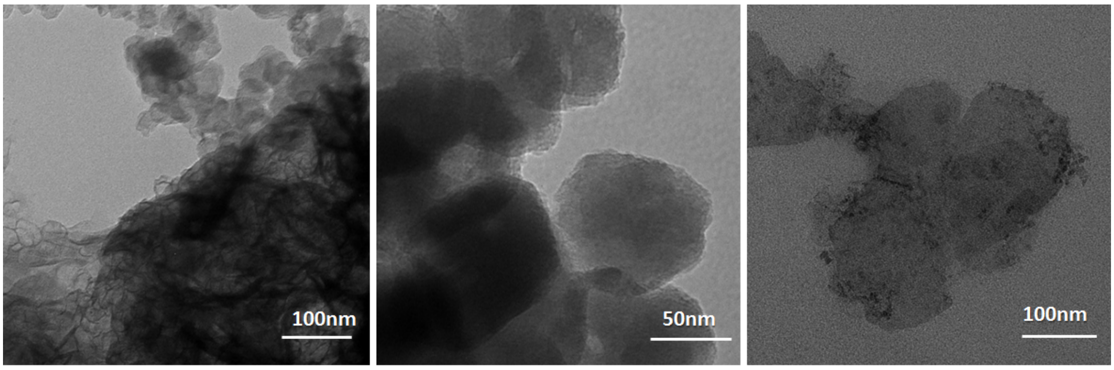

Figure S11: The specimens were collected after electrochemical test (from left to right: CoNi, NiFe, CoFe SUNOE with carbon). Though the morghologies changed comparing with pristine producets, the sheet structures persevered.

Electrochemical Impedance Spectroscopy (EIS) Analysis

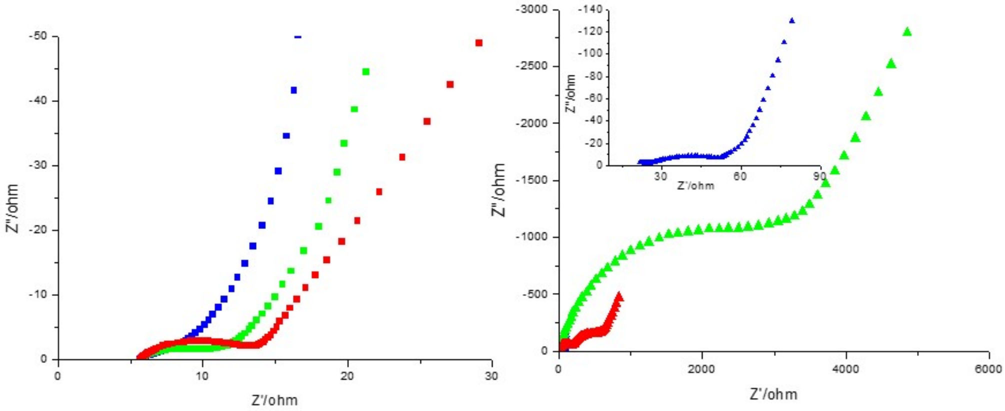

Figure S12: Nyquist plots of as prepared products, SUNOE with carbon are drawn at left side (square) and SUNOE without carbon are drawn at right side (trangle). The plots show that mixing with carbon would increase the conductivities, especially for CoNi and NiFe SUNOE.

Study on Co(IV) species (Taking CoFe SUNOE as an example)

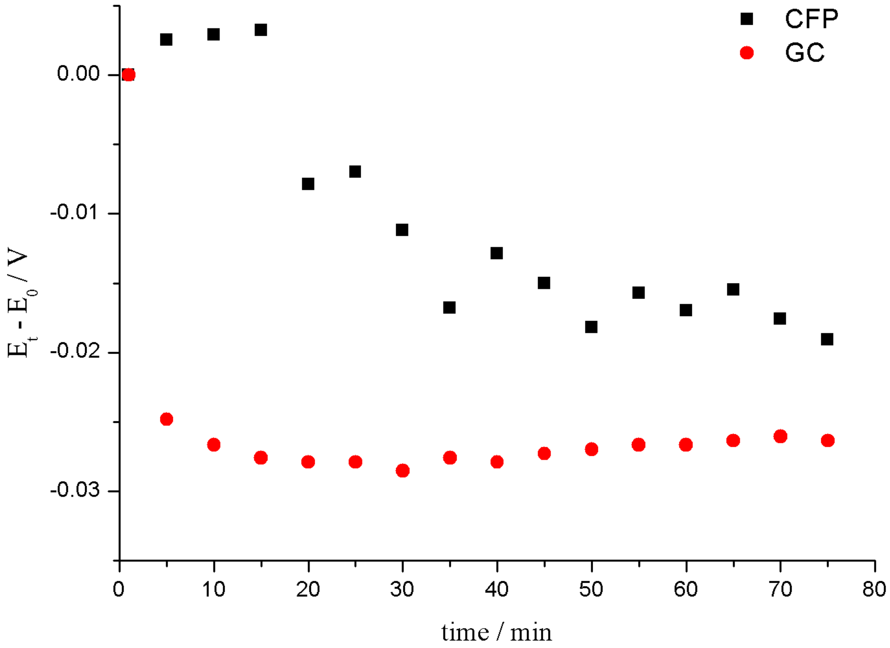

Figure S13: Potential changes under current density at 20 mA/cm^2 on carbon fiber paper (CFP) and glassy carbon (GC) substrates. Both of the potentials decreased along time, however, the changes were smaller when using CFP as substrate, comparing with GC. This may be due to the reductivity nature of CFP and inhibit the formation of Co(IV) species, thus hindered the decrease of potential.

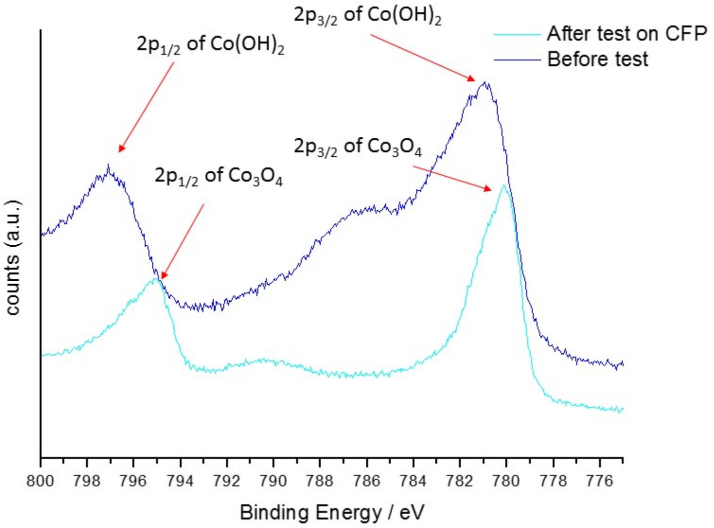

Figure S14: The pristine CoFe SUNOE shows XPS signal similar with $Co(OH)_2$[6], however, after chronopotential test under 20 mA/cm^2 on CFP, the signal resembles Co_3O_4[7]. This suggests the formation of high valence of Co species. However, Co(IV) species are highly active with reductive CFP, thus we cannot directly Co(IV) species by XPS, *in situ* analysis method may be used to debunk the question.

Specific Capacities:

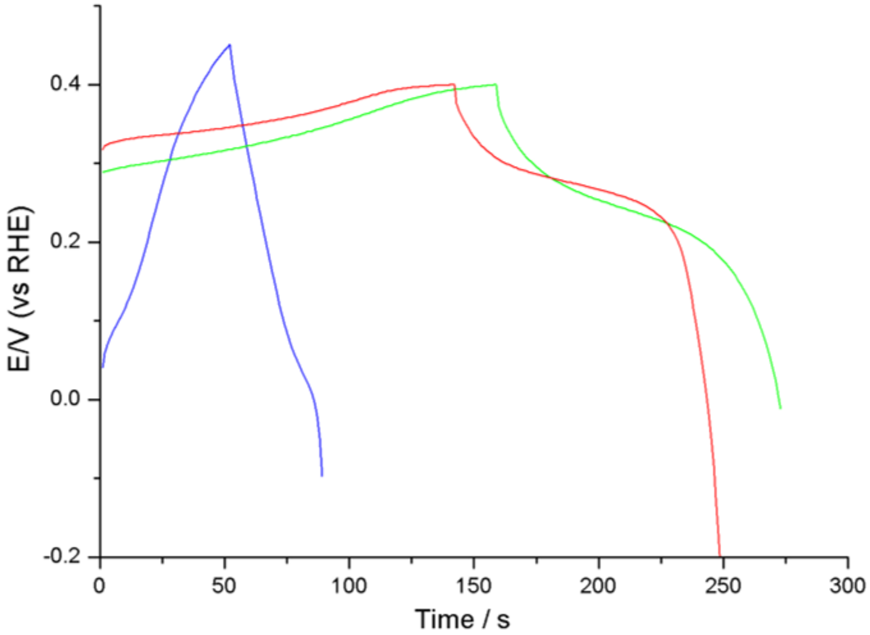

Figure S15: charge-discharge properties of different SUNOE, red line stands for NiFe SUNOE, green line for CoNi SUNOE and blue line for CoFe SUNOE. The specific capacitance is 176.7 F/g (NiFe SUNOE), 285 F/g (CoNi SUNOE) and 67.3 F/g (CoFe SUNOE). The charge-discharge efficiency is 0.741 (NiFe SUNOE), 0.717 (CoNi SUNOE) and 0.698 (CoFe SUNOE). And the percentage of oxidized cations is 0.25 (NiFe SUNOE), 0.20 (CoNi SUNOE) and 0.06 (CoFe SUNOE).

Additional Reference:

1. L. Yu, L. Zhang, H. B. Wu and X. W. Lou, *Angew. Chem. Int. Ed.*, 2014, **53**, 3711-3714.
2. M. Gao, W. Sheng, Z. Zhuang, Q. Fang, S. Gu, J. Jiang and Y. Yan, *J. Am. Chem. Soc.*, 2014, **136**, 7077-7084.
3. P. Jeevanandam, Y. Koltypin and A. Gedanken, *Nano Lett.*, 2001, **1**, 263-266.
4. N. H. W., L. D. and B. G. M., *Phys. Chem. Minerals.*, 2000, **27**, 357-366.
5. Y. E. Roginskaya, O. V. Morozova, E. N. Lubnin, Y. E. Ulitina, G. V. Lopukhova and S. Trasatti, *Langmuir*, 1997, **13**, 4621-4627.
6. B. J. Tan, K. J. Klabunde and P. M. A. Sherwood, *J. Am. Chem. Soc.*, 1991, **113**, 855-861.
7. N. S. McIntyre, D. D. Johnston, L. L. Coatsworth, R. D. Davidson and J. R. Brown, *Surf. Interface Anal.*, 1990, **15**, 265-272.