Electronic Supplementary Material (ESI) for Dalton Transactions.

A Binder-free Fe-Doped $NiCo_2O_4/Ni_3S_4$ Hollow Heterostructure Nanotubes for Highly Efficient Overall Water Splitting

Zhaohui Liu, Bolin Zhao, Chenhao Pan, Hang Zhao*

School of Material Science and Engineering, Shanghai Jiao Tong University,

Shanghai 201100, China

*Corresponding author

Email: h-zhao@foxmail.com

Electrochemical measurements details

The turnover frequency (TOF, s^{-1}) for HER was calculated with the following equation:

$$TOF=(|J|\times A)/2Fn \quad (1)$$

Where $|J|$ ($A\cdot cm^{-2}$) is the current density at a fixed voltage during the LSV measurement, A is the geometric area of the working electrode (1 cm^2), the factor of 2 is the corresponding electron transfer numbers, F is the Faraday constant (96485 $C\cdot mol^{-1}$), and n is the number of active sites (mol).

$$n=Q/2F \quad (2)$$

The number of active sites (n) was determined by the cyclic voltammetry (CV) with a scan rate of 10 mV s^{-1}. The number of the voltammetric charges (Q) could be determined by integrating.

The turnover frequency (TOF, s^{-1}) for OER was calculated with the following equation:

$$TOF=(|J|\times A)/4Fn \quad (3)$$

$$n=Q/4F \quad (4)$$

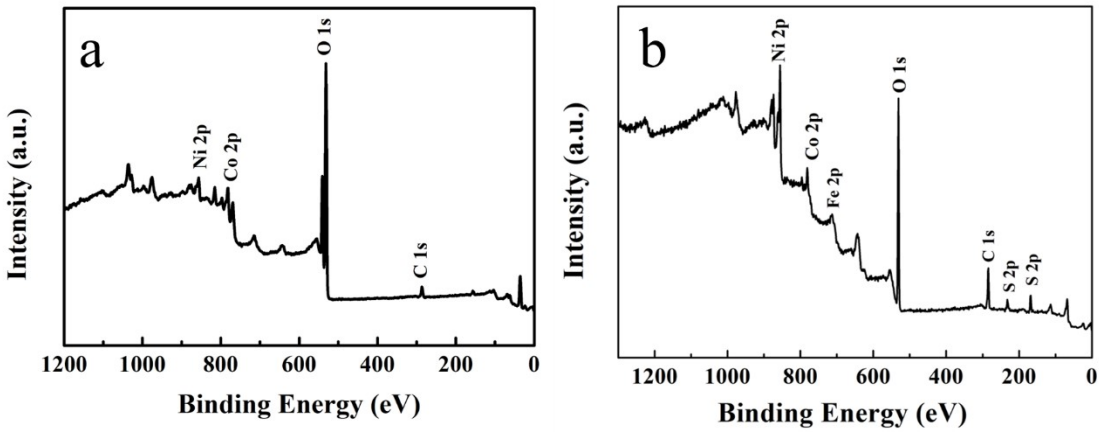


Fig.S1 XPS survey spectra of Ni-O (a) and Ni-O-S (b).

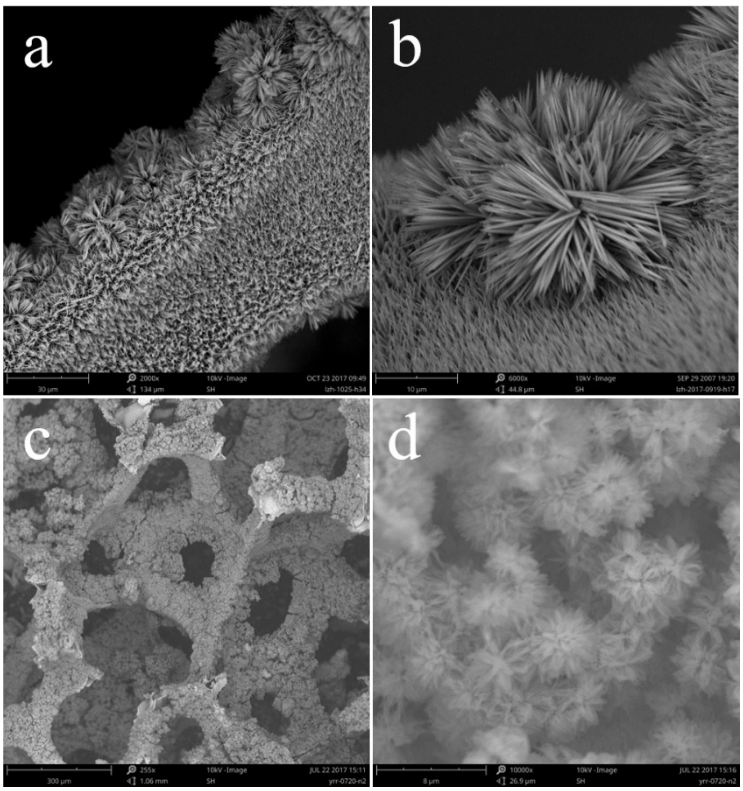
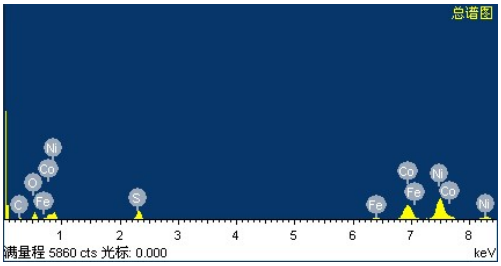


Fig. S2 SEM image of Ni-O (a, b) and Ni-S (c, d).



Element	Weight (%)	Atomic (%)
C K	0.20	0.88
O K	3.35	10.96
S K	3.09	5.04
Fe K	1.05	0.98
Co K	32.00	28.41
Ni K	60.31	53.74

Fig. S3 EDS and element content of Ni-O-S.

Comment [P]: Revised: "The element concent of Ni-O-S" was added.

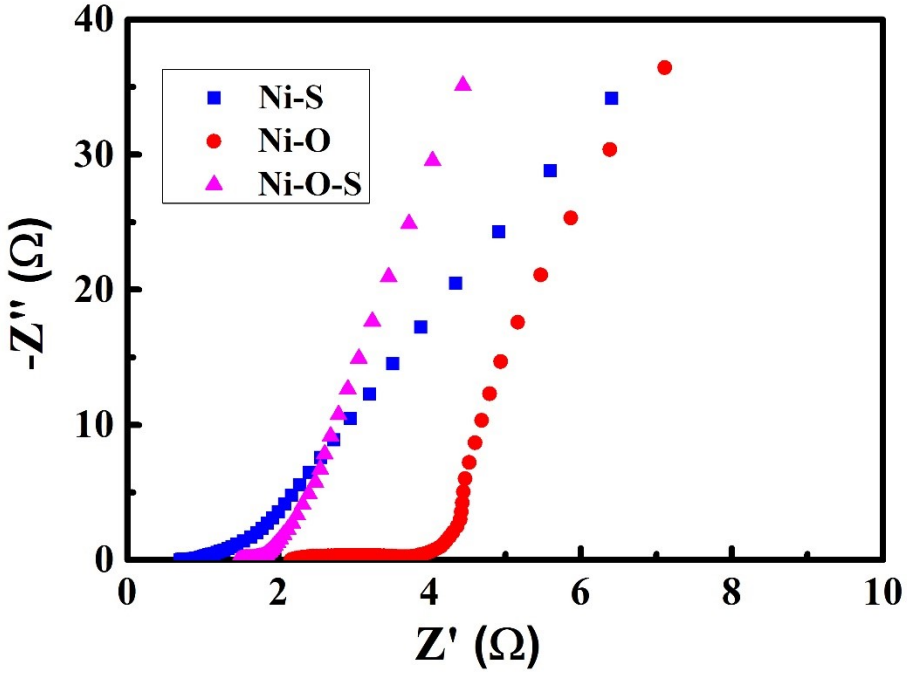


Fig. S4 Nyquist plots of various as-prepared samples.

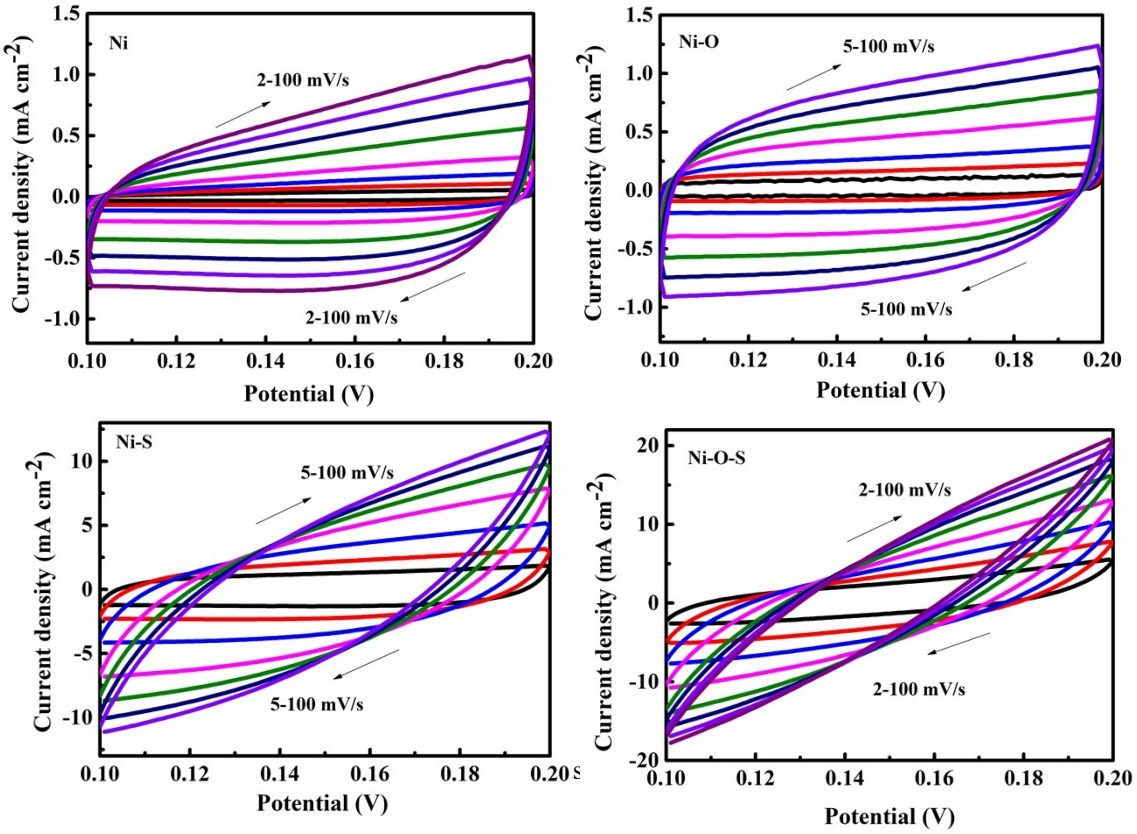
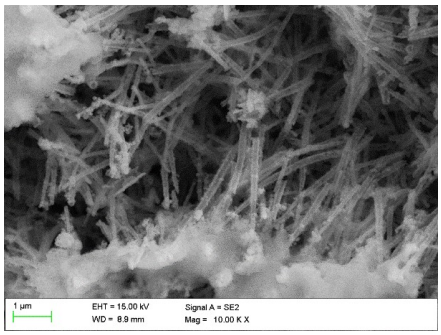


Fig. S5 CV curves of the different catalysts for the HER in 1 M KOH.



Element	Weight (%)	Atomic (%)
O K	2.45	8.32
S K	1.81	3.07
Fe K	1.45	1.41
Co K	33.79	31.18
Ni K	60.50	56.03

Fig. S6 SEM image and element content of Ni-O-S after stability test.

Comment [P]: Revised: Fig. S6 was added.

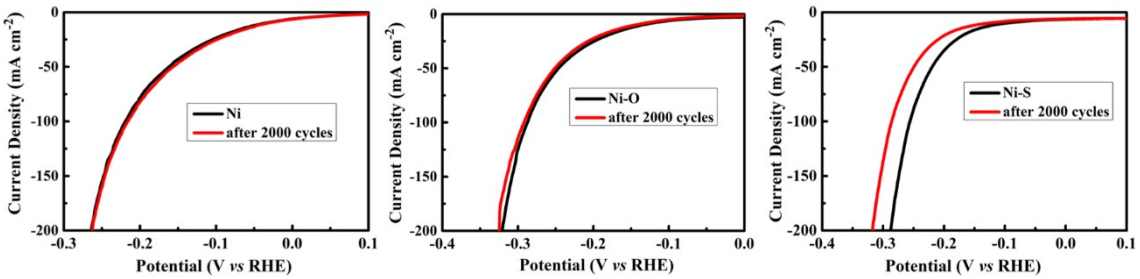


Fig. S7 polarization curves of Ni, Ni-O, Ni-S before and after 2000 potential cycles for HER.

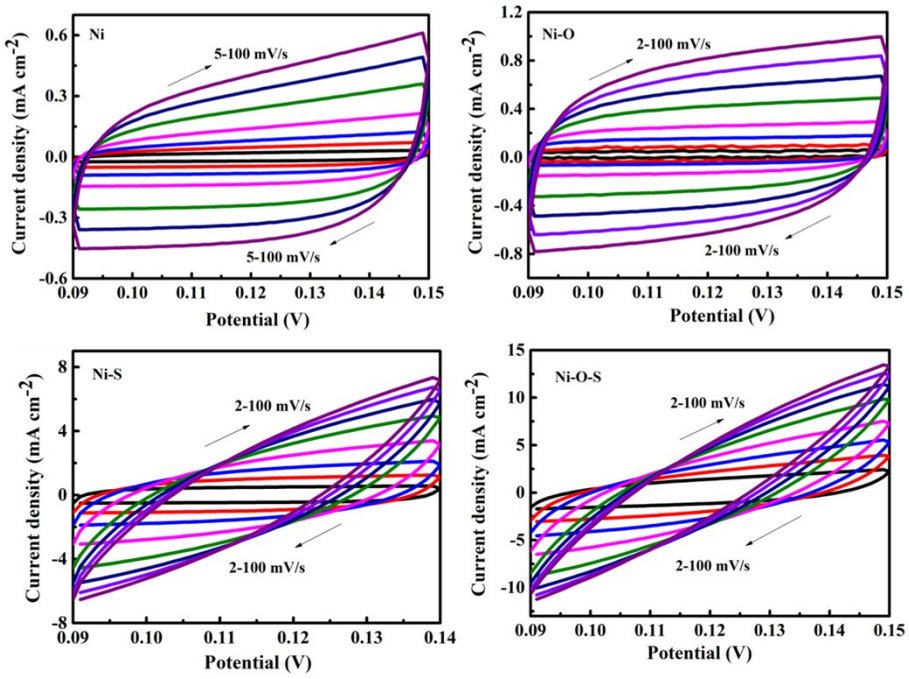


Fig. S8 CV curves of the different catalysts for the OER in 1 M KOH.

Comment [P]: Revised: "Fig. S7" was changed to "Fig. S8".

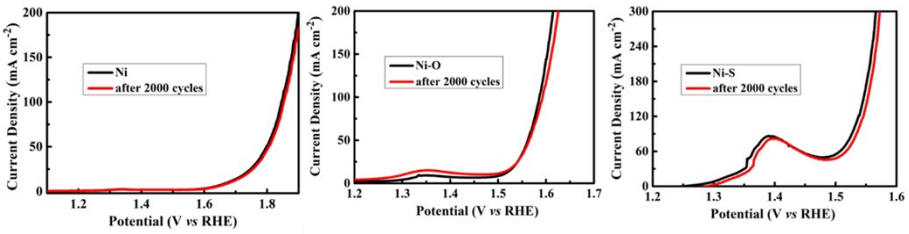


Fig. S9 polarization curves of Ni, Ni-O, Ni-S before and after 2000 potential cycles for OER.

Comment [P]: Revised: "Fig. S8" was changed to "Fig. S9".

Fig. S10 A digital image of overall water splitting.

Comment [P]: Revised: “Fig. S9” was changed to “Fig. S10”.

Table S1. Comparison of some recently reported representative electrocatalysts for overall water splitting in 1 M KOH electrolyte.

Catalyst	Overpotential for HER at 10 mA cm^{-2} (mV)	Overpotential for OER at 10 mA cm^{-2} (mV)	Cell voltage (V)	literature
$NiCo_2O_4/Cu_xO$	92	213	1.61	[2]
NiFe-LDH@CoS_x	136	206	1.537	[3]
CoMoNiS-NF-31	113	166	1.54	[5]
Fe-Co-O/Co@NC-mNS/NF	112	257	1.58	[15]
$Ni_xFe_{1-x}(OH)_2$	-	244	1.64	[24]
MoS_2-Ni_3S_2	98	249	1.50	[33]
Mo-Ni_3S_2/Ni_xP_y/NF	109	238 (50 mA)	1.46	[40]
$NiCo_2O_4$@$NiMo_2S_4$	159	310 (20 mA)	1.63 (50 mA)	[41]
Ni-O-S	29.1	259 (100 mA)	1.45	This work

Comment [P]: Revised: "Table S1" was added.