Electronic Supplementary Information

Dual-valence Nickel Nanosheets Covered with Thin Carbon as Bifunctional Electrocatalysts for Full Water Splitting

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Results and discussion

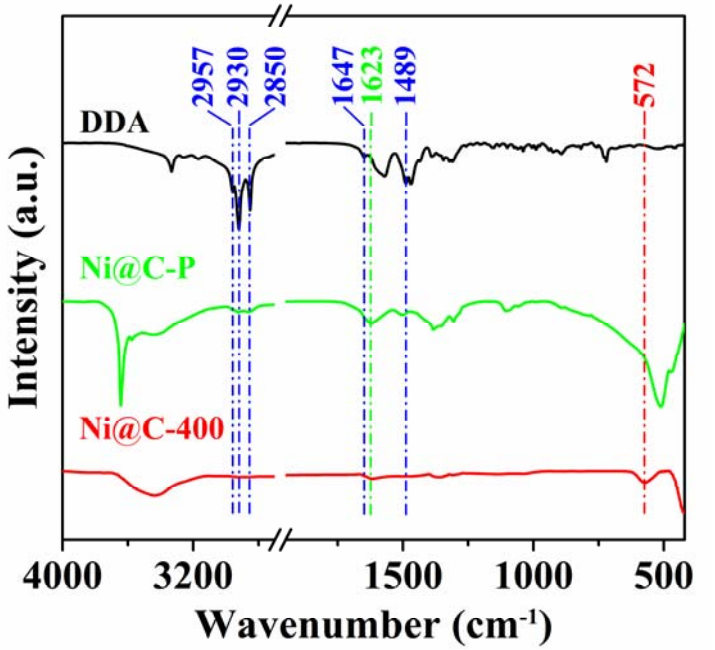

Fig. S1 FT-IR spectra of DDA, Ni@C-P, and Ni@C-400.

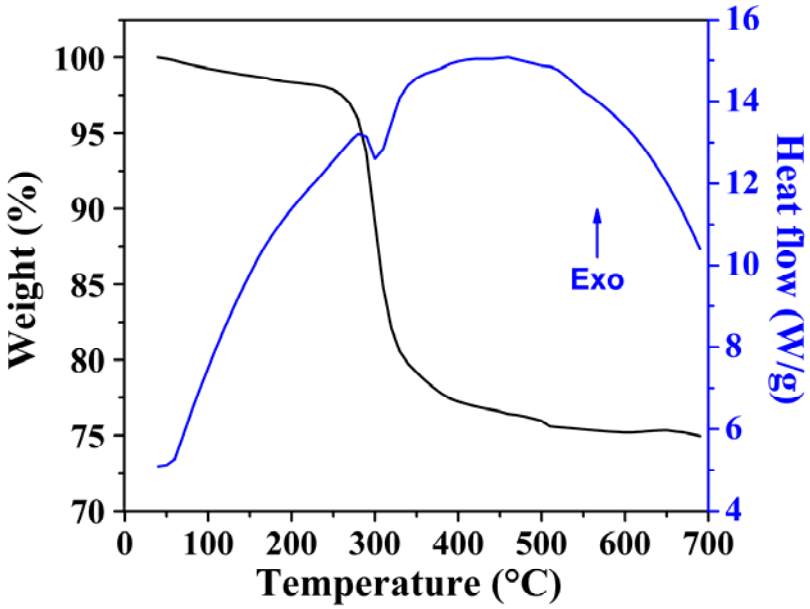

Fig. S2 TG and DSC curves of Ni@C-P in N_2.

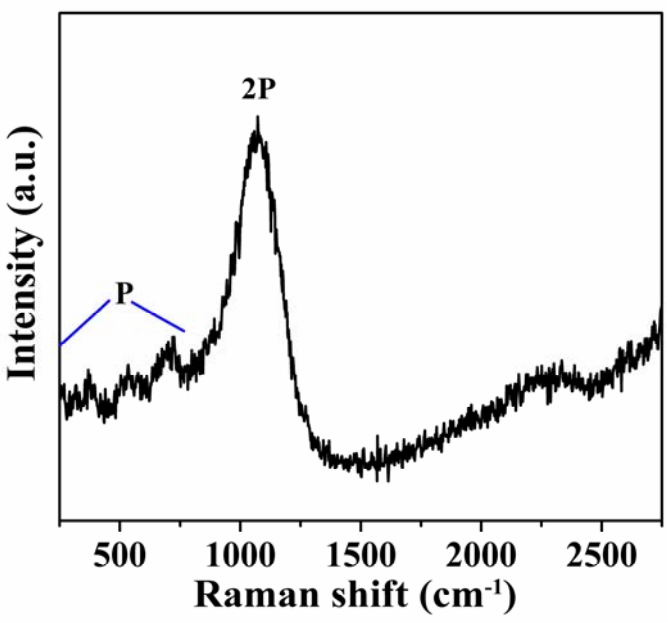

Fig. S3 Raman spectrum of Ni@C-400 NSs.

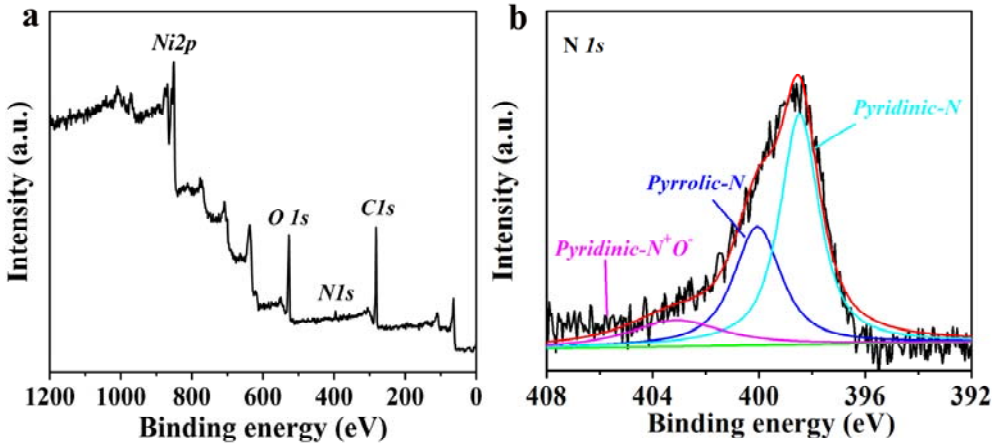

Fig. S4 (a) XPS survey spectrum and (b) the high-resolution *N 1s* XPS spectrum of Ni@C-400 NSs.

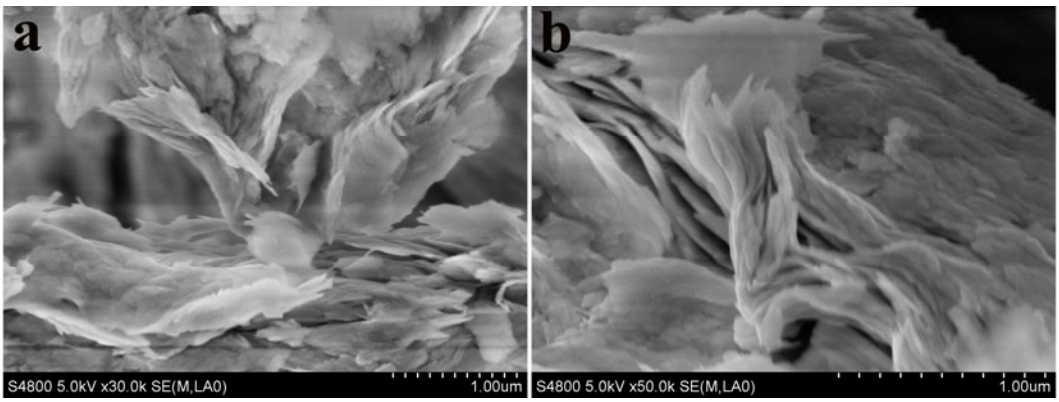

Fig. S5 SEM images of Ni@C-P NSs.

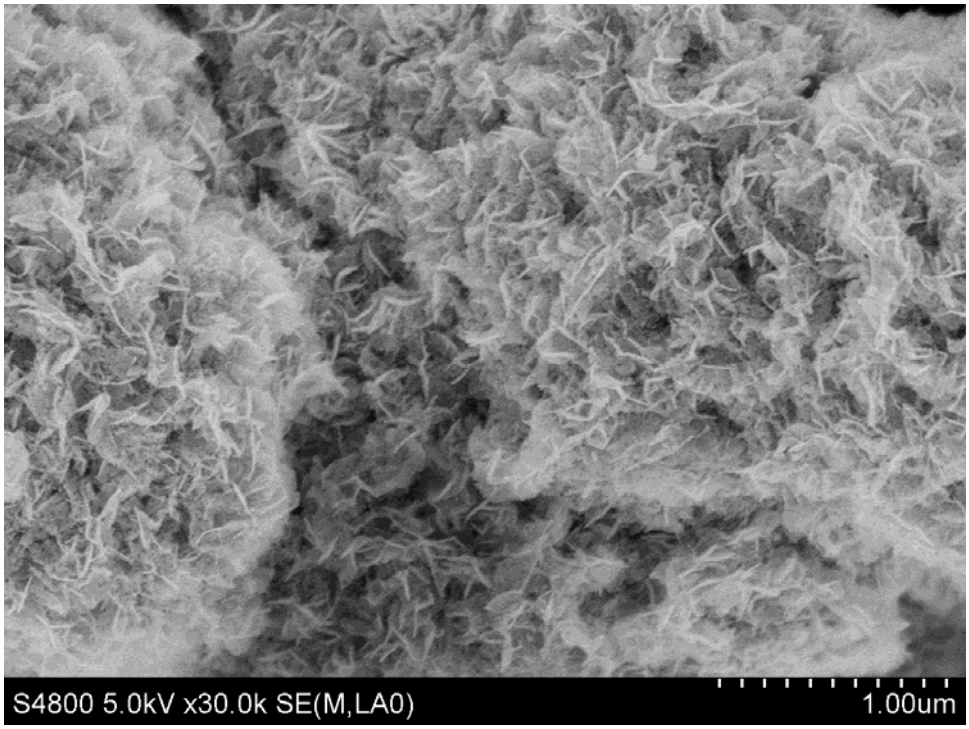

Fig. S6 SEM image of Ni@C-400 NSs.

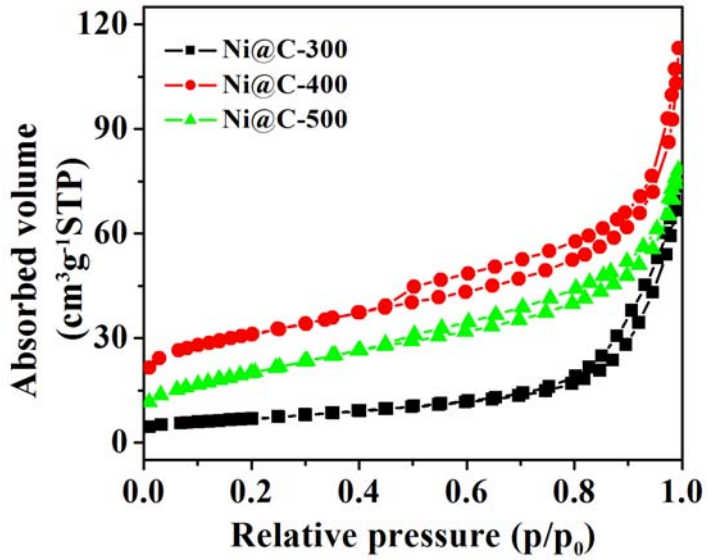

Fig. S7 N_2 adsorption-desorption isotherms of Ni@C-300, Ni@C-400 NSs and Ni@C-500 NSs.

Table S1. Comparison of BET surface area and pore diameter of various Ni@C NSs.

Sample name	BET Surface area ($m^2 \cdot g^{-1}$)	Pore diameter (nm)
Ni@C-300	24.31	13.44
Ni@C-400	109.51	10.08
Ni@C-500	72.08	7.91

Fig. S8 The photograph of DDA dispersed in ethylene glycol (a) and water (b); SEM image of Ni@C NSs prepared without ethylene glycol (c).

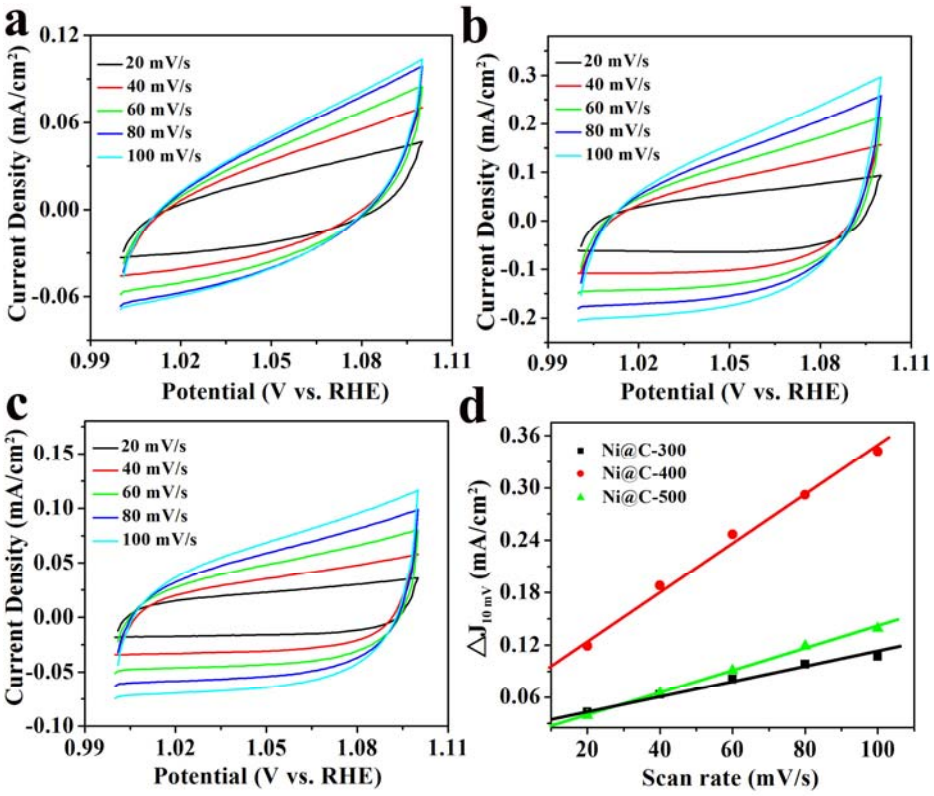

Fig. S9 (a-c) CVs for Ni@C-300, Ni@C-400 NSs and Ni@C-500 NSs at various scan rate (10, 20, 40, 60 and 80 $mV \cdot s^{-1}$); (d) the capacitive current at 0.15 V *vs.* RHE as a function of scan rate for Ni@C-300, Ni@C-400 NSs and Ni@C-500 NSs ($\Delta j_0 = j_a - j_c$).

Table S2. Comparison of catalytic performance of Ni@C-400 NSs for OER to reported Ni-based catalysts.

Materials	Electrode	Onset potential (V vs RHE)	Potential (at 10 $mA \cdot cm^{-2}$, V vs RHE)	Tafel slope (mV/dec)	electrolyte	Ref
NiCo LDH NTAs [1]	GC	1.540	1.690	65	---	S1
Ni NTAs [1]	Ni foil	1.604	1.890	145	---	
NiFe LDH/CNT [2]	GC	1.500	---	35	---	S2
NG-NiCo LDH [3]	GC	1.580	1.63 (at 145.3 $mAcm^{-2}$)	614	---	S3
CoCo LDHs	GC	1.638	1.840	---	---	S4
NiCo LDH/Ni foam	GC	1.520	1.650	113	1 M KOH	S5
$Ni_{2/3}Fe_{1/3}$-rGO	Ni foam	1.440	1.470	40	1 M KOH	S6
CoO/N-CG [4]	GC	---	1.570	71	---	S7
$NiCo_2O_4$ HNSs [5]	GC	1.500	1.590	64.4	---	S8
PNG-$NiCo_2O_4$ [6]	GC	1.540	---	156	---	S9
NG-$NiCo_2O_4$[3]	graphite carbon	1.570	---	249		
$NiCo_2O_4$ nanosheets	GC	1.550	---	30	1M KOH	S10
$Ni_{0.6}Co_{2.4}O_4$/Ni foil	Ni foil	1.570	1.760		---	S11
Co_3O_4/N-rGO [7]	GC	---	1.540	67	---	S12
N/C-NiO_x [8]	GC	---	1.650	---	---	S13
Ni-NG [3]	GC	1.550	---	188	---	S14
NiO-MWCNT[9]	ITO	1.92		137	0.1 M KBi	S15
Ni@NC [10]	GC		1.62	40	0.1 M KOH	S16
Co@NC [10]	GC	1.50	---	---	1 M KOH	
CoP/C	GC		1.59	66	0.1 M KOH	S17
Ni-NiO/N-rGO [7]	Ni foam	1.47		43	1 M KOH	S18
NiSe	Ni foam		1.50	64	1 M KOH	S19
$NiCo_2S_4$	carbon cloth	1.50	1.51	141	1 M KOH	S20
Ni@C-400 NSs	GC	1.53	1.56	145	1 M KOH	This work
	Ni foam	1.49	1.54	95	1 M KOH	

[1] NTAs, abbreviation for nanotube arrays;
[2] CNT, abbreviation for carbon nanotubes;
[3] NG, abbreviation for nitrogen doped graphene;
[4] N-CG, abbreviation for nitrogen doped hollow crumpled grapheme;
[5] HNSs, abbreviation for hollow nanosponges;
[6] PNG, abbreviation for 3D hybrid film of porous N-doped graphene;
[7] N-rGO, abbreviation for nitrogen doped reduced graphene oxide;
[8] N/C-NiO_x, abbreviation for nickel/nickel oxide nanoparticles was strongly bound to a porous nitrogen doped carbon matrix;
[9] MWCNT, abbreviation for multi-walled carbon nanotubes;
[10] NC, abbreviation for nitrogen doped carbon.

Table S3. Comparison of catalytic performance of Ni@C-400 NSs for HER to reported Ni-based catalysts.

Materials	Electrode	Onset potential (V vs RHE)	Potential (at -10 mA·cm^{-2}, V vs RHE)	Tafel slope (mV/dec)	Electrolyte	Ref
Ni_3S_2/MWCNT [1]	GC	---	-480	---	---	S21
Ni_2P	GC	---	-130	---	0.5 M H_2SO_4	S22
Ni_2P nanoparticles	GC	---	-225	100	1 M KOH	
NiO/Ni-CNT [2]	GC	-0.095	---	---	1 M KOH	S23
Ni-Mo powder	GC	---	-0.07/-20	---	2 M KOH	S24
	Ni foam	---	-0.08/-20	---	2 M KOH	
$Fe_{0.43}Co_{0.57}S_2$	GC	-150	---	56	0.5 M H_2SO_4	S25
CoMo nanoparticles	Ti foil	---	-75	---	1 M KOH	S26
EG/$Co_{0.85}$Se/NiFe-LDH [3]	graphite foil	-0.24	---	160	1 M KOH	S27
Ni_3N	Ni foam	-0.08	-180	120	1 M KOH	S28
Co-Ni-C [4]	GC	-1.15 vs. SCE	---	97.2	6 M KOH	S29
Ni dendrite	GC	-1.45 vs. SCE	---	102	6 M KOH	S30
Co-P-300 [5]	GC	---	-280	94.1	1 M KOH	S31
Ni-Co-P-300 [6]		--	-150	60.6		
NiP_2 nanosheet arrays	GC	---	-102	65	1 M KOH	S32
Ni_5P_4 films	GC	---	-150	53	1 M KOH	S33
Ni_3S_2/CNT [2]	GC	-400	---	167	1 M KOH	S21
Ni_xCo_{10-x}/C nanoflakes	GC	-200	---	126	0.1 M NaOH	S34
NiSe nanofiber	GC	-200	---	64	0.5 M H_2SO_4	S35
Ni@C-400 NSs	GC	-150	-270	143	1 M KOH	This work
	Ni foam	-50	-110	95		

[1] MWCNT, abbreviation for multi-walled carbon nanotubes;
[2] CNT, abbreviation for carbon nanotubes;
[3] LDH, abbreviation for layer double hydroxide;
[4] Co-Ni-C, abbreviation for Co-Ni alloys with grapheme;
[5] Co-P-300, abbreviation for Co-Co prussian blue analogue was phosphidation at 300 ºC;
[6] Ni-Co-P-300, abbreviation for Co-Ni prussian blue analogue was phosphidation at 300 ºC.

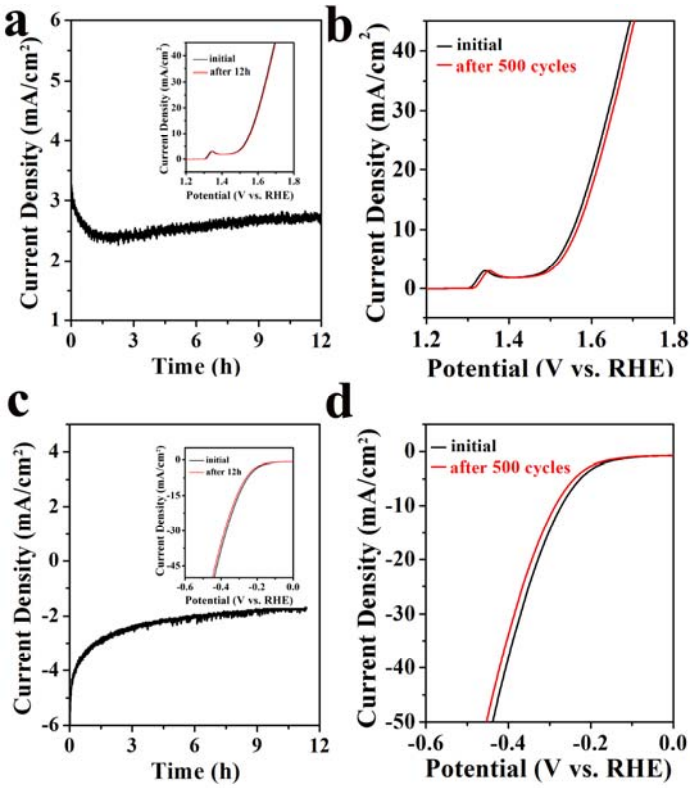

Fig. S10 (a, c) chronoamperometric response of Ni@C-400 NSs at a constant potential of 1.53 V and -0.16 V, respectively; the insets are the corresponding *iR*-compensated LSV curves of Ni@C-400 NSs before and after stability test for OER and HER; (b, d) OER and HER polarization curves for Ni@C-400 NSs initially and after 500 CV sweeps between -0.6 and 0 V *vs.* RHE.

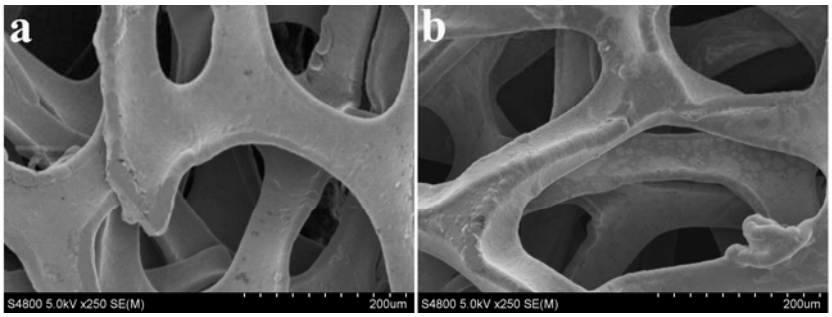

Fig. S11 SEM images of the cleaned Ni foam (a) and the self-standing electrode prepared without nickel salt (b).

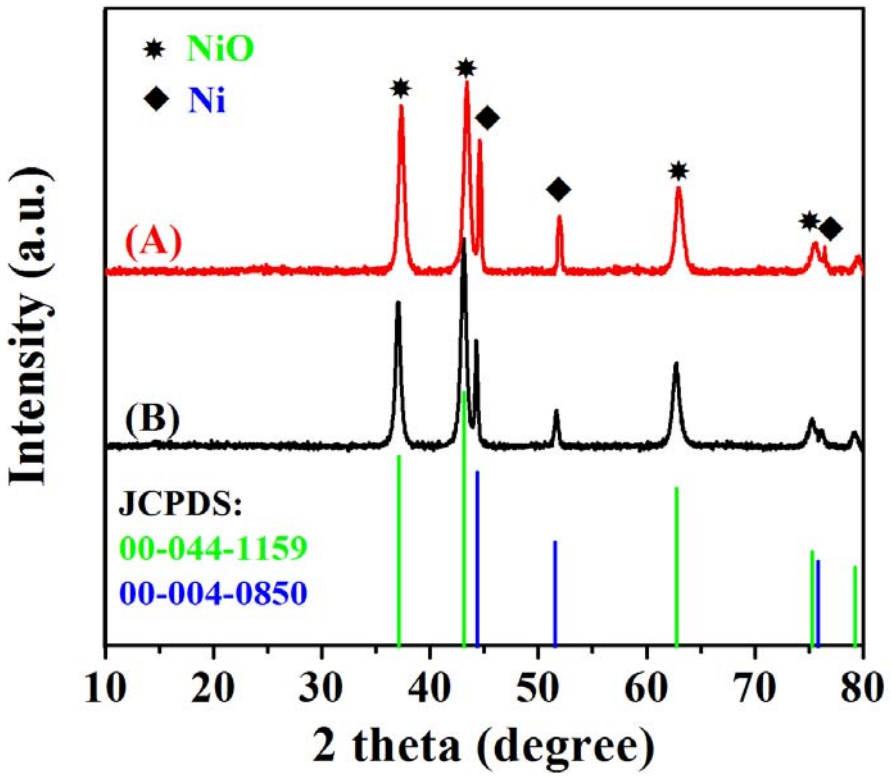

Fig. S12 Powder XRD patterns of Ni@C-400 NSs, (A) and (B) scraped off from Ni foam.

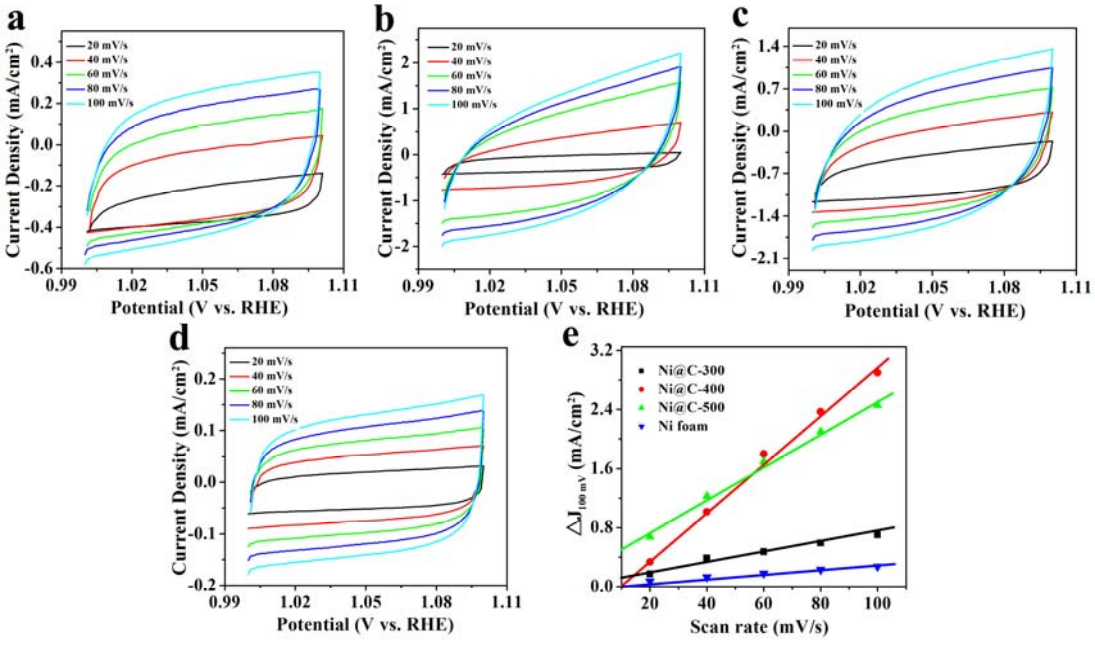

Fig. S13 CVs for at the self-standing Ni@C NSs/Ni foam electrode at various scan rate (10, 20, 40, 60 and 80 mV·s^{-1}), (a-d) Ni@C-300/Ni foam, Ni@C-400 NSs/Ni foam, Ni@C-500 NSs/Ni foam, and Ni foam, respectively; (d) the capacitive current at 0.15 V *vs.* RHE as a function of scan rate for various self-standing Ni@C NSs/Ni foam electrode ($\Delta j_0 = j_a - j_c$).

Table S4. Comparison of catalytic performance of Ni@C-400 NSs and Ni@C-400/Ni foam for OER and HER.

Catalyst	OER			HER		
	Onset potential (V vs. RHE)	Potential (at 10 mA·cm^{-2}, V vs. RHE)	Tafel slope (mV·dec^{-1})	Onset potential (V vs. RHE)	Potential (at -10 mA·cm^{-2}, V vs. RHE)	Tafel slope (mV·dec^{-1})
Ni@C-400 NSs	0.30	0.33	145	0.15	0.27	143
Ni@C-400 NSs/Ni foam	0.26	0.31	95	0.05	0.11	95

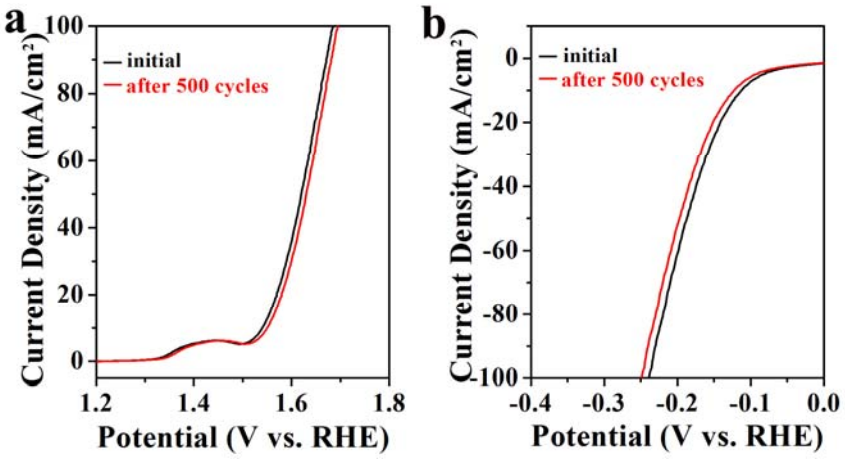

Fig. S14 (a, b) OER and HER polarization curves for Ni@C-400 NSs/Ni foam electrode initially and after 500 CV sweeps.

Table S5. Comparison of catalytic performance of Ni@C-400 NSs for full water splitting to reported Ni-based catalysts.

Materials	Onset potential (V vs RHE)	Potential (at 10 mA·cm^{-2}, V vs RHE)	Elctrolyte	Ref
NiFe LDH/Ni foam	-	1.7	1 M KOH	S36
$Ni(OH)_2$/Ni foam	-	1.82		
Pt/C-Ni foam	-	1.67		
NiSe	-	1.63	1 M KOH	S19
CoP	1.56	-	1 M KOH	S37
Ni_2P	-	1.63	1 M KOH	S38
NiMo-HNR [1]	-	1.64	1 M KOH	S39
RuO_2/TiM [2]	-	1.57		
Co_3O_4/NCs [3]	-	1.91	1 M KOH	S40
Co-P/NCs [3]	1.55	---	1 M KOH	S41
Ni@C-400 NSs/Ni foam	1.57	1.64	1 M KOH	This work

[1] HNR, abbreviation for the hollow nanorod arrays;
[2] TiM, abbreviation for Ti mesh;
[3] NCs, abbreviation for carbon fiber papers.

Additional References

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