Electronic Supplementary Information

Experimental Section

Materials: $Ni(NO_3)_2 \cdot 6H_2O$ was purchased from Aladdin Ltd. in Shanghai. Ammonium fluoride **(**NH_4F), urea and nitric acid (HNO_3) were purchased from Beijing Chemical Works. Acetone and ethanol were purchased from Tianjin Chemical Corporation. Carbon cloth (CC) was provided by Hongshan District, Wuhan Instrument Surgical Instruments business, and was cleaned by sonication sequentially in acetone, water and ethanol several times to remove the surface impurities. The water used throughout all experiments was purified through a Millipore system.

Preparation of $Ni(OH)_2$ NA/CC and Ni_3N NA/CC: In a typical procedure, 4.5 mmol $Ni(NO_3)_2 \cdot 6H_2O$, 8 mmol NH_4F and 20 mmol urea were dissolved in 80 mL distilled water and stirred to form a clear solution. Then the above solution and a piece of cleaned CC (2 cm × 3 cm) were transferred to a 50 mL Teflon-lined stainless-steel autoclave and maintained at 120 °C for 6 h. After the autoclave cooled down naturally, the resulting CC was taken out and washed with distilled water and ethanol, followed by drying 2 h at 60 ºC to obtain $Ni(OH)_2$ NA/CC. To prepare Ni_3N NA/CC, $Ni(OH)_2$ NA/CC was placed in a tube furnace, and heated at 380 °C for 3 h with a heating speed of 5 ºC min^{-1} in NH_3 atmosphere, and then naturally cooled to ambient temperature under NH_3. Finally, the black Ni_3N NA/CC were collected for further characterization.

Characterizations: XRD data were acquired on a RigakuD/MAX 2550 diffractometer with Cu Kα radiation (λ=1.5418 Å). SEM images were collected on a XL30 ESEM FEG scanning electron microscope at an accelerating voltage of 20 kV. TEM images were collected on a HITACHI H-8100 electron microscopy (Hitachi, Tokyo, Japan) with an accelerating voltage of 200 kV. XPS measurements were performed using an ESCALABMK II X-ray photoelectron spectrometer with the exciting source of Mg.

Electrochemical measurements: Electrochemical measurements were performed

with a CHI 660E electrochemical analyzer (CH Instruments, Inc., Shanghai) in a standard three-electrode system using Ni_3N NA/CC as the working electrode, a platinum wire as counter electrode and Hg/HgO as the reference electrode. The potentials reported in this work were calibrated to RHE, using the following equation: E (RHE) = E (Hg/HgO) + (0.098 + 0.059 pH) V. Polarization curves were obtained by linear sweep voltammetry with a scan rate of 5 mV s^{-1}. All experiments were carried out at 25 °C.

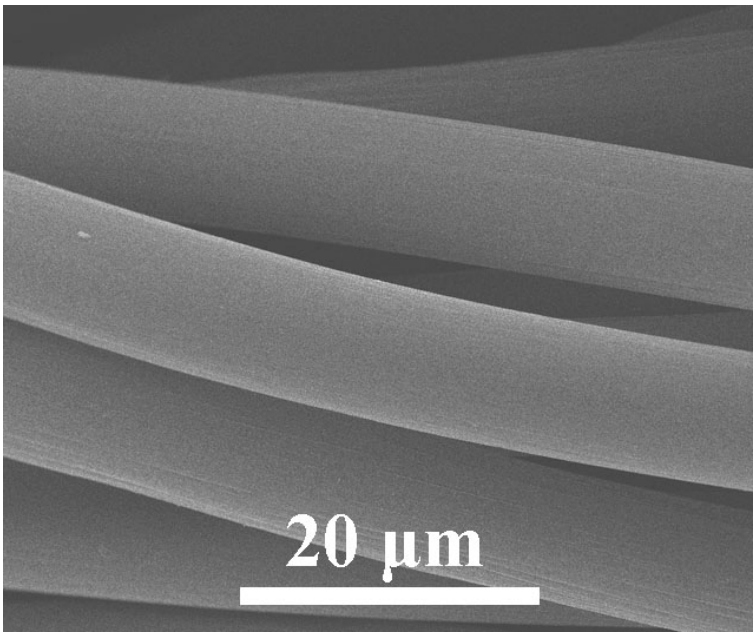

Fig. S1. SEM image of bare CC.

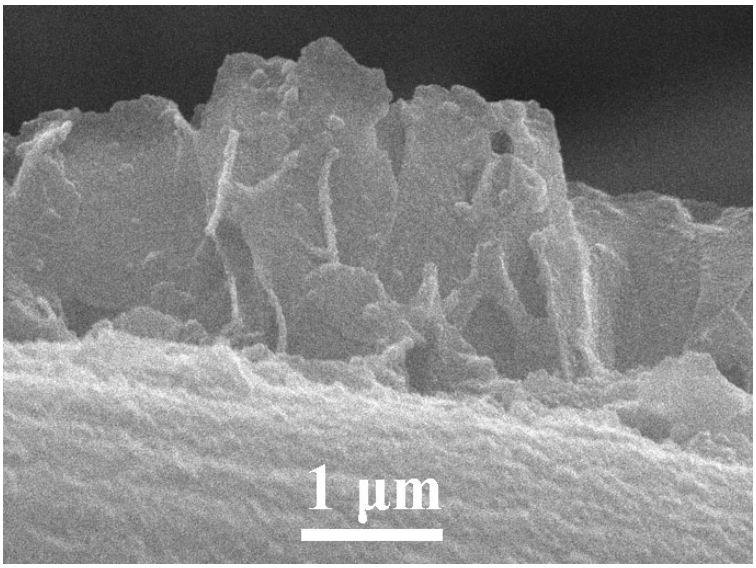

Fig. S2. Cross-section SEM image of Ni_3N NA/CC.

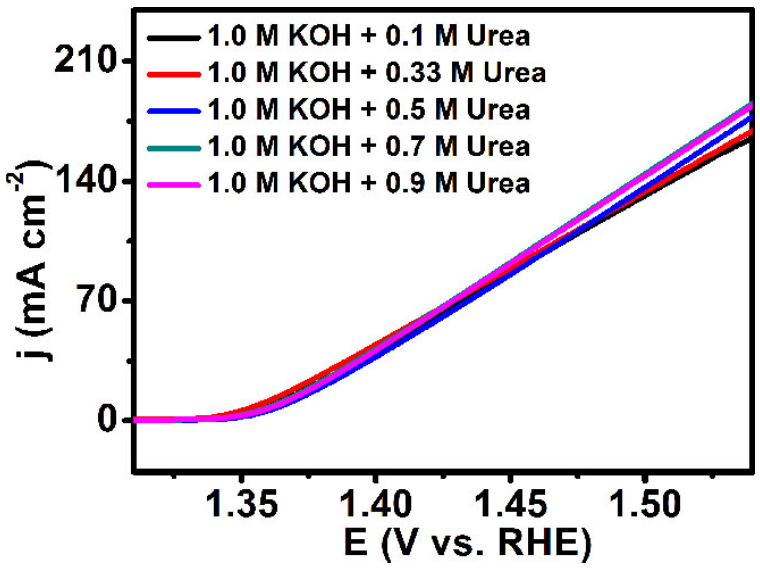

Fig. S3. LSV curves of Ni_3N NA/CC in 1.0 M KOH with 0.1, 0.33, 0.5, 0.7, and 0.9 M urea.

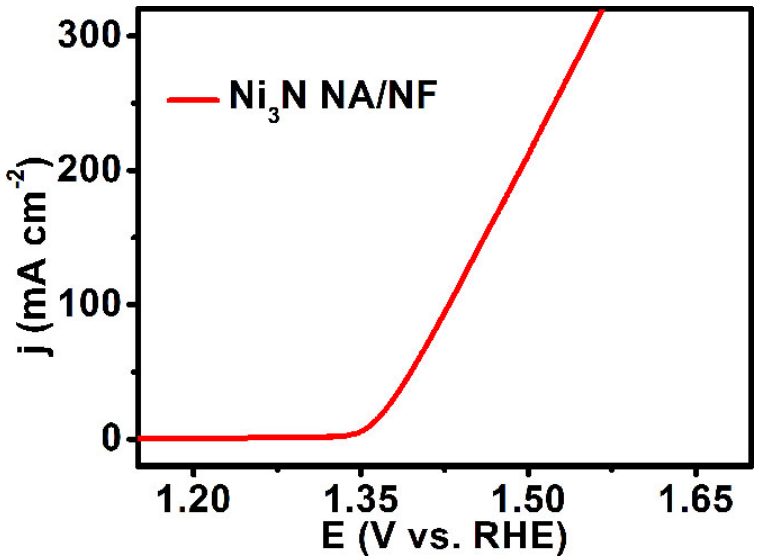

Fig. S4. LSV curves of Ni_3N NA/NF in 1.0 M KOH with 0.33 M urea.

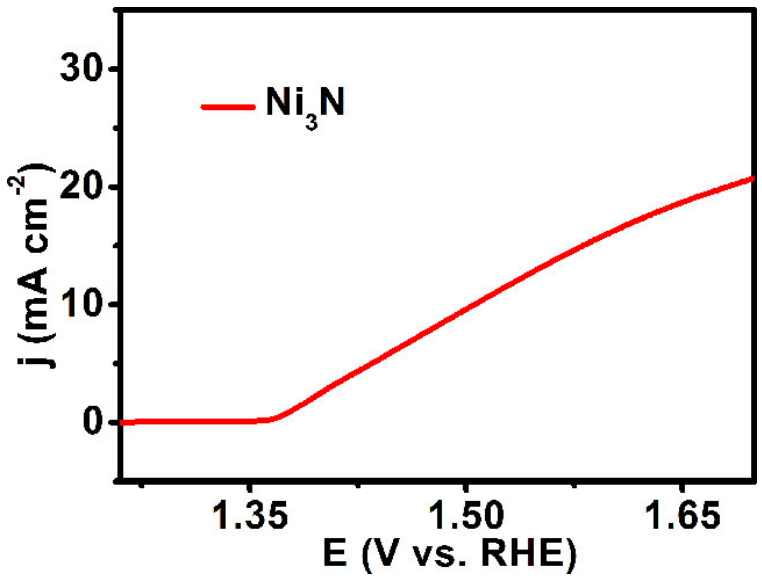

Fig. S5. LSV curves of pure Ni_3N in 1.0 M KOH with 0.33 M urea.

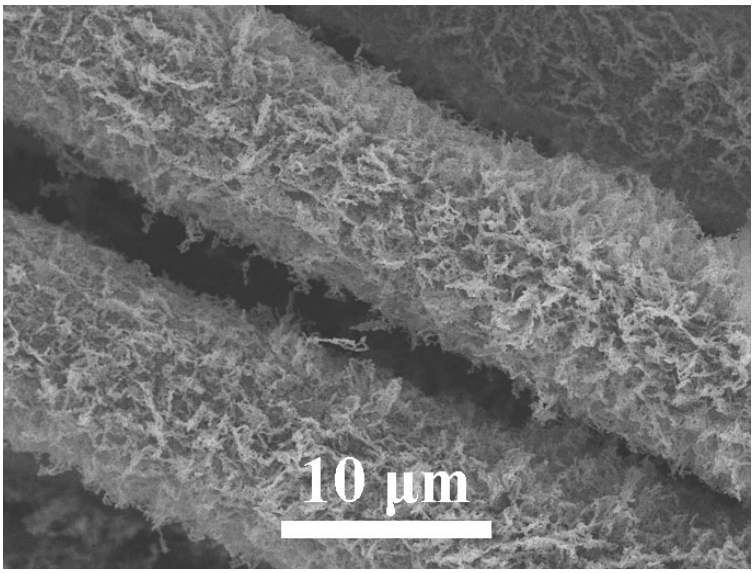

Fig. S6. SEM images for Ni_3N NA/CC after long stability test.

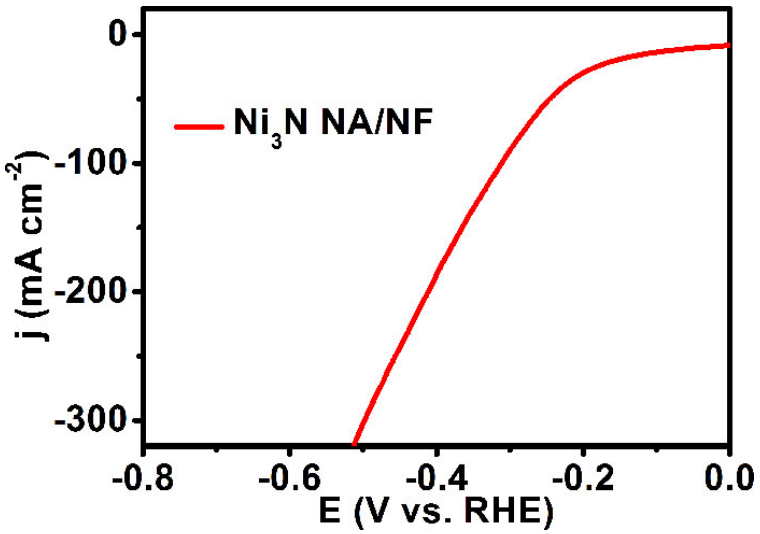

Fig. S7. LSV curves of Ni_3N NA/NF in 1.0 M KOH with 0.33 M urea.

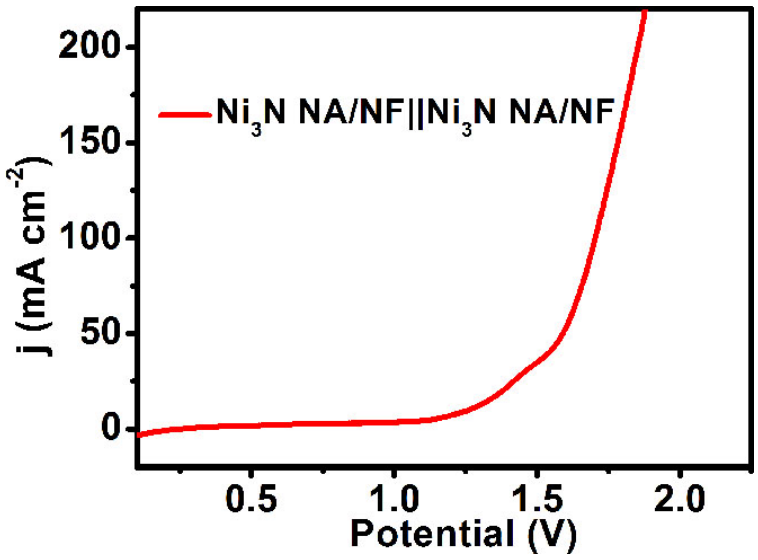

Fig. S8. Polarization curves for Ni_3N NA/NF||Ni_3N NA/NF in 1.0 M KOH with 0.33 M urea at scan rate of 5 mV s^{-1}.

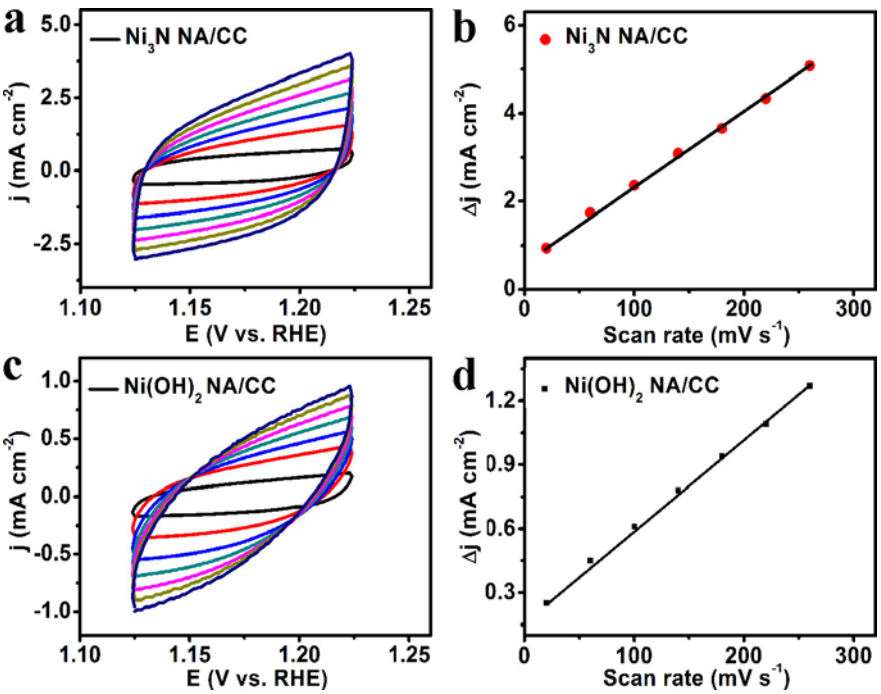

Fig. S9. (a) Ni_3N NA/CC and (c) $Ni(OH)_2$ NA/CC in the non-faradaic capacitance current range at scan rates of 20, 60, 100, 140, 180, 220 and 260 mV s^{-1}. (b) and (d) the capacitive currents at 1.175 V as a function of scan rate for Ni_3N NA/CC and $Ni(OH)_2$ NA/CC.

Table S1. Comparison of the UOR activity for several recently reported catalysts.

Catalyst	Potential at 10 mA cm^{-2} (V vs. RHE)	Mass loading (mg cm^{-2})	Ref.
L-MnO_2	1.37	1.5	1
Ni_2P NF	1.37	0.92	2
$Ni(OH)_2$ nanosheet	1.52	0.125	3
Rhodium-Ni	1.47	0.7	4
$Ni(OH)_2$ nanotube-NF	1.41	-	5
Graphene $Ni(OH)_2$	1.52	0.25	6
$Ni(OH)_2$ nanocube	1.55	0.3	7
NiO nanosheet array	1.38	0.27	8
NiMo sheet array	1.37	0.75	9
NiCo alloy	1.53	10	10
Pt	1.50	2.5	11
Ni foil	1.40	2	12
Rh-Ni	1.44	2	12
Nickel nanowire	1.44	1.3	13
Nickel film	1.48	1.3	13
ERGO-Ni	1.45	-	14
Ni_3N NA/CC	1.35	1.90	This work

Reference

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