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

Supporting Information

Large-current-stable bifunctional nanoporous Fe-rich nitride electrocatalysts for highly efficient overall water and urea splitting

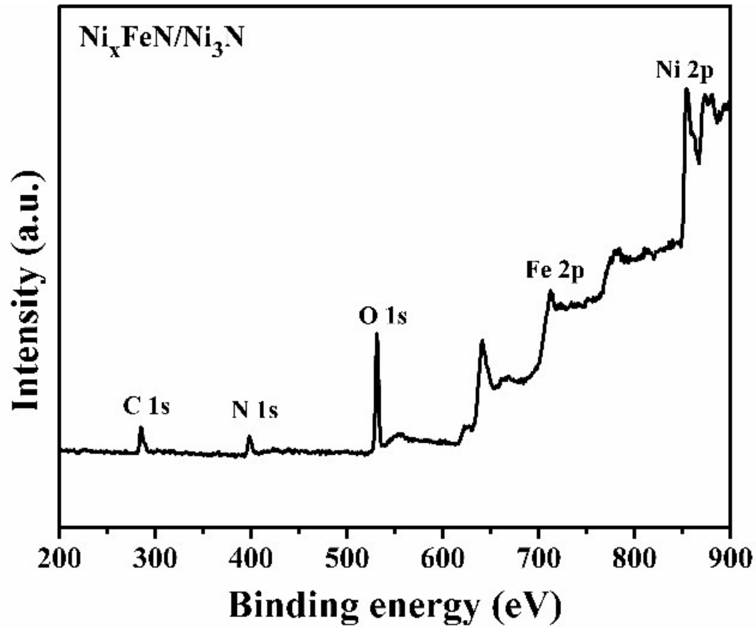

Figure S1. XPS survey spectrum of the as-prepared Ni$_x$FeN/Ni$_3$N hybrid on Ni foam.

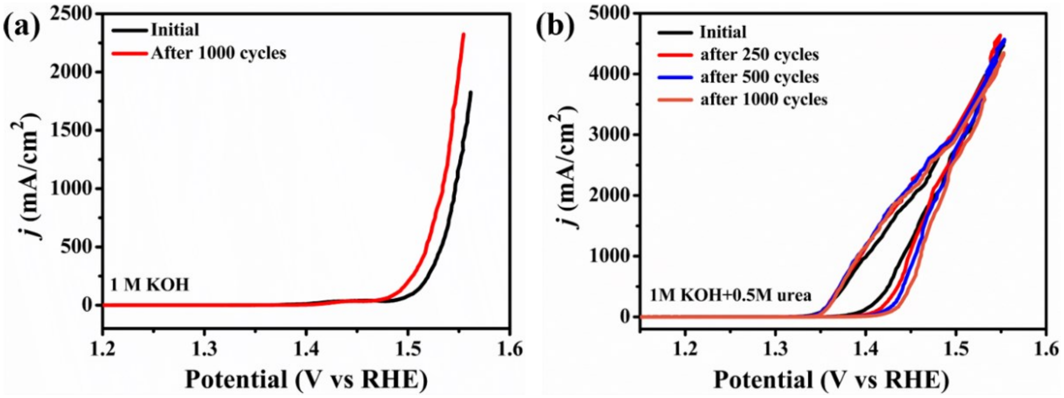

Figure S2. (a) The polarization curves for OER in 1M KOH and (b) cyclic voltammetry curves of the Ni$_x$FeN/Ni$_3$N catalysts for UOR in 1M KOH + 0.5M urea.

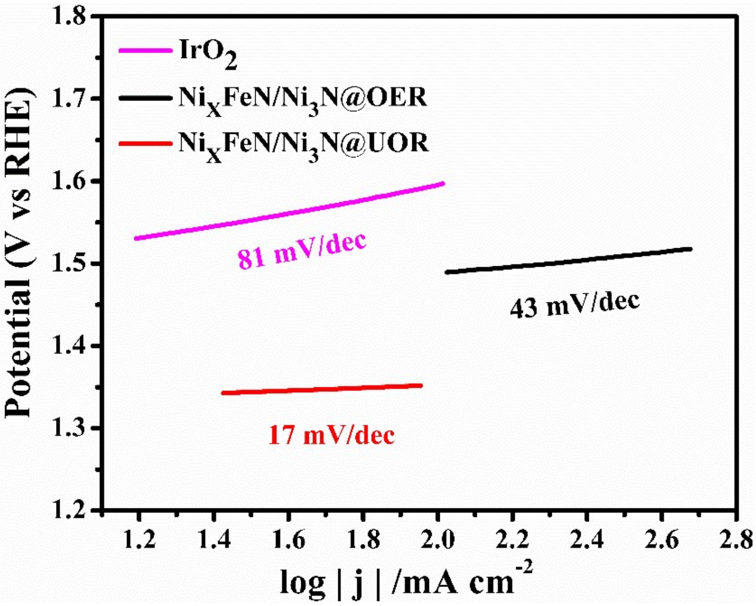

Figure S3. Tafel plots for the OER and UOR derived from corresponding polarization curve.

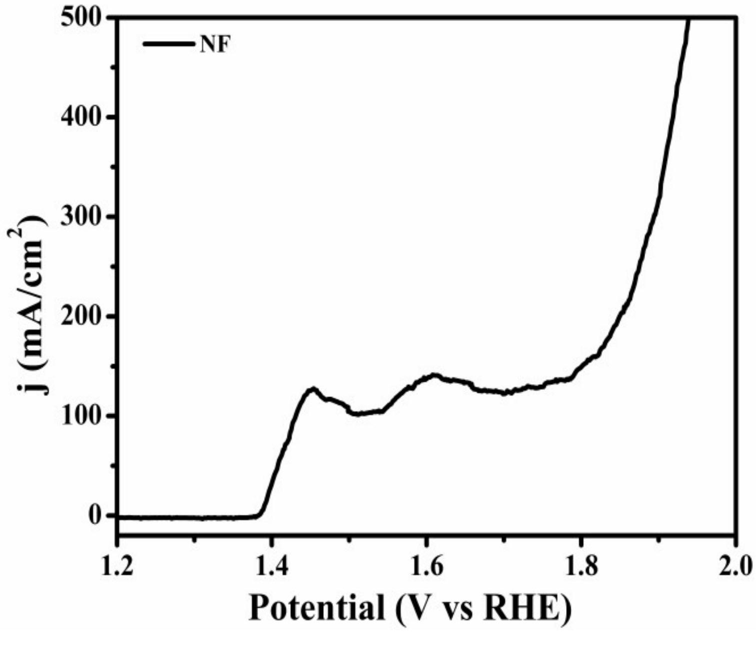

Figure S4. A steady-state potential polarization curve recorded on a piece of Ni foam in 1M KOH with 0.5M urea.

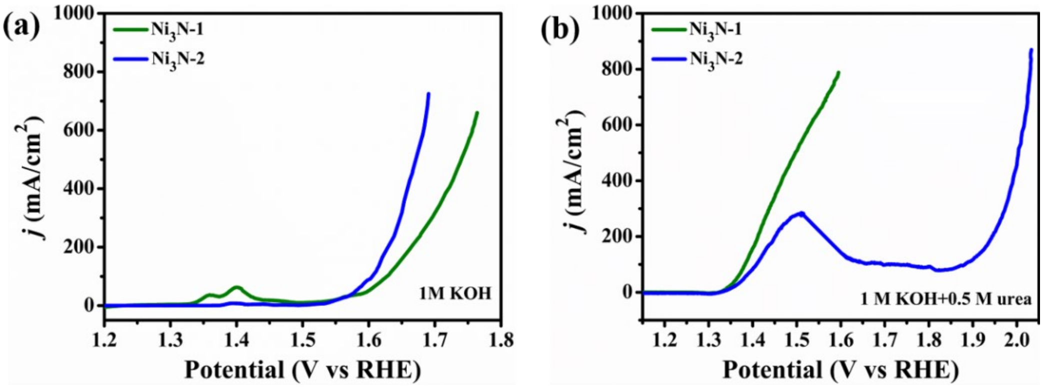

Figure S5. The polarization curves of the Ni_3N-1 and Ni_3N-2 catalysts for the OER in 1M KOH (a) and UOR in 1M KOH + 0.5M urea (b).

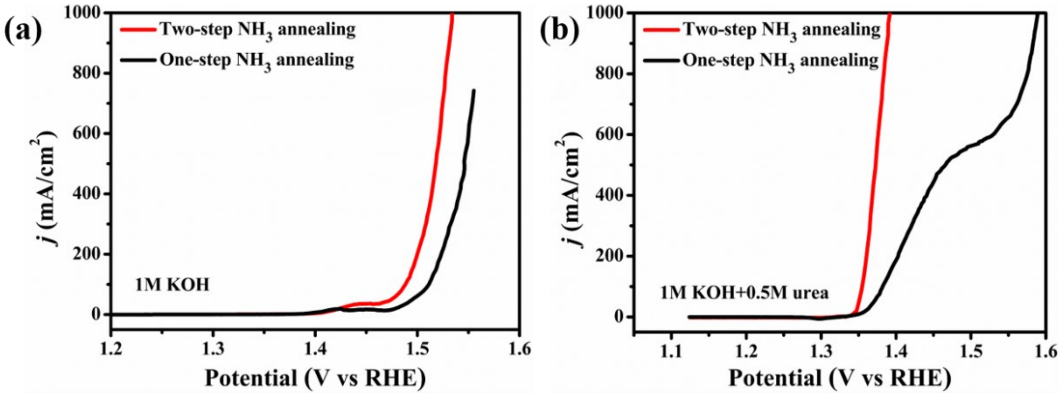

Figure S6. The comparison on the polarization curves of the Ni_xFeN/Ni_3N hybrid electrocatalyst using one- and two-step nitridation. (a) OER in 1M KOH. (b) UOR in 1M KOH containing 0.5M urea.

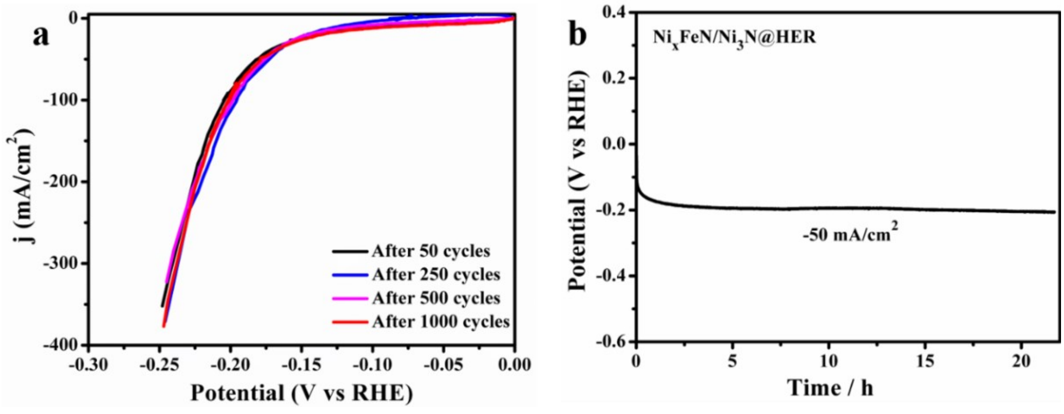

Figure S7. (a) The HER polarization curves of Ni_xFeN/Ni_3N in 1M KOH. (b) Chronopotentiometry test at a current density of 50 mA/cm^2 for Ni_xFeN/Ni_3N in alkaline medium.

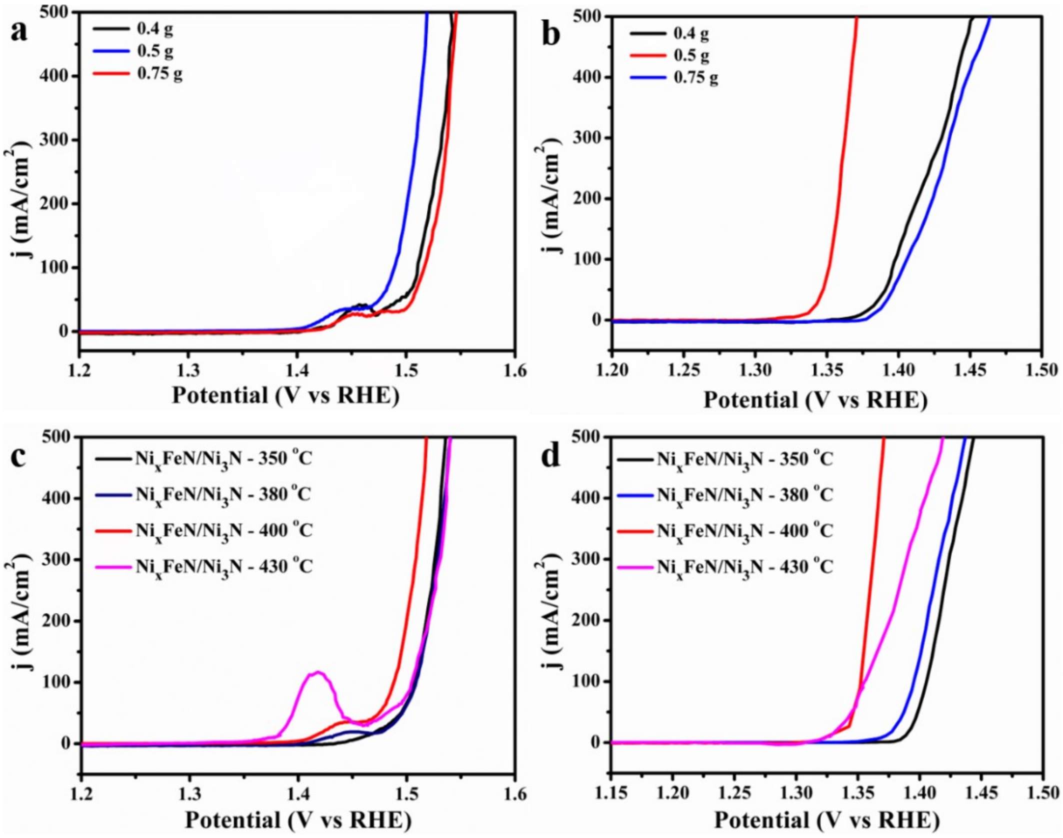

Figure S8. The optimization of the catalytic properties by tuning the growth conditions. (a) OER and (b) UOR properties of the Ni_xFeN/Ni_3N samples with different concentrations of $Fe(NO_3)_3$ precursor in 5 mL ethanol solution. Temperature: 400 °C. (c) OER and (d) UOR properties of the Ni_xFeN/Ni_3N hybrids with different nitridation temperature. Precursor concentration: 0.1 g/ml.

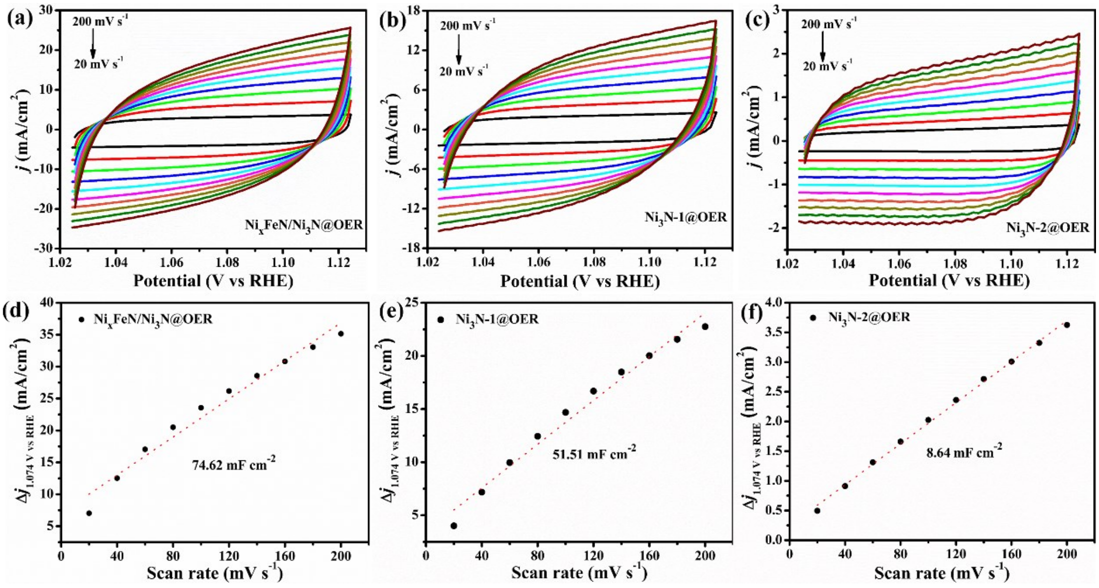

Figure S9. Double-layer capacitance measurements of the Ni_xFeN/Ni_3N hybrid, Ni_3N-1 and pure Ni_3N-2 electrodes in 1M KOH. (a-c) Typical cyclic voltammetry curves at the scan rates from 20 mV/s to 200 mV/s. (d-f) Capacitive ΔJ (= $J_a - J_c$) versus the scan rates.

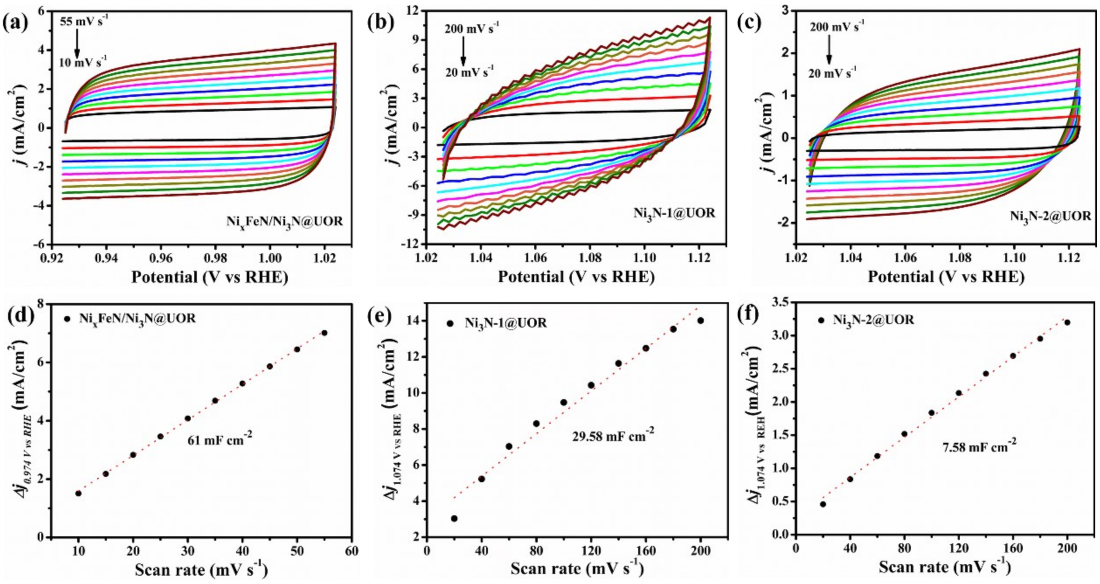

Figure S10. Double-layer capacitance measurements of the Ni_xFeN/Ni_3N hybrid, Ni_3N-1 and pure Ni_3N-2 electrodes in 1M KOH with 0.5 M urea. (a) Typical cyclic voltammetry curves at the scan rates from 10 mV s^{-1} to 55 mV s^{-1}. (b,c) Typical cyclic voltammetry curves at the scan rates from 20 mV s^{-1} to 200 mV s^{-1}. (d-f) Capacitive ΔJ (= $J_a - J_c$) versus the scan rates.

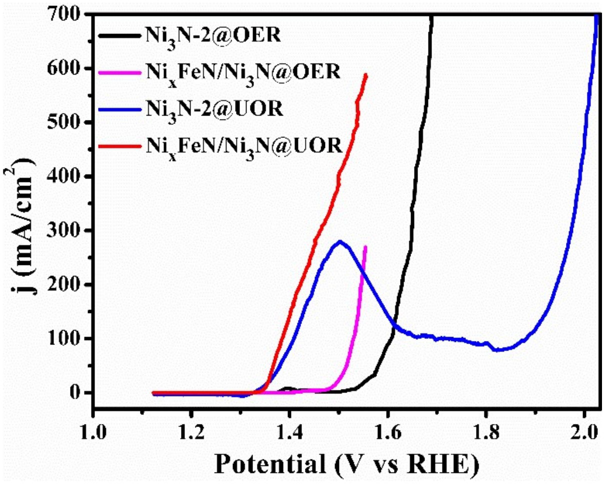

Figure S11. The normalized polarization curves of the Ni_xFeN/Ni_3N and pure Ni_3N-2 electrodes by C_{dl} difference in 1M KOH with and without 0.5M urea.

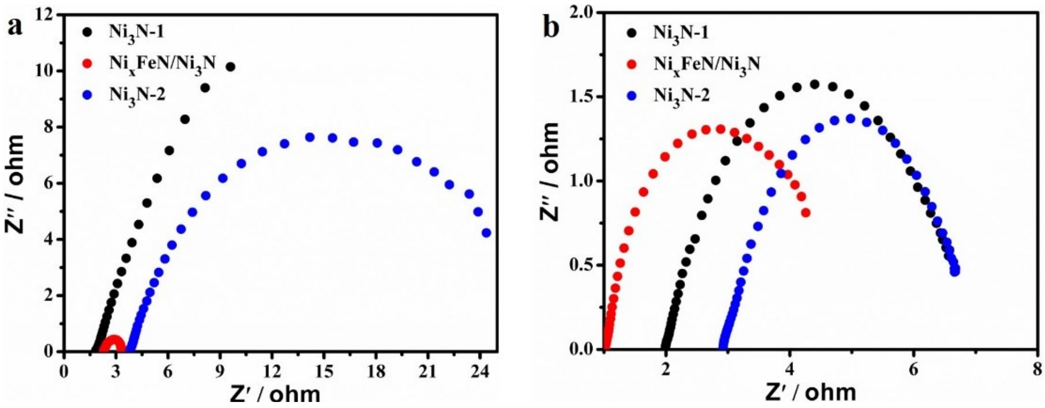

Figure S12. Nyquist plots of Ni_xFeN/Ni_3N, Ni_3N-1 and pure Ni_3N-2 in 1M KOH (a) and 1 M KOH containing 0.5 M urea (b).

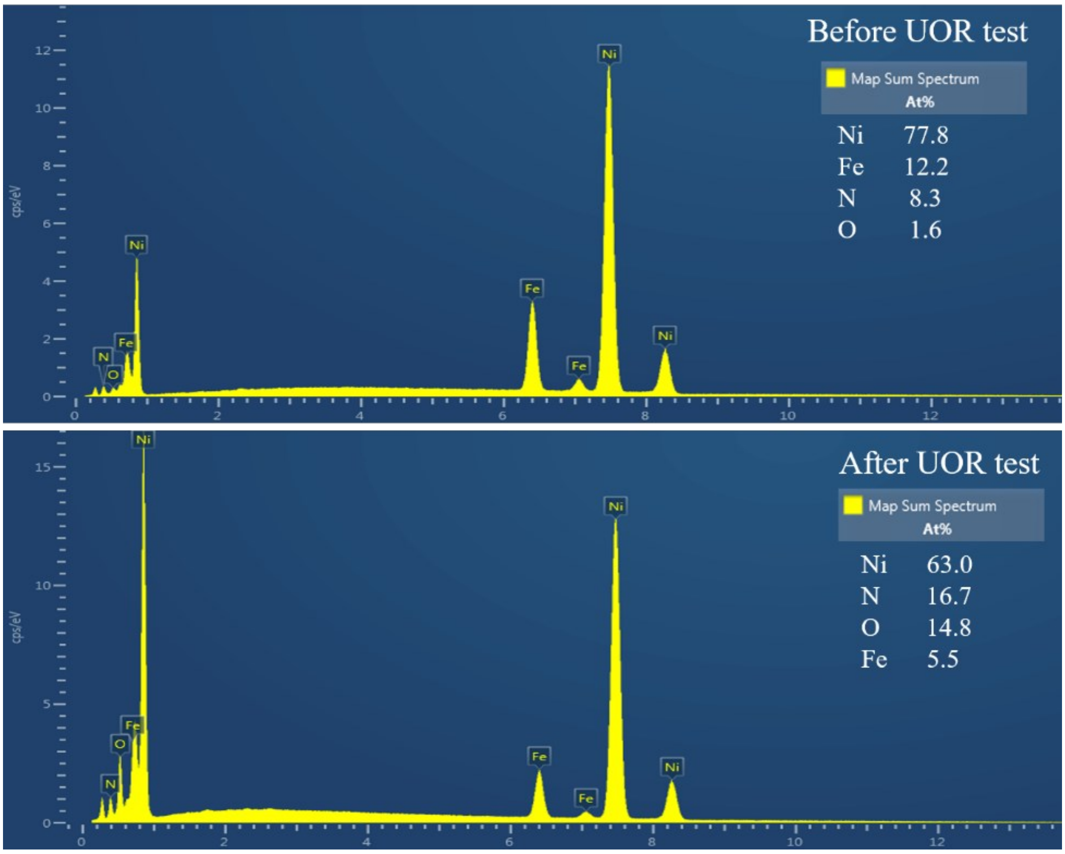

Figure S13. The EDX spectra of the Ni_xFeN/Ni_3N hybrid catalyst before (a) and after UOR testing (b).

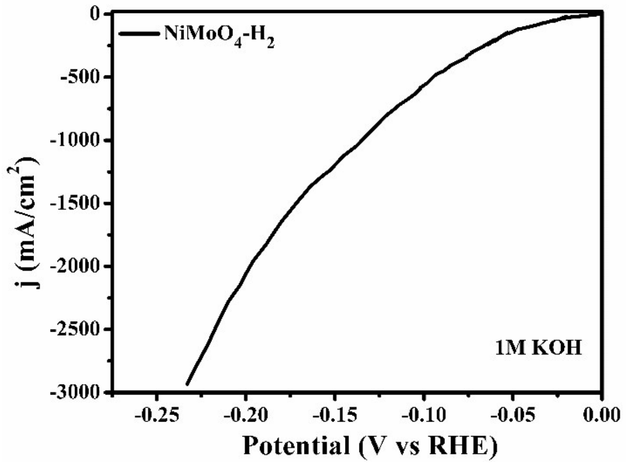

Figure S14. Hydrogen-evolving activity of the $NiMoO_4$-H_2 electrocatalyst in base.

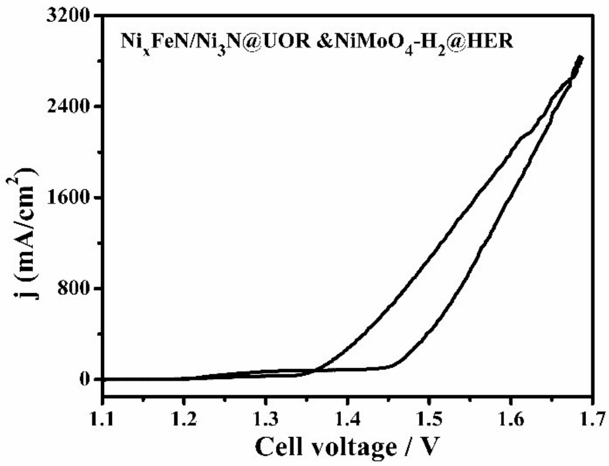

Fig. S15. A typical CV curve of urea electrolysis at a scan rate of 1 mV s^{-1}.

Table S1. Comparison of the OER activity of the Ni$_x$FeN/Ni$_3$N hybrid with other available electrocatalysts reported presently.

Electrocatalyst	OER overpotential @10 mA/cm^2	OER overpotential @100 mA/cm^2	Tafel slope	Ref
Ni$_x$FeN/Ni$_3$N	~ 211 mV	258 mV	43 mV/dec	This work
NiCoFeP/C	270 mV	335 mV	65 mV/dec	*Chem. Commun.* **55**, 10896-10899 (2019)
N-Ni$_3$S$_2$/NF	260 mV	330 mV	70 mV/dec	*Adv. Mater.* **29**, 1701584 (2017)
Co$_2$P/C	310 mV	375 mV	50 mV/dec	*ACS Energy Lett.* **1**, 169-174 (2016)
Ni$_{1.5}$Fe$_{0.5}$P/CF	264 mV	293 mV	55 mV/dec	*Nano Energy* **34**, 472-480 (2017)
NiFe LDH/Cu nanowire arrays	199 mV	281 mV	28 mV/dec	*Energy Environ. Sci.* **10**, 1820-1827 (2017)
Co-P	345 mV	392 mV	47 mV/dec	*Angew. Chem. Int. Ed.* **127**, 6349-6352 (2015)
Ni$_{0.7}$Fe$_{0.3}$S$_2$	198 mV	287 mV	56 mV/dec	*J. Mater. Chem. A* **5**, 15838-15844 (2017)
Ni$_x$Fe$_{1-x}$Se$_2$-DO	195 mV	226 mV*	28 mV/dec	*Nat. Commun.* **7**, 12324 (2016)
Gelled FeCoW/Au	191 mV	265 mV*	NA	*Science*

foam				**352**, 333-337 (2016)
$NiSe_2$-Ni_2P/NF	249 mV	274 mV	45 mV/dec	*J. Catal.* **377**, 600-608 (2019)
$Co_{0.9}S_{0.58}P_{0.42}$	266 mV	~ 350 mV	48 mV/dec	*ACS Nano* **11**, 11031-11040 (2017)
NiCoP/CC	242 mV	330 mV	64 mV/dec	*ACS Catal.* **7**, 4131-4137 (2017)
O-CoMoS	272 mV	310 mV	71 mV/dec	*ACS Catal* **8**, 4612-4621 (2018)
Ni-Co-P HNBs	270 mV	346 mV	76 mV/dec	*Energy Environ. Sci.* **11**, 872 (2018)
FeP/Ni_2P	154 mV	224 mV	23 mV/dec	*Nat. Commun.* **9**, 1551 (2018)

Table S2. Comparison of the UOR activity of Ni_xFeN/Ni_3N with other reported electrocatalysts in 1M KOH.

Electrocatalyst	UOR 50 mA/cm^2 (V vs RHE)	UOR 200 mA/cm^2 (V vs RHE)	Urea	Ref
Ni_xFeN/Ni_3N	1.347 V	1.358 V	0.5 M	This work
NF/NiMoO-Ar	1.398 V	1.475 V	0.5 M	*Energy Environ. Sci.* **11**, 1890 (2018)
Ni-Mo nanotube	1.39 V	~ 1.49 V	0.1 M	*Nano Energy* **60**, 894-902 (2019)
NiClO-D	1.385 V	1.534 V	0.33 M	*Angew. Chem. Int. Ed.* **58**, 16820-16825 (2019)
Ni_2P NF/CC	1.447 V	1.642 V	0.5 M	*J. Mater. Chem. A* **5**, 3208-3213 (2017)
$Ni_{0.9}Fe_{0.1}O_x$	1.386 V	1.429 V	0.33 M	*Chem. Commun.* **55**, 6555-6558 (2019)
$Ni(OH)_2$ nanoflakes	1.48 V	1.72 V	0.33 M	*Appl. Catal. B: Environ.* **259**, 118020 (2019)
NiCoP/CC	1.455 V	~ 1.70 V	0.5 M	*J. Mater. Chem. A* **7**, 9078-9085 (2019)
S-MnO_2-G-NF	1.414 V	1.564 V	0.5 M	*Angew. Chem. Int. Ed.* **55**, 3804-3808 (2016)
r-$NiMoO_4$/NF	1.405 V	1.577 V	0.5 M	*ACS Catal.* **8**, 1-7 (2018)

Ni_3N/NF	1.37 V	1.473 V	0.5 M	*ACS Appl. Mater. Interfaces.* **11**, 13168-13175 (2019)

Table S3. Comparison of the oveall water and urea electrolysis performance of our paired electrodes $Ni_xFeN/Ni_3N^{(+)}//NiMoO_4\text{-}H_2^{(-)}$ with other available water or urea electrolyzers reported thus far.

Electrolyzer configurations	**Water electrolysis @ 200 mA/cm^2**	**Water electrolysis @ 500 mA/cm^2**	**References**
$Ni_xFeN/Ni_3N^{(+)}\|NiMoO_4\text{-}H_2^{(-)}$	1.576 V	1.623 V	This work
$NiMoN@NiFeN^{(+)}//NiMoN^{(-)}$	1.610 V	1.696 V	*Nat. Commun.* **10**, 5106 (2019)
$Co_3Mo/Cu^{(+/-)}$	1.680 V	1.801 V	*Nat. Commun.* **11**, 2940 (2020)
CoFeZr oxides/NF$^{(+/-)}$	1.820 V	~ 1.86 V	*Adv. Mater.* **31**, 1901439 (2019)
$Ni_3FeN/r\text{-}GO^{(+/-)}$	> 2.10 V	NA	*ACS Nano* **12**, 245-253 (2018)
$Fe\text{-}O_2$ cat$^{(+)}$// $Fe\text{-}H_2$ cat$^{(-)}$	1.86 V	2.012 V	*Chem* **4**, 1139-1152 (2018)
NiFe LDH/Cu nanowire arrays$^{(+/-)}$	1.785 V	NA	*Energy Environ. Sci.* **10**, 1820-1827 (2017)
$Ni_{0.7}Fe_{0.3}S_2$/Ni foam$^{(+/-)}$	1.91 V	~ 2.07 V	*J. Mater. Chem. A* **5**, 15838-15844 (2017)
np-$Co_{1.04}Fe_{0.96}P^{(+/-)}$	1.65 V	~ 1.743 V	*Energy Environ. Sci.* **9**, 2257-2261 (2016)
NiFe LDH$^{(+)}$// $Ni@Cr_2O_3^{(-)}$	1.670 V	1.670 V	*Angew. Chem. Int. Ed.* **127**, 12157-12161 (2015)
NiFe LDH$^{(+)}$// NiO/Ni-CNT$^{(-)}$	~ 1.667 V	NA	*Nat. Commun.* **5**, 4695 (2014)
Electrolyzer configurations	**Urea electrolysis @ 200 mA/cm^2**	**Urea electrolysis @ 500 mA/cm^2**	**References**
$Ni_xFeN/Ni_3N^{(+)}//$ $NiMoO_4\text{-}H_2^{(-)}$	1.373 V	1.472 V	This work
NiMoO-Ar$^{(+)}$//	1.671 V	~ 1.85 V	*Energy Environ. Sci.*

NiMoO-$H_2^{(-)}$			**11**, 1890-1897 (2018)
CoFeCr LDH/$NF^{(+)}$ //Pt-C/$NF^{(-)}$	1.739 V	2.162 V	Appl. Catal B: Environ. 2020, 272, 118959
Co(OH)F/$NF^{(+)}$// CoP/$NF^{(-)}$	1.648 V	NA	*J. Mater. Chem. A* **7**, 3697-3703 (2019)
NiMo $nanotube^{(+/-)}$	~ 1.985 V	NA	*Nano Energy* **60**, 894-902 (2019)
$Zn_{0.08}Co_{0.92}P/TM^{(+/-)}$	2.064 V	NA	*Adv. Energy Mater.* **7**, 1700020 (2017)
CoS_2-$MoS_2^{(+/-)}$	1.575 V	1.673 V	*Adv. Energy Mater.* **8**, 1801775 (2018)
Ni_2P NF/$CC^{(+/-)}$	1.820 V	~ 2.250 V	*J. Mater. Chem. A* **5**, 3208-3213 (2017)
$Fe_{11.1\%}$-Ni_3S_2/Ni foam $^{(+/-)}$	1.980 V	NA	*J. Mater. Chem. A* **6**, 4346-4353 (2018)
MoP@NiCo-$LDH^{(+/-)}$	1.544 V	1.809 V	*J. Mater. Chem. A* DOI: 10.1039/d0ta06030e (2020)
$Ni_3N/NF^{(+/-)}$	1.501 V	1.705 V	*ACS Appl. Mater. Interfaces* **11**, 13168-13175 (2019)
MS-$Ni_2P/Ni_{0.96}S^{(+/-)}$	1.580 V	1.830 V	*ACS Appl. Mater. Interfaces* **12**, 2225-2233 (2020)

Supplementary Note 1: Synthesis of the Ni_3N-1 catalyst on Ni foam.

To synthesize this kind of samples, we just replaced the precursor from iron nitrate to nickel nitrate with other conditions similar to the growth of Ni_xFeN/Ni_3N hybrid, so as to get a similar mass loading of these two catalysts and compare the corresponding catalytic UOR or OER properties.

Supplementary Note 2: Synthesis of the Ni_3N-2 catalyst on Ni foam.

After directly treated at 400 ^oC in an ammonia environment (NH_3: 100 sccm), the Ni foam was dipped in an ethanol solution, which was dried in air naturally. Subsequently, the pre-modified Ni foam was placed at the middle of a tube furnace for a second nitridation under the same conditions as the Ni_xFeN/Ni_3N to gain Ni_3N/NF.