Supplementary Information

Dealloyed RuNiOₓ as a robust electrocatalyst for oxygen evolution reaction in acidic media

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Experiment Section

Materials: Ruthenium (III) chloride hydrate ($RuCl_3 \cdot xH_2O$), Cobalt (II) nitrate hexahydrate ($Co(NO_3)_2 \cdot 6H_2O$), Nickel (II) nitrate hexahydrate ($Ni(NO_3)_2 \cdot 6H_2O$) and PVP ($M_W=360,000$) were purchased from Aladdin Industrial Corp. Iron (III) nitrate nonahydrate ($Fe(NO_3)_3 \cdot 9H_2O$) was obtained from Sinopharm Chemical Reagent Co.,Ltd. All the chemicals were used as received without further purification. The carbon fiber paper (TORAY) substrate was clean by ethanol and then dried under nitrogen flow.

Synthesis of RuMOₓ: The ruthenium oxides were directly synthesized on CFP electrode by a dip-coating method with the prepared solution. For Ru-Ni oxides, the solution was prepared by mixing 0.2g $RuCl_3 \cdot xH_2O$, 0.2035g $Ni(NO_3)_2 \cdot 6H_2O$ and 0.16g PVP with 4ml ultra-pure water. CFPs (1cm × 2cm) were treated by O_2 plasma for 2min before dipping into the precursor. After dipping for about 10 seconds, CFPs were subsequently taken out. The obtained CFPs were annealed at 350℃ for 3 hours (ramping rate: 10℃ min⁻¹) in air atmosphere. The RuO_2, $RuFeO_x$ and $RuCoO_x$ were synthesized by similar procedure with adding 0.2g $RuCl_3 \cdot xH_2O$, 0.2828g $Fe(NO_3)_3 \cdot 9H_2O$ and and 0.2037g $Co(NO_3)_2 \cdot 6H_2O$.

Catalysts mass loading was calculated by the difference between the pristine CPFs and after annealed electrode. TGA test of RuO_2 has been investigated to prove the mass loading is accurate by this way. The tested electrode shows RuO_2 accounts for 13% (figure S10) of the electrode weight which is close to 12% (0.0021g of 0.0176g) calculated by the weighing difference.

Characterizations

The XRD analysis of all samples were carried out on mini Flex Guidance with Cu Kα radiation ($\lambda = 1.5406nm$ Å). For SEM, EDS results were taken from S-4800. The XPS scans were collected by AXIS Ultra DLD.

Electrochemical Measurements

All electrochemical measurements were taken under the three-electrodes test system by using a CHI 660E electrochemical analyzer (CH instrument, Inc., Shanghai). Since materials were in-situ grown on CFP, it directly can

be used as the working electrode. Carbon electrode and a saturated calomel electrode (SCE) were used as the counter and reference electrodes. OER measurements were conducted in O_2-saturated 0.5 M H_2SO_4 electrolyte. LSV analysis was recorded under a scan rate at 0.01V s^{-1} between 1-1.5V (vs. SCE).

ECSA were carry out by CV analysis under different scan rate: from 0.01 to 0.05 V s^{-1}. The CV cycles under different scan rate were turned out into a linear relationship between current and scan rate. The double layer capacitances (Cdl) were used to calculate ECSA where Cdl of RuO_2 is considered as a standard value represented to one square centimeter of Ru electrochemical activity surface area. Dealloying treatment and durability performance can be reflected in CV tests between 1.0 -1.4 V (vs. SCE) under a scan rate at 0.5 V s^{-1}. De-alloyed Ru-M oxides were obtained after 1,000 CV cycles tests of post Ru oxides.
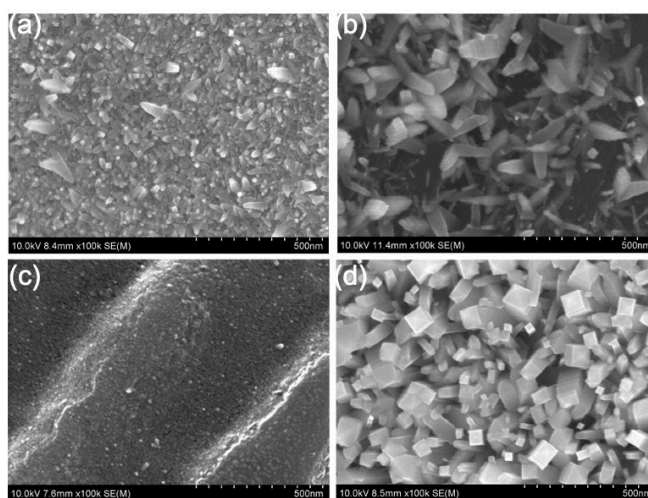

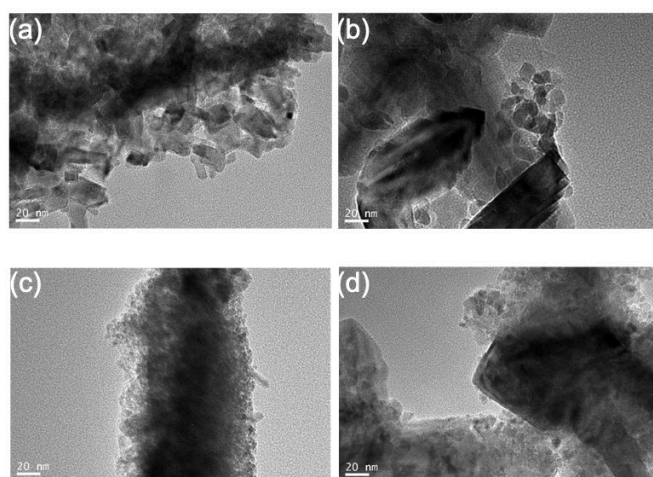Figure S1: SEM patterns of (a) RuO_2, (b) $RuFeO_x$, (c) $RuCoO_x$ and (d) $RuNiO_x$.

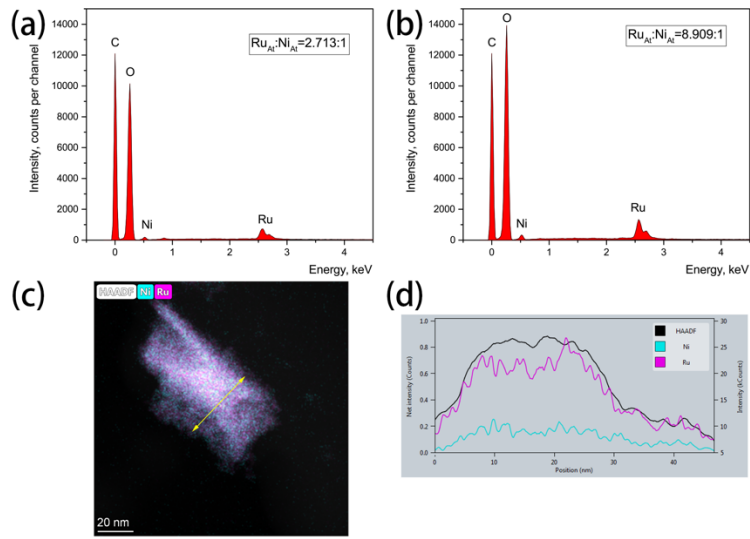Figure S2. TEM patterns of (a) RuO_2 (b) $RuFeO_x$, (c) $RuCoO_x$ and (d) $RuNiO_x$.

Figure S3: EDS results of RuNiO$_x$ (a)before and (b) after dealloying treatment; Ni and Ru distribution of the dealloyed particle (c) and the line across the particle(d).
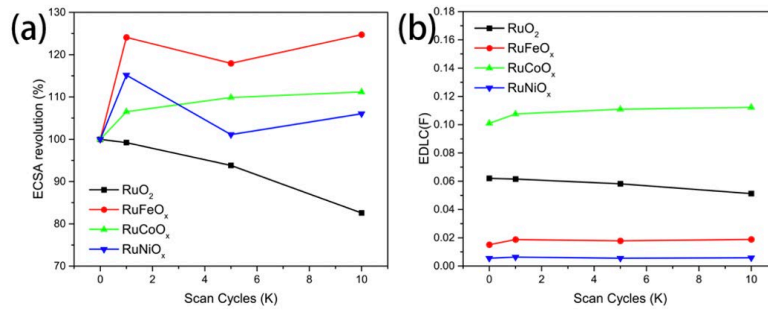

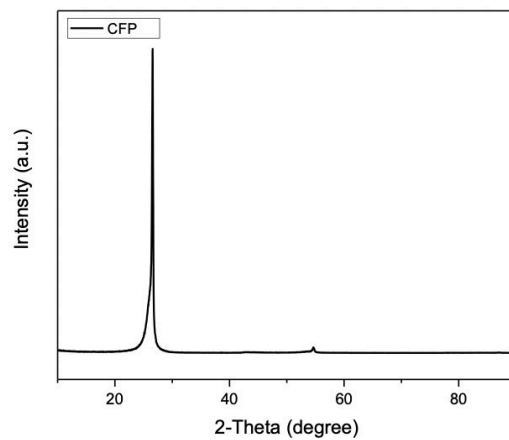Figure S4. ECSA (a) revolution and (b) EDLC change of RuO$_2$, RuFeO$_x$, RuCoO$_x$ and RuNiO$_x$.

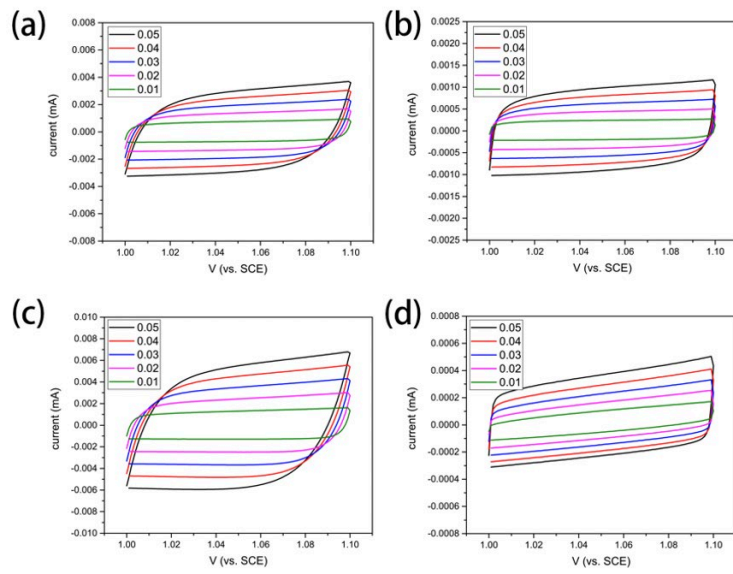Figure S5. XRD pattern of carbon fiber paper substrate

Figure S6. CV cycles under scan rate at 0.01-0.05V s^{-1} of (a) RuO$_2$, (b) RuFeO$_x$, (c) RuCoO$_x$ and (d) RuNiO$_x$.
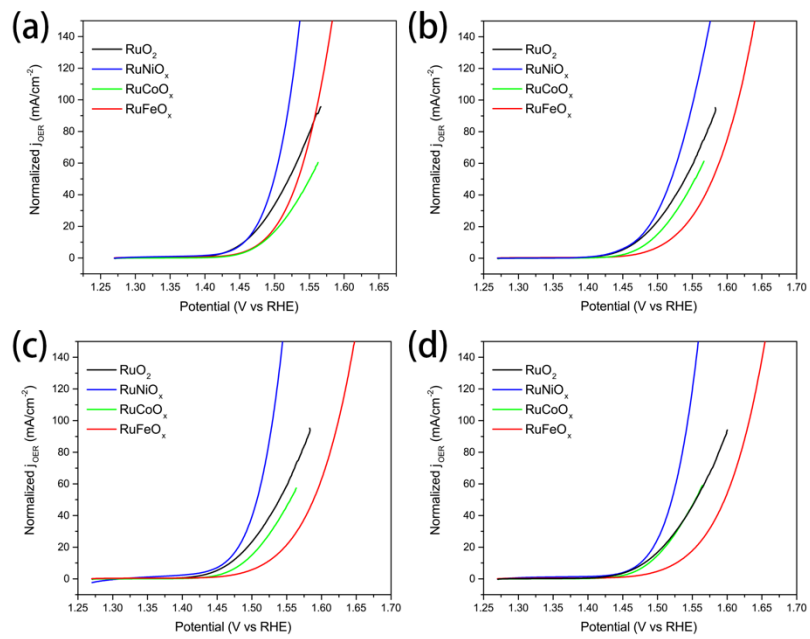

Figure S7. LSV of RuO$_2$, RuFeO$_x$, RuCoO$_x$ and RuNiO$_x$ after (1) 0, (2) 1,000, (3) 5,000 and (4) 10,000 CV cycles.
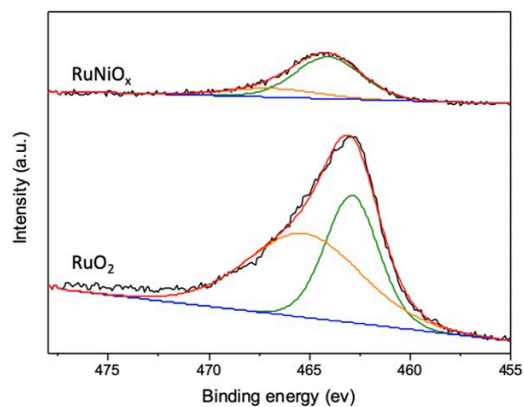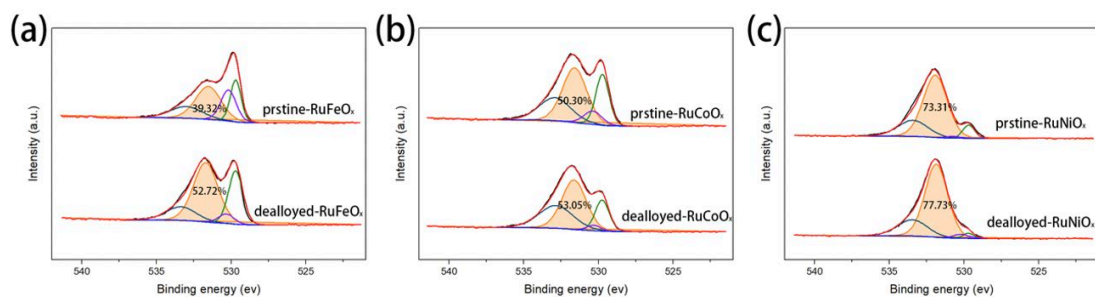
Figure S8. XPS spectra of Ru 3p.

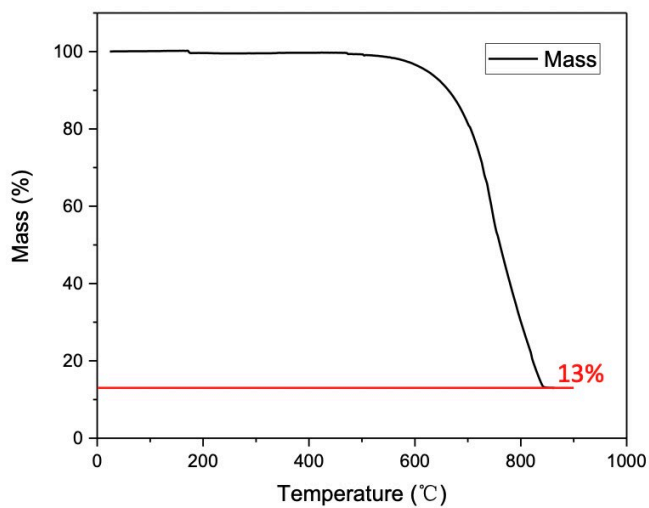Figure S9. O1s XPS spectra of pristine and dealloyed (a) RuFeO$_x$, (b) RuCoO$_x$ and (c) RuNiO$_x$.

Figure S10. TGA analysis of RuO$_x$.

Table S1. Double layer capacitance (F) of RuO2, RuFeOx, RuCoOx and RuNiOx.

Samples	Pristine (F)	1,000 cycles (F)	5,000 cycles (F)	10,000 cycles (F)
RuO2	0.06233	0.06225	0.05832	0.04977

RuFeOx	0.01429	0.01829	0.01749	0.01816
RuCoOx	0.10946	0.11667	0.12143	0.12051
RuNiOx	0.00456	0.00461	0.00464	0.00608

Table S2. Atom ratio of Ru to Ni after 1,000, 5,000 and 10,000 cycles.

	As prepared	1,000 cycles	5,000 cycles	10,000 cycles
Ru/Ni	3.965	6.797	5.327	4.947