



## Supporting Information

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Oxygen-Rich Carbon Nitrides from an Eutectic Template Strategy Stabilize Ni, Fe Nanosites for Electrocatalytic Oxygen Evolution

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## Supplementary information

### Oxygen-rich carbon nitrides from a eutectic template strategy stabilize Ni, Fe nanosites for electrocatalytic oxygen evolution

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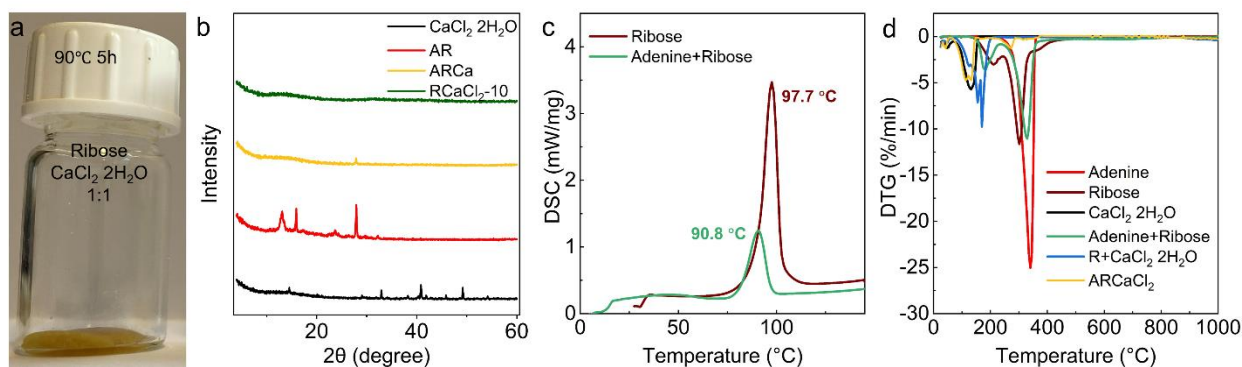


Figure S1 (a) picture of ribose and  $\text{CaCl}_2 \cdot 2\text{H}_2\text{O}$  in a 90 °C oven for 5 hours, (b) XRD, (c) DSC, and (d) DTG of the mixture of precursors and salt.

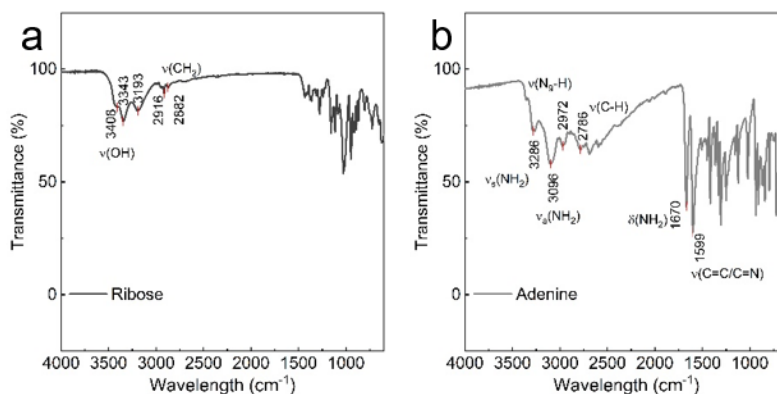


Figure S2 FTIR of (a) D-Ribose, (b) adenine

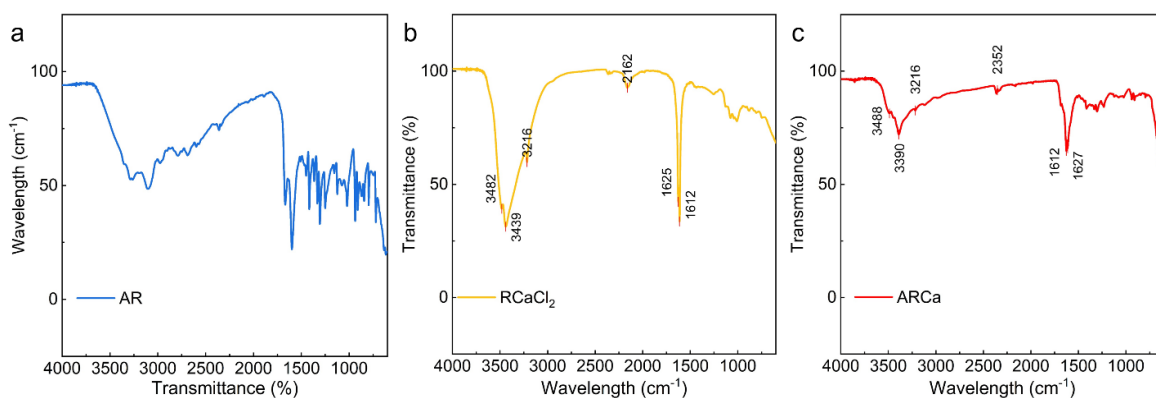


Figure S3 FTIR of (a) adenine and ribose, (b) ribose and CaCl<sub>2</sub>·2H<sub>2</sub>O, and (c) adenine, ribose, and CaCl<sub>2</sub>·2H<sub>2</sub>O.

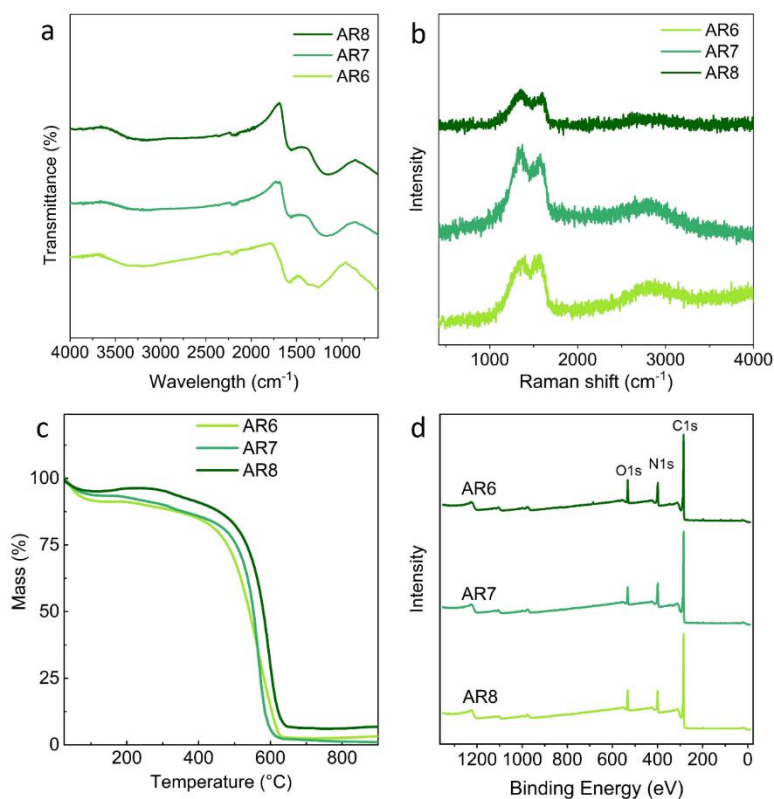


Figure S4 (a) FTIR spectra, (b) Raman spectra, (c) TGA curves, and (d) XPS survey spectra of AR6, AR7, and AR8.

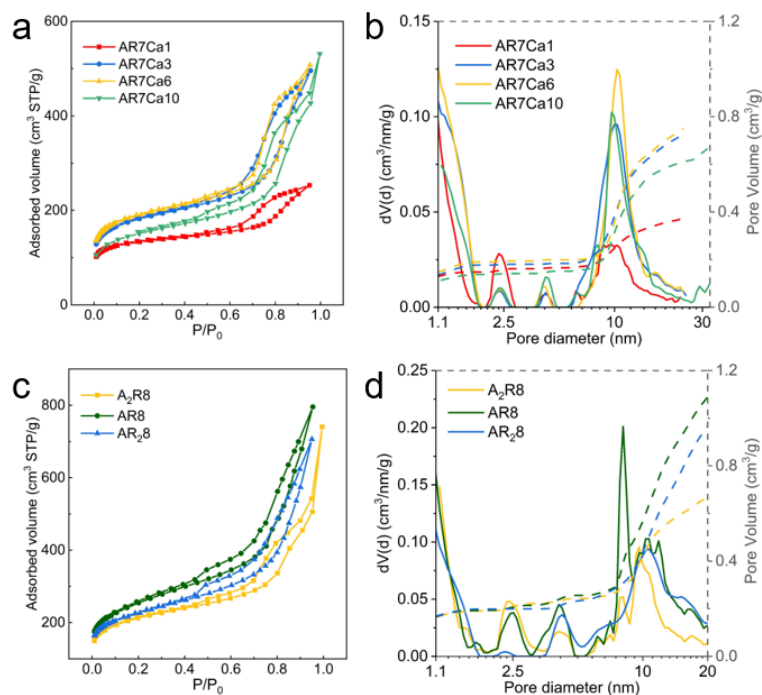


Figure S5 (a) N<sub>2</sub> adsorption-desorption isotherms (b) pore distribution of samples with different salt/precursor ratios and (c, d) samples with different adenine/ribose ratios.

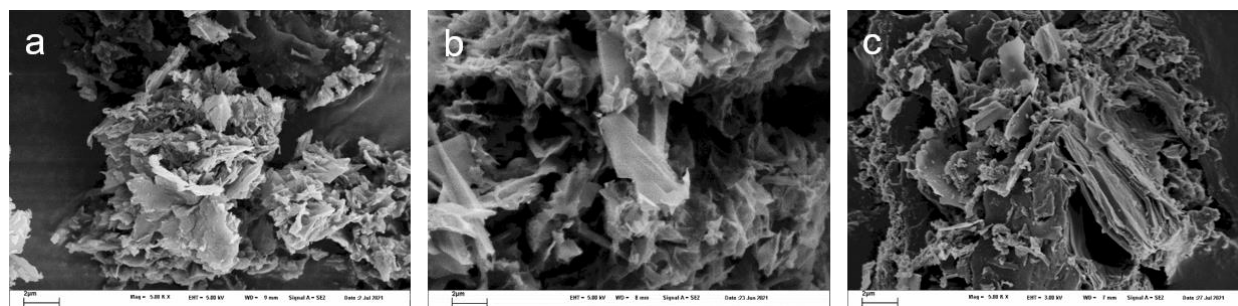


Figure S6 SEM images of (a) AR6, (b) AR7, and (c) AR8

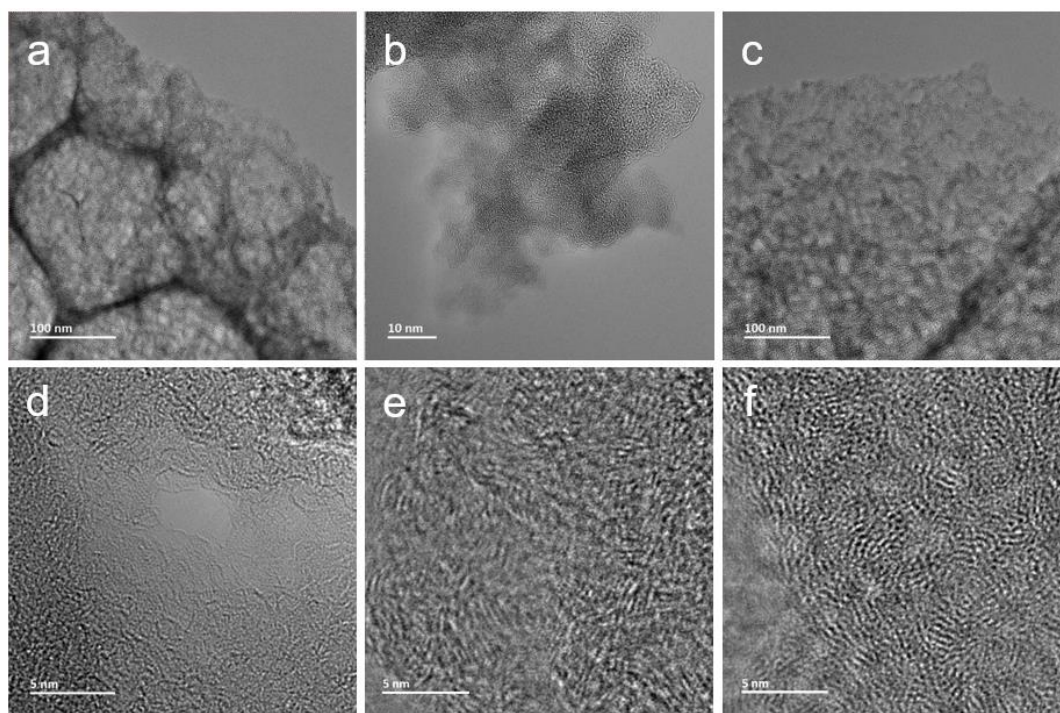


Figure S7 TEM image of (a) AR6, (b) AR7, and (c) AR8, HRTEM images of (d) AR6, and (e, f) AR7

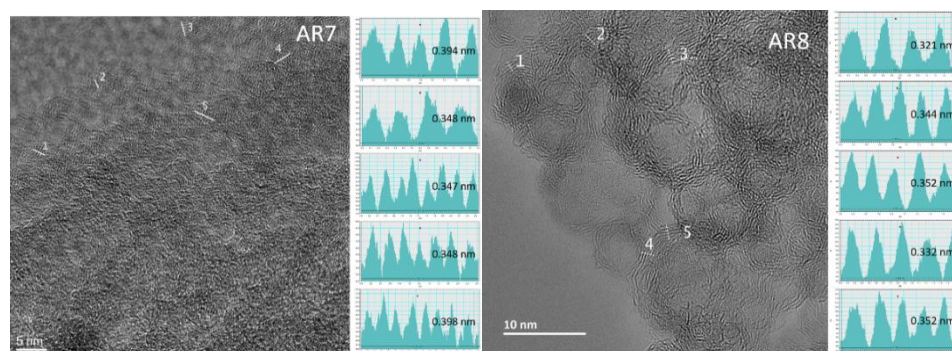


Figure S8 TEM images and high profiles of AR7 and AR8.

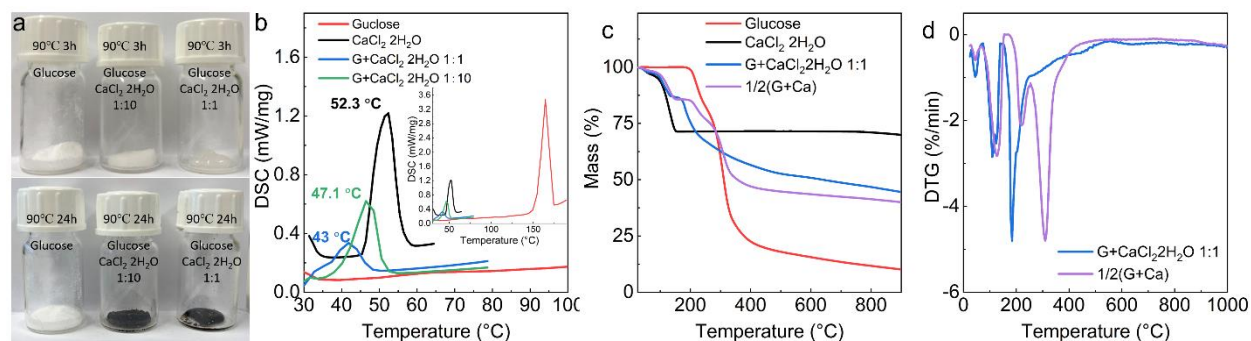


Figure S9 (a) digital photo of glucose, and the mixture with  $\text{CaCl}_2 \cdot 2\text{H}_2\text{O}$  in a 90 °C oven after 3 and 24 hours, (b) DSC curves, (c) TGA curves, and (d) DTG curves of glucose,  $\text{CaCl}_2 \cdot 2\text{H}_2\text{O}$  and their mixture. The label 1/2(G+ Ca) is mathematically integrated by the individual glucose and  $\text{CaCl}_2 \cdot 2\text{H}_2\text{O}$ .

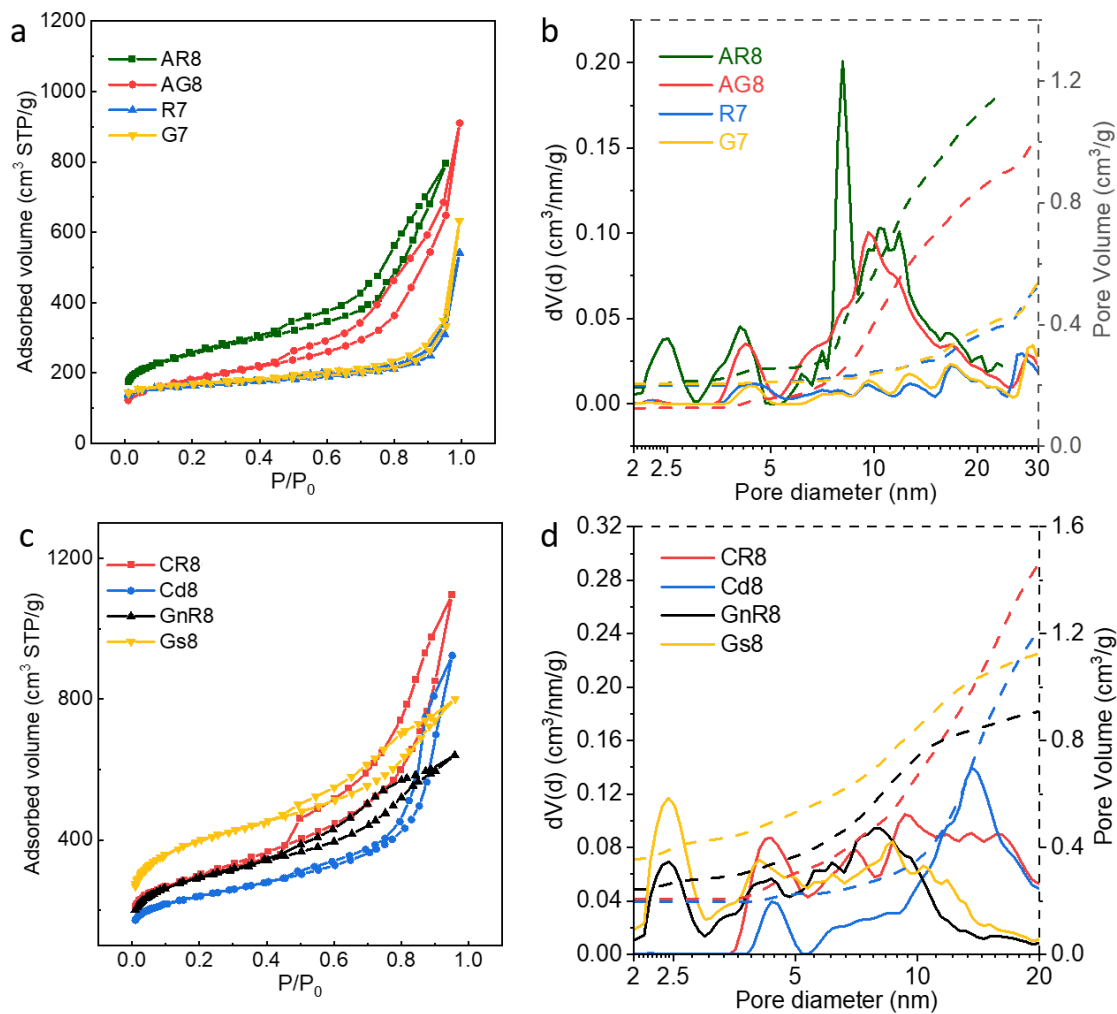


Figure S10 (a) N<sub>2</sub> sorption-desorption isotherms, (b) pore volume and pore distribution of AR8, AG8, R7, and G7. (c) N<sub>2</sub> sorption-desorption isotherms, (d) pore volume and pore distribution of CR8, Cd8, GnR8

and Gs8.

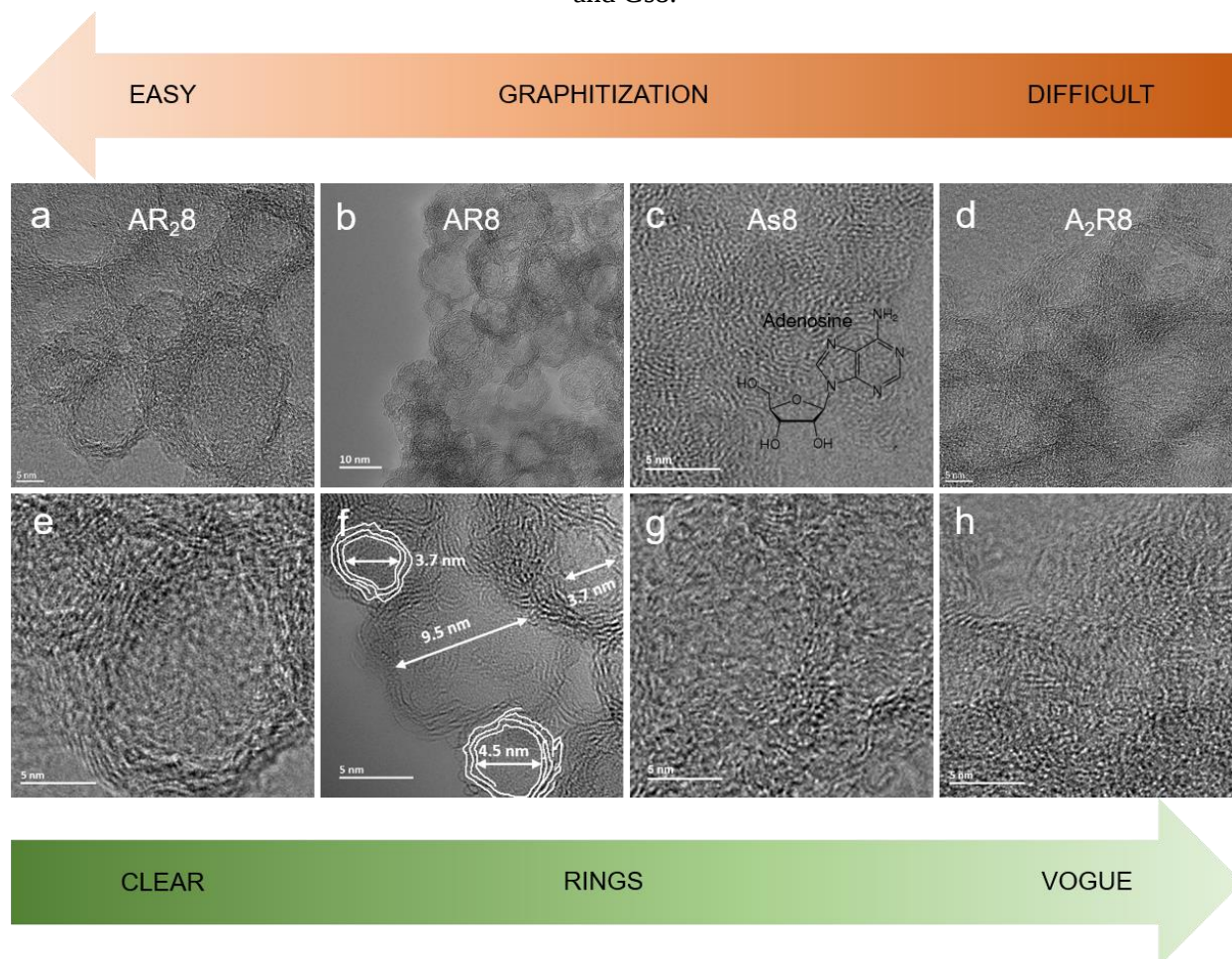


Figure S11 TEM images of (a, e) AR<sub>2</sub>8, (b, f) AR8, (c, g) As8, and (d, h) A<sub>2</sub>R8.

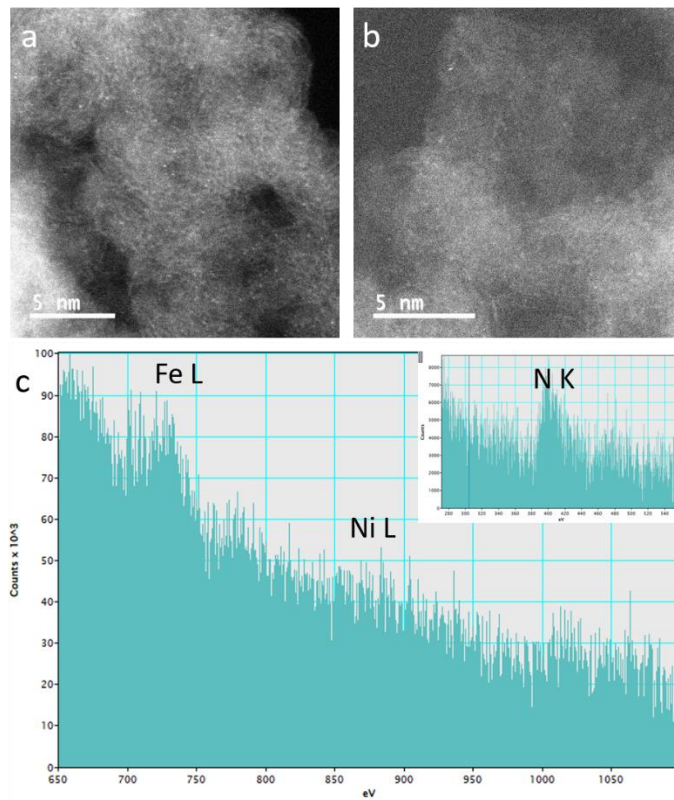


Figure S12 (a, b) HAADF-STEM images of AR8\_Ni<sub>1</sub>Fe<sub>0.2</sub>\_A. and (c) EELS atomic spectra of Fe, Ni, and N elements from the bright dots in Figure 5b.

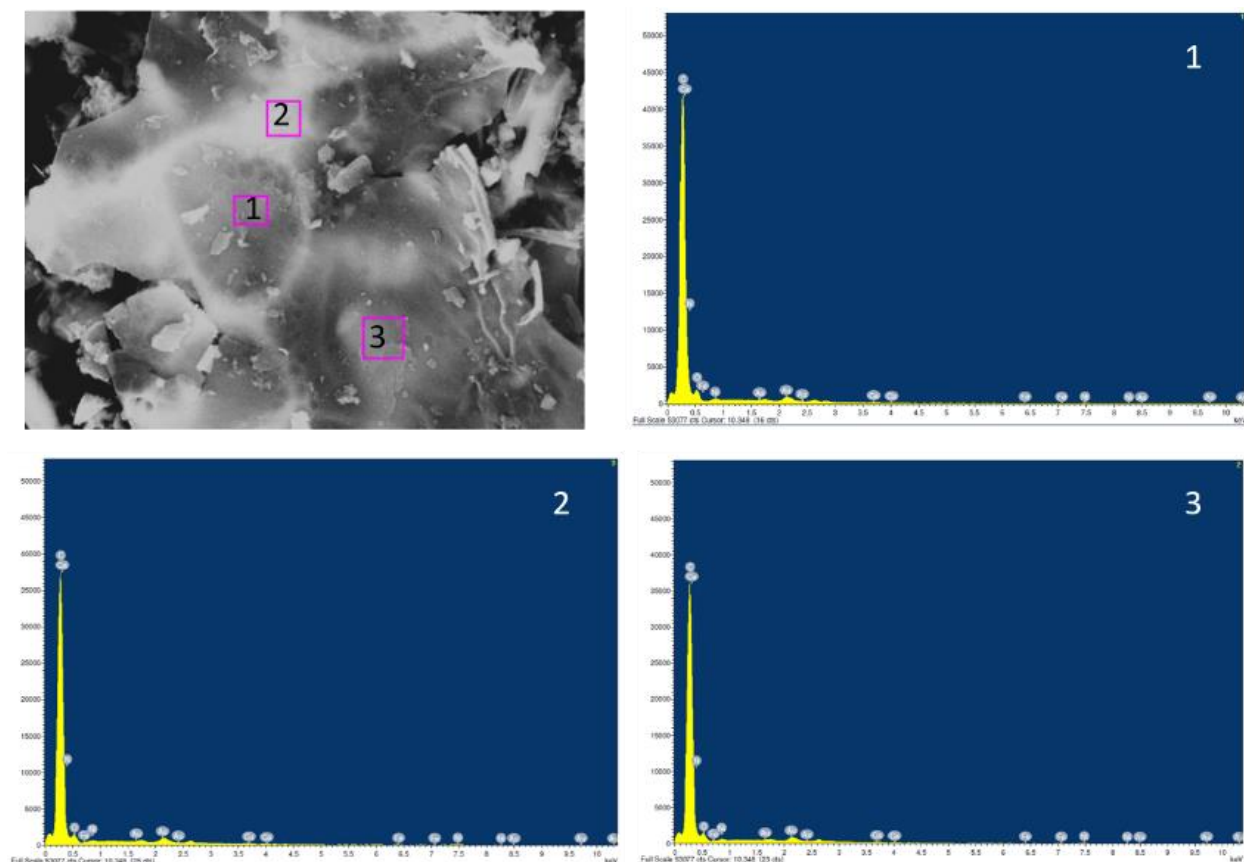


Figure S13. SEM micrograph and EDX spectrum of AR8\_Ni<sub>1</sub>Fe<sub>0.2</sub>\_A.

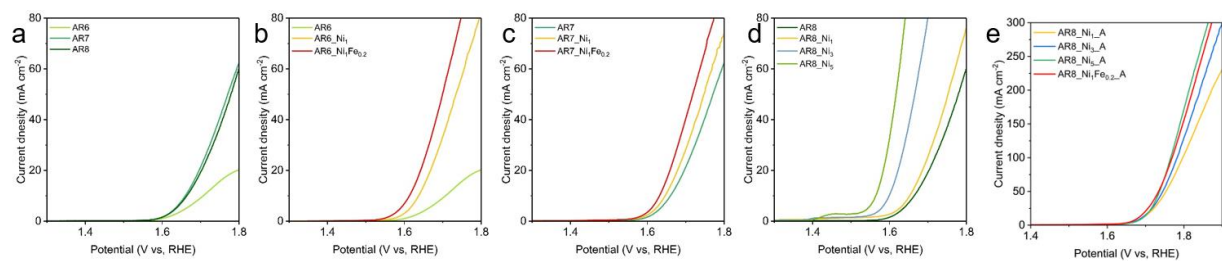


Figure S14 LSV curves of (a) CNOs, and (b-e) their comparison after loading metals.

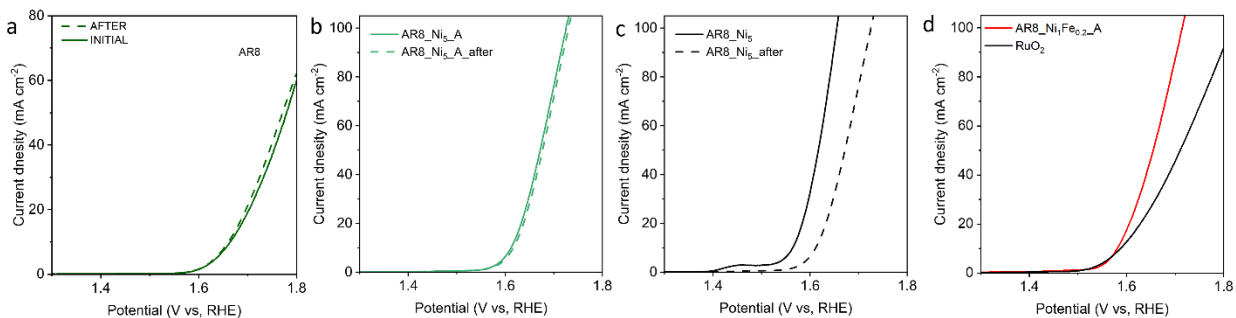


Figure S15 LSV curves of (a) AR8, (b) AR8\_Ni<sub>5</sub>, and (c) AR8\_Ni<sub>5</sub>\_A before and after 1000 cycles CV and (d) comparison of AR8\_Ni<sub>5</sub>Fe<sub>0.2</sub>\_A and RuO<sub>2</sub>

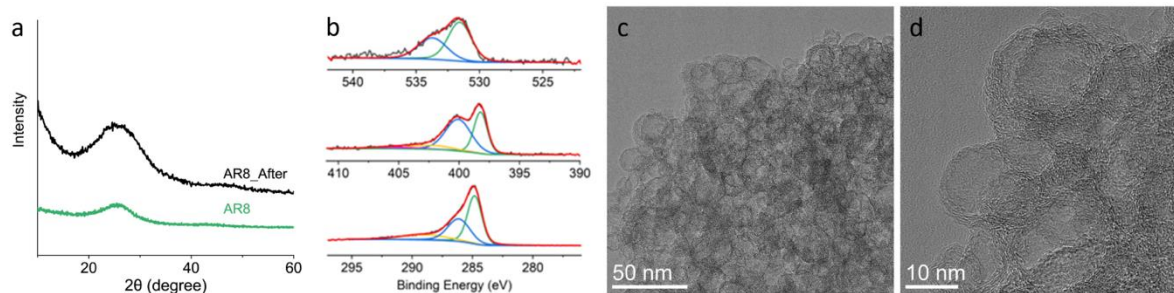


Figure S16 (a) XRD patterns of AR8 before and after durability test, (b) (Top to bottom) XPS deconvoluted O1s, N1s, C1s signals, and (c-d) TEM images of AR8 after 1000 cycles CV as durability test.

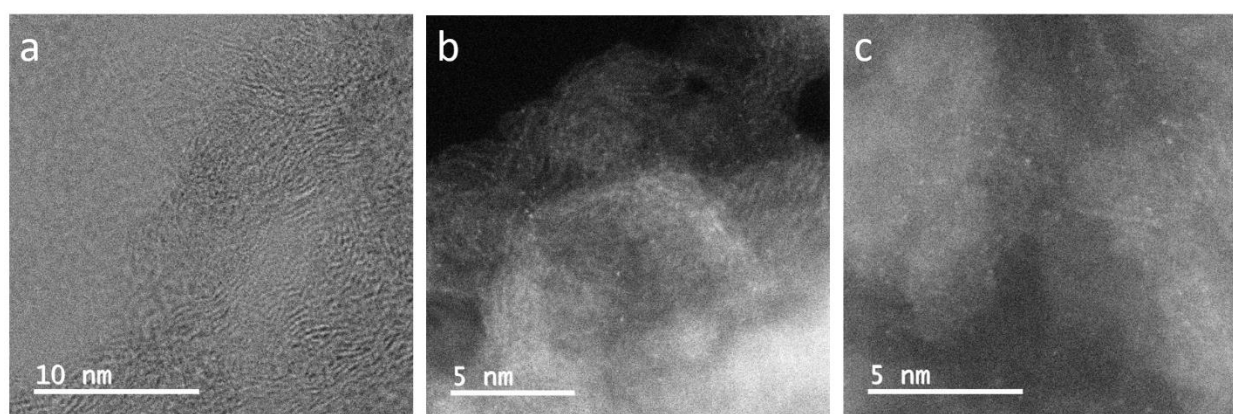


Figure S17 TEM image and HAADF-STEM images of AR8\_Ni<sub>1</sub>Fe<sub>0.2</sub>\_A after stability test.

Table S1: Element analysis results

| Sample    | C[wt%] | N[wt%] | O[wt%] | H[wt%] | C/N  | C/N(atomic) | Ca   |
|-----------|--------|--------|--------|--------|------|-------------|------|
| AR7Ca1    | 55.6   | 23.4   | 19     | 2      | 2.38 | <b>2.78</b> |      |
| AR7Ca3    | 59.6   | 25     | 13.4   | 2      | 2.38 | <b>2.78</b> |      |
| AR7Ca6    | 61.3   | 26     | 10.5   | 2.2    | 2.36 | <b>2.75</b> |      |
| AR7(Ca10) | 63.8   | 20.5   | 13.1   | 2.6    | 3.1  | <b>3.62</b> | 0.25 |
| AR8       | 63.7   | 20.7   | 13.2   | 2.4    | 3.1  | <b>3.62</b> | 0.27 |
| AR6       | 63.8   | 20.5   | 12.75  | 2.95   | 3.1  | <b>3.62</b> | 0.11 |

Table S2 Peak information from XPS

|               | Sample | C1<br>C=C | C2<br>C-N | C3<br>C=N | N1<br>pyridinic | N2<br>pyrrolic | N3<br>quaternary | N4<br>N-O | O1<br>O-H | O2<br>O-C |
|---------------|--------|-----------|-----------|-----------|-----------------|----------------|------------------|-----------|-----------|-----------|
| Peak position | AR6    | 284.75    | 286.23    | 288.79    | 398.7           | 400.47         | 402.64           | 405.22    | 532.19    | 533.7     |
|               | AR7    | 284.78    | 286.32    | 288.74    | 398.3           | 400.1          | 402.09           | 404.3     | 531.99    | 533.54    |
|               | AR8    | 284.8     | 286.33    | 288.73    | 398.1           | 400            | 401.61           | 404.3     | 531.8     | 533       |
| Atomic %      | AR6    | 67.5      | 24.8      | 7.7       | 43.2            | 42             | 8.1              | 6.7       | 77        | 23        |
|               | AR7    | 65        | 22.2      | 12.8      | 36.1            | 42.1           | 14.3             | 7.5       | 65.7      | 34.3      |
|               | AR8    | 63.2      | 23.7      | 13.1      | 33.2            | 40.4           | 16.7             | 9.7       | 65.3      | 34.7      |

Table S3: Summary of surface area and pores size distribution derived from  $N_2$  adsorption experiments.

| Sample            | $S_{BET}$<br>[m <sup>2</sup> /g] | Total pore<br>volume<br>(cc/g) |
|-------------------|----------------------------------|--------------------------------|
| AR7Ca1            | 499                              | 0.364                          |
| AR7Ca3            | 670                              | 0.692                          |
| AR7Ca6            | 699                              | 0.707                          |
| AR7Ca10           | 545                              | 0.683                          |
| AR6               | 275                              | 0.49                           |
| A <sub>2</sub> R8 | 766                              | 0.883                          |
| AR8               | 906                              | 1.17                           |
| AR <sub>2</sub> 8 | 818                              | 1.034                          |
| AG8               | 641                              | 1.01                           |
| R7                | 626                              | 0.482                          |
| G7                | 643                              | 0.518                          |

Table S4 Content of metals from ICP and overpotentials of the samples

| Sample                                | Ni[wt%]        | Fe[wt%] | Ni[wt%]       | Fe   | Overpotential (mV) @<br>j=10 mA cm <sup>-2</sup><br>Before/after etching |
|---------------------------------------|----------------|---------|---------------|------|--------------------------------------------------------------------------|
|                                       | Before etching |         | After etching |      |                                                                          |
| AR6_Ni <sub>1</sub>                   | 2.2            |         |               |      | 407                                                                      |
| AR6_Ni <sub>1</sub> Fe <sub>0.2</sub> | 1.4            | 0.13    |               |      | 383                                                                      |
| AR7_Ni <sub>1</sub>                   | 2.7            |         |               |      | 416                                                                      |
| AR7_Ni <sub>1</sub> Fe <sub>0.2</sub> | 2.8            | 0.18    |               |      | 401                                                                      |
| AR8_Ni <sub>1</sub>                   | 2.6            |         | 0.61          |      | 424/387                                                                  |
| AR8_Ni <sub>1</sub> Fe <sub>0.2</sub> | 1.9            | 0.21    | 0.6           | 0.04 | 351                                                                      |
| AR8_Ni <sub>3</sub>                   | 5.7            |         | 0.73          |      | 368/383                                                                  |
| AR8_Ni <sub>5</sub>                   | 16.2           |         | 0.64          |      | 334/382                                                                  |
| AR8_Fe <sub>1</sub> _A                |                |         |               | 0.26 | 433                                                                      |
| AR8_Fe <sub>3</sub> _A                |                |         |               | 0.38 | 435                                                                      |
| AR8_Fe <sub>5</sub> _A                |                |         |               | 0.32 | 443                                                                      |

Table S5 Comparison of the OER performances of different transition-metal single atoms on carbon materials.

| Catalyst                                                                                              | Overpotential<br>j=10 mA cm <sup>-2</sup> @ | Electrolyte | +AC | Ref                                    |
|-------------------------------------------------------------------------------------------------------|---------------------------------------------|-------------|-----|----------------------------------------|
| S NiNx-PC/EG<br>Ni: 0.2 wt. %                                                                         | 280                                         | 1.0<br>KOH  | M   | Nat Commun 10, 1392<br>(2019)          |
| Ni-NHGF<br>(0.275 mg cm <sup>-2</sup> ) Ni: 0.05 at %                                                 | 330                                         | 1.0<br>KOH  | M N | Nat. Catal. 2018, 1, 63                |
| FeCo-Nx-CN (single or multi-atom)<br>(0.1 mg cm <sup>-2</sup> ) Fe: 0.40 at % ,Co: 0.12 at %          | 370                                         | 1.0<br>KOH  | M N | Angew. Chem. Int. Ed. 2018, 57, 1856   |
| S,N-Fe/N/C-CNT<br>(0.6 mg cm <sup>-2</sup> ) Fe: 0.8 at %                                             | 370                                         | 0.1<br>KOH  | M N | Angew. Chem. Int. Ed. 2017, 56, 610    |
| A-Ni@DG<br>(0.262 mg/cm <sup>-2</sup> ) Ni:1.24 wt %                                                  | 270                                         | 1.0<br>KOH  | M N | Chem 4, 285–297                        |
| NiFe@g-C <sub>3</sub> N <sub>4</sub> /CNT<br>(0.382 mg/cm <sup>-2</sup> ) Ni: 0.84 at %, Fe:0.92 at % | 326                                         | 1.0<br>KOH  | M N | J. Mater. Chem. A, 2018,6, 6840-6846   |
| Ni-CN-200<br>(79 µg cm <sup>-2</sup> ) Ni:2.4 at %                                                    | 310@1 mA cm <sup>-2</sup>                   | 1.0<br>KOH  | M N | Carbon 124 (2017): 180-187             |
| Ni@NC (Ni nanoparticles)<br>(0.4 mg cm <sup>-2</sup> ) Ni: 10wt %                                     | 390                                         | 0.1<br>KOH  | M N | Adv. Energy Mater. 2015, 5, 1401660    |
| nNiFe LDH/3D MPC (0.26 mg cm <sup>-2</sup> ) Ni:3.31 at%                                              | 340                                         | 0.1<br>KOH  | M N | J. Mater. Chem. A, 2018,6, 14299-14306 |
| NiFe LDH nanosheets                                                                                   | 340                                         | 1.0<br>KOH  | M N | Nano Energy, 81, 105606.               |
| AR8_Ni <sub>5</sub> (1 mg cm <sup>-2</sup> ) Ni: 0.6 wt%, Fe: 0.04 wt%                                | 351                                         | 0.1<br>KOH  | M N | <b>Our work</b>                        |