# Supporting Information

## N-doped 3D porous Ni/C bifunctional electrocatalysts for alkaline water electrolysis

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total number of tables : 2; total number of equations : 1

Figure 2 shows the particle size distribution histogram for the Ni/C electrocatalyst, determined neglecting the few agglomerated or very large nanoparticles. The diameters of 300 randomly selected particles were measured and the Ni/C nanoparticles particle averaged diameter was calculated to be 16 nm according to the formula:

$$d = \sum f_i d_i^3 / \sum f_i d_i^2 \qquad \text{S1}$$

where $f_i$ is the ratio of particles, $d_i$ is diameter.

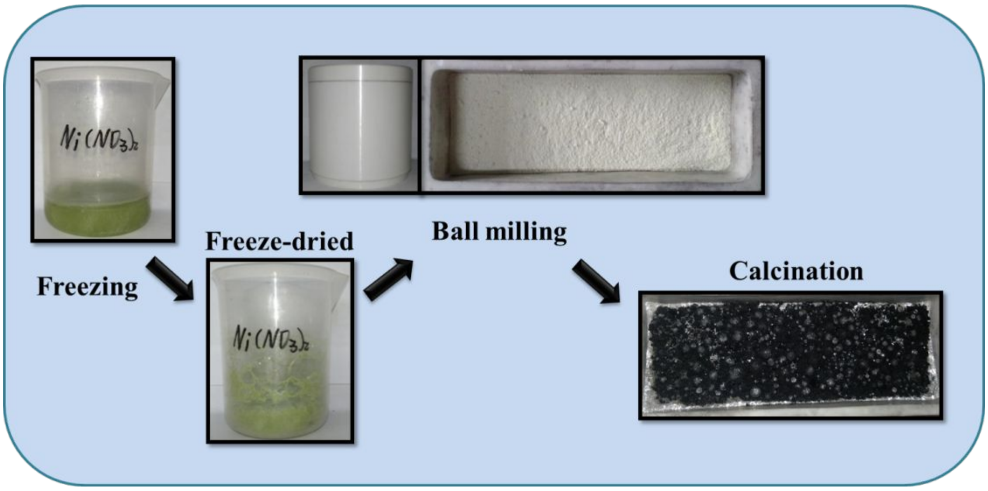


**Figure S1.** Experiment procedure of preparing Ni/C samples.

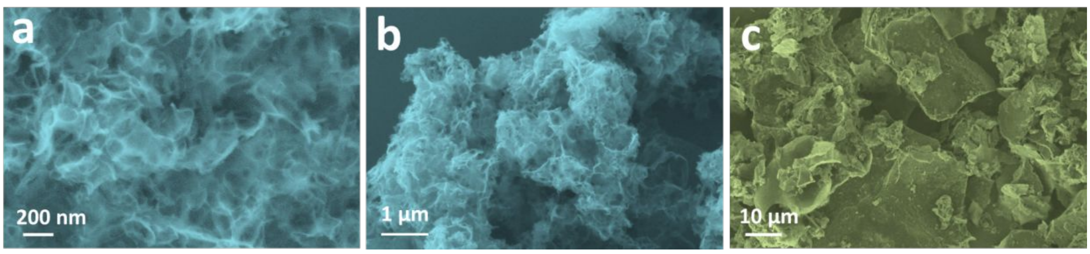


**Figure S2.** (a) SEM images of the C; (b) the low magnification SEM image of Ni-2; (c) SEM images of the C synthesized products without NaCl.

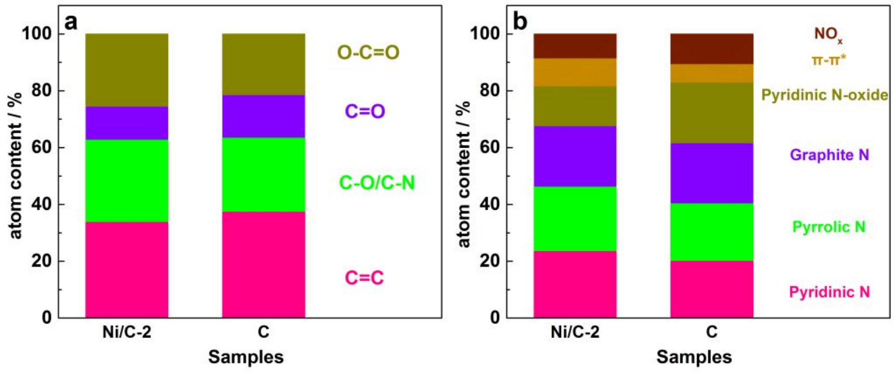


**Figure S3.** C (a) and N (b) surface composition of C and Ni-2.

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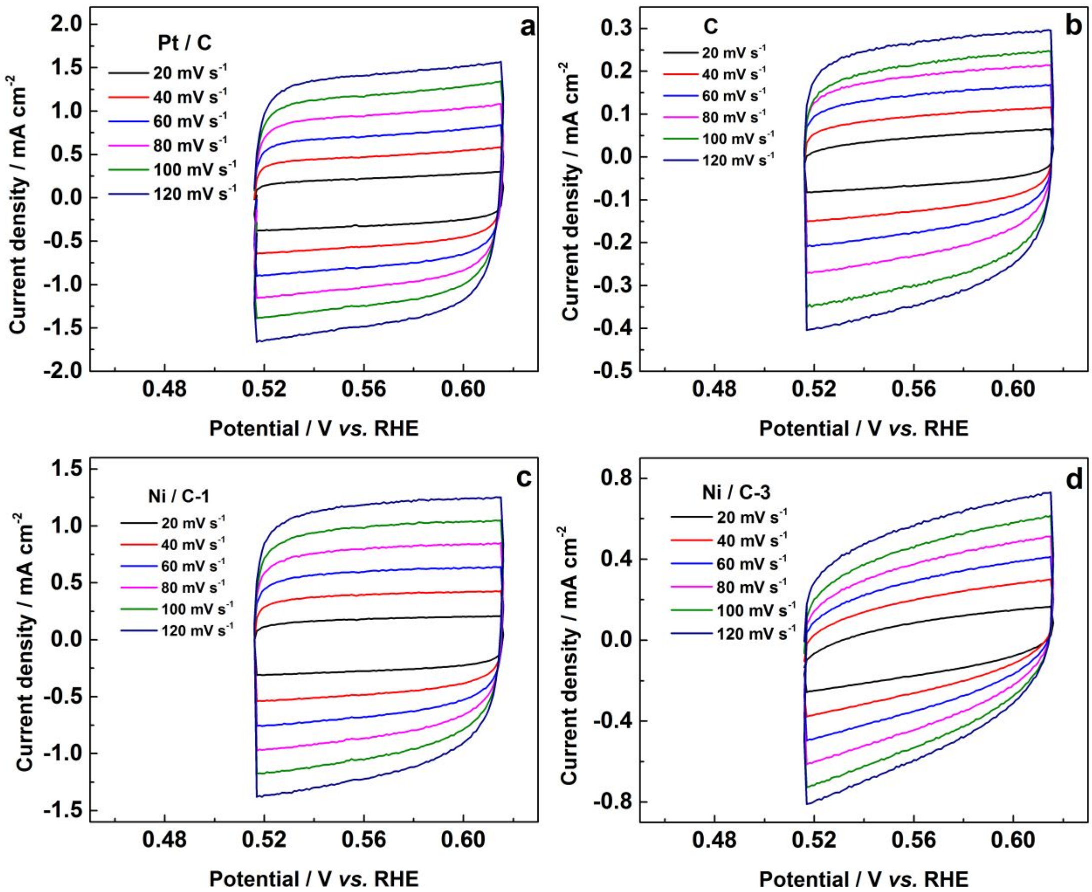


**Figure S4.** Electrochemical double-layer capacitance measurements. (a-d) Electrochemical cyclic voltammogram of as-grown catalysts at different potential scanning rates. The scan rates are 20, 40, 60, 80, 100 and 120 mV $s^{-1}$. The selected potential range where current was observed is 0.516 to 0.616 V vs. RHE.

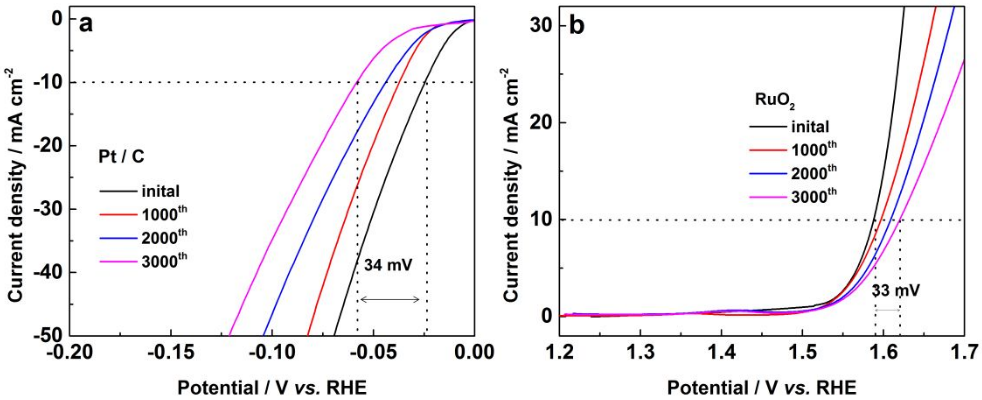


**Figure S5.** (a) HER LSV of the different cycle points on the Pt/C electrode during stability testing; (b) OER LSV of the different cycles points on the $RuO_2$ electrode during stability testing.

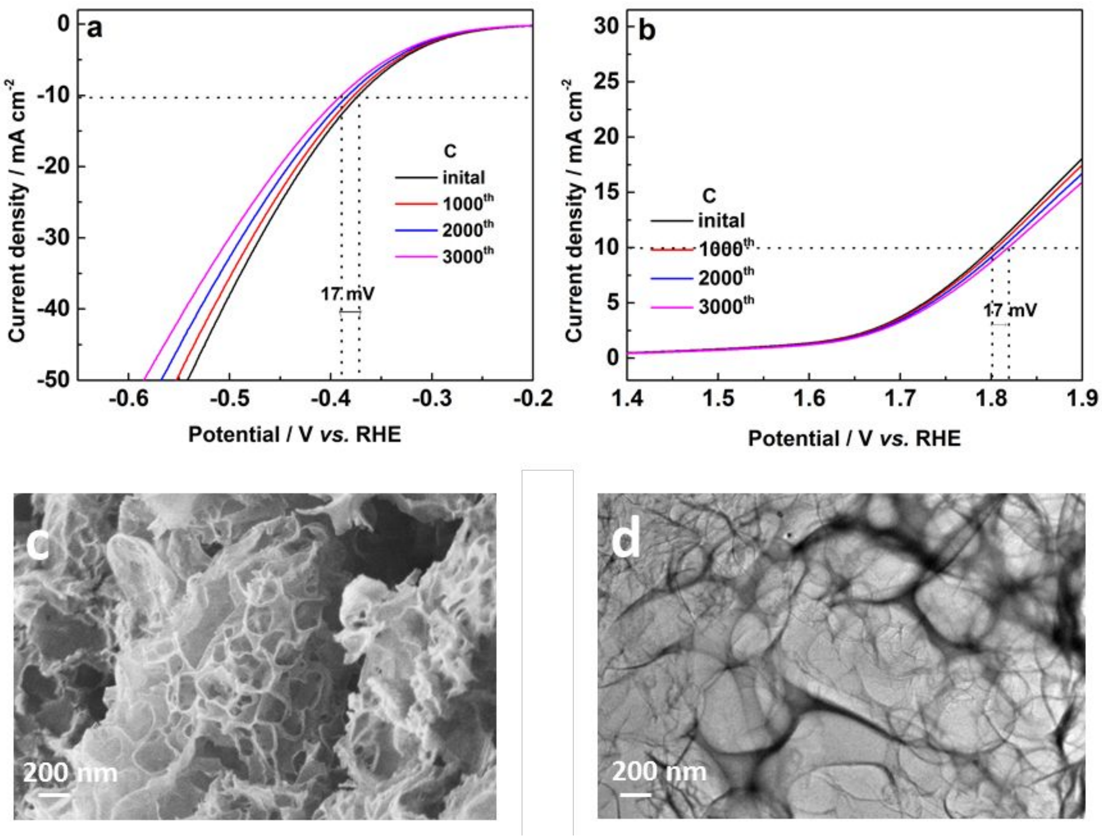


**Figure S6.** (a) HER LSV and (b) OER LSV of the different cycles points on the C electrode during stability testing; Morphology of C after 3000 cycles (c) SEM and (d) TEM.

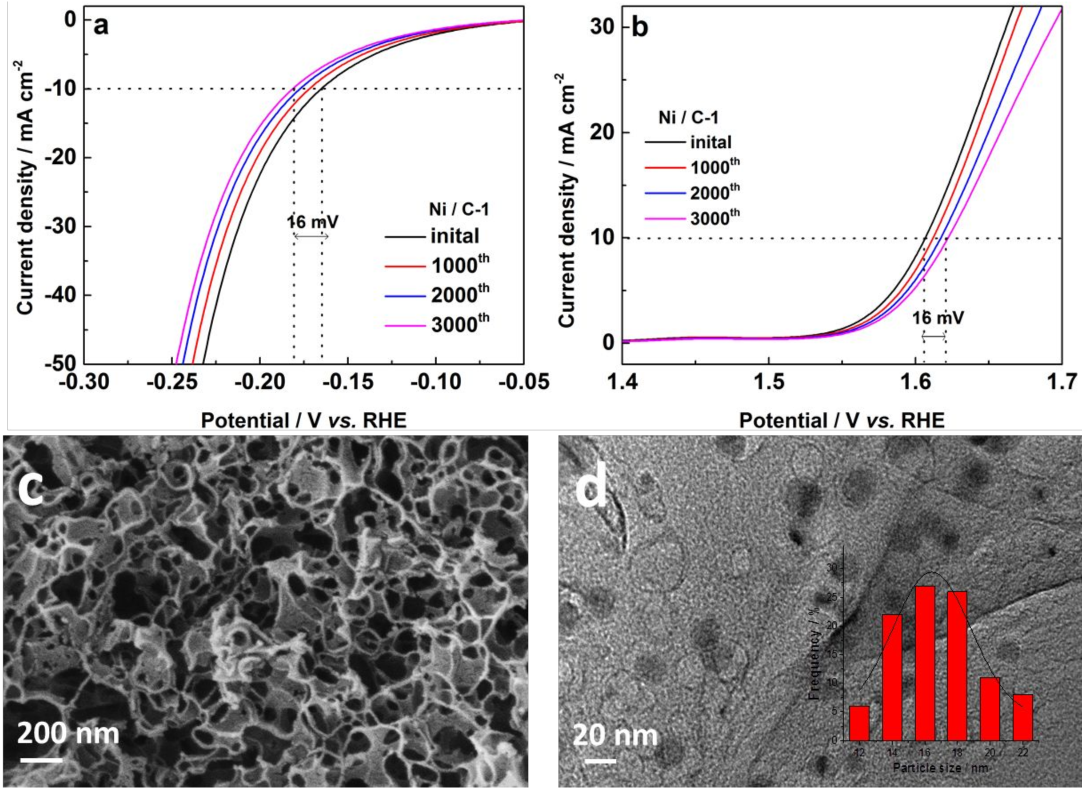


**Figure S7.** (a) HER LSV and (b) OER LSV of the different cycles points on the Ni-1 electrode during stability testing; Morphology of Ni-1 after 3000 cycles (c) SEM and (d) TEM.

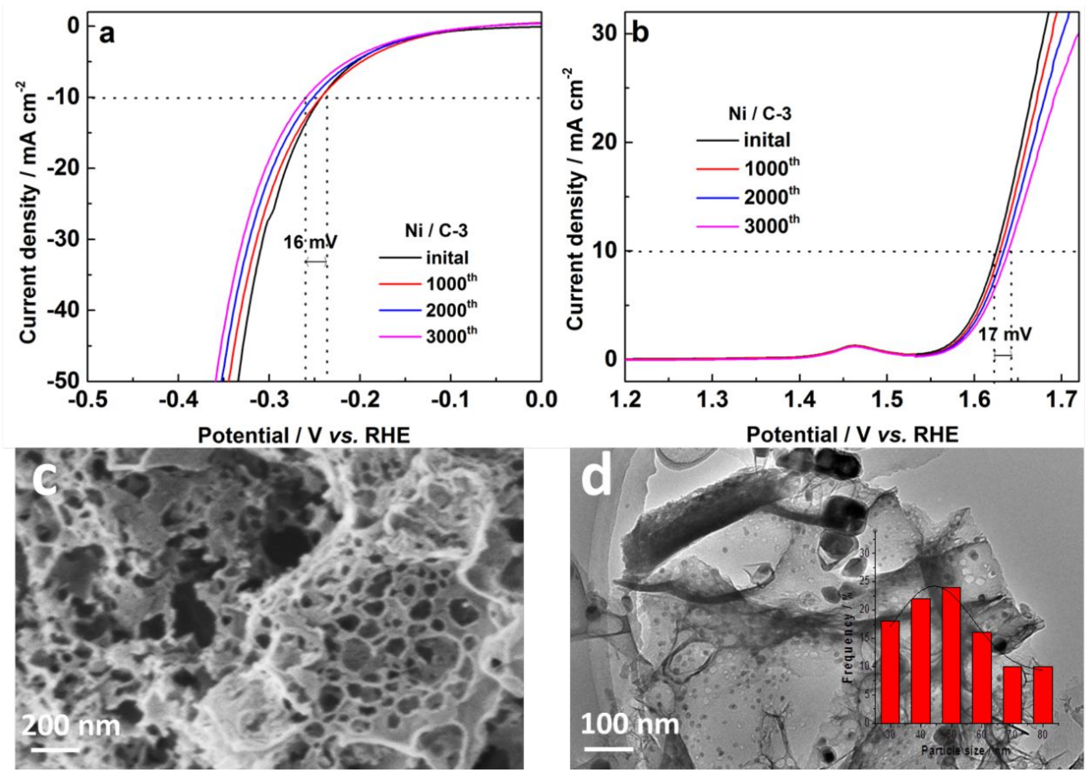


**Figure S8.** (a) HER LSV and (b) OER LSV of the different cycles points on the Ni-3 electrode during stability testing; Morphology of Ni-3 after 3000 cycles (c) SEM and (d) TEM.

**Table S1.** A benchmark of our Ni/C with the value obtained from some other independent literaures.

| Samples | Electrolyte | HER Overpotential (10 mA cm$^{-2}$) | Tafel Slope (mVdec$^{-1}$) | Reference |
|---|---|---|---|---|
| Ni-2 | 1M KOH | 94 mV | 52 | This Work |
| $Ni_3Se_2$/EG | 1M KOH | 150 mV | 83 | Nano Lett,2017,17,4202-4209 |
| CoOx@NC | 1M KOH | 250 | -- | J. Am. Chem. Soc2015,137,2688-2694 |
| $Mo_2C$/C | 1M KOH | 100mV | 72 | ACS Appl. Mater. Interfaces 2017,9,41314-41322 |
| NiO/Ni-CNT | 1M KOH | 85 mV | 82 | Nat.Commun. 2014, 5, 4695 |

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|---|---|---|---|---|
| N,S-CNT | 1M KOH | 400 | 133 | Adv. Energy Mater. 2017, 1602068 |
| CoP-NW/Hb | 1M KOH | 100 | 88 | Nano Eesearch 2017,10(3);1010-1020 |
| Ni@NC | 0.1M KOH | 190 mV | -- | Adv. Energy Mater. 2015, 5, 1401660. |

**Table S2.** A benchmark of our Ni/C with the value obtained from some other independent literatures.

| Samples | Electrolyte | OER Overpotential (10 mA $cm^{-2}$) | Tafel Slope ($mVdec^{-1}$) | Reference |
|---|---|---|---|---|
| Ni-2 | 1M KOH | 350 mV | 56 | This Work |
| NiNCN-22 | 0.1M KOH | 470 mV | 139 | J. Mater. Chem. A, 2016,4, 4864-4870 |
| NiOx-N/C | 1M KOH | 250 mV | -- | Nature communications 4 (2013): 2390 |
| Ni@NC | 0.1M KOH | 390 mV | 44 | Adv. Energy Mater. 2015, 5, 1401660. |
| Co-N-GCI | 0.1M KOH | 420 mV | 69 | ACS Sustainable Chem.Eng.2016,4,4131-4136 |
| S,N-Fe/N-CNT | 0.1M KOH | 370 mV | 82 | Angew. Chem. Int. Ed. 2017, 56, 610 –614 |
| $Ni_3Se_2$ | 0.3M KOH | 370 mV | 99.6 | Energy Environ. Sci., 2016,9, 1771-1782 |
| N,P-GCNs | 0.1M KOH | 356 mV | 70 | ACS Catal. 2015,5,4133-4142 |

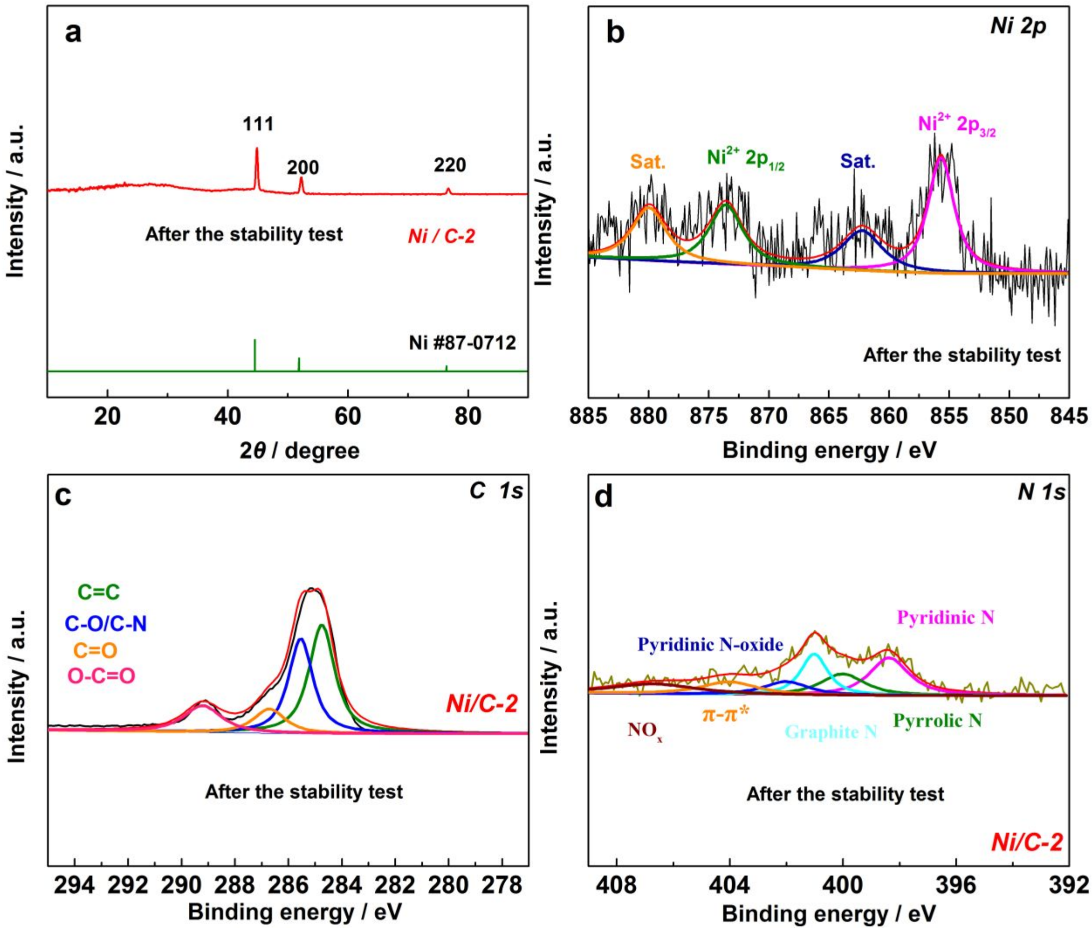


**Figure S9.** (a) XRD patterns of the post-stability Ni-2. Deconvoluted high resolution XPS spectra of Ni 2p (b), C 1s (c), N 1s (d).