

Supporting information

Gram-Scale Synthesis of Carbon-Supported Sub-5 nm PtNi

Nanocrystals for Efficient Oxygen Reduction

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Supporting Information

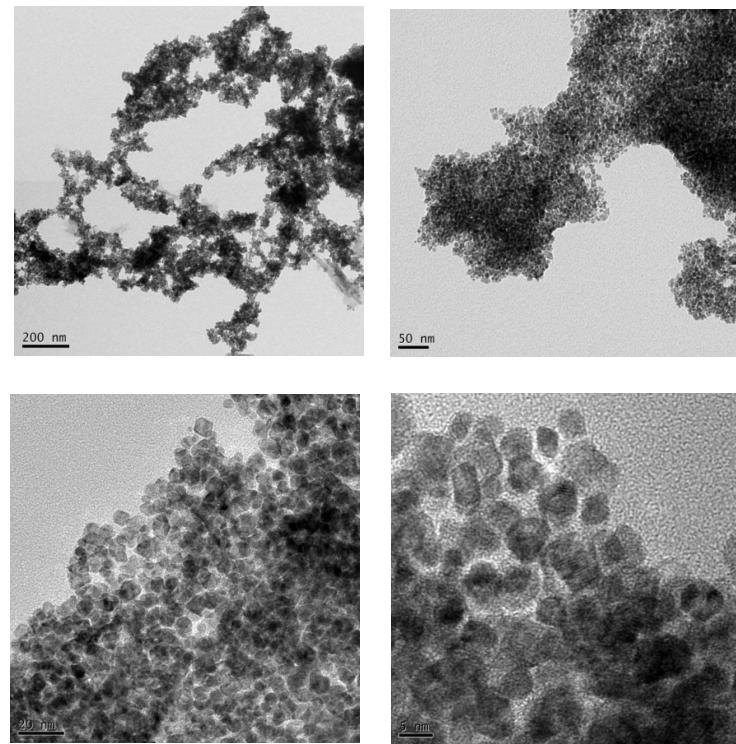


Figure S1. TEM images of PtNi nanocrystals (200°C, Pt:Ni=1:2).

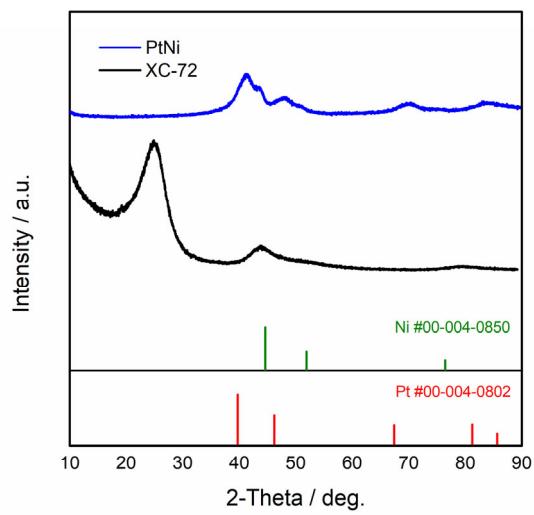


Figure S2. XRD patterns of PtNi nanocrystals (200°C, Pt:Ni=1:2) and Vulcan XC-72.

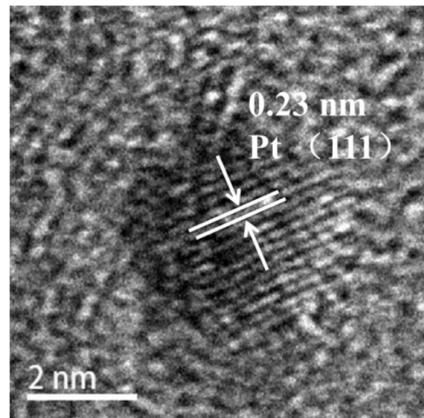


Figure S3. HRTEM image of the initial Pt/C.

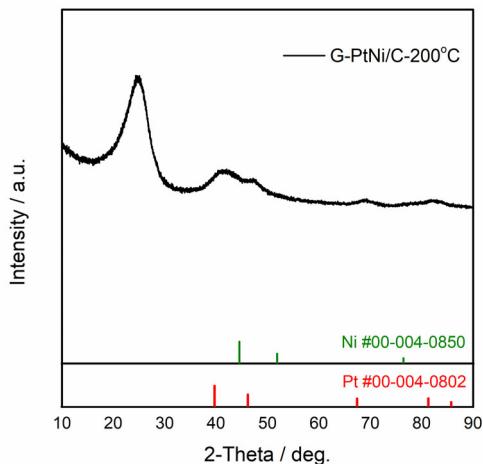


Figure S4. XRD patterns of G-PtNi/C-200°C nanocrystals.

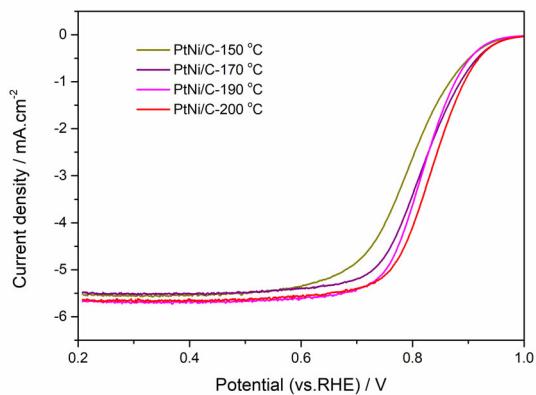


Figure S5. The ORR polarization curves of PtNi/C-150 °C, PtNi/C-170 °C, PtNi/C-190 °C and PtNi/C-200 °C catalysts were conducted in 0.1 M KOH with saturated oxygen.

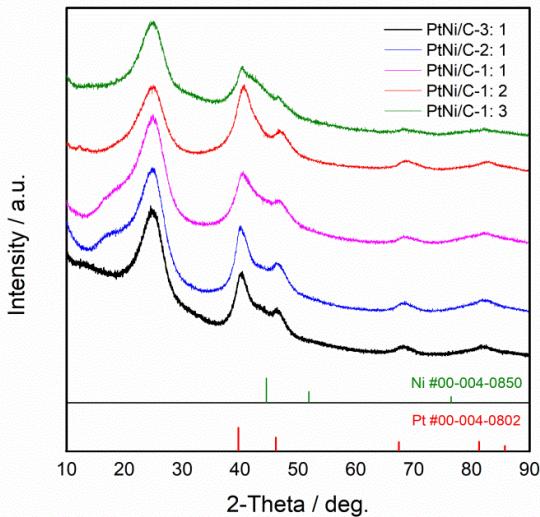


Figure S6. XRD patterns of PtNi/C-3: 1, PtNi/C-2: 1, PtNi/C-1: 1, PtNi/C-1: 2 and PtNi/C-1: 3 nanocrystals.

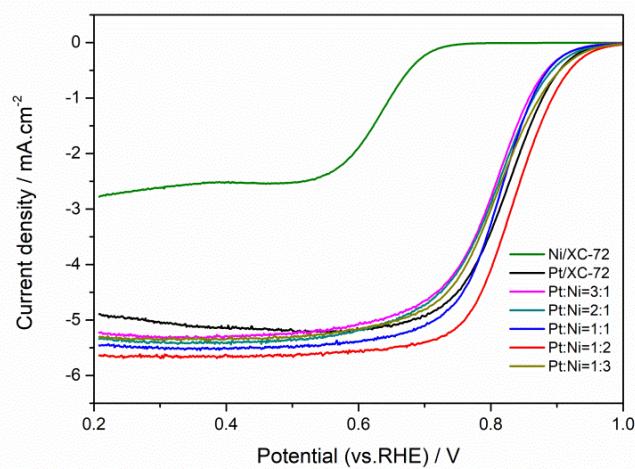


Figure S7. The ORR polarization curves of Ni/XC-72, Pt/XC-72, PtNi/C-3: 1, PtNi/C-2: 1, PtNi/C-1: 1, PtNi/C-1: 2 and PtNi/C-1: 3 catalysts were conducted in 0.1 M KOH with saturated oxygen.

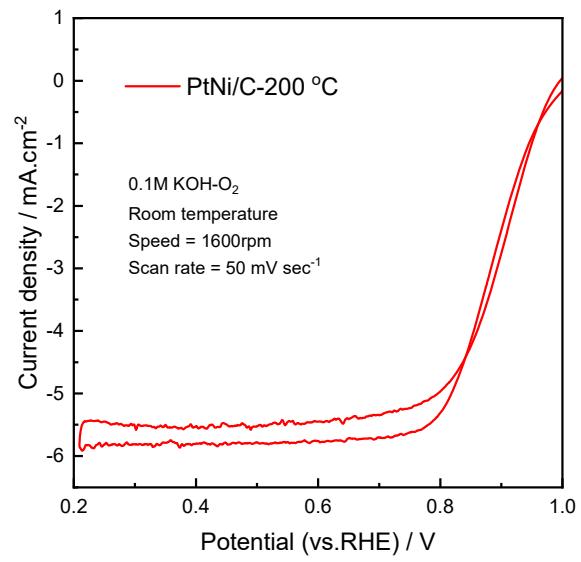


Figure S8. The CV curves of PtNiC-200 catalysts.

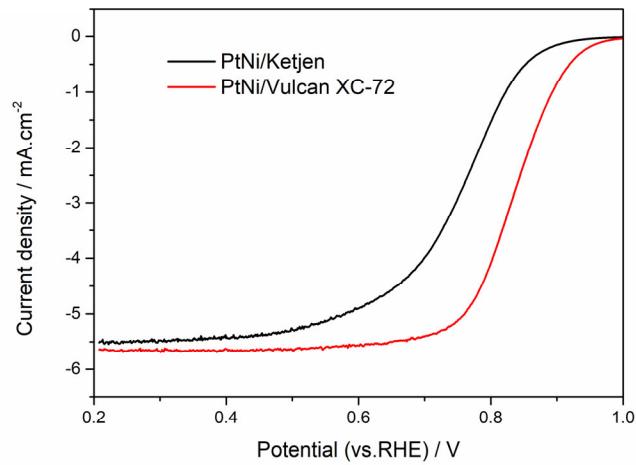


Figure S9. The ORR polarization curves of PtNi/Ketjen Black, PtNi/XC-72 catalysts were conducted in 0.1 M KOH with saturated oxygen.

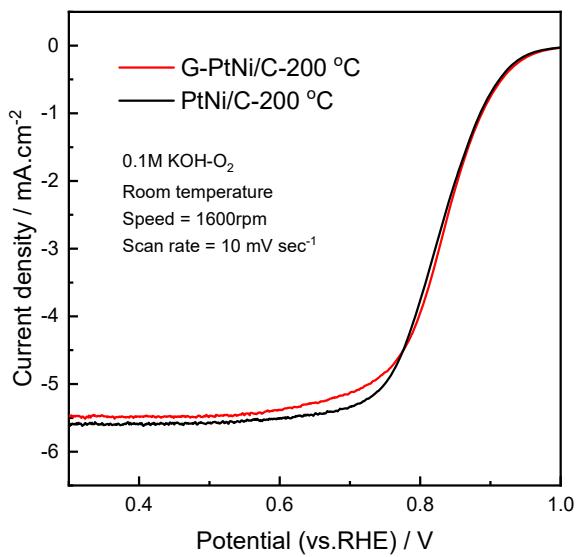


Figure S10. The ORR polarization curves of G-PtNi/C-200 °C, PtNi/C-200 °C in O₂-saturated 0.1 M KOH.

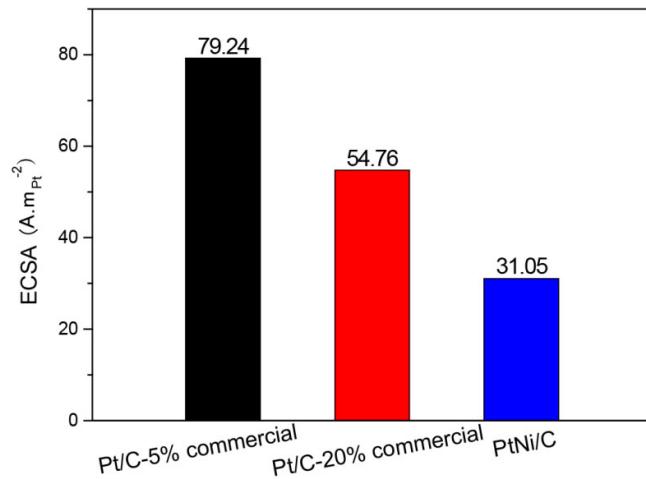


Figure S11. ECSA of commercial Pt/C (platinum content is 5% and 20%) and PtNi/C at 0.9 V (vs. RHE).

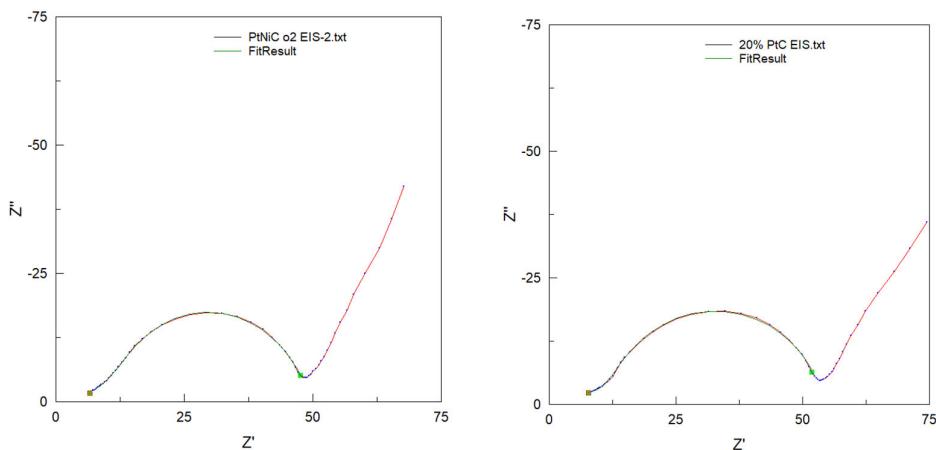


Figure S12. Nyquist plots of PtNi/C-200 and commercial Pt/C-20%.

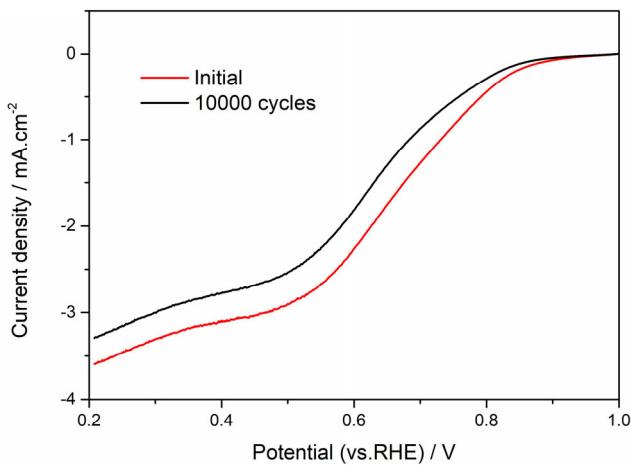


Figure S13. Long-term stability of commercial Pt/C (5 wt.%) catalyst. The ORR polarization curves were conducted in 0.1 M KOH with saturated oxygen.

Table S1. ICP-OES results for various PtNi/C samples.

| | Pt (mg/kg) | Ni (mg/kg) | Pt wt% | Ni wt% | Pt:Ni (atomic ratio) |
|------------|------------|------------|--------|--------|-------------------------|
| PtNi/C-3:1 | 33605.4 | 3683.43 | 3.36% | 0.37% | 1:0.36 |
| PtNi/C-2:1 | 32279.7 | 4869.51 | 3.23% | 0.49% | 1:0.50 |
| PtNi/C-1:1 | 36902.2 | 7870.31 | 3.69% | 0.79% | 1:0.71 |
| PtNi/C-1:2 | 30393.6 | 7870.31 | 3.04% | 1.29% | 1:1.41 |
| PtNi/C-1:3 | 30047.2 | 15411.8 | 3.00% | 1.54% | 1:1.71 |
| Pt/XC-72 | 31806.3 | -- | 3.18% | -- | -- |
| Ni/XC-72 | -- | 3831.75 | -- | 0.38% | -- |

Table S2. Fitting data of EIS results of Pt/C-20% commercial and PtNi/C in 0.1 M KOH.

| Catalyst | R ₁ (Ω) | R ₂ (Ω) | R ₃ (Ω) |
|---------------------|--------------------|--------------------|--------------------|
| Pt/C-20% commercial | 2.365 | 14.27 | 38.13 |
| PtNi/C | 4.06 | 23.12 | 25.79 |

R₁ is the resistance of the solution, R₂ is the resistance of the corrosion layer and R₃ is the charge transfer resistance on the electrode surface.

Table S3. Comparison of the alkaline ORR activity of different Pt-based catalysts

| Catalysts | E _{onset} (V vs.RHE) | E _{1/2} (Vvs.RHE) | Tafel slope (mv.dec ⁻¹) | Electron transfer numbers (n) | Durability test | Pt (wt%) | Reference |
|---------------------------------------|----------------------------------|-------------------------------|--|--|--------------------|-------------|-----------|
| PtP _{1.4} @Pt/C | -- | 0.88 | -- | -- | 27 (30 k cycles) | 32.3 | [1] |
| Pt/MnO | -- | 0.78 | -- | 4.0 | -- | -- | [2] |
| Pt ₆₇ Ni ₃₃ NCs | 0.92 | 0.82 | 61.8 | 3.7 | 7.1 (2.5 k cycles) | -- | [3] |
| Pt _L @Ni _L | -- | 0.68 | -- | -- | -- | 4.71 | [4] |
| P-PtNi/C | -- | 0.9 | -- | 4.08 | ~50 (2.5 k cycles) | 17.7 | [5] |
| Pt _{3.5%} Ni PF | 0.92 | 0.80 | -- | 3.90 | -- | -- | [6] |
| Pt ₇₅ Ni ₂₅ | 0.95 | 0.86 | -- | 3.90 | ~5mV (1 k cycles) | -- | [7] |
| PtNi/C | -- | 0.88 | 98 | 4.0 | 15mV (1 k cycles) | 22.75 | [8] |
| PtNi/C-200 | 0.98 | 0.84 | 77.08 | 4.0 | 5mV (10 k cycles) | 3.04 | This work |

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