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# Supplementary Information

# for

# Thiometallate precursors for the synthesis of supported Pt and PtNi nanoparticle electrocatalysts: Size-focusing by S capping

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## Experimental Section

**Chemicals.** Ammonium sulfide solution ($(NH4)_2S$, 40-48 wt% in $H_2O$, Aldrich), chloroplatinic acid solution ($H_2PtCl_6$, 8 wt% in $H_2O$, Aldrich), nickel(II) acetate tetrahydrate (98%, Aldrich), methyl alcohol (99.5%, Samchun), 2-propanol (99.5%, Samchun), toluene (99.5%, Samchun), sulfur (99.998%, Aldrich), ethyl alcohol(99.5%, Samchun) were used as received.

**Synthesis of thioplatinate complex.** Thioplatinate com-plex was synthesized by the method reported by our group. Typically, 5.0 mL of ammonium sulfide solution was diluted by adding 5.0 mL of distilled water. 3.0 g of sulfur was further added into this solution and was stirred until the color of solution turned from yellow to red, where ammonium polysulfide was formed. Then, 1.25 mL of chloroplatinic acid solution was added dropwise to the polysulfide solution and was stirred for longer than 12 h, which generated an orange colored precipitate. This precipitate was collected by centrifugation at 7000 rpm for 3 min. The precipitate was further washed with mixed solvents of methanol and toluene with volume ration of 1:14 by three times. The final product was dried under vacuum.

**Synthesis of thionickelate complex.** Thionickelate complex was synthesized by the method reported by our group. 5.0 mL of ammonium sulfide solution was diluted by adding 5.0 mL of methanol. 1.0 g of sulfur was further added into this solution and was stirred until the color of the solution turned from yellow to clear red, where ammonium polysulfide solution was formed. 0.4 g of nickel acetate tetrahydrate was added and simultaneously temperature was increased to 45 $^{o}$C. Reaching that temperature, the precipitate and supernatant was separated by centrifugation at 4000 rpm for 3 min. The supernatant was further washed with IPA by two times. The final product was dried under vacuum.

**Synthesis of Pt-S/C and PtNi-S/C.** Pt-S/C was synthesized by simply mixing carbon and thioplatinate complex. To make 25% Pt-S/C, 0.9157 g of thioplatinate and 1 g of carbon was mixed by adding ethanol with stirring for 12 h. After mixing, the solution was heated at 140 $^{o}$C to evaporate ethanol. The remained powder was heated in the tube furnace at appropriate temperatures. PtNi-S/C was made with the same method, but 0.4185 g of thionickelate was added with other components before mixing. The Pt content in the synthesized Pt-S/C (15 wt%) was measured by inductively coupled plasma-mass spectrometry (ICP-MS; NexION 300D; Perkin Elmer)

**Characterization of materials.** Transmission electron microscopy (TEM) images of nanocrystals were collected using a JEOL-2100 instrument operated at 200 kV. The samples dispersed in non-polar solvents were prepared by drop-casting on carbon-coated TEM grids and dried under air while the samples dispersed in polar solvents were dried under vacuum. Scanning TEM (STEM) and Energy dispersive X-ray spectroscopy (EDX) characterization was conducted in a Cs probe aberration-corrected FEI Titan Cube TEM with an electron monochromator operated at 80 kV. X-ray diffraction (XRD) patterns were obtained using a Rigaku D/Max2500V diffractometer equipped with a Cu-rotating anode X-ray source. Electronic states of Pt species were obtained using a ThermoFisher K-alpha X-ray photoelectron spectrometer. The absorption spectra of thiometallates were acquired using a UV-Vis spectrophotometers (Shimadzu UV-2600). Extended X-ray absorption fine-structure (EXAFS) measurements for Pt $L_3$-edge was done at 1D XRS KIST-PAL beamline of Pohang Accelerator Laboratory, South Korea.

**Electrochemical half-cell test**. Electrochemical properties were tested by using an AutoLab potentiostat. A saturated calomel electrode was used as the reference electrode and a Pt plate was used as the counter electrode. The working electrode was coated with the electorcatalyst on glassy car-bon rotating disk electrode (RDE). To prepare the catalyst slurry ink, 5 mg of commercial Pt/C (Pt 20 wt%. Tanaka), synthesized Pt-S/C catalysts were used in 500 μL of IPA and 50 μL of Nafion solution (5 wt% solution, Aldrich). Then, 5 μL of catalyst ink was transferred onto the glassy carbon. Cyclic voltammetry curves were recorded in an Ar-saturated 0.1 M $HClO_4$ solution at a scan rate of 20 mV/s and oxygen reduction reaction (ORR) curves were recorded in an $O_2$-saturated 0.1 M $HClO_4$ solution at a scan rate of 5 mV/s and the rotation disk electrode (RDE) was rotated at 1,600 rpm. An ADT was conducted in which potential cycling was carried out over the range of 0.6 to 1.1 V in an Ar-saturated conditions at a scan rate of 50 mV/s. All potentials are represented on a scale with respect to the reversible hydrogen electrode (RHE).

**Membrane electrode assembly test.** To prepare the membrane electrode assembly (MEA) for the single-cell test, the anode and cathode catalysts were loaded through a spray method onto Nafion 211 membrane. Pt loading of the catalyst layers were 0.2 mg/cm$^2$ for anode and 0.4 mg/cm$^2$ for cathode respectively; the active areas were 5 cm$^2$. Commercial Pt/C (Pt 20 wt%, Tanaka) catalysts were sprayed on the anode side and commercial Pt/C and Pt-S/C catalysts were sprayed on the cathode side. The anode and cathode were placed in an $H_2$/air (RH100%) flow, at a flow rate of 200/600 sccm with ambient pressure, while the temperature was maintained at 80 $^oC$.

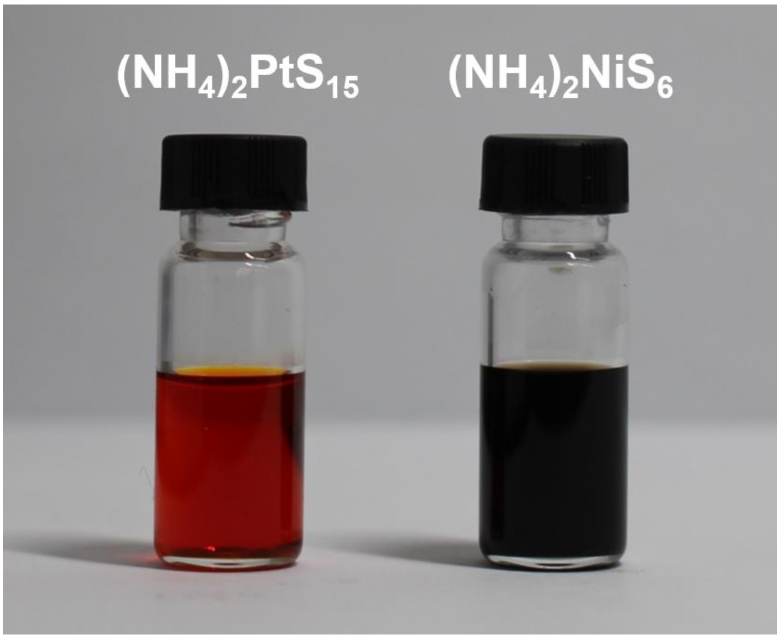


**Figure S1.** Photographs showing the synthesized thioplatinate and thionickelate solution in NMF

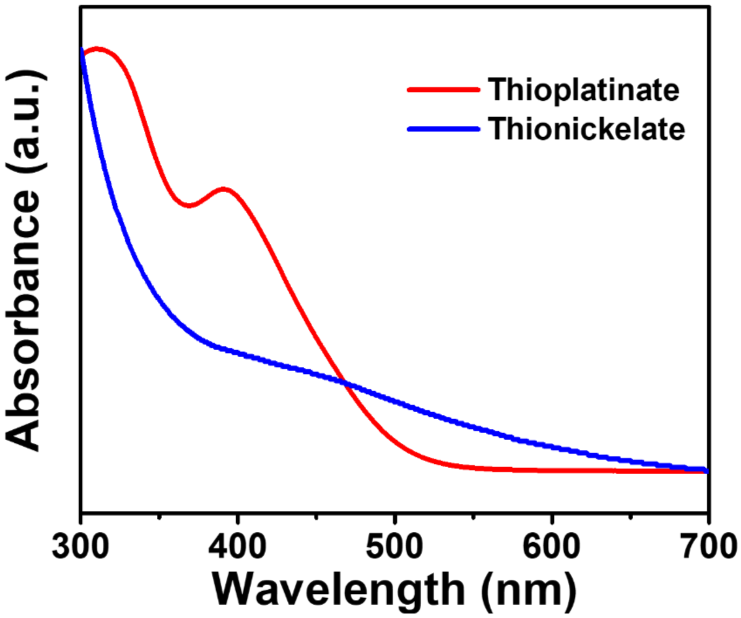


**Figure S2.** UV−Vis absorption spectra of ammonium thioplatinate and ammonium thionickelate.

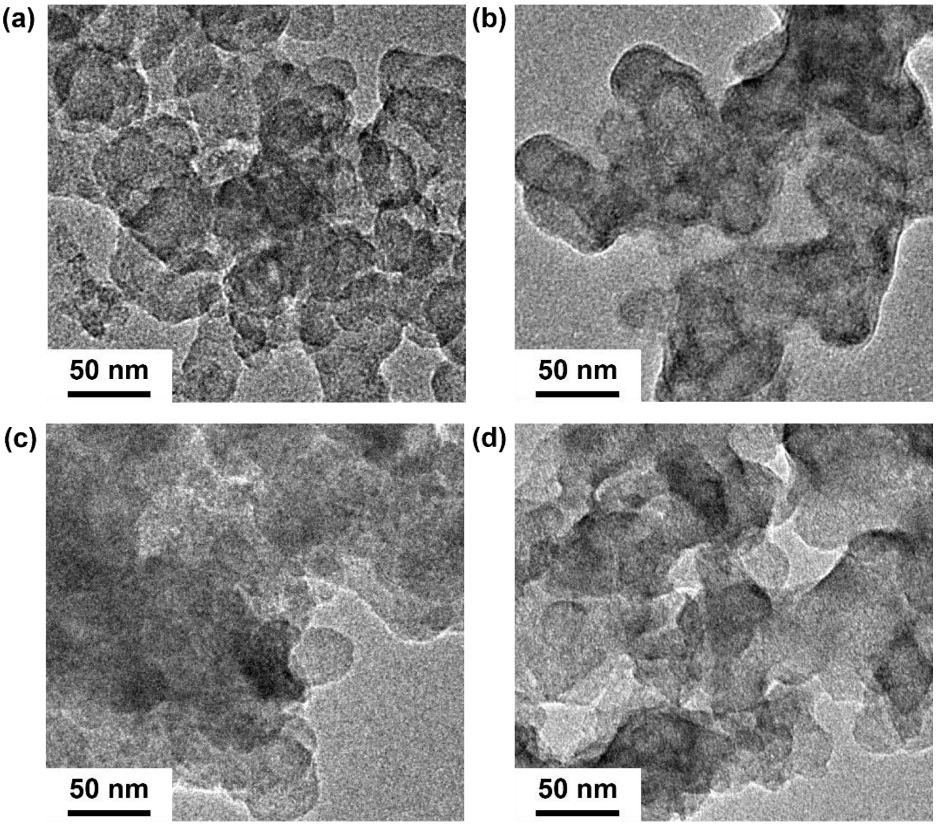


**Figure S3.** TEM images of (a) the Vulcan carbon and as-deposited (b) thioplatinate, (c) thionickelate, and (d) mixture of thioplatinate and thionickelate on the Vulcan carbon.

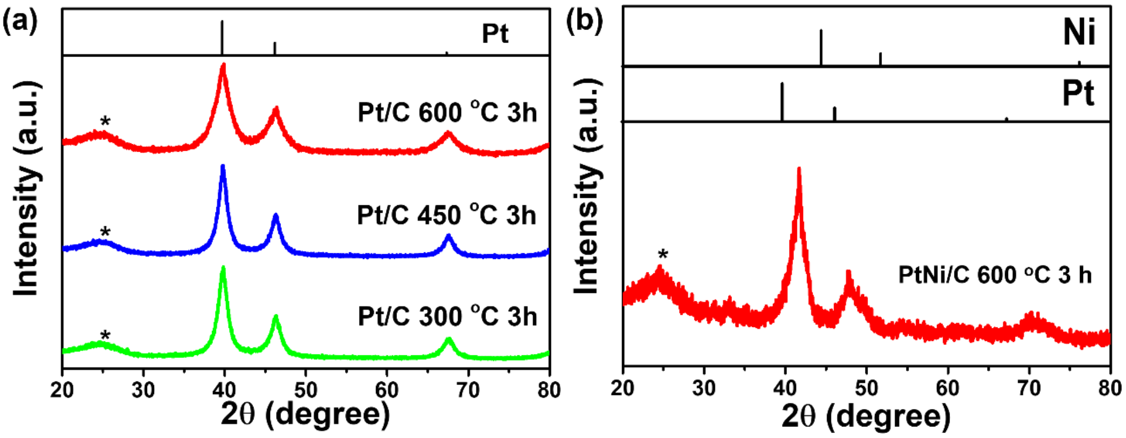


**Figure S4.** XRD patterns of (a) the synthesized Pt/C at 300 °C, 450 °C, and 600 °C, and (b) PtNi/C at 600 °C. The star marks in the panel indicate the peak to be indexed to the carbon. The vertical lines indicate the reference pattern of Pt(JCPDS 00-004-0802) and Ni(JCPDS 00-004-0850).

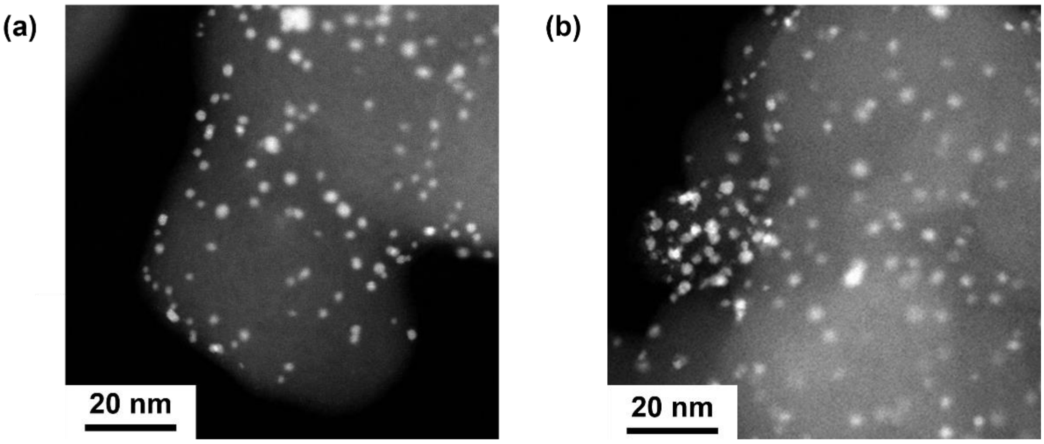
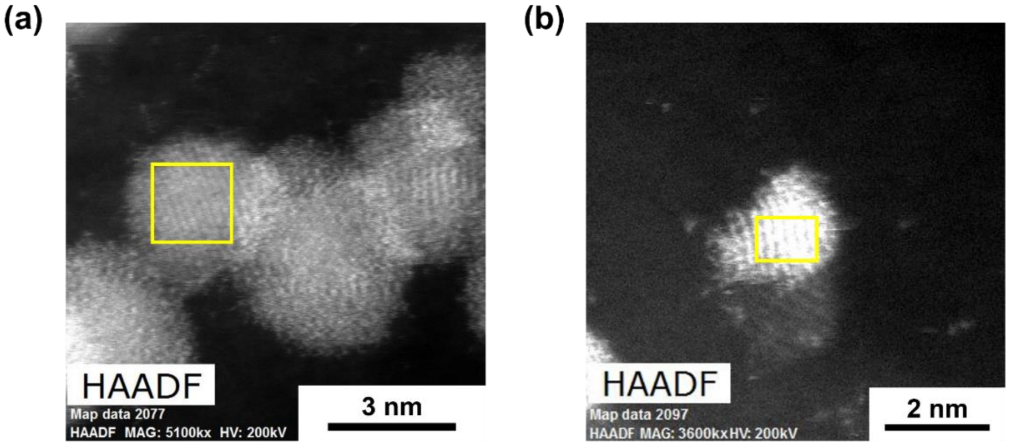


**Figure S5** STEM image of a) Pt/C and b) PtNi/C



(c)

| Element | wt.% | at.% |
|---|---|---|
| Pt | 99.42 | 96.54 |
| S | 0.58 | 3.46 |

(d)

| Element | wt.% | at.% |
|---|---|---|
| Pt | 43.38 | 64.90 |
| Ni | 37.05 | 30.29 |
| S | 19.57 | 4.81 |

**Figure S6** TEM-EDX mapping images of (a) Pt-S/C and (b) PtNi-S/C samples. Content of the elements in (c)Pt-S/C and (d) PtNi-S/C.

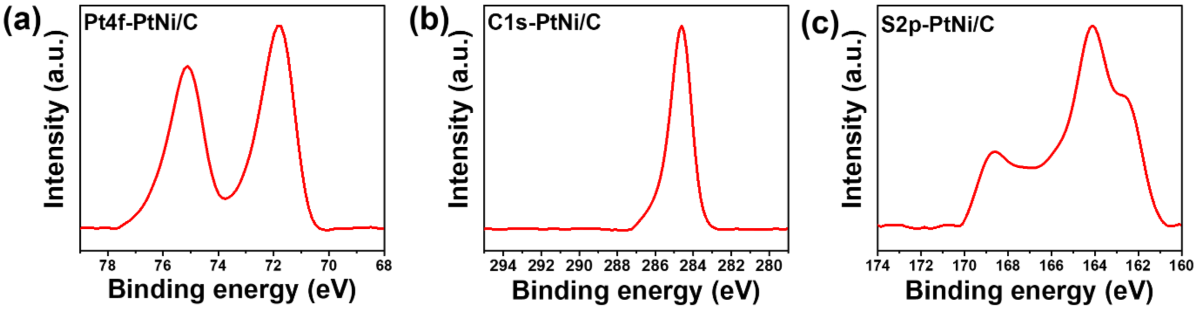


**Figure S7.** XPS spectra of (a) Pt 4f, (b) C 1s, and (c) S 2p of the synthesized PtNi/C.

| Shell | N | R | $\sigma^2$ (Å) | $\epsilon_o$ (eV) | R-Factor |
|---|---|---|---|---|---|
| Pt Foil | | | | | |
| Pt-$Pt_I$ | 12.2±0.7 | 2.761±0.003 | 0.003±0.0004 | 8.2±0.5 | 0.005 |
| Pt-$Pt_{II}$ | 5.7±0.9 | 3.902±0.001 | 0.004 | | |
| **Pt-S/C** | | | | | |
| Pt-C | 0.3±0.9 | 1.965 | 0.013 | 6.5 | 0.012 |
| Pt-S | 1.50±0.4 | 2.27±0.02 | 0.01710.002 | | |
| Pt-$Pt_I$ | 9.1±1.2 | 2.763±0.003 | 0.004±0.001 | | |
| Pt-$Pt_{II}$ | 4.3±1.2 | 3.902±0.017 | 0.004±0.004 | | |
| **Commercial Pt/C** | | | | | |
| Pt-C | 1.9±0.8 | 2.000±0.017 | 0.006±0.005 | 7.728 | 0.02 |
| Pt-$Pt_I$ | 8.1±1.3 | 2.754±0.004 | 0.005±0.001 | | |
| Pt-$Pt_{II}$ | 2.1±1.7 | 3.915±0.046 | 0.009 | | |

**Figure S8.** Results from the quantitative analysis of the EXAFS data providing the coordination number (N), radial distance (R) and Debye-Waller factor ($\sigma^2$) for the samples.

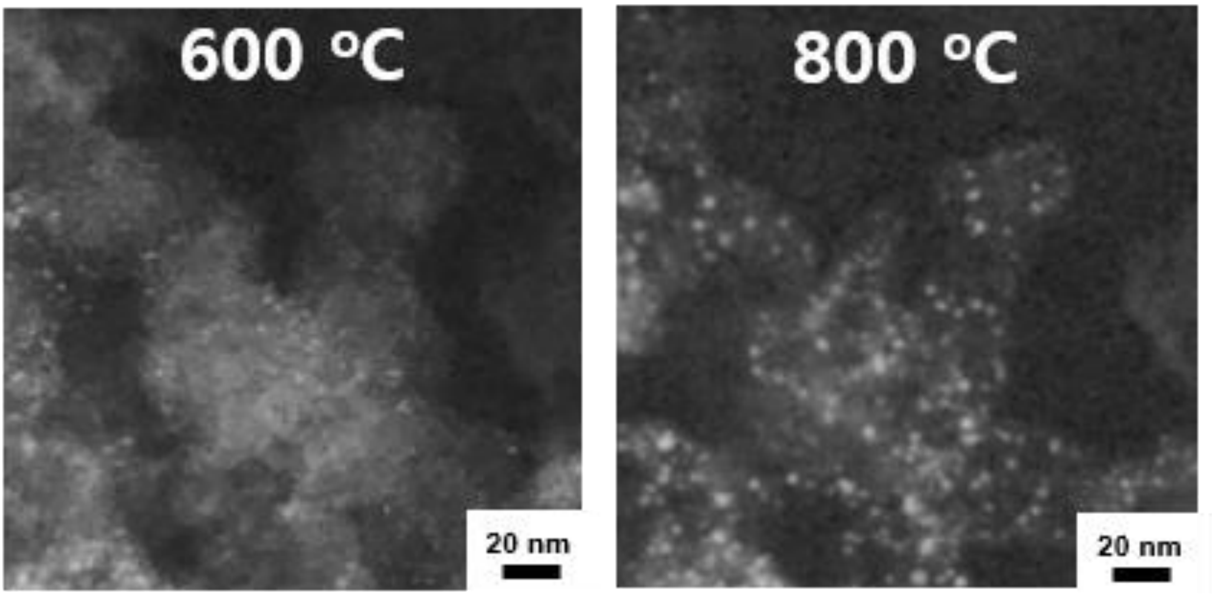


**Figure S9.** HAADF-STEM images showing the synthesized Pt-S/C during heating from 600 °C to 800 °C under $H_2$ environment.

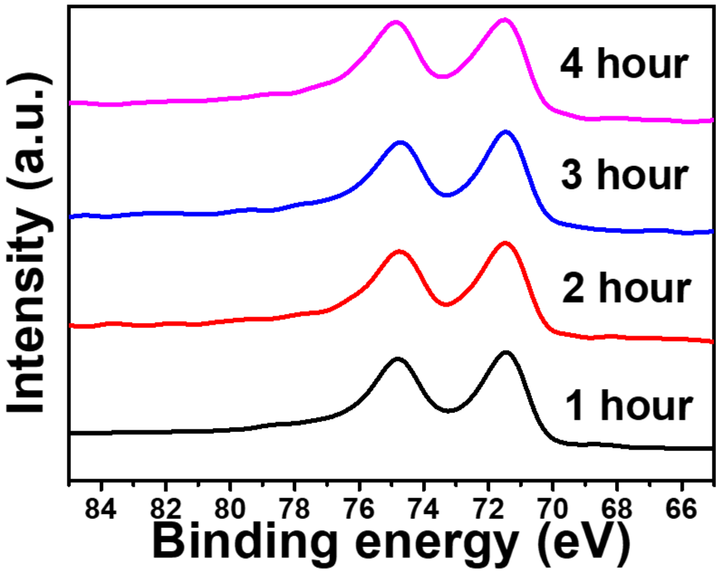


**Figure S10.** XPS spectra of the synthesized Pt/C at 600 °C for 1 h, 2 h, 3 h, and 4 h.

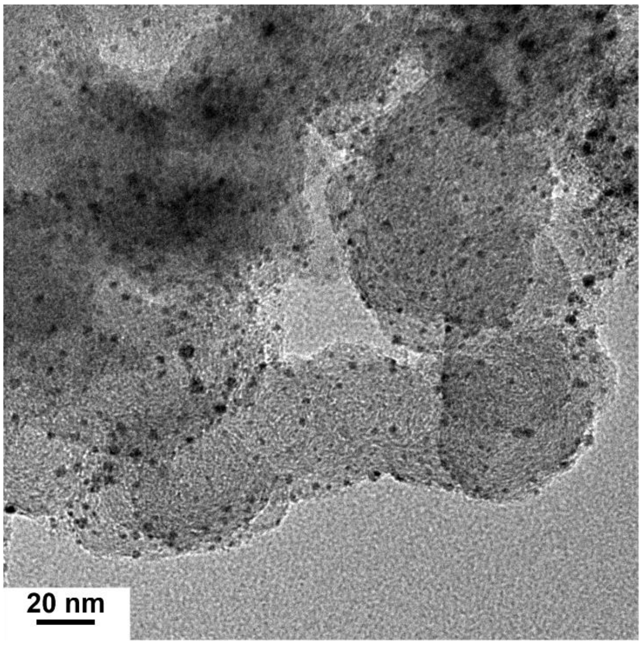


**Figure S11.** TEM image of Pt/C sample further heated at 600 ºC for 7 h.

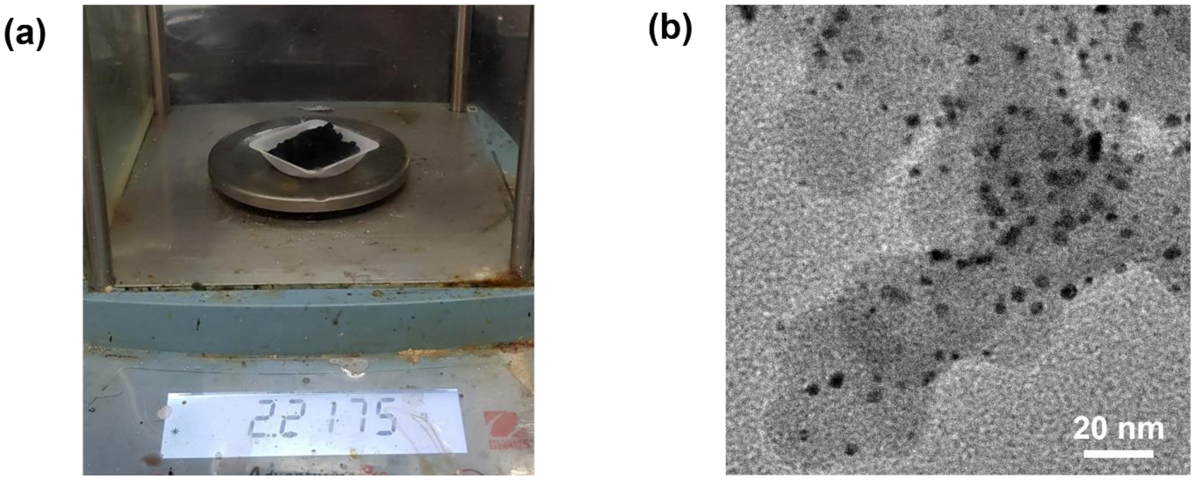


**Figure S12. (**a) A photograph showing multigrams of the Pt/C catalyst synthesized in a large scale and (b) the corresponding TEM image.

**Table S1.** Oxygen reduction reaction (ORR) activity parameters of Pt-S/C catalysts and previously reported Pt-based catalysts.

| **Catalysts** | **ECSA** | **Mass activity (@ 0.9 V)** | **Specific activity (@ 0.9 V)** | **Ref** |
|---|---|---|---|---|
| | ($m^2/g_{Pt}^{-1}$) | ($A/mg_{Pt}^{-1}$) | ($mA/cm^{-2}$) | |
| **Pt-S/C** | **70.6** | **0.11** | **0.16** | **This work** |
| Pt/C synthesized by physical vapor deposition | 64.7 | 0.12 | - | S1 |
| Pt nanoassembly | 40.8 | 0.11 (@0.85 V in $H_2SO_4$) | 0.72 | S2 |
| Mesoporous Pt nanospheres | 21.6 | 0.07 | 0.40 | S3 |
| Pt skeleton NTs | 21.1 | 0.21 | 1.00 | S4 |
| Porous strained Pt | 32.8 | 0.16 | 0.49 | S5 |
| Meso-PtNi | 15.7 | 0.11 | 0.70 | S6 |
| Pt/Nb-$TiO_2$ nanofiber | - | 0.081 | - | S7 |

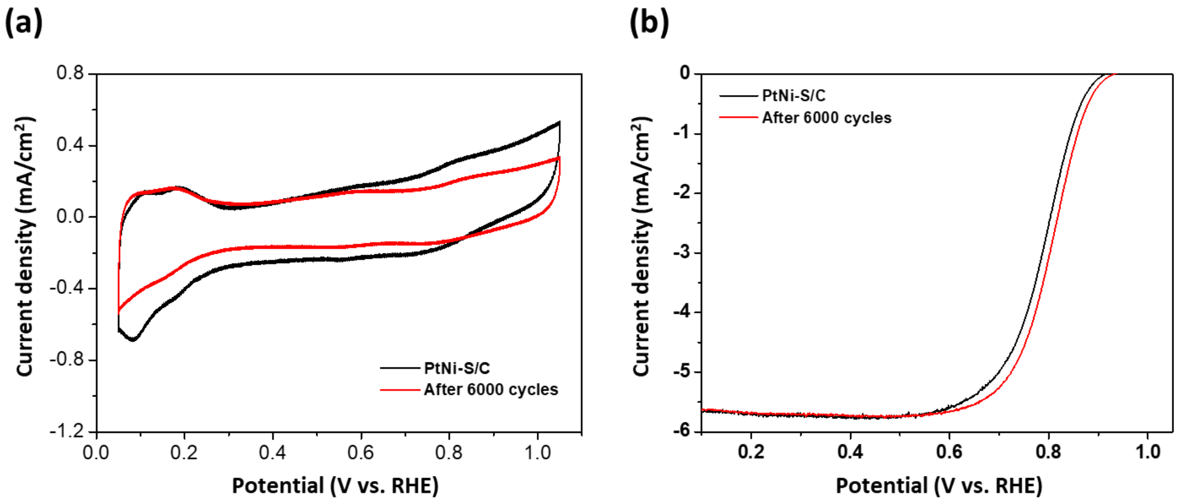


**Figure S13.** (a) Cyclic voltammetry curves and (b) oxygen reduction (ORR) curves of PtNi-S/C before and after accelerated degradation test (ADT) in the 0.6-1.1 V range for 6000 cycles.

## References

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