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Chemical tuning of electrochemical properties of Pt-skin surface for highly active oxygen reduction reactions

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Preparation of catalysts

As-prepared carbon-supported PtNi (PtNi/C-asp) alloy nanoparticles with a Pt/Ni molar ratio of 1 were prepared via conventional $NaBH_4$ reduction. 0.15 g of carbon black (Vulcan XC-72R) was dispersed in anhydrous ethanol (150 mL, Aldrich), and the mixture solution was stirred at 500 rpm for 1 h, followed by sonication for 1 hr. $PtCl_4$ (0.0853 g, Aldrich), $NiCl_2 \cdot 6H_2O$ (0.0602 g, Aldrich), and sodium acetate (0.9143 g, Aldrich) were added to the ethanol solution containing dispersed carbon black. Stirring for 2 h and sonication for 10 min of the solution were repeated two times. The amount of sodium acetate added to the mixture was adjusted so that the molar ratio of sodium acetate to total metal was 22. After stirring and sonication of the solution, 20 mL of anhydrous ethanol solution with $NaBH_4$ (Aldrich) was quickly introduced with vigorous stirring (750 rpm). The resultant solution was stirred for 4 h to complete the reduction of metal precursors, followed by filtration, washing, and drying in an oven at 60 ˚C.

These PtNi/C-asp nanoparticles were then immersed in 0.5 M $HClO_4$ solution (500 mL) with stirring for 2.5 h in order to leach out the surface Ni atoms, forming de-alloyed PtNi/C with a Pt-skeleton surface as a starting material (PtNi/C-acid). After the acid treatment, the catalyst solution was washed by filtration with excessive D.I. water, and the catalyst powder was dried in an oven at 60 ˚C. This was subsequently annealed in a H_2 atmosphere to smoothen the corrugated surface, resulting in a Pt-skin structure on the nanoparticles (PtNi/C-acid/heat). The annealing temperature was elevated from 20 to 250 ˚C for 30 min, and then was kept at 250 ˚C for 30 min. After that, the catalyst was slowly cooled to room temperature in the furnace, and Ar gas was introduced into the furnace at room temperature for 2 h. As an alternative method for forming a Pt-skin structure, additional Pt atoms were slowly chemically deposited onto the surface of the PtNi/C-acid material to make highly active Pt-skin structure for the ORR (Pt@PtNi/C-acid). L-ascorbic acid (0.15 g, Aldrich) was dispersed in anhydrous ethanol (200 mL) for 10 min by sonication. PtNi/C-acid (0.09 g) was introduced in the solution, and mixed by sonication for 10 min and stirred for 1 h. After $PtCl_4$ (0.0173 g, Aldrich) as a precursor for additional Pt overlayer was dispersed in the solution, the solution was refluxed and stirred at 80 ˚C for 2 h. The solution was then washed by filtration with excessive D.I. water, and dried in an oven at 60 ˚C.

Physical analysis

The particle distribution and size of the prepared PtNi/C catalysts were investigated by high resolution-transmission electron microscope (HR-TEM) (JEOL 2010, at 200 kV). The element analyzer (EA) (EA1112, CE Instrument) was used to identify the weight percent of the catalysts. Total metal loading was calculated by subtracting the weight of C, H, N in each sample. Inductively coupled plasma-atomic emission spectroscopy (ICP-AES) (Optima-4300 DV, Perkin-Elmer) was performed to the compositions of prepared PtNi/C catalysts. By X-ray diffraction (XRD) (Rigaku, D/MAX 2500) with Cu Kα radiation (40 kV, 200 mA), the diffraction patterns of PtNi/C catalysts were obtained in 2 theta ranges between 20 and 80 °.

Pt L_{III} edge and Ni K edge X-ray absorption spectroscopy (XAS) was recorded at the Pohang Light Source (PLS) using the 10C beamline with a ring current of 120-170 mA at 2.5 GeV. A Si(111) monochromator crystal was used with intensity detuned to 85% to eliminate high-order harmonics. Data were collected in fluorescence and transmission modes. Energy calibrations were performed for all measurements using either Pt foil or Ni foil placed in front of the third ion chamber. The University Washington data analysis program was the data analysis package used for X-ray absorption near-edge structure spectroscopy (XANES). The XANES spectra were first subjected to background removal by fitting pre-edge data to a Victoreen-type formula over a range of 200-40 eV below the edge, followed by extrapolation over the energy range of interest and subtraction from the data. After removal of all background, second derivatives calculated from inflection points of data from the reference channel were used to correct the spectra for edge-shifts. Normalization was performed by the conventional procedures. The normalization value was chosen as the absorbance at the inflection point of one extended X-ray absorption fine structure (EXAFS) oscillation. The spectra were thus normalized by dividing each datum point by the normalization value. The obtained data were processed in the usual way to obtain the absorbance and analyzed with ATHENA and ARTEMIS in the suite of IFEFFIT software programs. The obtained data were processed in the usual way to obtain the absorbance and analyzed with ATHENA and

ARTEMIS in the suite of IFEFFIT software programs. Pre-edge absorption due to the background and detector were subtracted using a linear fit to the data in the range of -200 to -60 eV relative to E0. E0 was defined as the first inflection point on the rising absorption edge. Each spectrum was then normalized by a constant, extrapolated value to E0 of third-order polynomial fit over absorption at 150-900 eV relative to E0. To isolate EXAFS signal, the post-edge background function was approximated with a piecewise spline that could be adjusted so that the low-R component of pre-Fourier transformed data were minimized. After calculation of EXAFS function $\chi(k)$, k3-weighted EXAFS function in momentum (k) space was Fourier transformed to reveal the neighboring atoms arranged according to distance from a central As atom in R-space. The k range of the transform varied between a kmin of 2.0-3.0 Å-1 and a kmax of 12.0-13.0 Å-1. Kaiser-Bessel function was adopted as a window function and the windowsill of dk=1.5 was also used in the transform. A shell of interest in R-space was back-transformed into the momentum space with Kaiser-Bessel window function and windowsill of dR=0.1. Fourierfiltered spectra derived from the experiments were fitted by using of the theoretical standards generated with the ab-initio FEFF 8.2 code.

X-ray photoelectron spectroscopy (XPS) was additionally measured at the PLS. Binding energies were calibrated with respect to Au 4f XPS peak. Experimental data were curve-fitted using XPSPEAK4.1 software. Atomic ratios of Pt oxidation states and O species in the samples were estimated from the area of the respective Lorentzian-Gaussian peaks.

Electrochemical analysis

All electrochemical measurements were conducted in a standard three-compartment electrochemical cell using a glassy carbon electrode of the rotating disk electrode (RDE), Pt wire, and saturated calomel electrode (SCE) as working, counter, and reference electrodes, respectively. All measurements were reported versus reversible hydrogen electrode (RHE), and performed at 20 ˚C in 0.1 M $HClO_4$. The catalyst ink slurry was prepared by mixing each catalyst with 20 μL of DI water, 54.7 μL of 5 wt % Nafion solution as a binding material, and 630 μL of 2-propanol. Following mixing and ultrasonication, a

drop of ink slurry was loaded onto a glassy carbon substrate (0.196 cm^2, geometric surface area). The dried electrode was then transferred to the electrochemical cell.

In the CO oxidation measurement, CO was adsorbed on prepared PtNi/C catalysts at 0.05 V during the introduction of 100 % CO gas for 20 min. The electrolyte was purged by Ar gas for 25 min after CO_{ad} adsorbed on the catalyst surfaces, and CO_{ad} was then oxidized by the potential sweep between 0.05 and 1.05 V with a scan rate of 20 mV s^{-1}. The ORR test was conducted to confirm the ORR activity of prepared samples. Before the ORR test, a blank CV was measured with rotating speed of 1600 rpm by 5 mV s^{-1} from 0.05 to 1.05 V in Ar-saturated 0.1 M $HClO_4$. After O_2 gas was purged for 30 min, the potential was scanned with rotating speed of 1600 rpm by 5 mV s^{-1} from 0.05 to 1.05 V with purging O_2 gas. The ORR curve was corrected by the anodic current of the blank CV. The accelerated degradation test (ADT) was performed to ensure the durability of the Pt-skin catalysts after the potential cycling of 3,000 times (scan rate = 50 mV s^{-1}) between 0.6 and 1.0 V in O_2-saturated 0.1M $HClO_4$. After 3,000 cycles, the ORR tests of the catalysts were repeated O_2-saturated 0.1M $HClO_4$, and the results were compared to the ORR activities before the ADT.

Table S1 Surface Pt oxidation states of PtNi/C-acid, PtNi/C-acid/heat, and Pt@PtNi/C-acid.

	Oxidation States	Binding Energy / eV	Ratio / %
PtNi/C-acid	Pt (0)	71.3	32.7
	Pt (II)	72.2	27.4
	Pt (IV)	73.7	39.9
PtNi/C-acid/heat	Pt (0)	71.3	44.0
	Pt (II)	72.1	28.1
	Pt (IV)	73.5	27.9
Pt@PtNi/C-acid	Pt (0)	71.3	45.5
	Pt (II)	72.1	34.4
	Pt (IV)	73.5	20.1

Table S2 Binding energy and ratio of O species of PtNi/C-acid, PtNi/C-acid/heat, and Pt@PtNi/C-acid.

	O species	Binding Energy / eV	Ratio / %
PtNi/C-acid	Metal-O or metal-like	530.7	20.5
	-CO	532.1	54.5
	Carbon functional group	533.7	25.0
PtNi/C-acid/heat	Metal-O or metal-like	530.6	14.1
	-CO	532.0	52.9
	Carbon functional group	533.7	33.0
Pt@PtNi/C-acid	Metal-O or metal-like	530.7	9.0
	-CO	532.2	56.4
	Carbon functional group	533.8	34.6

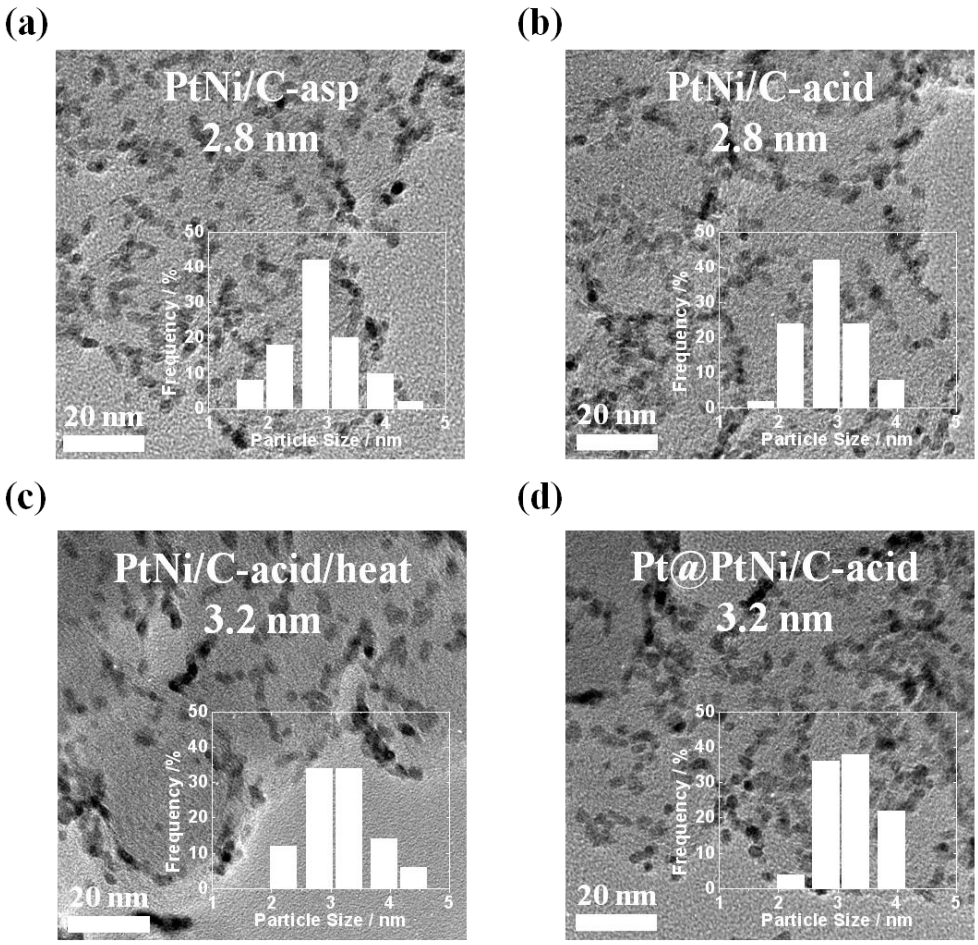

Fig. S1 TEM images, average particle sizes and particle size distributions of (a) PtNi/c-asp, (b) PtNi/C-acid, (c) PtNi/C-acid/heat, and (d) Pt@PtNi/C-acid.

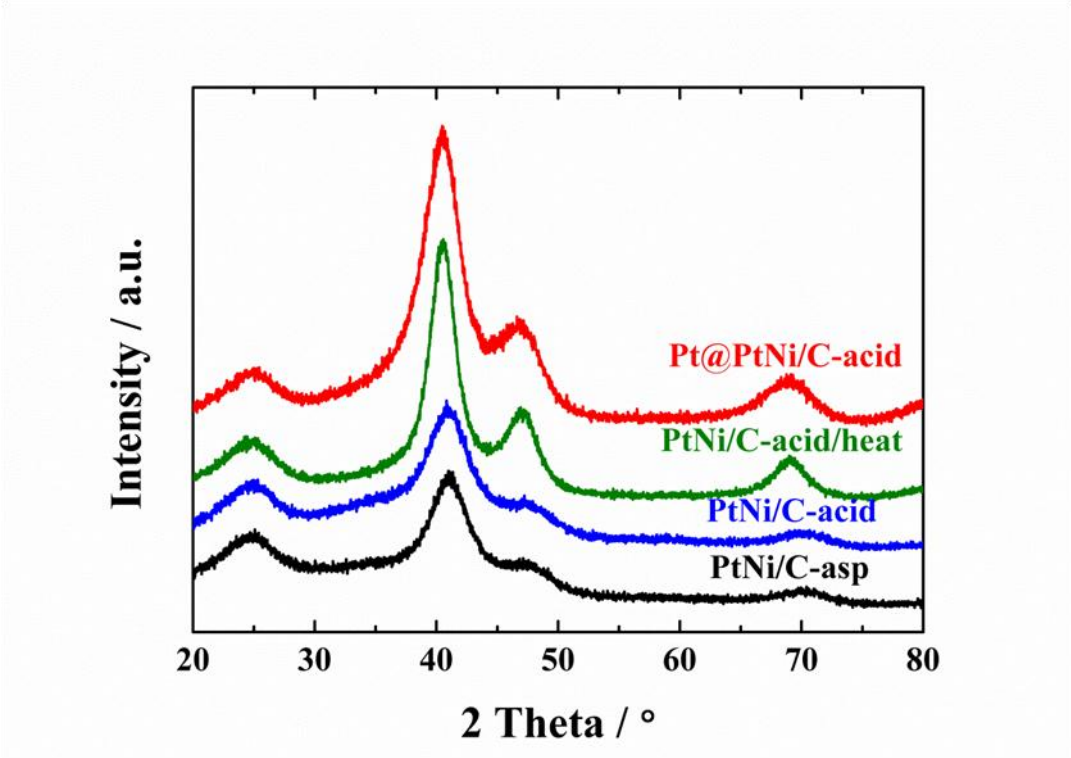

Fig. S2 XRD patterns of PtNi/C-asp, PtNi/C-acid, PtNi/C-acid/heat, and Pt@PtNi/C-acid.

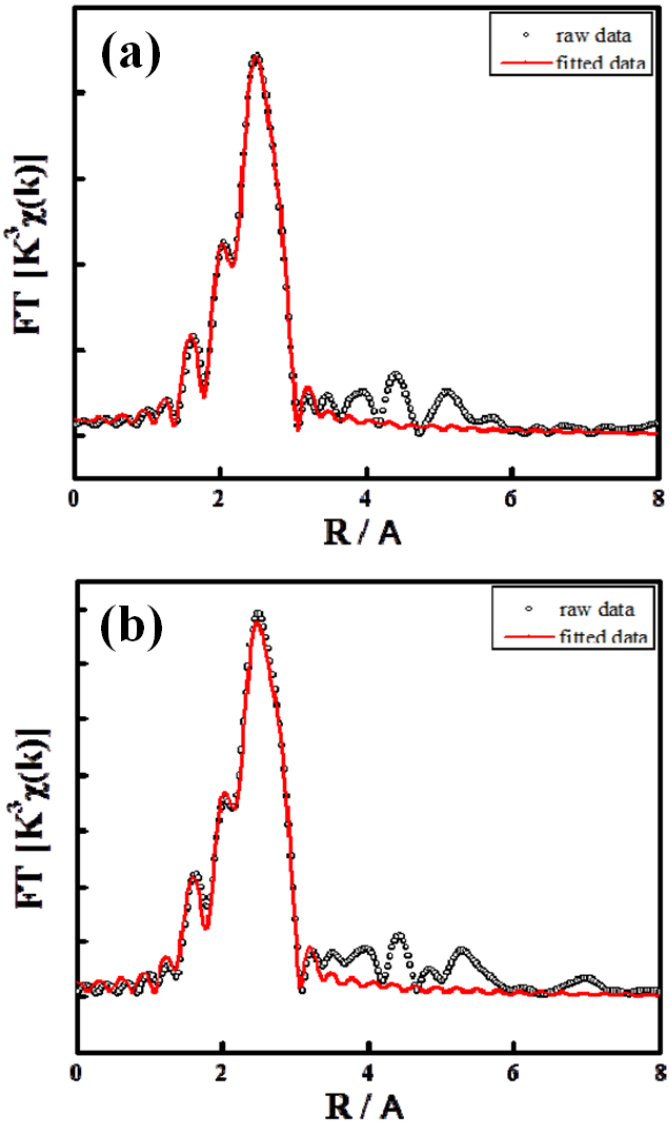

Fig. S3 EXAFS raw and fitted data (Pt L_{III}-edge) of (a) PtNi/C-acid/heat and (b) Pt@PtNi/C-acid samples in r-space with the high quality for the nearest Pt-Pt pair.

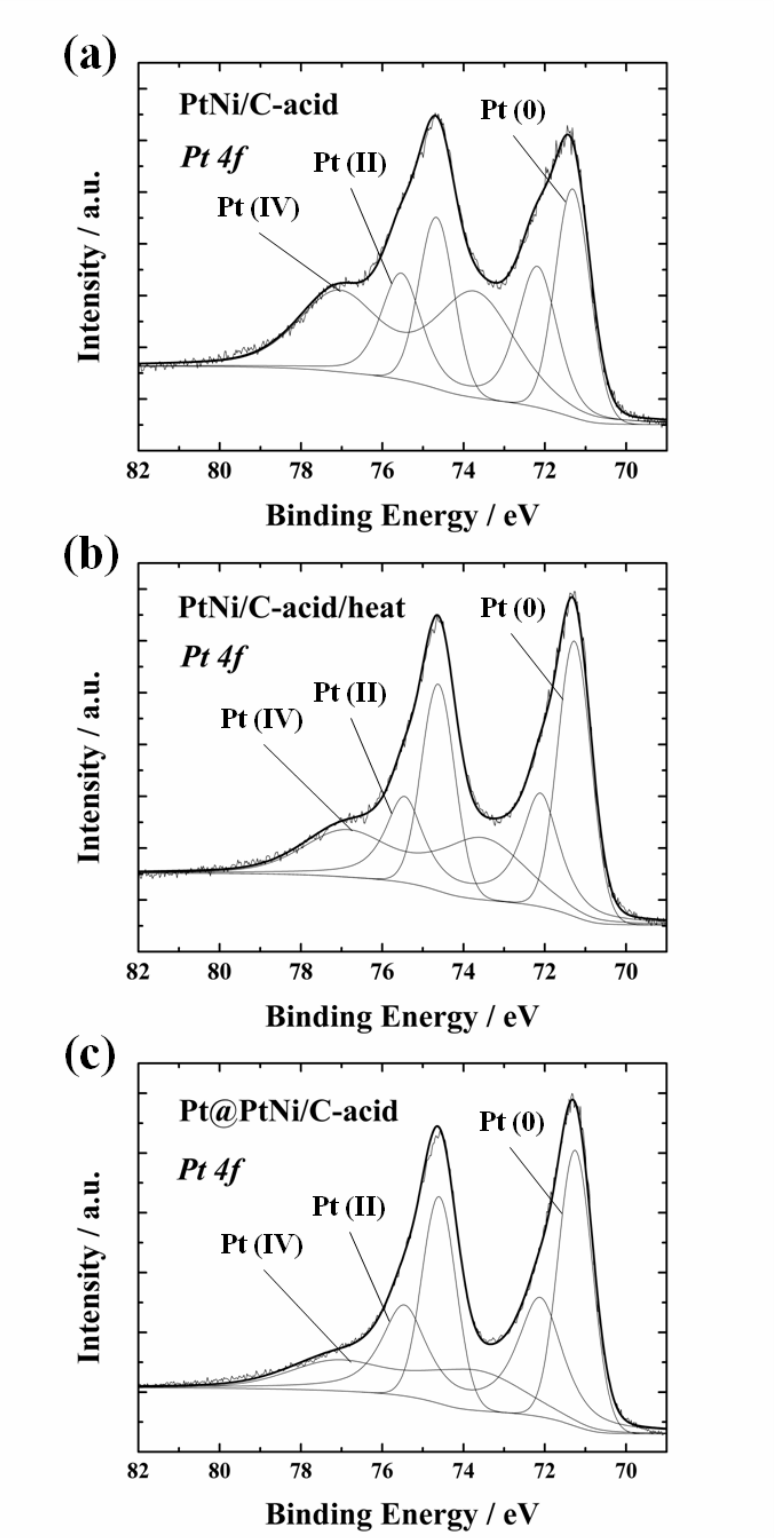

Fig. S4 Pt 4f XPS peaks and fitting curves of (a) PtNi/C-acid, (b) PtNi/C-acid/heat, and (c) Pt@PtNi/C-acid.

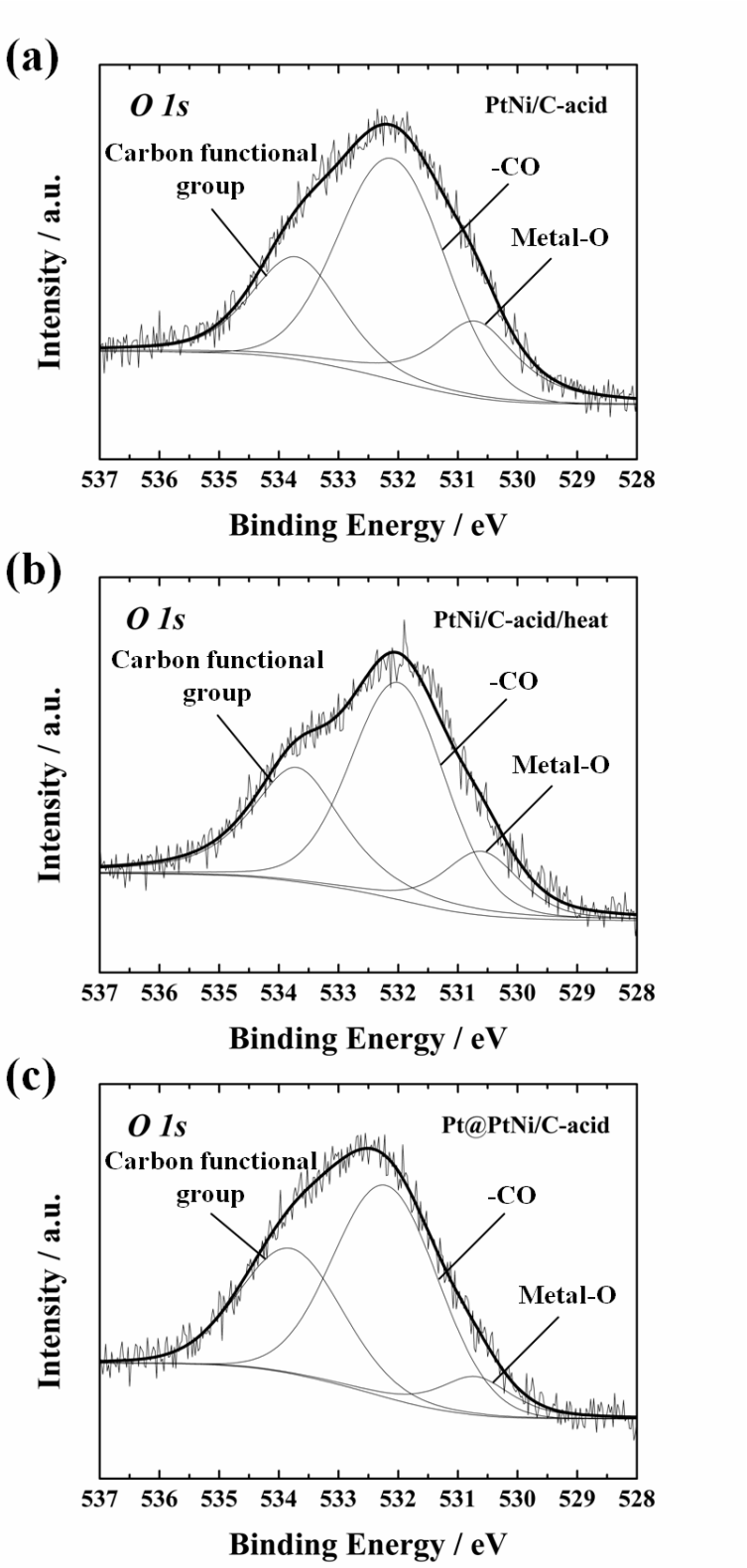

Fig. S5 O 1s XPS peaks and fitting curves of (a) PtNi/C-acid, (b) PtNi/C-acid/heat, and (c) Pt@PtNi/C-acid.

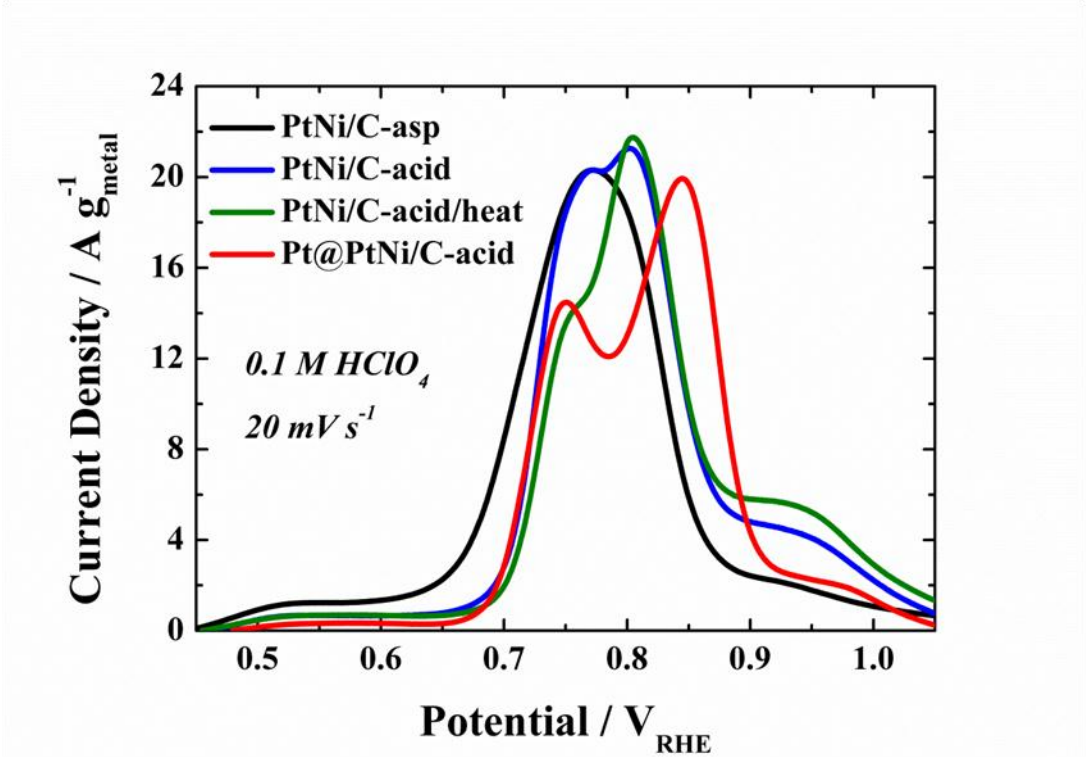

Fig. S6 CO oxidation peaks of PtNi/C-asp, PtNi/C-acid, PtNi/C-acid/heat, and Pt@PtNi/C-acid in 0.1 M $HClO_4$.

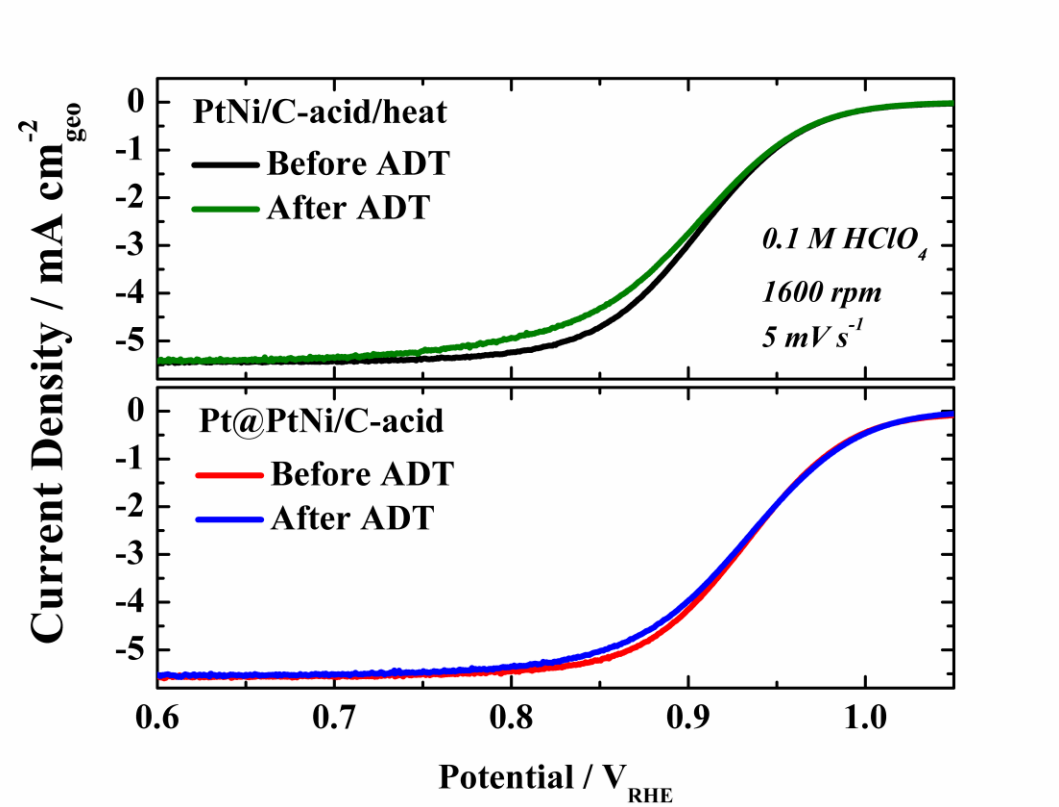

Fig. S7 The ORR polarization curves of PtNi/C-acid/heat and Pt@PtNi/C catalysts with Pt-skin surfaces before and after the ADT.