Supplementary information

Title: Shell thickness effects on restructure of NiOcore-Ptshell anodic catalysts in high current density direct methanol fuel cell

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1. Pt L3-edge XAS analysis

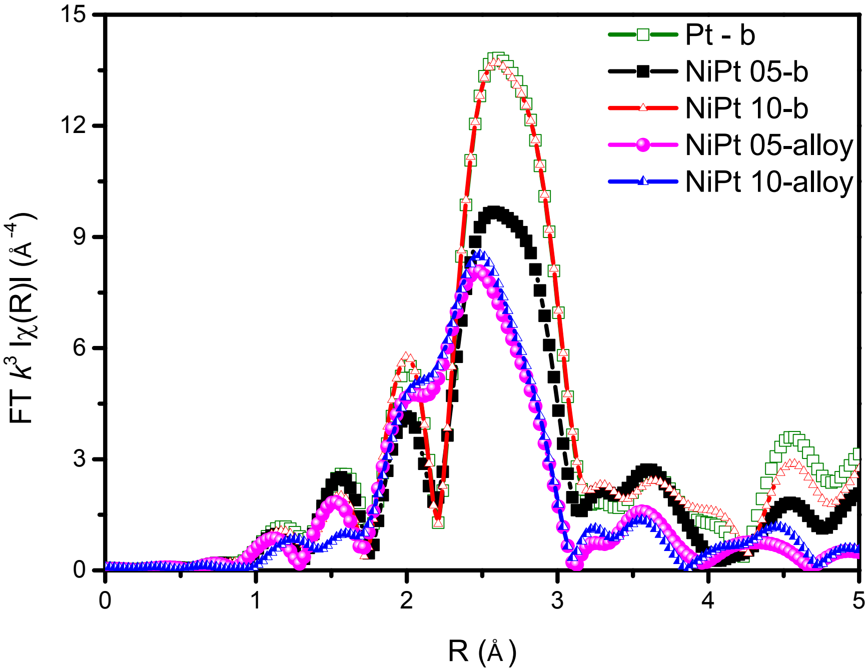

Fig. S1 Fourier transofrmed Pt L3-edge EXAFS spectra of PtRu, NiPt05, and NiPt10 NPs w/o experiencing long-term work cycle of DMFC

2. Nanostructure goemetric modeling

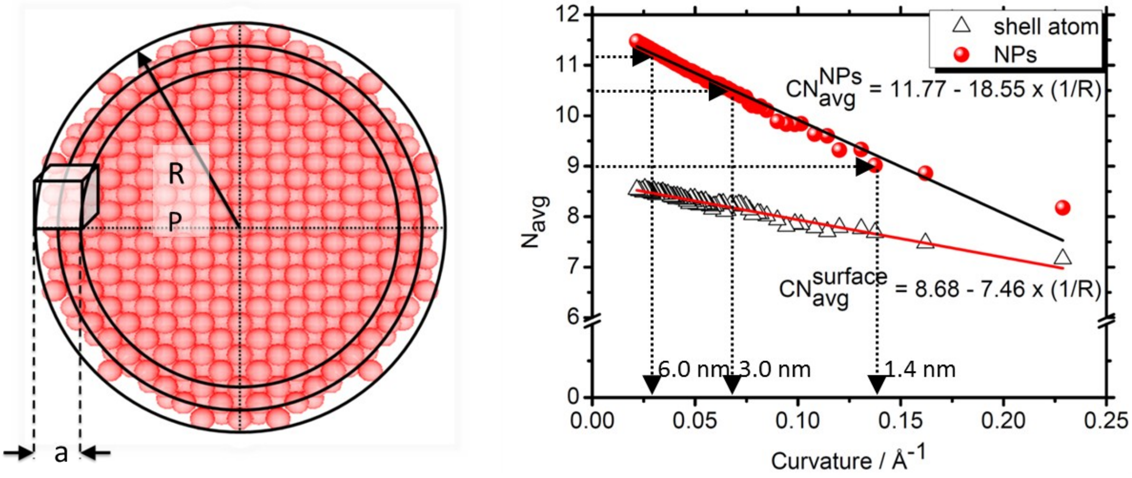

Figure S2. The average coordination numbers of surface atoms as changes with particle curvature ($1/R_P$). Where R_P is the radii of particle and a is the lattice constant of crystal. The surface atoms are set to be atoms having coordination neighbors less than 12. From this constrain, the thickness of surface atoms are set in a lattice constant deep.

3. DMFC characterizations

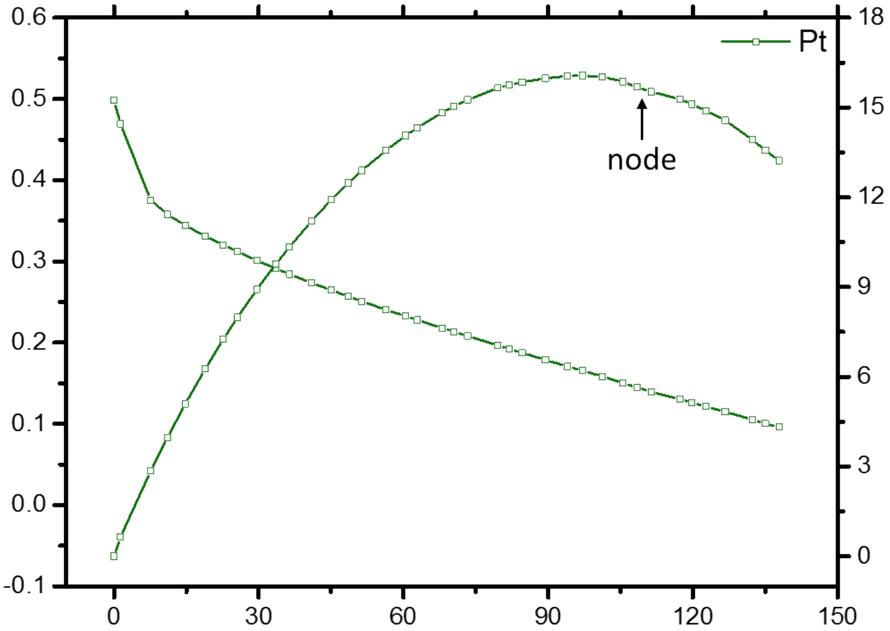

Figure S3. Polarization curves for DMFC with Pt anode at 70°C.

Table S1 Electrochemical properties of experiment NC in DMFC anode.

NC	**I_{DMFC} (NC) (mA cm^{-2})**	**ΔI_{DMFC} (NC vs. Pt) (%)**	**ECSA (cm^{-2} mg^{-1})**	**Δ ECSA (NC vs. Pt) (%)**
Pt	140.0	0.0	37.7	0.0
PtRu	152.0	8.6	25.8	-31.6
NiPt05	450.0	221.4	34.9	-7.4
NiPt10	285.0	103.6	21.3	-43.5

For measuring ECSA, the CV test was conducted in the electrolyte of 0.5 M $H_2SO_{4(aq)}$. In long-term MOR, the electrolyte is mixture of 0.5 M methanol and $H_2SO_{4(aq)}$. During the DMFC measurements, the cell is heated to 70 ^{o}C and is fed with 1.0 M of methanol (MeOH) and H_2SO_4 solution with a flux of 60 ml h^{-1} at anode and the 100 sccm of oxygen flow at cathode.

ΔI_{DMFC} (NC vs. Pt, %) = ($I_{DMFC\_NC} - I_{DMFC\_Pt}$) / I_{DMFC_Pt} x 100%

Δ ECSA (NC vs. Pt) = (ECSA (NC) – ECSA (Pt)) / ECSA (Pt) x 100%

4. Ni K-edge XAS analysis

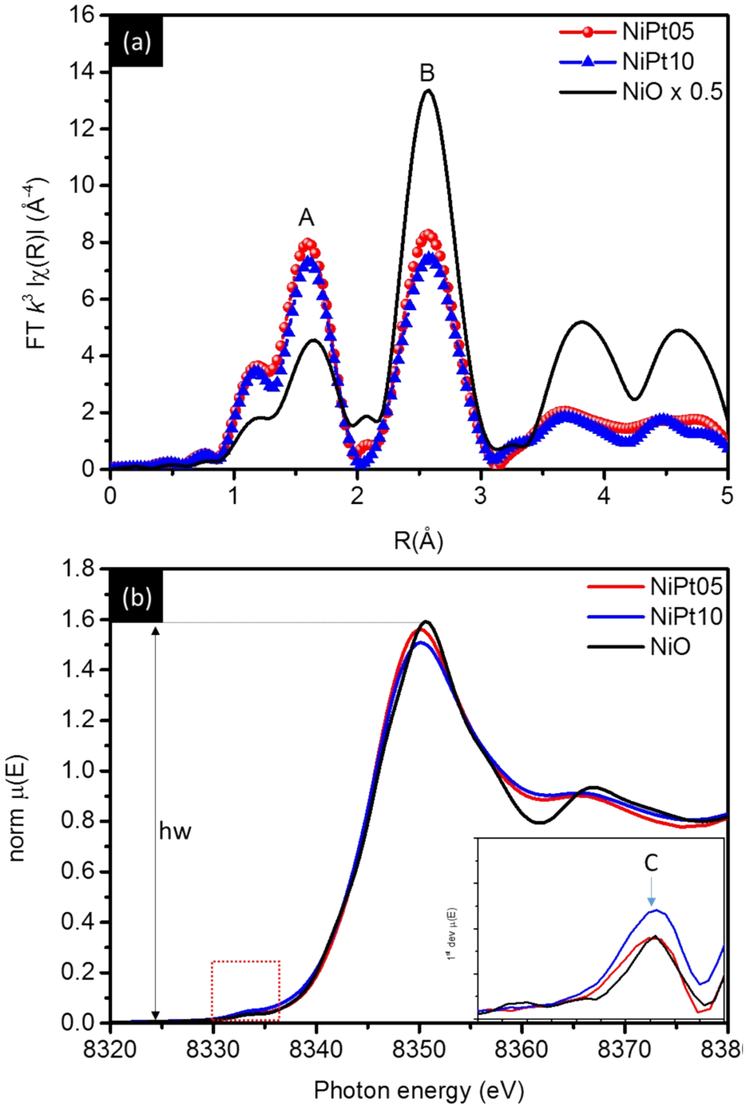

Fig. S4 (a) Fourier transformed extended X-ray fine structure spectra and (b) X-ray absorption near-edge spectra of experimental NiPt05, NiPt10 NPs and standard NiO sample (with the intensity multiplied by 0.5).

Fig. S4. The (a) Fourier transformed extended X-ray fine structure spectra (radial structure function) and (b) X-ray absorption near-edge spectra of experimental NiPt05, NiPt10 NPs and standard NiO sample. In Fig. R1a, the radial peaks A and B correspond to the contributions of X-ray interferences from bond pairs of 1st (Ni-O) and 2nd (Ni-Ni) coordination shells of NiO crystal. The significantly decreased peak B intensity depicts the lack of scattering matters of nanoparticles as compared to bulk NiO crystal.

The corresponding X-ray near-edge spectra are compared in Fig. S4b, where inset shows the 1st deviation results of the spectra. As indicated, the position of 1st deviation peak refer to the value of threshold energy for electron transitions from 1s to 3p or 4s orbitals. In a K-edge XANES spectrum, this value is proportional to the chemical states of targeting element. Accordingly, NiPt05 and NiPt10 NPs have similar chemical state to NiO. In addition, the whiteline intensity (hw) depicts the extent of empty state in 3p / 4s orbital of Ni in experimental sample. In this event, the hw (i.e., extent of electron relocation from Ni to neighboring atoms) of NiPt NPs is lower than that of NiO. In addition, the higher hw suggests the higher extent of Ni oxidation of NiPt05 as compares to NiPt10.