Electrical Supplementary Information

Title: Heterojunction Confinement on Atomic Structure Evolution of Near Monolayer Core-Shell Nanocatalysts in Redox Reactions of Direct Methanol Fuel Cell

Authors: Tsan-Yao Chen,[a,b,*] Guo-Wei Lee,[c,‡] Yu-Ting Liu,[d] Yen-Fa Liao,[e] Chun-Chih Huang,[a] Deng-Sung Lin,[c,*] and Tsang-Lang Lin[a]

Affiliations:

[a] Department of Engineering and System Science, National Tsing Hua University, Hsinchu 30013, Taiwan

[b] Institute of Nuclear Engineering and Science, Hsinchu 30013, Taiwan

[c] Department of Physics, National Tsing Hua University, Hsinchu 30013, Taiwan

[d] Department of Environmental Science and Engineering, Tunghai University, Taichung 40704, Taiwan

[e] National Synchrotron Radiation Research Center, Hsinchu 30013, Taiwan

[*]To whom correspondence should be addressed:

Tsan-Yao Chen, email: chencaeser@gmail.com Tel: +886-3-5715131#34271;

Deng-Sung Lin, email: dengsunglin@gmail.com

1. Characterization methods and parameters for measuring the DMFC module

After the DMFC stack was fixed, the MEA inside the stack was activated by flowing with 0.5 M of H_2SO_4 solution for 24 h and then connected with 850e cables and fuel suppliers prior to the electrochemical measurement. During the measurement, the stack was heated to 30, 50, and 70^{o}C and feed by 1.0 M of methanol solution with the flux of 60 ml/h at anode and the 100 sccm of oxygen flow at cathode at the identical temperature of the DMFC stack, respectively. The entire stack was stabilized for at least 30 min (or at a stable open circuit voltage) prior to the electrochemical (I-V curve and power density) measurement.

The polarization curves for the DMFC modules equipped with PtRu alloyed and PtS/RuC NCs are shown in Fig. S1.

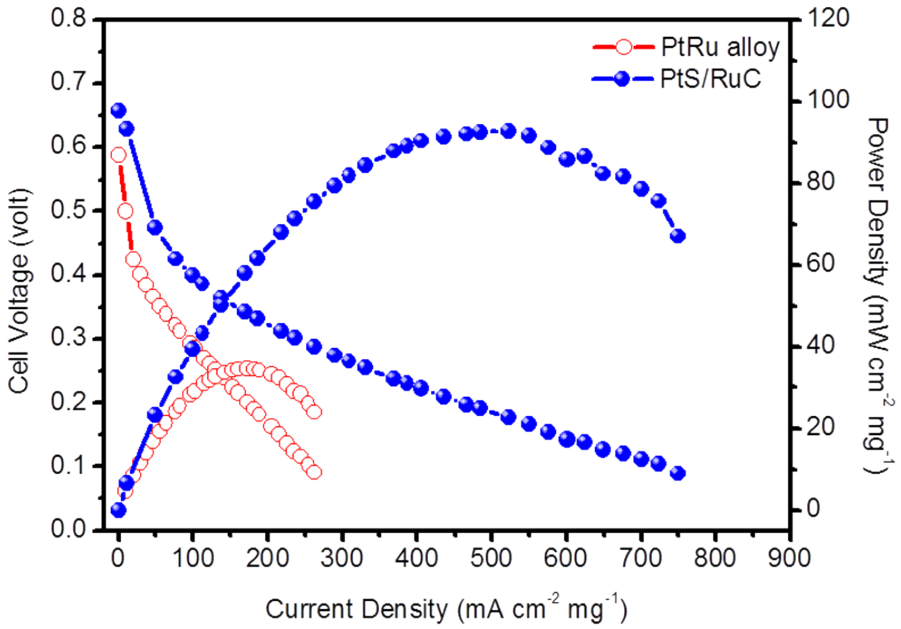


Fig. S1. The polarization curves of DMFC modules equipped with PtRu alloyed (open sphere with solid line) and PtS/RuC NCs (solid spheres with solid line) at anode.

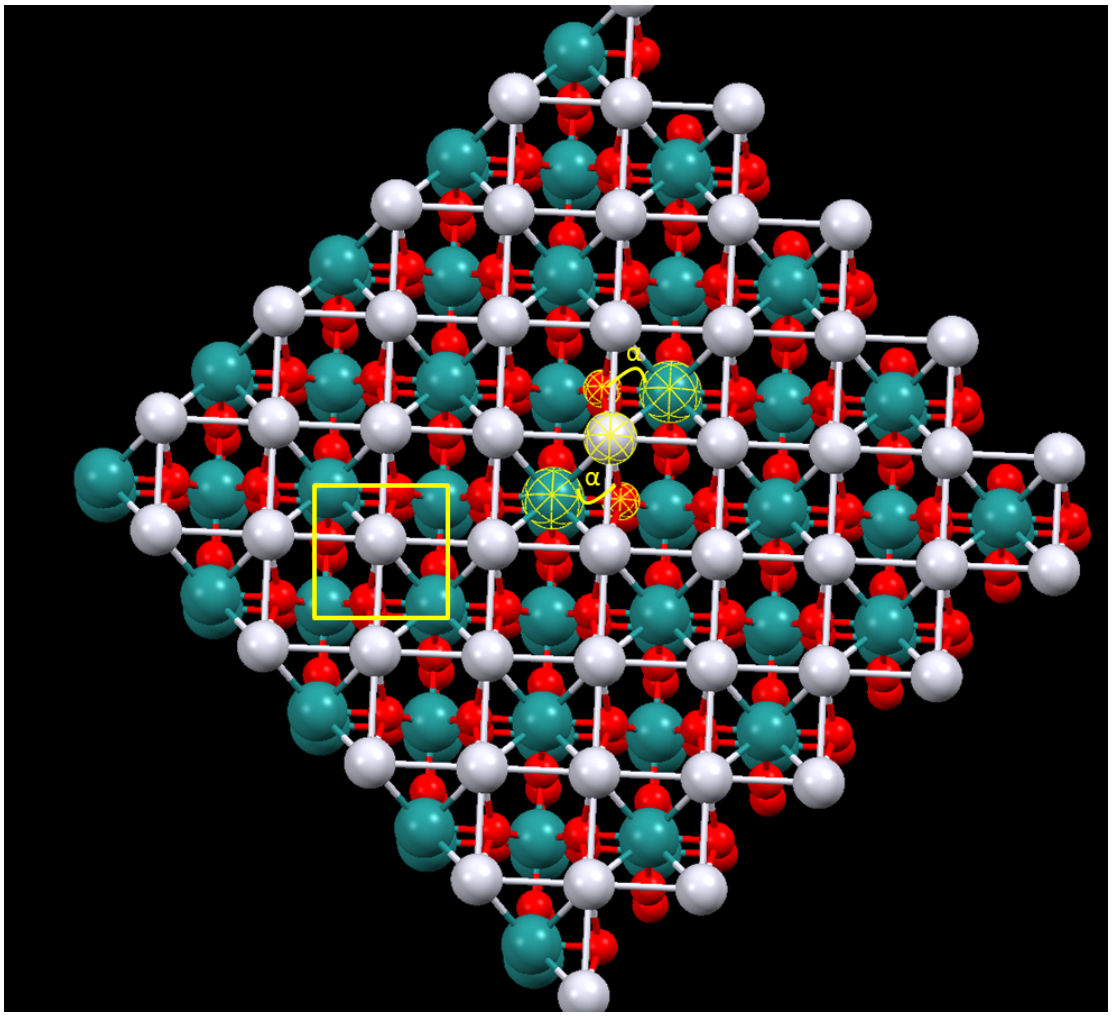


Fig. S2. The ball and stick plot for the simulated density function theory bimetallic models of (a) PtS/RuC NCs: Pt on (001) RuO_2 "4×4 RuO_2 + 32 Pt". The simble « α » refers to the bond angles for the Pt-O-Ru bonds.

2. XPS analysis on PtRu alloy and PtS/RuC NCs

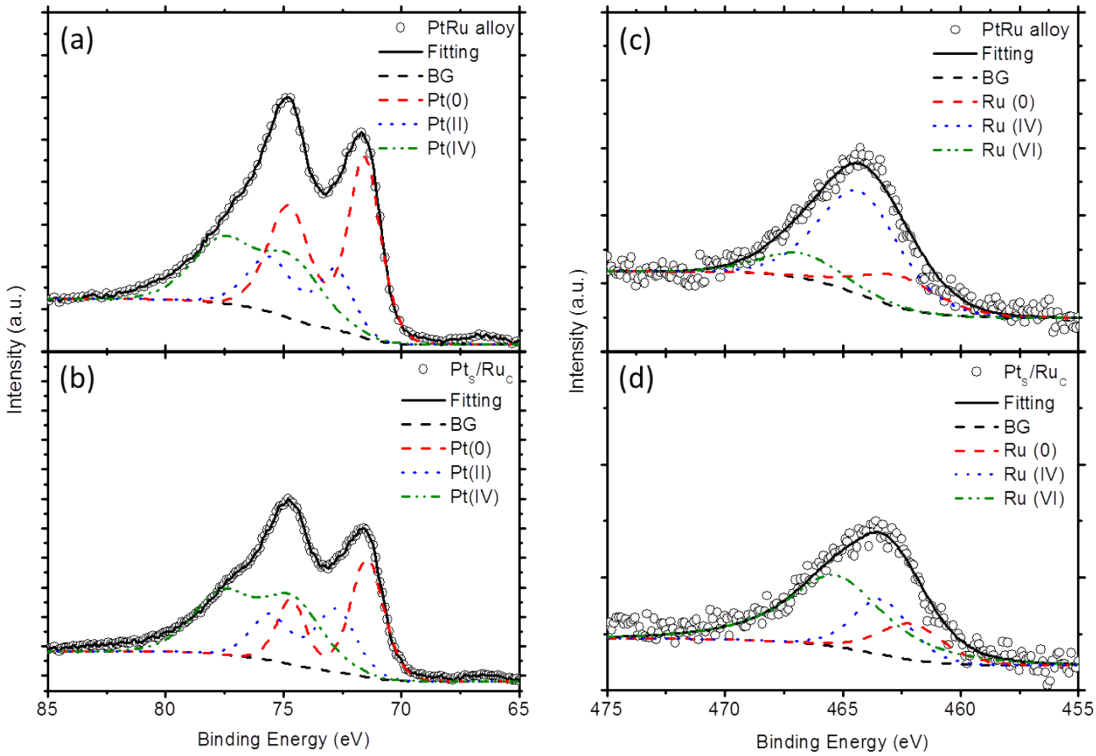


Fig. S3. The Pt4f XPS spectra of (a) PtRu alloy and (b) PtS/RuC NCs. (c) and (d) refer to the Ru 3p XPS spectra of the two samples (as denoted by the text in the figures), respectively.

Table S1. The XPS determined structure parameters of RuPt alloy and PtS/RuC NCs.

	Pt 4f			Ru 3p		
NCs	species	BE (eV)[b]	AR (%)[a]	species	BE (eV)	AR (%)
RuPt alloy	Pt(0)	71.57	47.45	Ru(0)	460.12	19.19
	Pt(II)	72.76	20.33	Ru(IV)	462.18	64.79
	Pt(IV)I	74.61	32.22	Ru(VI)	465.17	15.52
PtS/RuC	Pt(0)	71.25	42.95	Ru(0)	461.10	17.64
	Pt(II)	72.11	27.86	Ru(IV)	462.36	23.50
	Pt(IV)I	74.08	13.84	Ru(VI)	464.32	58.85
	Pt(IV)II	75.56	15.35			

[a] BE: binding energy. [b] AR: the relative area (composition) ratios of each specie.

3. TEM and SEM analysis

The TEM images with EDX results of PtS/RuC and PtRu alloyed NCs are shown in **Fig. S3**. The agglomeration of NCs is caused by the ultrasonic treatment upon preparing the TEM samples. Accordingly, the Pt/Ru ratio of PtS/RuC is determined to be 7/3 and can be attributed to a certain extent of fluorescence shielding effects on Ru signal by the Pt shell encapsulation. It is interesting to note the presence of rod like structure in the samples of PtRu alloyed NCs. From EDX analysis, we notice that these nanorods are composed of RuO_2 nanocrystallites and again revealing the Ru dissolution and crystal regrow as that was proposed by XAS analysis.

The high resolution and low resolution SEM images of the PtS/RuC and PtRu alloyed NCs are shown in Fig. S4. As clearly indicated, the PtS/RuC NCs is homogeneously dispersed at CNT. On the other hand, the agglomeration of PtRu alloyed NCs is evident.

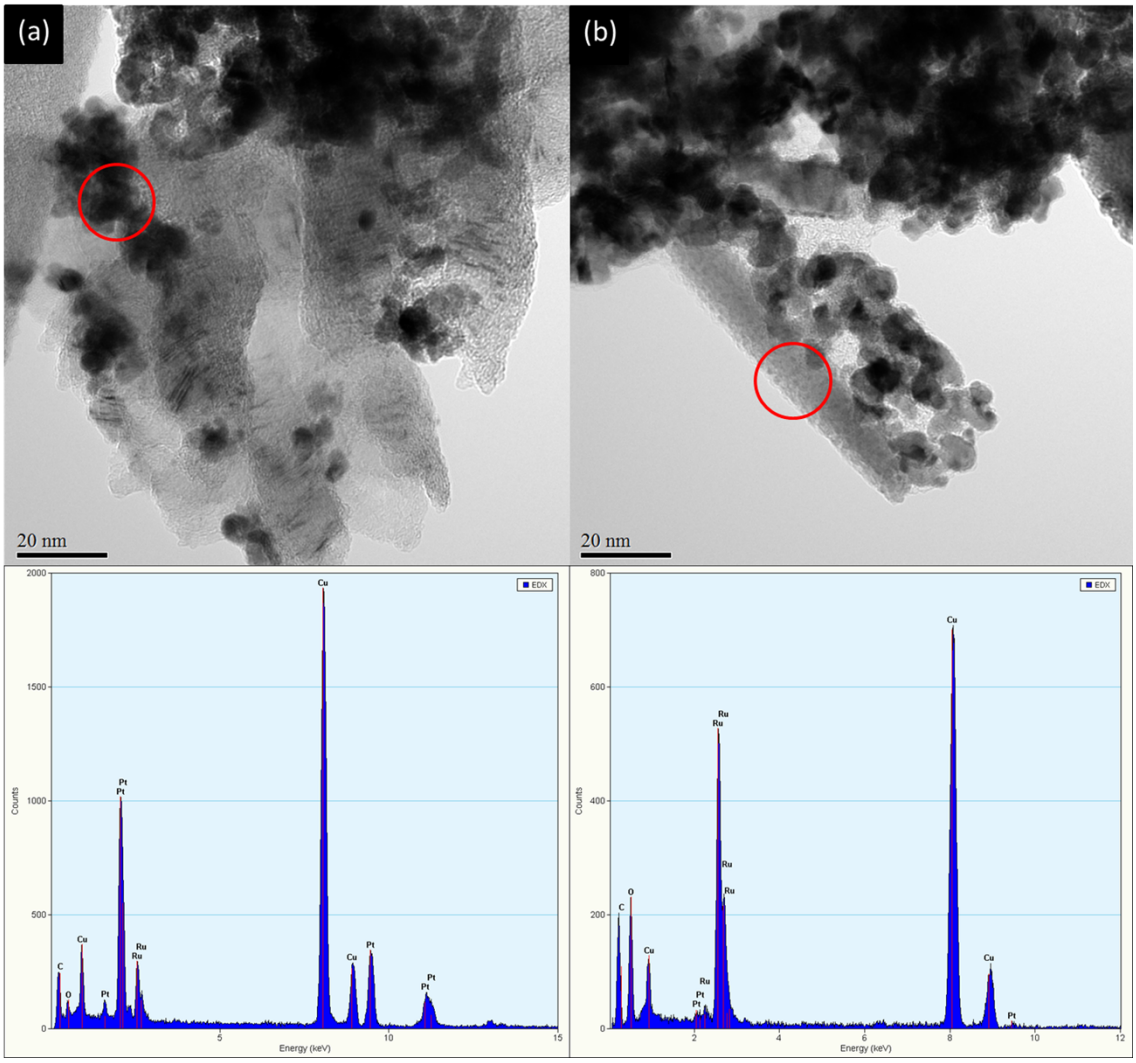


Fig. S3. TEM images with corresponding EDX results of PtS/RuC and PtRu alloyed NCs supported at CNT.

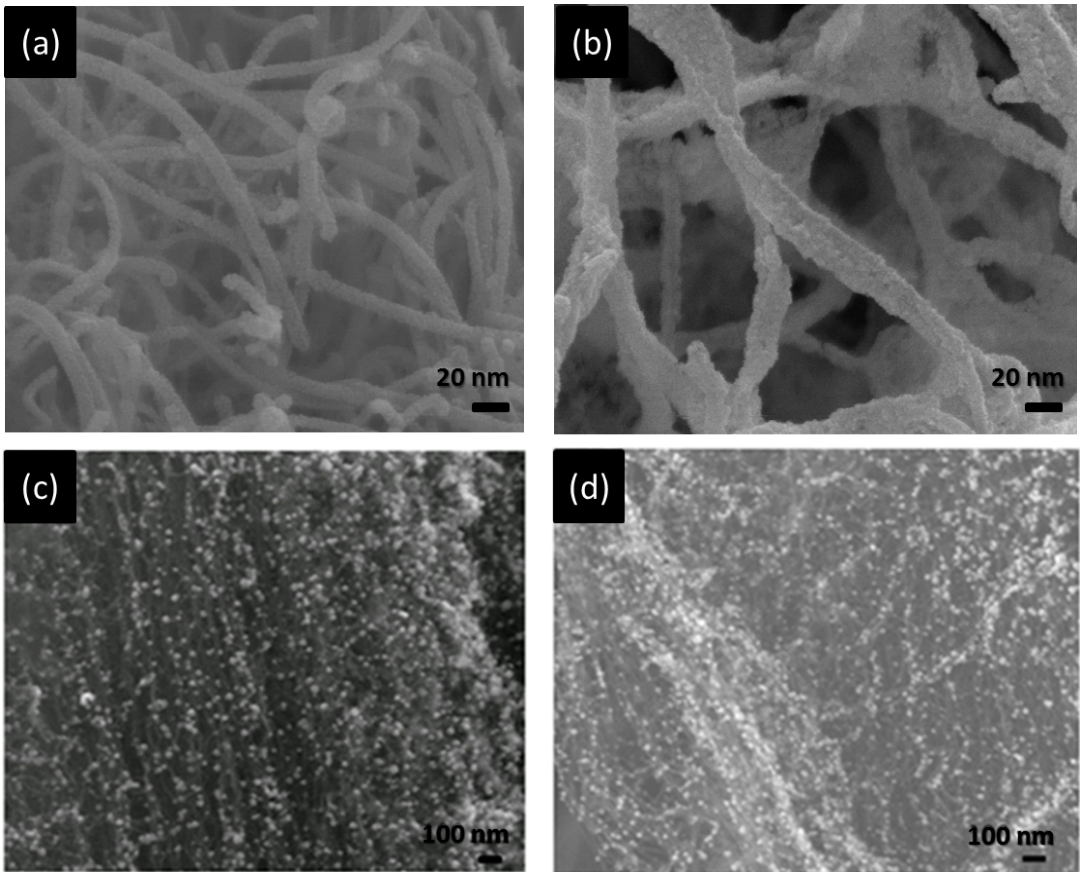
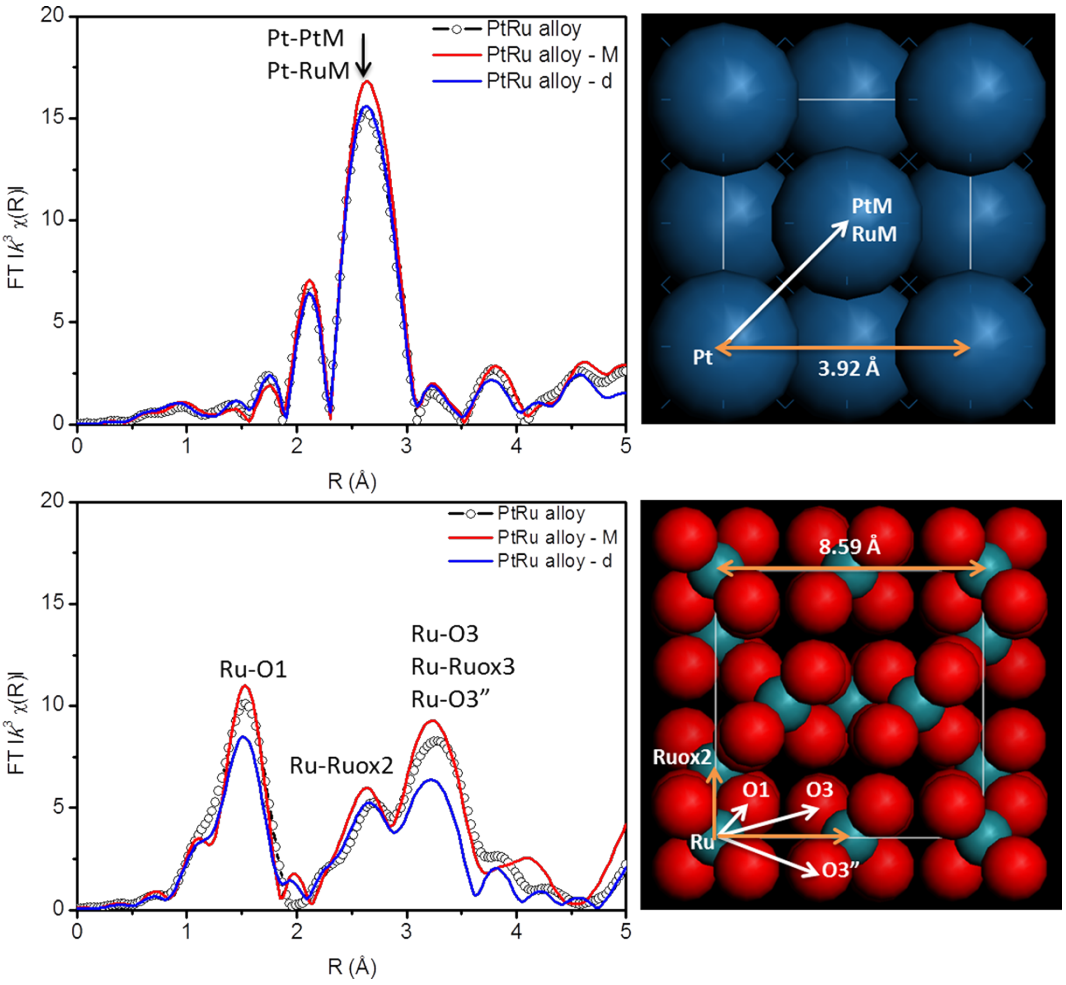


Fig. S4. High resolution images of (S4a) PtS/RuC and (S4b) PtRu alloyed NCs supported at CNT; where Figure (S4c) and (S4d) show the corresponding low resolution SEM images (S4a) and (S4b), respectively.

4. XAS analysis



Scheme S1. The radial structure function of PtRu alloyed NPs at Pt L_3 (top) and Ru K-edges (bottom) with the corresponding atomic structure models for center atoms (presented in the unit cells of Pt in f.c.c and RuO_2 in tetragonal phases).