Electronic Supplementary information (ESI) *for*

Ruthenium Core-activated Platinum Monolayer Shell High Redox Activity Cathodic Electrocatalysts for Dye-Sensitized Solar Cells

Tsan-Yao Chen,[a,b*] *Ha M. Nguyen,*[a] *Yu-Ting Liu,*[c] *Liang-Jen Fan,*[d] *Chiun-Yi Wu,*[a] *Tzy-Jiun Mark Luo,*[b] *Chih-Hao Lee,*[a,d] *Yaw-Wen Yang,*[d] *Ten-Chin Wen,*[e] *and Tsang-Lang Lin*[a*]

Affiliations:

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

[b] Department of Materials Science and Engineering, North Carolina State University, Raleigh, North Carolina 27695, USA

[c] Department of Civil and Environment Engineering, Duke University, Durham, North Carolina 27708, USA

[d] National Synchrotron Radiation Research Center, Hsinchu 30076, Taiwan

[e] Department of Chemical Engineering, National Cheng Kung University, Tainan 70101, Taiwan

[*]To whom correspondence should be addressed: Tsan-Yao Chen, email: chencaeser@gmail.com; Tsang-Lang Lin, email: tllin@mx.nthu.edu.tw; Tel: +886-3-5742671 (O); +886-3-5728445 (Fax)

1. surface ratio estimation by SAXS analysis

Assuming that the NPs are spherical particles, the Pt utilization (which is a qualification corresponding to the specific number density of surface reaction sites for electrocatalysts, ψ) can be estimated by equation 1:

$$\langle \psi \rangle = \frac{n_{Pt\_s}}{n_{Pt\_t}} \qquad \text{(S1)}$$

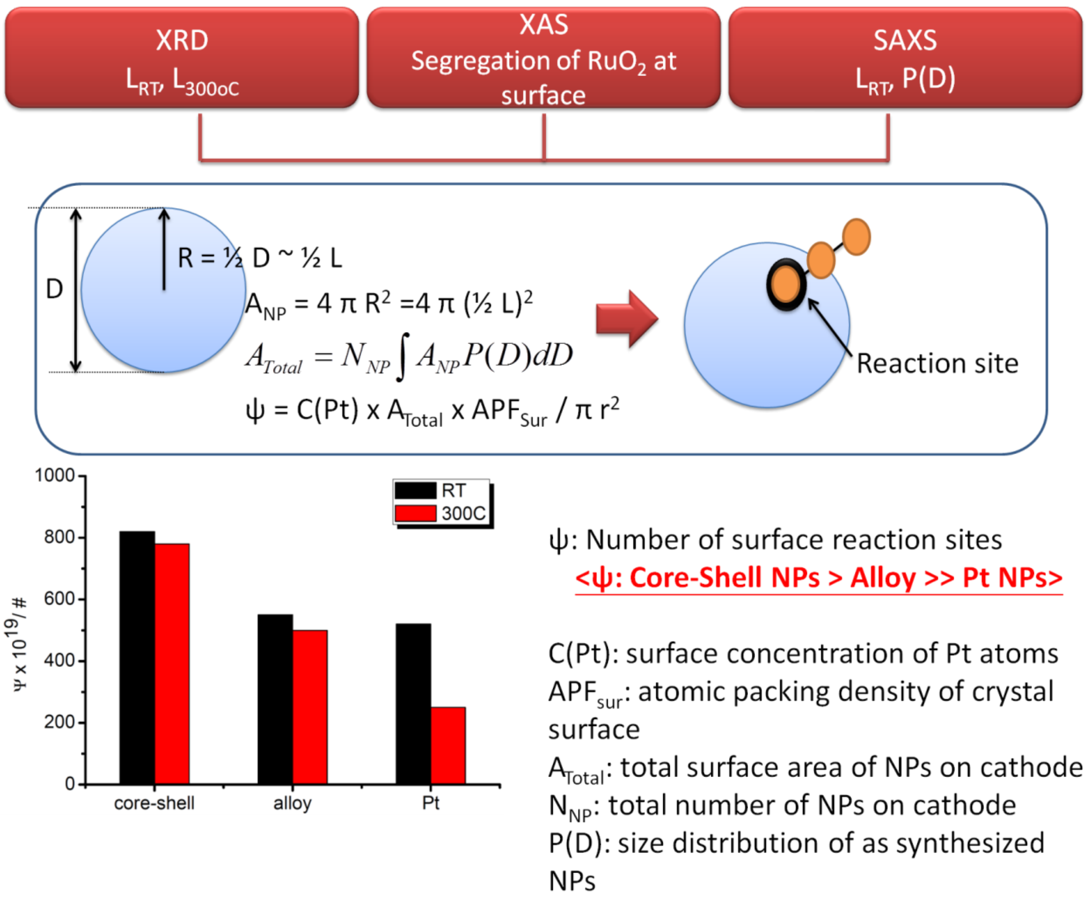
where n_{Pt_s} and n_{Pt_t} are the number of surface and total Pt atoms in a NPs, respectively. These two value can be represented by the D_{avg} and $P(D)$ as follow:

$$\frac{n_S}{n_t} = \frac{A_{NPs} \times P_S \times C_{Pt} \times r}{\left((\frac{D_{avg}}{2})^3 - (\frac{D_{avg}}{2} - t)^3 \right) \times P_L} \qquad \text{(S2)}$$

where A_{NPs} is the average surface area of NPs and C_{Pt} is the surface Pt concentration of NPs, respectively. P_S and P_L denote the atomic packing factor of surface and bulk of NPs. The details for numerical derivation are given in the SI. The A_{NPs} can be determined by an integral that taken over the whole range of particle size distribution ($D_{\text{min}} < D < D_{\text{max}}$, as a function of $P(D)$) in equation 3:

$$A_{NPs} = \int \pi D^2 P(D) dD \qquad \text{(S3)}$$

Accordingly, since the Pt shell is ~1.5 monolayers thick the Pt utilization (ψ) of Ru_{core}–Pt_{shell} NPs is determined to be ~90%, which is about 61% higher than that of Pt NPs.



Scheme S1. Strategies and results of the specific surface ratio and active sites for the nanoparticles combining SAXS, XRD, and XAS analyses.

2. Pt L-edges XAS analysis

Figure S1 compares the normalized Pt L_2-edge X-ray absorption near-edge spectra of Pt NPs and Ru_{core}-Pt_{shell} NPs with that of Pt foil. The intensity of peak A and the post-edge features (B and C) correspond to the extent of $2p_{3/2}$ to $5d_{3/2}$ charge transition probability and the multiple photoelectron interferences, respectively. In general, the higher the peak A intensity the higher the transition probability is expected. On the other hand, the higher the integrated intensity across the B and C area, the better local structure of the Pt domain. Hereby, the highest peak A with the smallest B and C amplitude of Ru_{core}-Pt_{shell} NPs are indications for the largest extent of charge donation from the 2p core level to the valence states among the three samples.

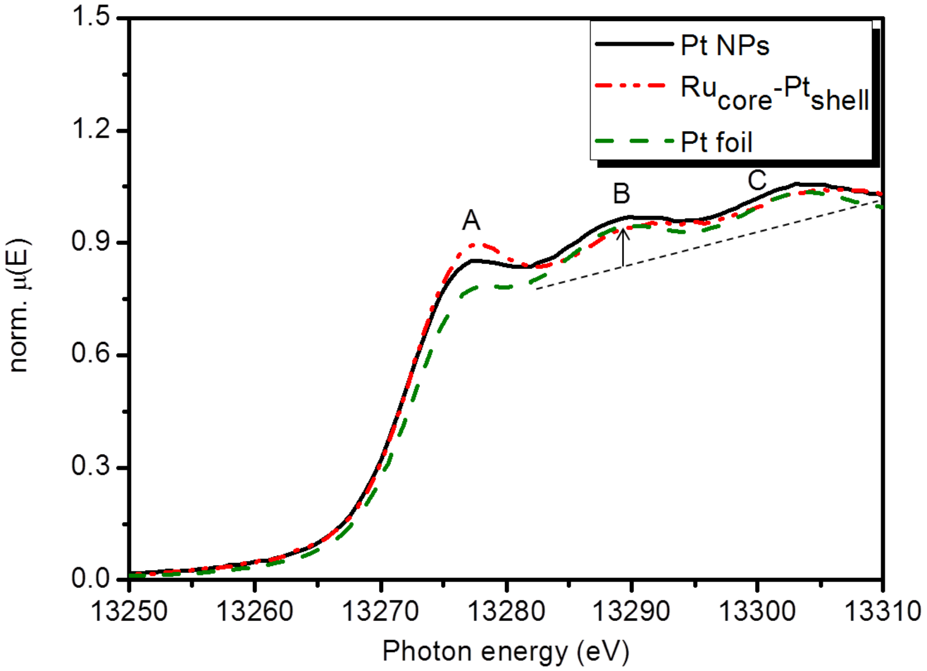


Figure S1. Pt L_2-edge XANES spectra of Pt NPs and Ru_{core}–Pt_{shell} NPs compared with Pt foil.

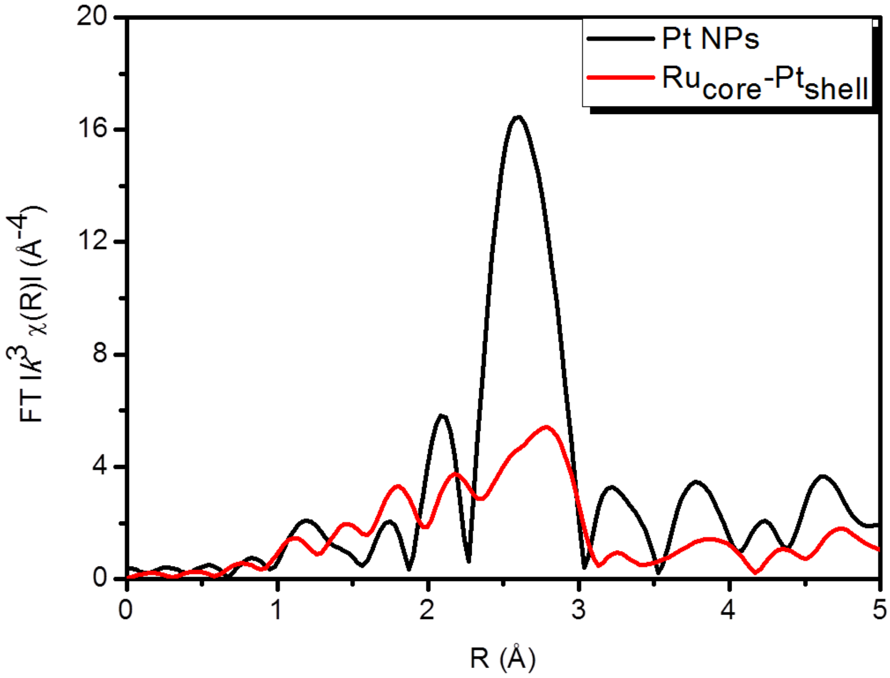


Figure S2. Pt L_3-edge EXAFS radial structure functions.

Table S1. XAS obtained structure parameters of Pt and Ru$_{core}$-Pt$_{shell}$ NPs.

NPs	CN_{Pt-Pt}	CN_{Pt-Ru}	CN_{total}	Sigma (Å^2)
Pt NPs	10.79	NA	10.79	0.008
Ru$_{core}$-Pt$_{shell}$	5.05	0.76	5.81	0.007

CN_{Pt-Pt} and CN_{Pt-Ru} denote the coordination number of Pt and Ru atoms around center Pt atom, respectively, and CN_{total} denotes the sum of the two.

According to the fitting results, the CN_{total} of Pt atoms in Ru$_{core}$-Pt$_{shell}$ NPs is determined to be 5.81. This number is about similar to the Pt atoms at interfacets edges. Presumably the Pt atoms would form a thin layer of shell structure at the truncated disk-like Ru core surface. In the meantime, consider that the average particle size of Pt NPs is 6.1 nm, a slight negative offset of CN_{total} (10.79) is found compared to that of theoretical prediction (10.9 - 11.0). This is possibly due to the formation of surface defects and the shape merging effects.

3. UPS and XPS analysis of Pt NPs, Rucore-Ptshell NPs, PtRu alloy, and Ru NPs

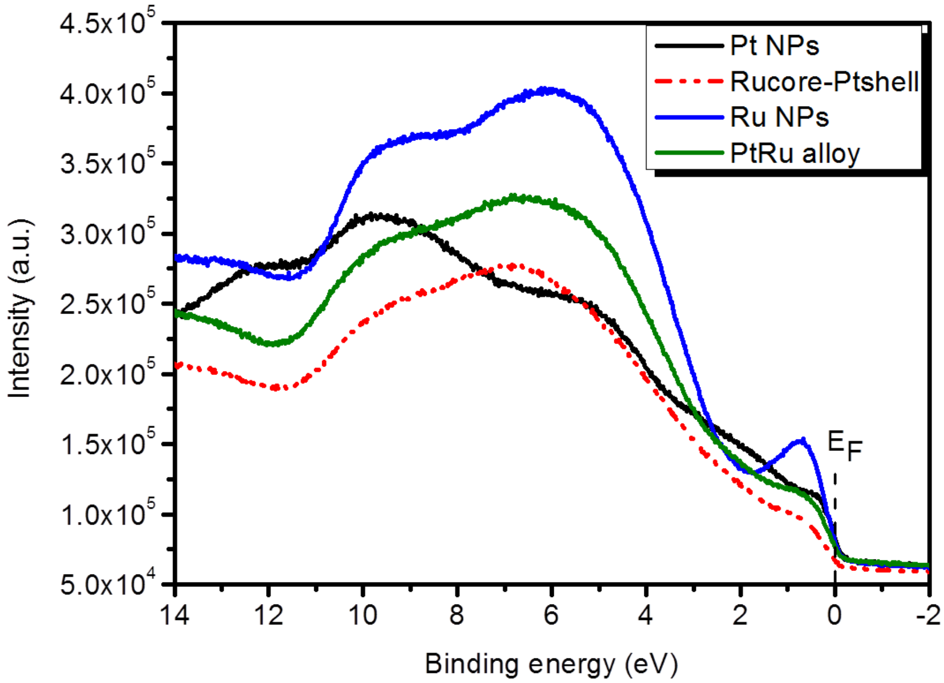


Figure S3. The VB spectra of Ru NPs and PtRu alloy compared with that of experiment NPs

5. Fabrication of DSCs module.

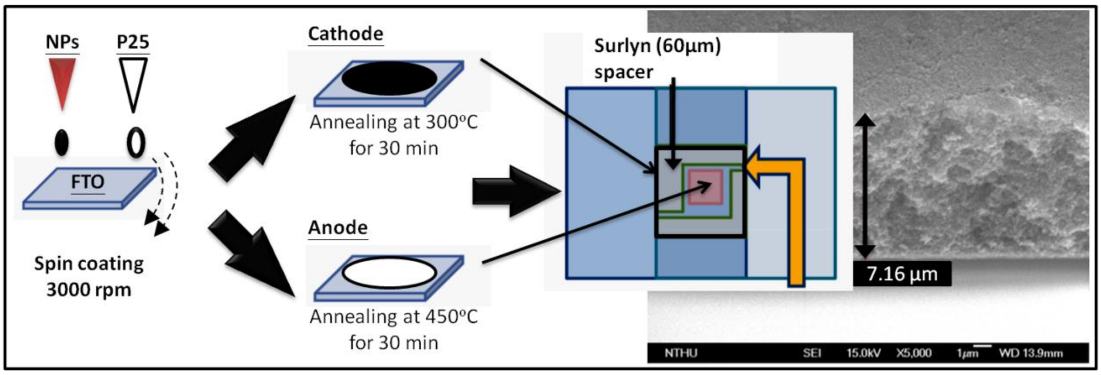


Figure S4. Schematic representation for the fabrication of NPs coated cathode and

Electronic Supplementary Material (ESI) for Journal of Materials Chemistry A

anode in a DSCs module.