

Supplementary Information For:

**Tailoring Ruthenium Exposure to Enhance the Performance of *fcc*
Platinum@Ruthenium Core-Shell Electrocatalysts in the Oxygen Evolution
Reaction**

Noktan M. AlYami,^a Alec P. LaGrow,^{a,b} Khurram S. Joya,^{c,d} Jinyeon Hwang,^e Khabiboulakh Katsiev,^f Dalaver H. Anjum,^g Yaroslav Losovyj,^h Lutfan Sinatra,^a Jin Young Kim,^e and Osman M. Bakr^{*,a}

^aDivision of Physical Sciences and Engineering, Solar and Photovoltaics Engineering Research, King Abdullah University of Science and Technology (KAUST), Thuwal 23955-6900, Saudi Arabia, E-mail: Osman.bakr@kaust.edu.sa

^bJEOL Nanocenter and Department of Physics, University of York, Heslington, York YO10 5DD, United Kingdom

^cLeiden University, Einsteinweg 55, P.O. Box 9502, 2300 RA, Leiden, The Netherlands

^dDepartment of Chemistry, University of Engineering and Technology (UET), GT Road, 54890 Lahore, Pakistan

^eFuel Cell Research Center, KIST, Hwarangno 14-gil 5, Seongbuk-gu, Seoul 136-791, Republic of Korea

^fSABIC Corporate Research and Development Center, King Abdullah University of Science and Technology (KAUST), Thuwal 23955- 6900, Saudi Arabia

^gImaging and Characterization Lab, King Abdullah University of Science and Technology (KAUST), Thuwal 23955-6900, Saudi Arabia.

^hDepartment of Chemistry, Indiana University, Bloomington, IN 47405, USA

Calculation method: The estimated values of Ru mass activity (A/g_{Ru}) of all catalysts were calculated from Ru loading ($mg_{Ru} cm^{-2}$) and measured current density ($mA cm^{-2}$) at overpotential (η) = 0.22 V vs. NHE by using this formula: mass activity = Ru loading/current density. From EDS (table S1), we assume that Ru atoms% is approximately 40% for all platinum-ruthenium catalysts. Based on that we calculated Ru loading by using this equation= $0.4 \times 30 \mu g = 12 \mu g$. For pure Ru nanoparticles, the loading is 30 μg .

Table S1. The particle and shell size of platinum-ruthenium nanocrystals extracted from HAADF-STEM images and XRD profiles by applying the Scherer formula. Also, the average compositional ratio of platinum and ruthenium from EDS analysis in Fig. 1.

Sample	Crystallite Size, nm (XRD)	Shell Size, nm (XRD)	Shell Size, nm (STEM)	Pt, atoms% (EDS)	Ru, atoms% (EDS)
Pt@Ru _{Cuboctahedral}	4.6	-	0.7 ± 0.2	61 ± 2%	39 ± 4%
Pt@Ru _{Dendritic}	6.2	2.3	1.8 ± 0.3	63 ± 3%	37 ± 5%
PtRu _{Alloy}	3.2	-		62 ± 4%	38 ± 5%

The particle size was extracted from the XRD pattern of the nanoparticles by fitting Gaussian peak functions to the (111) peak of PtRu nanoparticles.

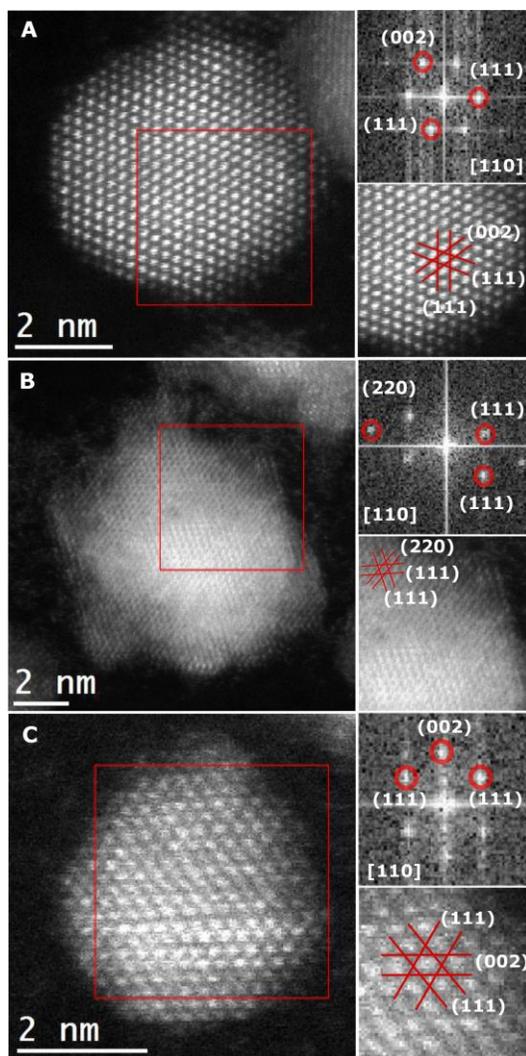


Fig. S3 High resolution STEM images of the single particle of **A)** Pt@Ru_{cuboctahedral}, **B)** Pt@Ru_{dendritic} and **C)** PtRu_{Alloy} that were shown in **Fig. 1** The FFT's were taken from the areas shown in the red boxes. The FFT's are indexed to the [110] zone axis. The corresponding lattice spacing are marked by red lines and circles.

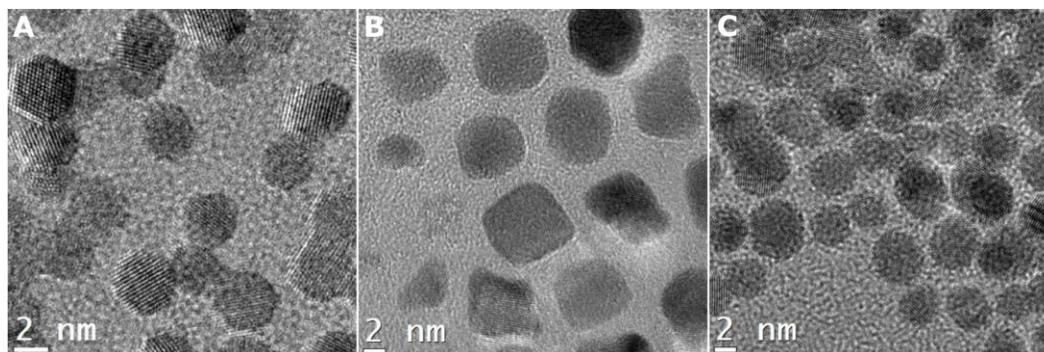


Fig. S4 High resolution TEM images of **A)** Pt cuboctahedra, **B)** Pt nanoparticle with random shapes (irregular) and **C)** Pt polyhedral shape that were shown in **Fig. 5**.

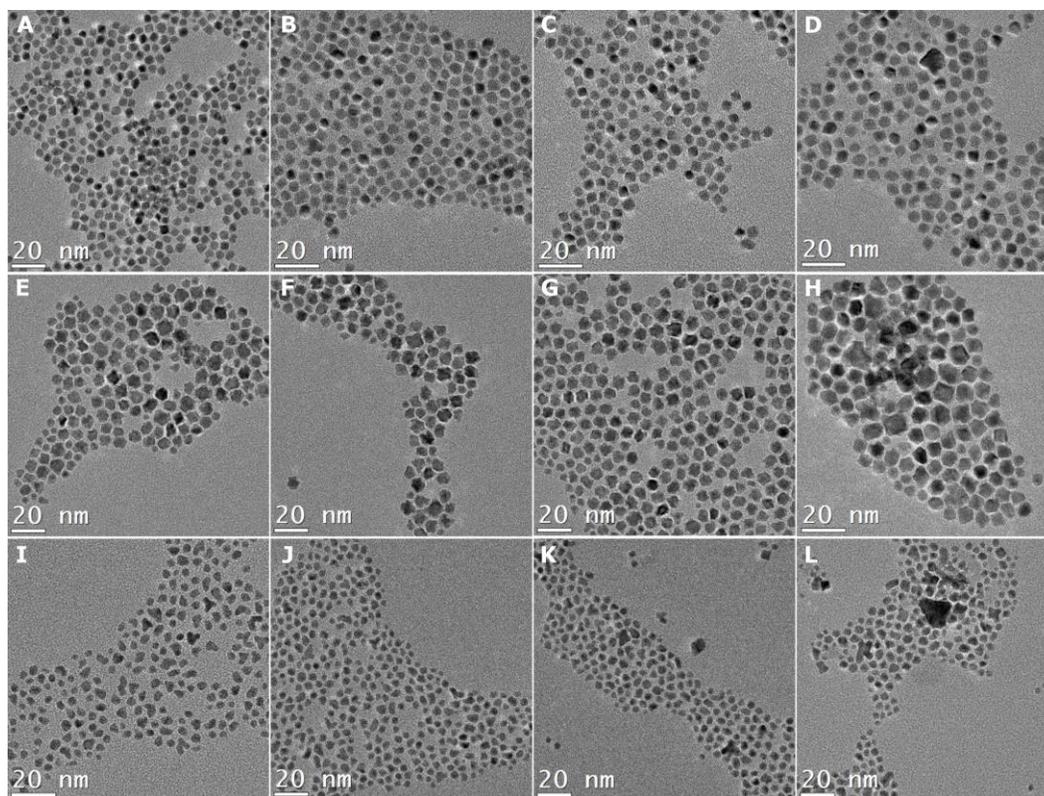


Fig. S5 Time-resolved TEM images of **A-D)** Pt@Ru_{Cuboctahedral}, **E-H)** Pt@Ru_{Dendritic} and **I-L)** PtRu_{Alloy} nanoparticles at 30 seconds, 1 minute, 2.5 minutes and 10 minutes respectively.

Table S2. The average compositional ratio of platinum and ruthenium from EDS analysis in **Fig. S6**.

Time	Sample	Pt, atoms%	Ru, atoms%
		(EDS)	(EDS)
30 seconds	Pt@Ru _{Cuboctahedral}	62 ± 2%	38 ± 5%
	Pt@Ru _{Dendritic}	73 ± 4%	27 ± 9%
	PtRu _{Alloy}	89 ± 5%	11 ± 7%
1 minute	Pt@Ru _{Cuboctahedral}	65 ± 3%	35 ± 6%
	Pt@Ru _{Dendritic}	66 ± 3%	34 ± 6%
	PtRu _{Alloy}	67 ± 3%	33 ± 6%
2.5 minutes	Pt@Ru _{Cuboctahedral}	64 ± 3%	36 ± 6%
	Pt@Ru _{Dendritic}	66 ± 2%	34 ± 4%
	PtRu _{Alloy}	71 ± 3%	29 ± 6%
10 minutes	Pt@Ru _{Cuboctahedral}	63 ± 3%	37 ± 7%
	Pt@Ru _{Dendritic}	64 ± 2%	36 ± 5%
	PtRu _{Alloy}	68 ± 3%	32 ± 7%

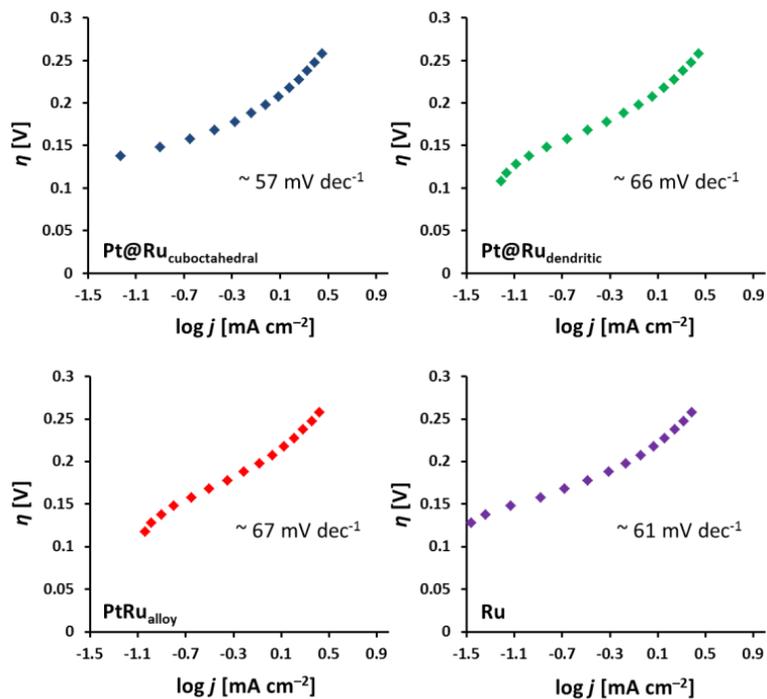


Fig. S6 Tafel plots (η vs. $\log j$) for the Pt@Ru core-shell (cuboctahedral and dendritic), PtRu alloy and pure Ru nanocrystals recorded in a 0.1 M HClO₄ solution.

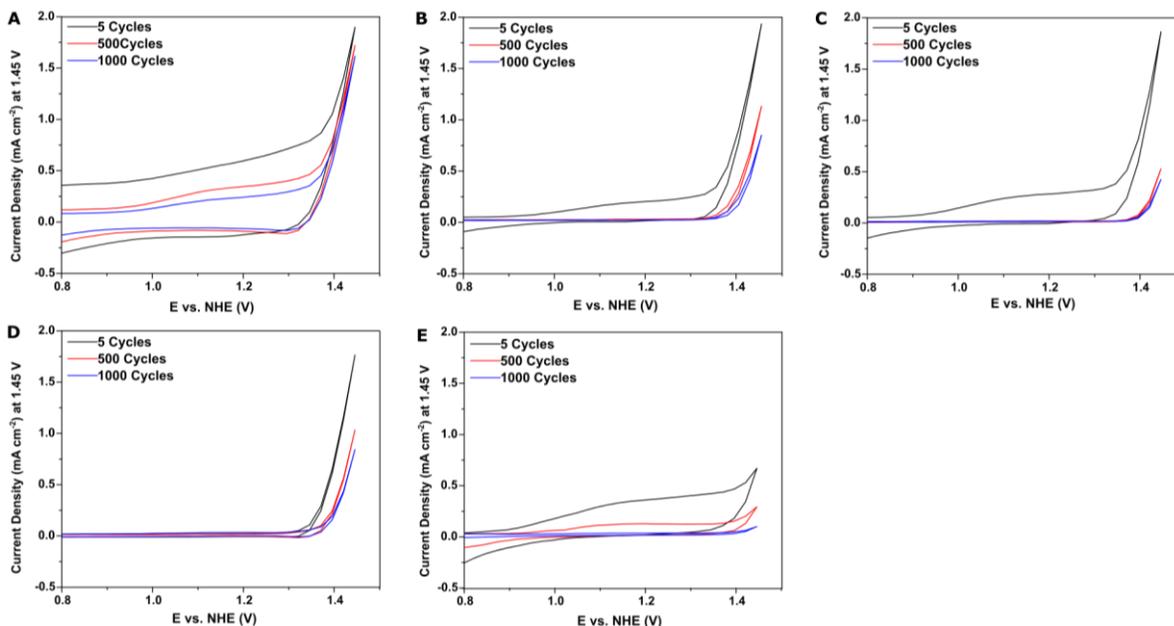


Fig. S7 Cyclic voltammograms of A) Pt@Ru_{cuboctahedral}, B) Pt@Ru_{dendritic}, C) PtRu_{Alloy} D) pure Ru and E) pure Pt nanoparticles in 0.1M HClO₄ solution at cycles 5,500 and 1000 that were shown in Fig. 7.

Table S3. The conversion of obtained potentials (V) from vs. NHE to vs. RHE that were shown in **table 1** and **Fig. 7 A&B**.

Sample	E vs. NHE (V)	E vs. RHE (V)	E vs. NHE (V)	E vs. RHE (V)
	HClO ₄	HClO ₄	H ₂ SO ₄	H ₂ SO ₄
Pt@Ru _{Cuboctahedral} (table 1)	1.31	1.37	1.33	1.39
Pt@Ru _{Dendritic} (table 1)	1.33	1.39	1.35	1.41
PtRu _{Alloy} (table 1)	1.33	1.39	1.35	1.41
Pure Ru(table 1)	1.35	1.41	1.36	1.42
Pure Pt(table 1)	1.39	1.45	1.40	1.46
Potential limit(Fig. 7 A&B)	1.45	1.51	-	-

E_{NHE} was calculated by using this equation (NHE at pH=0):

$$E_{\text{NHE}} = E_{\text{Ag/AgCl}} + 0.059 \text{ pH} + E^{\circ}_{\text{Ag/AgCl}} \quad (E^{\circ}_{\text{Ag/AgCl}} = 0.197 \text{ V})$$

For conversion of the potential from vs. NHE to vs. RHE, this formula was used: $E_{\text{RHE}} = E_{\text{NHE}} + 0.059 \text{ pH}$ where $\text{pH} = 1$