Supporting Information:

Reconciling the experimental and computational methanol electro-oxidation activity via potential-dependent kinetic mechanism analysis

Haijun Liu [1, 2, 3], Fengman Sun[1, 2, 3], Ming Chen[2, 3]*, Haijiang Wang [2, 3]*

[1]Harbin Institute of Technology, Harbin, 150001, China

[2]Department of Mechanical and Energy Engineering, Southern University of Science and Technology, Shenzhen, 518055, China

[3]Key Laboratory of Energy Conversion and Storage Technologies (Southern University of Science and Technology), Ministry of Education, Shenzhen 518055, China

E-mail: chenm3@sustech.edu.cn (M. Chen), wanghj@sustech.edu.cn (H. Wang)

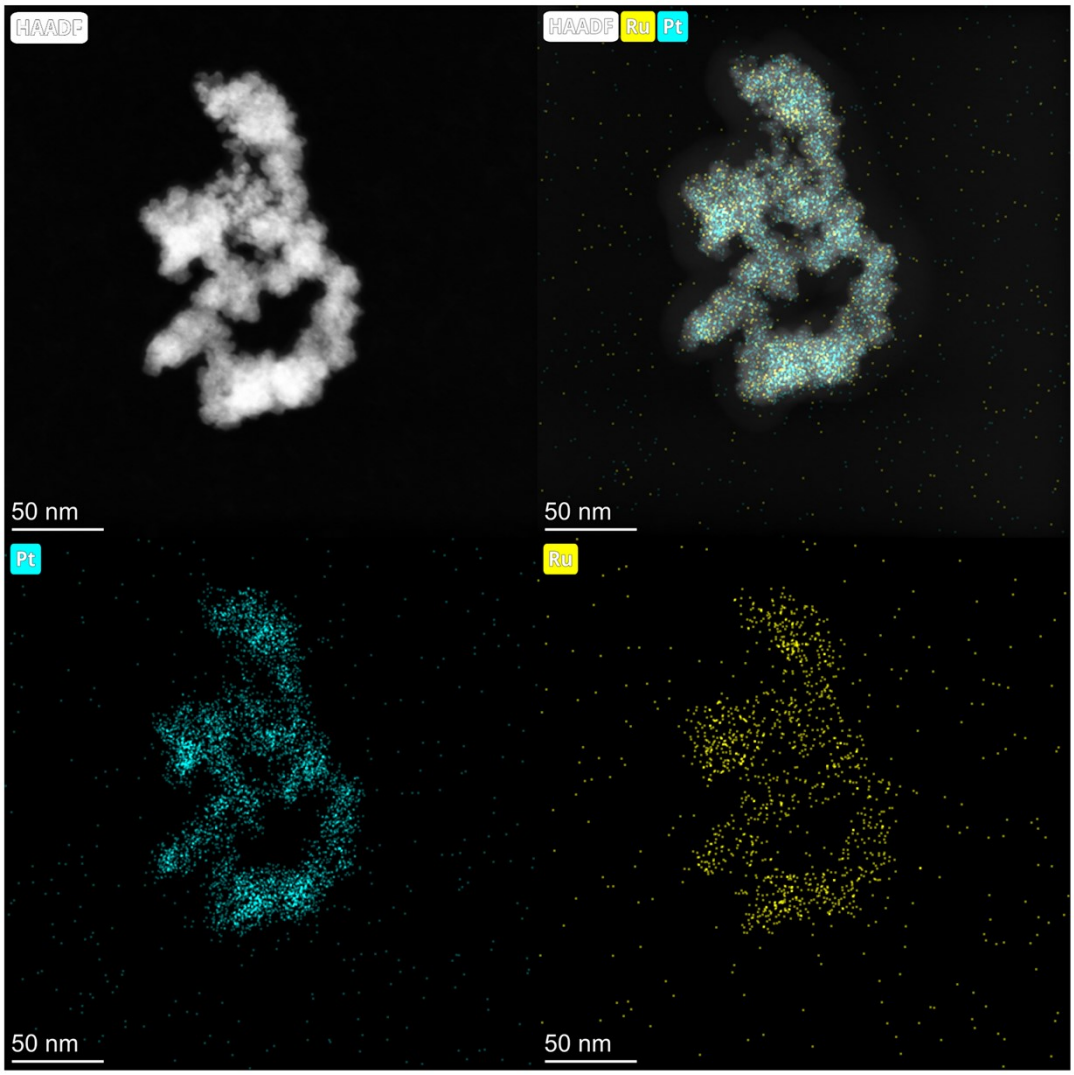

Fig. S1 HAADF and EDS elemernt mapcping of PtRu black

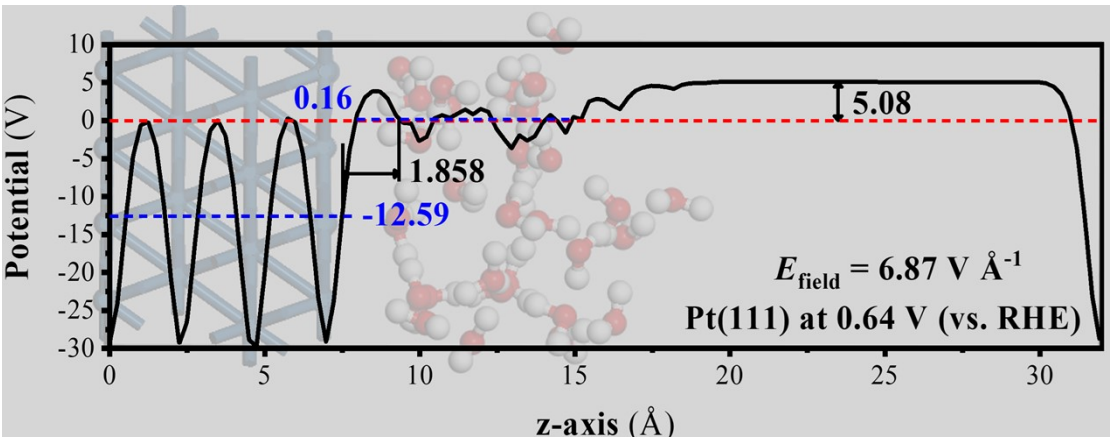

Fig. S2 The electrostatic potential profile average on the plane perpendicular to the z-axis as a function of the Pt(111)-electrolyte structure. The structure of Pt with a water layer is shown in the background. The Fermi level, the average potential on the Pt side and water side, and the thickness of the electrochemical double layer are marked by red, blue, and black lines and numbers. The work function is represented by a vertical two-way arrow with a black number.

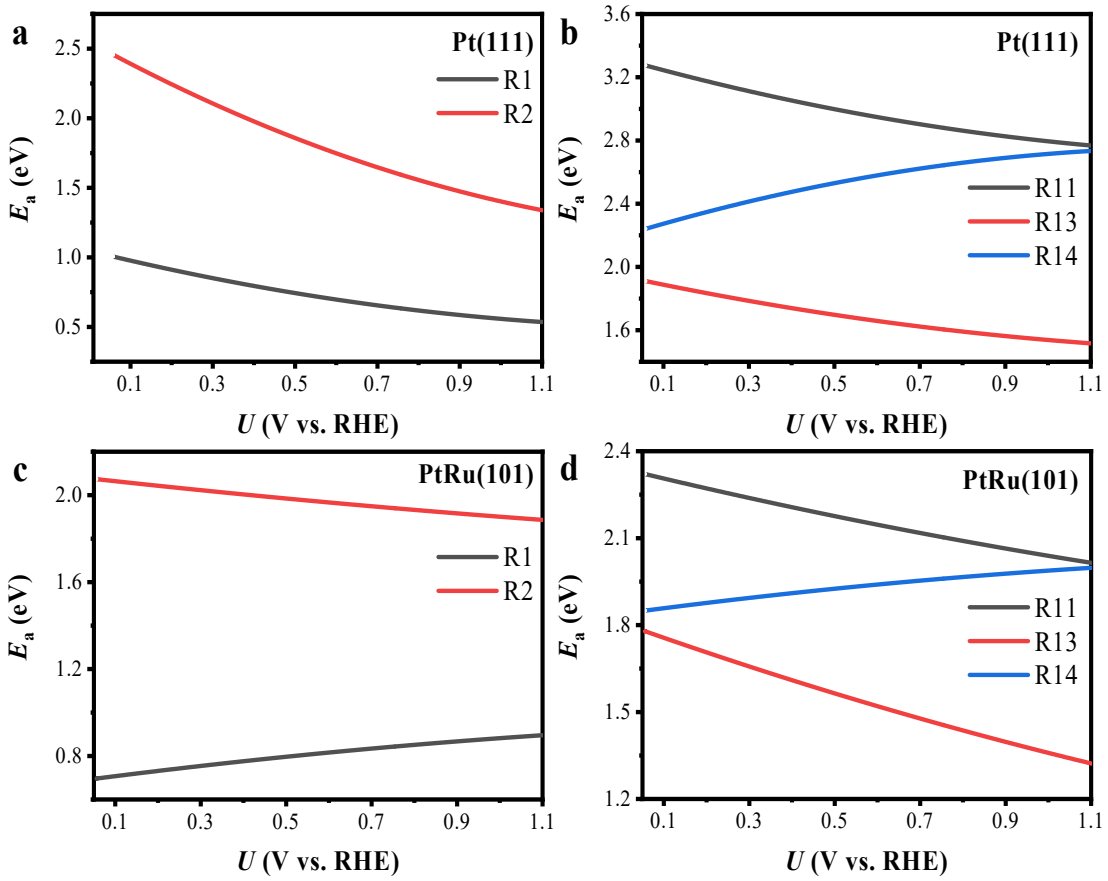

Fig. S3 Relationships of potential *U* with the free energy barriers of R1 and R2 (a, c) and R11, R13, and R14 (b, d) on Pt(111) (a, b) and PtRu(101) (c, d).

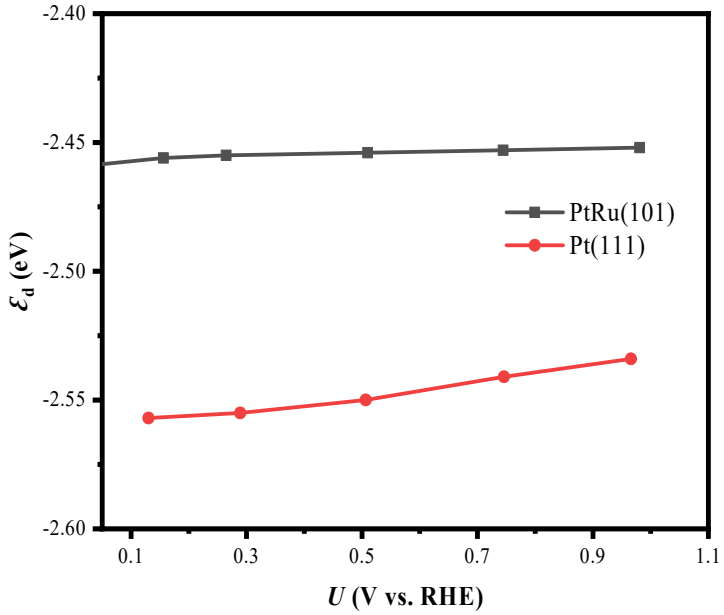

Fig. S4 Relationship of potential U with the d band center ε_d of Pt(111) and PtRu(101) surface atoms

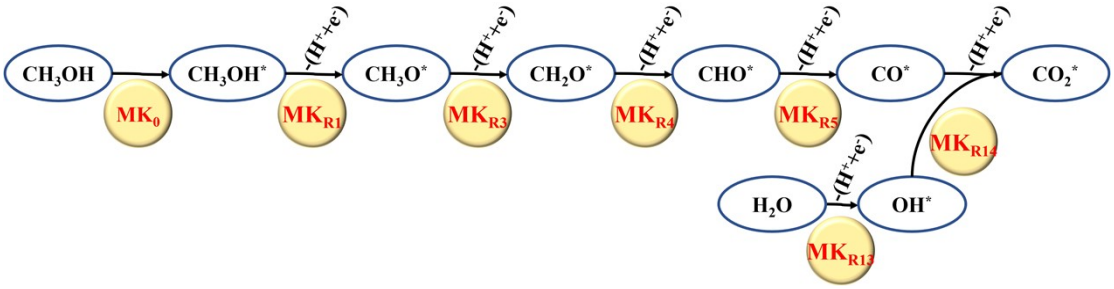

Fig. S5 The microkinetic modeling reaction pathways network for MOR $6e^-$ process.

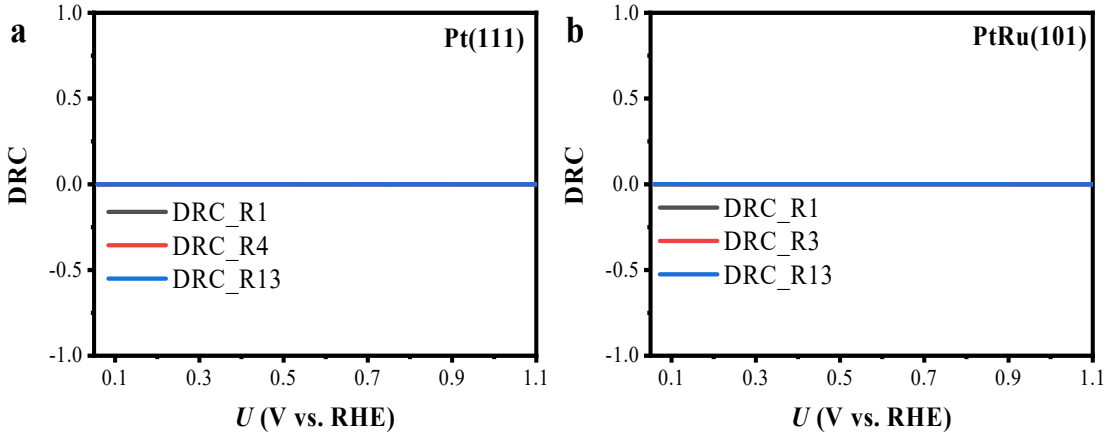

Fig. S6 Relationships between potential *U* and DRC on Pt(111) (a) and PtRu(101) (b).

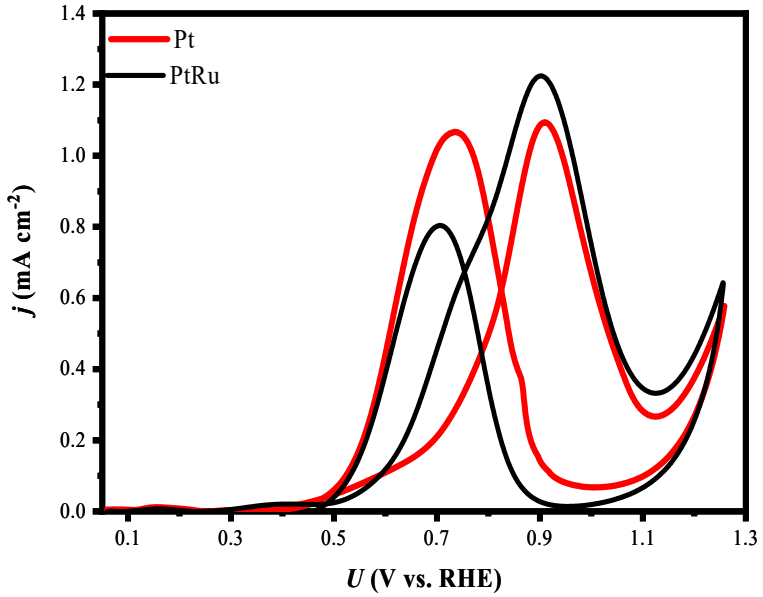

Fig. S7 Experimental MOR cyclic voltammograms for Pt and PtRu.

Table S1. Calculated and experimental lattice parameters of Pt and PtRu

lattice parameters	Pt	PtRu
calculated/Å	**a = 3.99**	**a = 3.86** **c/a = 1.02**
experimental/Å	**a = 3.92[1]**	**a = 3.88[2]** **c/a = 1.01**

[1] Travitsky N, Ripenbein T, Golodnitsky D, et al. Pt-, PtNi-and PtCo-supported catalysts for oxygen reduction in PEM fuel cells. J. Power Sources, 2006, 161 (2), 782-789.

[2] The lattice parameters are obtained from the material project database.

TableS2: The calculated free energy barriers of forward/backward elementary reactions as a function of potential *U* on the Pt(111) surface

Reaction	$\triangle G_f(U)$ (eV)	$\triangle G_b(U)$ (eV)
R1	$0.237U^2$-$0.726U$+1.047	$0.034U^2$-$0.118U$+1.543
R2	$0.470U^2$-$1.617U$+2.549	-$0.175U^2$+$0.407U$+1.800
R3	$0.692U^2$-$2.209U$+3.720	$0.510U^2$-$1.630U$+3.954
R4	$0.129U^2$-$0.429U$+2.824	-$0.533U^2$+$1.632U$+2.172
R5	-$0.659U^2$+$0.730U$+2.573	-$0.488U^2$+$1.391U$+3.035
R6	$0.245U^2$-$0.754U$+0.897	-$0.171U^2$+$0.535U$+0.706
R7	$0.043U^2$-$0.297U$+4.431	-$0.508U^2$+$1.411U$+3.537
R8	$0.287U^2$-$0.891U$+0.741	-$0.168U^2$+$0.533U$+0.090
R9	$0.301U^2$-$0.933U$+0.936	-$0.267U^2$+$0.871U$+0.772
R10	$0.332U^2$-$1.032U$+0.899	-$0.119U^2$+$0.378U$+*0.205*
R11	$0.233U^2$-$0.756U$+3.318	-$0.258U^2$+$0.780U$+2.173
R12	$0.234U^2$-$0.786U$+1.150	-$0.108U^2$+$0.382U$+1.339
R13	$0.175U^2$-$0.581U$+1.944	-$0.262U^2$+$0.841U$+1.656
R14	-$0.302U^2$+$0.823U$+2.194	-$0.477U^2$+$1.422U$+2.873

Table S3: The calculated free energy barriers of forward/backward elementary reactions as a function of potential *U* on the PtRu(101) surface

Reaction	$\triangle G_f(U)$ (eV)	$\triangle G_b(U)$ (eV)
R1	$-0.058U^2+0.258U+0.682$	$-0.088U^2+0.406U+1.213$
R2	$0.035U^2-0.220U+2.086$	$0.001U^2-0.052U+2.569$
R3	$0.097U^2-0.650U+1.948$	$-0.096U^2+0.603U+2.841$
R4	$0.054U^2-0.462U+2.080$	$-0.028U^2+0.298U+2.798$
R5	$0.008U^2-0.073U+2.037$	$-0.070U^2+0.639U+2.791$
R6	$0.037U^2-0.193U+0.855$	$-0.006U^2+0.024U+0.538$
R7	$-0.069U^2+0.304U+1.190$	$-0.105U^2+0.485U+1.523$
R8	$0.059U^2-0.306U+0.516$	$-0.044U^2+0.238U-0.038$
R9	$0.015U^2-0.121U+3.215$	$-0.094U^2+0.467U+2.929$
R10	$0.052U^2-0.290U+0.597$	$-0.038U^2+0.227U+0.249$
R11	$0.056U^2-0.358U+2.341$	$-0.007U^2+0.043U+1.922$
R12	$0.038U^2-0.230U+0.833$	$-0.031U^2+0.203U+0.213$
R13	$0.077U^2-0.526U+1.808$	$-0.001U^2-0.028U+1.900$
R14	$-0.048U^2+0.197U+1.839$	$-0.100U^2+0.525U+2.945$