Supporting information for

Tuning the electronic structure of PtRu bimetallic nanoparticles for promoting hydrogen oxidation reaction in alkaline media

Chang Long^{a,b,c,†}, Kun Wang^{c,†}, Yanan Shi^c, Zhongjie Yang^c, Xiaofei Zhang^{a,b,c}, Yin Zhang^c, Jianyu Han^c, Yini Bao^d, Lin Chang^c, Shaoqin Liu^{a,b}*, and Zhiyong Tang^c*

^a School of Materials Science and Engineering, Harbin Institute of Technology, Harbin 150080, P. R. China.

^b MOE Key Laboratory of Micro-systems and Micro-structures Manufacturing, Harbin Institute of Technology, Harbin 150080, P. R. China.

^c CAS Key Laboratory of Nanosystem and Hierarchical Fabrication CAS Center for Excellence in Nanoscience, National Center for Nanoscience and Technology, Beijing 100190, P. R. China.

^d West China Hospital of Stomatology, Sichuan University, Chengdu 610041, PR China

Corresponding address:

zytang@nanoctr.cn

shaoqinliu@hit.edu.cn

Supplementary Content

Figure S1. Polarization curves in Ar-saturated 0.1 M KOH.

Figure S2. Electrochemical behavior of Pt-H_{ad} interaction.

Figure S3. Electrochemical surface area measurements.

Figure S4. Tafel plots of PtRu bimetallic nanoparticles and Pt/C

Figure S5. Micro-kinetic polarization plots.

Figure S6. Polarization curves and Koutecky–Levich plots.

Figure S7. ECSA-normalized kinetic current densities.

Figure S8. HOR activity comparison.

Table S1. Summary of ICP-MS results for PtRu bimetallic nanoparticles.

Table S2. Summary of binding energies for Pt $4f_{7/2}$ and Pt $4f_{5/2}$ of PtRu bimetallic nanoparticles and Pt/C from XPS results

Table S3. Summary of electrochemical surface areas for PtRu bimetallicnanoparticles and Pt/C.

Table S4. Normalized exchange current densities for PtRu bimetallic nanoparticles and Pt/C.



Figure S1. Polarization curves of PtRu bimetallic nanoparticles, and Pt/C in Ar-saturated 0.1 M KOH at a scan rate of 5 mV s⁻¹ under rotating speed of 1600 r.p.m.



Figure S2. The impact of alloy degree on the $Pt-H_{ad}$ interaction determined by electrochemical behavior of as-prepared catalysts in degassed 0.1 M KOH solution.

As displayed in **Figure S2**, the negative shift of oxidation peak of H_{ad} has been observed and this result indicates that the hydrogen-binding strength can be weakened according to the increased alloy degree.



Figure S3. Electrochemical surface area measurements. a-c) Cu stripping on PtRu bimetallic nanoparticles for determining the specific surface area of Pt. d) H adsorption on Pt/C for determining the specific surface area of Pt.



Figure S4. Tafel plots of PtRu bimetallic nanoparticles and Pt/C.



Figure S5. Micro-kinetic polarization plots of PtRu bimetallic nanoparticles and Pt/C.



Figure S6. Polarization curves of PtRu bimetallic nanoparticles and Pt/C in H₂-saturated 0.1M KOH at a scan rate of 5mV/s at various rotating speeds. The followed is the corresponding Koutecky–Levich plots at an overpotential of 120mV.



Figure S7. ECSA-normalized kinetic current densities derived from Koutecky–Levich plots for PtRu bimetallic nanoparticles and Pt/C at overpotential of 120 mV.



Figure S8. HOR activity comparison. PtRu bimetallic nanoparticles prepared under different temperature.

	PtRu-220	PtRu-250	PtRu-280	PtRu-320
ratio of Pt	74%	71%	65%	<mark>62%</mark>
ratio of Ru	26%	29%	35%	<mark>38%</mark>
Lattice	<mark>3.91</mark>	<mark>3.90</mark>	<mark>3.89</mark>	<mark>3.91</mark>
parameter				

Table S1. Summary of ICP-MS results for PtRu bimetallic nanoparticles.

Catalyst	Binding energy (eV)			
	Pt 4f _{7/2}	$Pt^{2+} 4f_{7/2}$	Pt 4f _{5/2}	$Pt^{2+} 4f_{5/2}$
PtRu-280	71.66	72.61	75.01	75.96
PtRu-250	71.56	72.36	74.91	75.71
PtRu-220	71.41	72.26	74.76	75.61
Pt/C	71.31	72.51	74.66	75.86

Table S2. Summary of binding energies for Pt $4f_{7/2}$ and Pt $4f_{5/2}$ of PtRu-280, PtRu-250, PtRu-220 and Pt/C from XPS results.

Table S3. Summary of electrochemical surface areas for PtRu bimetallic nano	particles and
Pt/C.	

Sample	Electrochemical surface area (m ² /g)
Pt/C	50.5
PtRu-220	34.45
PtRu-250	31.42
PtRu-280	28.42

Sample	jo Micropolarization	<i>j</i> ⁰ Butler-Volmer fitting	
	(mA/cm ² ECSA)	(mA/cm ² ECSA)	
PtRu-280	4.16	4.00	
PtRu-250	3.41	3.28	
PtRu-220	2.75	2.64	
Pt/C	1.89	1.76	

Table S4. Normalized exchange current densities for PtRu bimetallic nanoparticles and Pt/C.