Supporting Information

Promoting Oxygen Reduction Reaction by Gold at Step/Edge Sites of Ni@AuPt Core-Shell Nanoparticles

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Table S1. Energy ordering for one Ni or Au atom exchanged to different location on $Ni/Au_1Pt_3(221)$ surface.

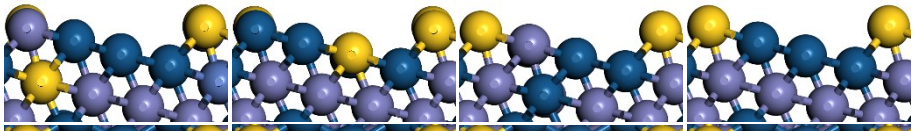
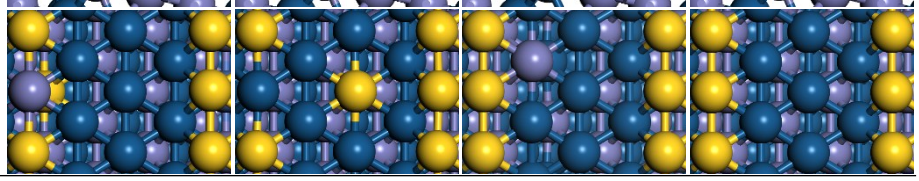
 Au Ni Pt	Ni@edge	Au@terrace	Ni@terrace	$Ni/Au_1Pt_3(221)$
ΔE (eV)	0.75	0.42	0.39	0
Side-view				
Top-view				

Table S2. Calculated binding energy (BE, in eV) for various ORR intermediates at different adsorption sites. (a) Pt(111) and Ni/Pt(111) facets, (b) Pt(221), Ni/Pt(221) and Ni/Au_1Pt_3(221) facets. BEs in bold denote the most favorable adsorption sites.

(a)

Surface	O*		OH*		OOH*
	fcc	hcp	bridge	top	bridge
Pt(111)	**1.29**	1.66	**0.72**	0.79	3.77
Ni/Pt(111)	**1.82**	2.02	**1.09**	ttb[a]	3.81

(b)

Surface	Site	BE-O*	Site	BE-OH*	Site	BE-OOH*
Pt	EU(h)	**1.25**	E(b)	**0.45**	E(b)[b]	2.63
(221)	UM(h)	1.64	U(b)	1.12	E(b)	**3.30**
	ML(h)	1.69	M(b)	1.05	U(b)	3.98
	LE(h)	1.62			M(b)	3.96
Ni/Pt	EU(h)	**1.44**	E(b)	**0.53**	E(b)	**3.57**
(221)	UM(h)	2.05	U(b)	1.32	U(b)	4.21
	ML(h)	2.25	M(b)	1.26	M(b)	4.18
	LE(h)	1.62				
Ni/Au_1Pt_3	EU(h)	2.25	E(b)	1.20	E(b)	4.23
(221)	UM(h)	**1.96**	U(b)	**1.07**	U(b)	**4.14**
	ML(h)	2.21	M(b)	1.18	M(b)	4.14
	LE(h)	2.43				

[a] ttb=top-to-bridge.

[b]The O-O cleavage OOH* → O*+OH* occurs during optimization.

Table S3. Calculated Bader charge (in e^-) for surface Pt atoms at E, U, M, L positions on Pt(221), Ni/Pt(221), and $Ni/Au_1Pt_3(221)$ surfaces.

Site	E	U	M	L
Pt(221)	-0.06	-0.02	-0.01	-0.02
Ni/Pt(221)	-0.15	-0.15	-0.18	-0.27
$Ni/Au_1Pt_3(221)$	-0.08 [a]	-0.20	-0.16	-0.29

[a] Calculated Bader charge of Au atoms.

Table S4. Correlation between calculated BE-O and d-band center at various surface sites.

Cat	BE-O (eV)	d-band center (eV)
Pt(111)(T)[a]	1.29	-2.35
Ni/Pt(111)(T)	1.82	-2.55
Pt(221)(S)[b]	1.64	-2.44
Pt(221)(E)[c]	1.25	-2.29
Ni/Pt(221)(S)	2.05	-2.67
Ni/Pt(221)(E)	1.44	-2.36
$Ni/Au_1Pt_3(221)(S)$	**1.96**	**-2.51**
$Ni/Au_1Pt_3(221)(E)$	**2.25**	**-3.17**

[a]T=terrace site;

[b]S=step site;

[c]E=edge site.

Table S5. Calculated binding energy (BE, in eV) and O-O bond length (BL, in Å) for O_2 adsorbed at various sites.

Surface	Step/BL	Edge/BL
Pt(111)	-0.87/ 1.38	\
Ni/Pt(111)	-0.41/1.35	\
Pt(221)	-0.57/1.38	-1.20/1.38
Ni/Pt(221)	-0.19/1.35	-0.34/1.37
$Ni/Au_1Pt_3(221)$	-0.13/1.35	-0.19/1.35

Table S6. Calculated activation energies (Ea, in eV), reaction energy (ΔE, in eV) and imaginary frequency (i-freq, in cm^{-1}) of transition state for O_2 dissociation and the first protonation reaction.

Surface	$*O_2 \rightarrow *O+*O$	$*H+*O \rightarrow *OH$
	Ea/ΔE/i-freq	Ea/ΔE/i-freq
Pt(111)	0.77/-0.87/123	1.00/-0.12/607
Ni/Pt(111)	0.98/-0.65/319	0.78/-0.59/261
Pt(221)(S)	0.73/-1.26/283	0.94/-0.23/167
Pt(221)(E)	\	1.01/-0.11/468
Ni/Pt(221)(S)	0.95/-0.76/376	0.72/-0.54/235
Ni/Pt(221)(E)	\	0.90/-0.40/354
$Ni/Au_1Pt_3(221)(S)$	1.07/-0.63/388	0.78/-0.67/265
$Ni/Au_1Pt_3(221)(E)$	1.14/-0.58/120	0.56/-1.01/175

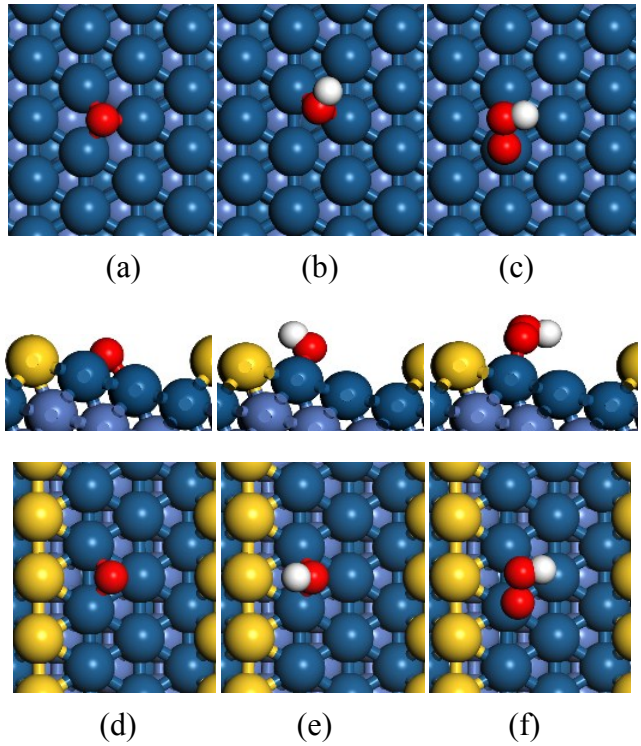


Fig. S1. (a)-(c) Most stable configuration for the adsorbates on Ni/Pt(111) facet (a) O* at fcc site, (b) OH* at bridge site, (c) OOH* at bridge site. (d)-(f) Most stable configuration for the adsorbates on $Ni/Au_1Pt_3(221)$ facet (d) O* at EU(h) site, (e) OH* at M(b) site, (f) OOH* at M(b) site.

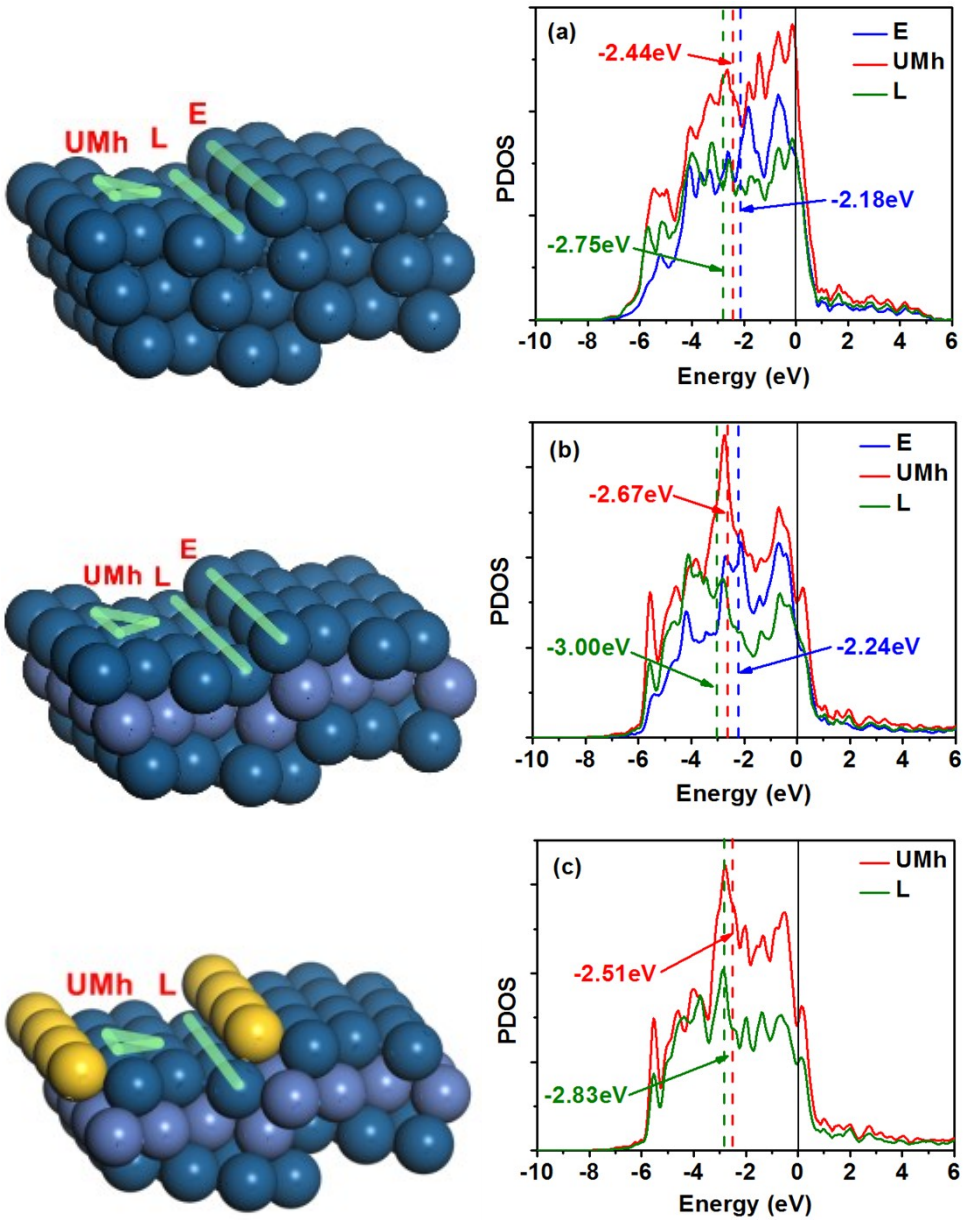


Fig. S2. Calculated 5d-PDOS and d-band center of surface Pt atoms at E, UMh, and L sites (CN=7, 9, and 11, respectively). (a) Pt(221), (b) Ni/Pt(221), and (c) Ni/Au_1Pt_3 (221). PDOS is drawn by using 2, 3, and 2 surface Pt atoms, respectively.