Support information

Understanding Composition-Dependent Synergy of PtPd Alloy Nanoparticles in Electrocatalytic Oxygen Reduction Reaction

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Synthesis of Pt_nPd_{100-n} nanoalloy. Pt_nPd_{100-n} nanoalloys with different bimetallic compositions are synthesized by wet chemical method in dioctyl ether solvent. The general synthesis involved the use of metal precursors, $Pt(acac)_2$ and $Pd(acac)_2$, in controlled molar ratios. These precursors were mixed into dioctyl ether solvent. Oleic acid and oleylamine as capping agents involving were also added into the solvent as well as 1, 2-hexadecanediol as the reducing agent. In a typical procedure for the synthesis of $Pt_{47}Pd_{53}$, 0.3933 g $Pt(acac)_2$, 0.3046 g $Pd(acac)_2$, 0.6201 g 1, 2-hexadecanediol and 40 mL dioctyl ether were added to a 3-neck flask under stirring. 1 mL oleylamine and 1mL oleic acid were also added to the mixed solution. The solution was heated to 105 ^oC under N_2, at which the metal precursors started to decompose and the solution turned dark. Then N_2 purging was stopped and the mixture was further heated up to 220 ^oC with reflux for 30 mins. After cooling to room temperature, the product was precipitated out by ethanol washing and centrifugation. The synthesis of other ratios nanoalloys, $Pt_{14}Pd_{86}$ and $Pt_{64}Pd_{36}$, followed the protocol of $Pt_{47}Pd_{53}$, and the only difference was the amount of metal precursors. 0.1966 g $Pt(acac)_2$ and 0.4570 g $Pd(acac)_2$ were used for the synthesis of $Pt_{14}Pd_{86}$, while 0.5810 g $Pt(acac)_2$ and 0.1523 g $Pd(acac)_2$ were added for $Pt_{64}Pd_{36}$.

Table S1 Compositions of the composition in as-synthesized PtPd NPs vs. feeding ratio in the synthesis

PtPd feeding ratio	as synthesized NPs
25:75	14:86
50:50	47:53
75:25	64:36

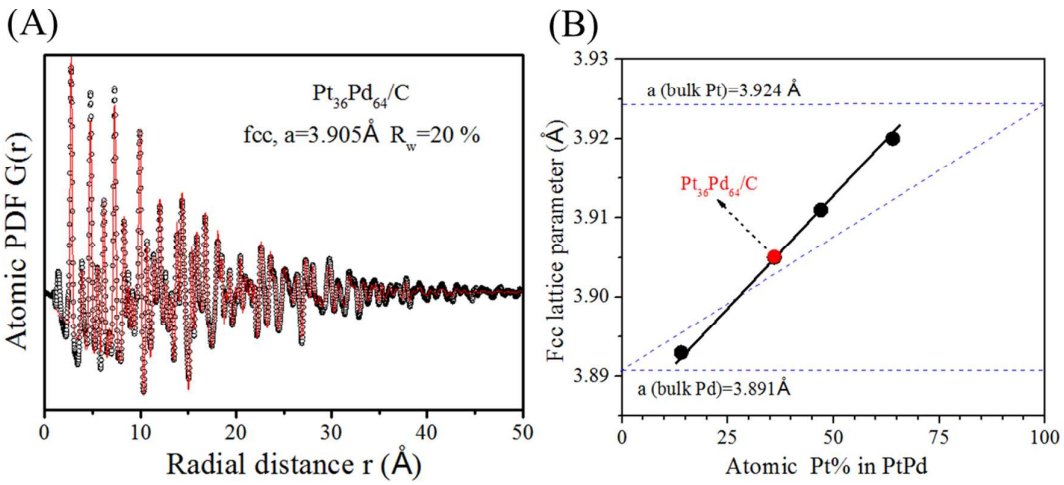


Figure S1. (A) Experimental (symbols) and model-derived (lines) atomic PDFs for carbon supported $Pt_{36}Pd_{64}$ nanoparticles thermal-treated under N_2+H_2; Lines in red represent the best model approximation to the experimental data. (B) plot of the fcc-lattice parameters as a function of relative Pt content in Pt_nPd_{100-n} (n=14, 47 and 64) nanoparticles.

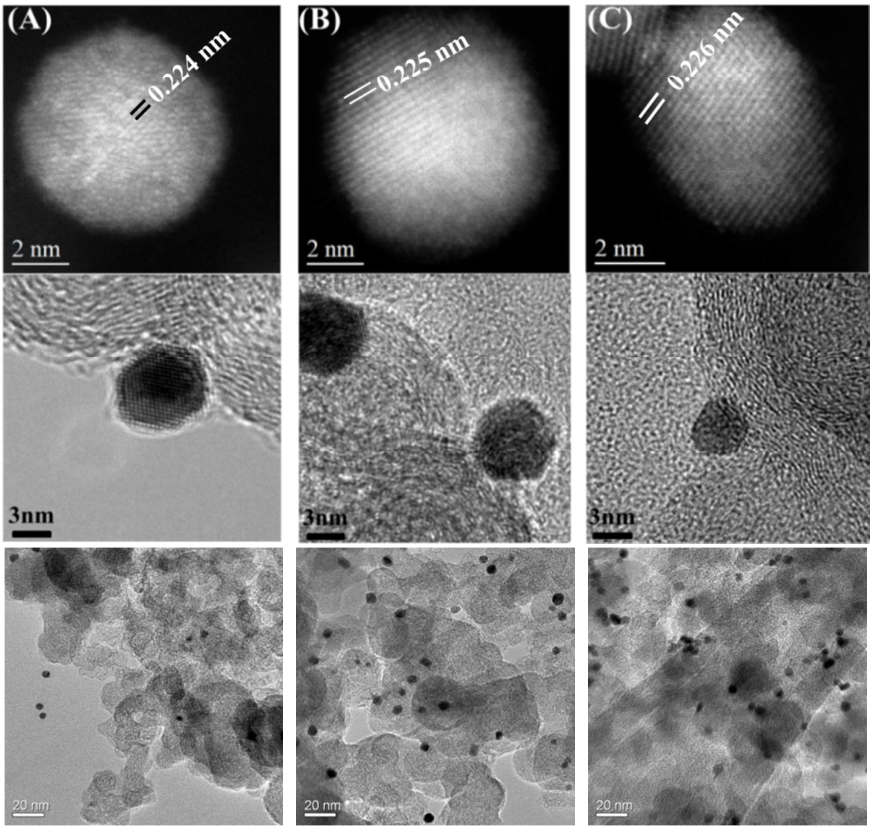


Figure S2. High-angle annular dark field scanning TEM (upper panel), High-resolution TEM (middle panel) and TEM images (bottom panel) for (A) $Pt_{14}Pd_{86}$/C, (B) $Pt_{47}Pd_{53}$/C, (C) $Pt_{64}Pd_{36}$/C nanoparticles

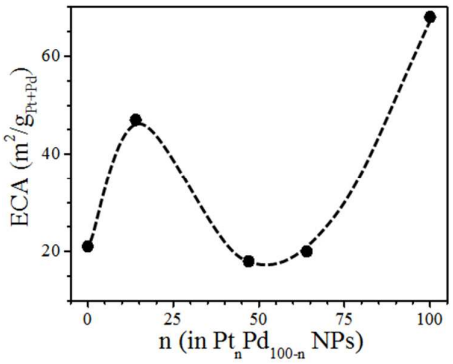
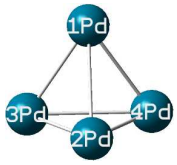
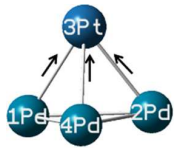
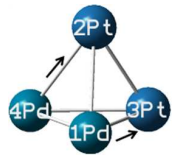
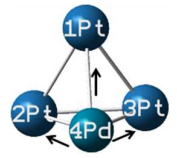


Figure S3. Comparison of ECA (A), mass activities and specific activities (B) for Pt_nPd_{100-n}/C (n=14, 47, 64) catalysts. Electrode: Glassy carbon (0.196 cm^2) inked with 10 μg catalysts; Electrolyte: O_2-saturated 0.1 M $HClO_4$

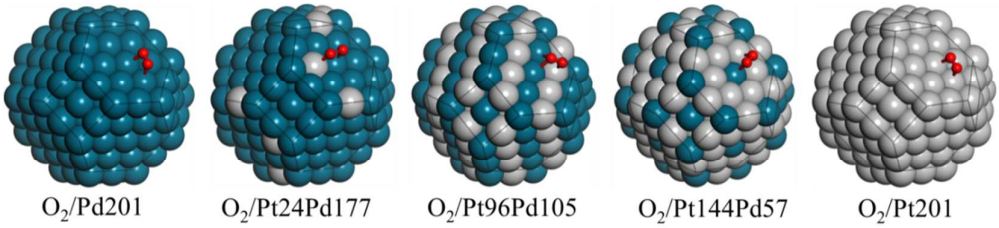
Table S2. Comparison of ECA, mass activity and specific activity normalized to Pt mass loading and metal mass loading for PtPd/C catalysts in 0.1 M $HClO_4$ solution

Catalyst	ECA (m^2/g_{pt+Pd})	Mass Activity (A/ mg_{Pt+Pd})	Specific activity (mA/cm^2_{Pt+Pd})
E-tek Pt/C	69	0.185	0.27
E-tek Pd/C	26	0.049	0.64
$Pt_{14}Pd_{86}$/C	46	0.196	0.42
$Pt_{47}Pd_{53}$/C	18	0.038	0.21
$Pt_{64}Pd_{36}$/C	20	0.104	0.24

Table S3. The electron configuration and natural atomic charge of the optimized structure of PtxPd4-x (x=0, 1, 2, 3, 4) clusters

cluster	Atom No.	Electron Configuration	charge	e-transfer
Pd4	1Pd	$5s^{0.51}4d^{9.41}5p^{0.08}$	0.00	
	2Pd	$5s^{0.51}4d^{9.41}5p^{0.08}$	0.00	
	3Pd	$5s^{0.51}4d^{9.41}5p^{0.08}$	0.00	
	4Pd	$5s^{0.51}4d^{9.41}5p^{0.08}$	0.00	
Pt1Pd3	1Pd	$5s^{0.40}4d^{9.44}5p^{0.08}$	0.09	
	2Pd	$5s^{0.40}4d^{9.44}5p^{0.08}$	0.09	
	3Pt	$6s^{1.00}5d^{9.15}6p^{0.10}$	-0.24	
	4Pd	$5s^{0.33}4d^{9.55}5p^{0.06}$	0.06	
Pt2Pd2	1Pd	$5s^{0.26}4d^{9.56}5p^{0.06}$	0.12	
	2Pt	$6s^{0.86}5d^{9.16}6p^{0.10}$	-0.12	
	3Pt	$6s^{0.86}5d^{9.16}6p^{0.10}$	-0.12	
	4Pd	$5s^{0.26}4d^{9.56}5p^{0.06}$	0.12	
Pt3Pd1	1Pt	$6s^{0.70}5d^{9.18}6p^{0.14}6d^{0.01}$	-0.02	
	2Pt	$6s^{0.70}5d^{9.18}6p^{0.14}6d^{0.01}$	-0.02	
	3Pt	$6s^{0.70}5d^{9.18}6p^{0.14}6d^{0.01}$	-0.02	
	4Pd	$5s^{0.25}4d^{9.60}5p^{0.03}6p^{0.07}$	0.06	

Pt4	1Pt	$6s^{0.76}5d^{9.17}6p^{0.07}$	0.00	
	2Pt	$6s^{0.76}5d^{9.17}6p^{0.07}$	0.00	
	3Pt	$6s^{0.76}5d^{9.17}6p^{0.07}$	0.00	
	4Pt	$6s^{0.76}5d^{9.17}6p^{0.07}$	0.00	



O_2/Pd201 O_2/Pt24Pd177 O_2/Pt96Pd105 O_2/Pt144Pd57 O_2/Pt201

Figure S4. The stable adsorption configurations of O_2 on surface of PtxPd201-x (x=0, 24, 96, 144, 201) clusters

Table S4 Adsorption energy for O_2 on PtxPd201-x (x=0, 24, 96, 144, 201) clusters

	Pt201	Pt144Pd57	Pt96Pd105	Pt24Pd144	Pd201
O_2	-1.86 eV	-1. 82 eV	-2.08 eV	-2.40 eV	-2.11 eV