Electrical Supplementary Information

Title: Atomic scale Pt decoration promises oxygen reduction properties of Co@Pd nanocatalysts in alkaline electrolyte for 310k redox cycles

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## 1. Benchmark of heterogeneous catalysts in oxygen reduction applications

Some of recent advances for heterogeneous nanocatalysts in oxygen reduction application are summarized in Table S1. Accordingly, most bimetallic and ternary catalysts possess a mass activity (MA) from 120 – 1400 mA mg<sup>-1</sup> against Pt (noble metal) both in 0.1 m KOH and 0.1 M HClO<sub>4</sub> electrolytes. There are some more catalysts achieve a maximum MA above 2000 mA mg<sup>-1</sup> against Pt in less than 2% among research papers. In the existing literatures, hetero-atomic cluster in cluster or core-shell structure substantially improve the structural complexity in a nanocatalysts. Such an architecture raises the interatomic diffusion barrier in a nanocrystal. It thus suppresses the atomic restructure and thus improves the stability of nanocatalysts in redox reaction. Among them, rarely research works perform a redox durability without current decay both in acid or basic electrolytes above 200k potential cycles. Strong homoatomic bond strength between Pt atoms are mainly responsible for the decay of redox activity in a Pt-based nanocatalyst. Such an intrinsic material's nature triggers the formation of local Pt cluster in a presence of applied potential at NC. To prevent or suppress such a homoatomic Pt cluster formation, a robust liquid state atomic deposition method by controlling time, concentration, and sequences of reduction steps is developed in our study. The presented catalyst comprises nanostructure of Co(Co oxide) capped by Pd nanoparticle with sub-nanometer Pt clusters in surface. It shows outstanding durability in ORR owing to an extensively increased heteroatomic intermix, local lattice compression, and local electron relocation to Pt from neighbouring atoms.

year	sample	MA @ 0.9 volt	ADT (cycle)	electrolyte	ref
		(mA mg-1 Pt)			
2010	PtNi nano alloy	122	NA	0.1 M HClO4	Nano Lett. 2010, 10, 638-644
2012	Nicore-Ptshell	900	35000		Nano Lett. 2012, 12, 6266-6271
2013	Ptcore-Coshell	520	5000	-	Nature Materials, 2013, 12, 81
2015	<u>Co@Pd</u>	600	NA	-	ACS Catal. 2015, 5, 5317-5327
2015		7000	10000	-	ACS Appl. Mater. Interfaces 2015, 7,
2015	Pu( <i>u</i> )Pt INKS	/000	10000	_	17162-17170
2016	CuPt or CoPt	600	NA	_	Top Catal (2016) 59:1628–1637
2017	Ni(OH)2@Pt/C	700	5000		Electrochimica Acta 247 (2017) 958–969
2010	Co@Pt	300	100000	0.1 M KOH	Angew. Chem. Int. Ed. 2010, 49, 8602-
				_	8607
2014	Ag(Au)/CuPd	200	48000		J. Am. Chem. Soc. 2014, 136, 15026-
					15033
2015	<u>Co, Cu, Pd</u>	200 - 600	1000 - 10000	_	ACS Catal. 2015, 5, 4643-4667
2017	Pd2FeCo/C	1400	10000	_	J. Mater. Chem. A, 2017, 5, 9867-9872
2017	AgCu	200 (@0.85 volt)	9000	_	small 2017, 13, 1603387

Table S1 Recent advances of heterogeneous catalysts in oxygen reduction applications

## 2. XRD analysis on Pt-CNT, Pd-CNT, and Pd@Pt NCs.

In Figure 1, XRD pattern of Pt-CNT, peaks A, B, and C at ~17.56, 20.26, and 28.87° indicate diffraction lines of (111), (200), and (220) facets for fcc phase Pt crystallite. In this NC, lattice spaces  $(d_{(hkl)}) / D_{(hkl)}$  are 2.257 Å / 65.3 Å for (111), 1.958 Å / 48.9 Å for (200), and 1.382 Å / 51.5 Å for (220) facets. The lattice constant is 3.891 Å which is slightly compressed (0.22%) from that of standard Pt metal crystal (3.92 Å) due to a strong homo-atomic bond between Pt atoms. A small preference growth in (111) facet is noticed by an abnormal peak intensity  $(h_{(hkl)})$  ratio of  $h_{(111)}/h_{(200)} = 2.88$  (which is 2.0 for fcc crystal without preferential growth) and is consistently revealed by high-resolution transmission electron microscopy (HRTEM) image (**Figure 2a**). Such a (111) preference is accounted to differences of surface free energy ( $\gamma$ ) in an absence of stabilizers upon Pt NC growth<sup>13</sup>. Pd-CNT is a metallic fcc phase NC. It's  $D_{avg}$  about ~20% larger than that of Pt-CNT and can be attributed to a minimization of surface free energy by increasing crystal size or formation of metal oxide in low Z transition metal elements<sup>6</sup>.

For CNT supported Pd NC with Pt decoration (namely Pd@Pt), peaks A, B, and C are shifted to a lower angle by  $0.065^{\circ}$  (A'  $\rightarrow$  A),  $0.11^{\circ}$  (B'  $\rightarrow$  B), and  $0.11^{\circ}$  (C'  $\rightarrow$  C) denoting a lattice expansion by 0.31% for (111), 0.61% for (200), and 0.43% for (220) facets as compared to that of Pd-CNT due to formation of surface alloying. Such an uneven lattice expansion could be accounted to preferential alloying of Pt atoms with substantial displacement between Pt-Pd atoms (also proved by XAS characterization in latter section) and suppressed crystal growth by capping Pt atoms in sorption sites of Pd open facets (I.e. (200) and (220))<sup>4</sup>. Such hypothesis is consistently revealed by uneven growth of  $D_{(hkl)}$  with identical trend to lattice strain in the three facets ( $D_{(111)}$  = 61.4 Å,  $D_{(200)} = 40.9$  Å, and  $D_{(220)} = 43.1$  Å). A small  $D_{avg}$  in high lattice expansion facets suggesting that a slight galvanic replacement occurs between Pt<sup>4+</sup> ion and metallic Pd at both (200) and (220) facets. With limited metal ion source in crystal growth, such a slight galvanic replacement leaves Pt clusters in nucleation stage and thus suppresses the subsequent heterogeneous crystal growth at both two facets. Given that identical carbon support is employed for all NPs, asymmetry shape tailing to two sides of peak A and B (denoted by Q, Q' and Q" implies a considerable extent of out-of-phase scattering by surface alloying of Pt and Pt oxide clusters to Pd crystal in Pd@Pt.

3. HRTEM analysis on Pt-CNT, Pd-CNT, and Pd@Pt NCs.



Figure S1 HRTEM images of (a) Pt-CNT, (b) Pd-CNT, and Pd@Pt NC.

Surface morphology, atomic structure, and crystal structure of experimental NCs are elucidated by using HRTEM analysis. As demonstrated in Figure S1, all control NCs (Pt-CNT and Pd-CNT) are fcc metal and preferentially grown at (111) facets in different extents. Variations in NC shape are resulted from competitions between factors in crystal growth rate including, surface free energy, surface oxidation, and heteroatomic intermix in different facets. Figure S1a shows HRTEM image of Pt-CNT. The aspect ratio of particle size in longitude (D<sub>1</sub>) and transverse (D<sub>t</sub>) axes (D<sub>1</sub>/D<sub>t</sub>) is ~1.8 with a lattice fringe of (111) in D<sub>1</sub> (d-space "d(111) = 2.262 Å  $\pm$  0.03 Å) indicating a preferential growth in (111) facets. Shown in Figure S1b, Pd NPs are drop-like particles with indistinct inter-particle boundaries and amorphous atomic arrangements (denoted by yellow arrows) revealing a severe inter-particle collapse and oxidation of Pd NCs as consistently depicted by Pd K-edge XAS analysis. Denoted by yellow arrows, Pd-CNT possesses prevailing defects particularly in NC surface. Such a phenomenon is attributed to the absence of stabilizers in crystal growth therefore resulting in random displacement of interatomic distances in NC (R1, R2, R3, and R4 shown in line histogram). Above characteristics reveal the fatal issues of high surface free energy defect sites and a lack of heteroatom bonding for Pd NPs in electrochemical reactions. Those issues cause an easy corrosion (atomic restructure) in electrochemical reactions. Therefore, it is expectable to see the low durability of Pd-CNT in an accelerated degradation test (ADT) of oxygen reduction reaction (ORR) (see Figure 4). Consequently, it is inevitable for Pd-CNT to face low electrochemical performances in both ORR and ADT (Figure 5). Figure S1c shows that Pd@Pt are decahedron-like crystal; where  $d_{(111)}$  is 2.294 ± 0.03 Å and  $d_{(200)}$  is 2.000 ± 0.03 Å. Compared to that of Pt-CNT,  $d_{(111)}$  and  $d_{(200)}$  of Pd@Pt are expanded by 1.41% and 2.09%, respectively. The uneven lattice displacement indicates the preference of Pt allocation at open facets with prevailing surface defects at incoherent interface between Pd and Pt crystal.



### 4. Pd K-edge X-ray absorption spectroscopy analysis on experimental NCs

Figure S2 Pd K-edge (a) XANES and (b) FT EXAFS spectra of Co@Pd-Pt compared with experimental NCs (Co@Pd, Pd@Pt, and Pd-CNT). Co K-edge (c) XANES of Co@Pd-Pt compared with Co metal and CoO, (d) EXAFS of Co-CNT compared with that of CoO (CoO-cal),  $Co_3O_4$  (Co<sub>3</sub>O<sub>4</sub>-cal), and Co metal (Co fcc-cal and Co hcp-cal) calculated by theoretical atomic models, (e) XANEs of Co-CNT compared with that of standard samples of Co metal foil, CoO,  $Co_3O_4$ , and  $Co_2O_3$ .

Figure S2a compares Co K-edge Co@Pd-Pt with that of Co@Pd, Co-CNT, and metallic Co foil. Near edge position (inflection point) of all experimental NCs are posited between that of Co metal and CoO. Such a characteristic reveals the formation

of partially oxidized Co. Symmetry of local structure around Co atoms is illustrated in pre-edge profile (Figure S2a inset). Accordingly, two shoulders in pre-edge region (X1 and X2) denote the typical features of electron transition from 1s to 3d (eg and t2g) orbitals of Co atoms in octahedral sites in metal. A substantially reduced nearedge intensity and merge of two shoulders into single hump (O) depict the formation of tetragonal sites in local structure in CoO. For Co-CNT, Co are located in mainly tetragonal sites as revealed by presence of single hump in near-edge region. Meanwhile, an insignificant X2" shoulder with wide band in near-edge region are evidences for partial oxidation of Co (CoOx). Such a hypothesis is further confirmed in corresponding EXAFS spectrum in Figure S2b. As for Co@Pd and Co@Pd-Pt, upshift and merge of near-edge intensity of all NCs are stay between those of Co metal and CoO suggesting formation of highly disordered Co-O sites as consistently revealed by ED pattern and HRTEM images (Figure 2).

Pd K-edge XANES spectra of Co@Pd-Pt, Co@Pd, Pd@Pt, and Pd-CNT are shown in Figure S2c. Two near-edge peaks (A and A\*) features that Pd atoms are stay mainly in metallic state and the highest intensity of valley bottom (A') resembles the highest oxidation state of Pd-CNT among experimental NCs. Compared to that of Pd-CNT, Co@Pd shows a reduced A' intensity indicating the suppression of surface amorphous structure upon positing Pd atoms in a "soft template" (i.e., highly disordered CoOx). By positing Pt atoms in Co@Pd interfaces (Co@Pd-Pt), oxidation of Pd is depicted by a substantially increased near-edge peaks (A and A\*). Compared to that of Pd-CNT, suppressed near-edge peaks indicate reduction of oxidation by shielding effects of Pt atoms in Pd surface both in Pd@Pt and Co@Pd-Pt NCs.

## 5. X-ray photoemission spectroscopy inspection



**Figure S3** and shows UPS spectra of control samples including Silicon wafer (substrate for mounting CNT supported NCs) and CNT supported NC on Silicon wafer, where energy is calibrated in a way that the Fermi level is located at 0 eV binding energy.

Table S2 Work function of Co@Pd-Pt compared with substrate and experimental NCs.

Sample	Calibrated WF
Si wafer*	4.803
CNT	5.052
Pt-CNT-ink	4.743
Pd-CNT	5.235
Co-CNT	4.82
Pd@Pt	4.689
Co@Pd	5.003
Co@Pd-Pt	4.513
J.MPt	4.711
J.MPt ink	5.048

\* All UPS spectra are measured from CNT supported NC that casting on Si wafer.

## 6. Electrochemical inspection on NC in ORR

Oxygen reduction performances of experimental NCs at 0.9 volt vs. RHE are summarized in Table S3. Accordingly,  $MA_{Pt} / MA_{total}$  possesses the same trend with that obtained at 0.85 volt vs. RHE. Obtained results are mostly compatible or superior to that of most literatures in Table S1.



Figure S4 LSV curves of experimental NCs for (S4a) J.M.-Pt, (S4b) Co-CNT (S4c) Co@Pt, (S4d) Pd@Pt, (S4e) Co@Pd, and (S4f) Co@Pd-Pt on electrode spinned at different rotation speed (400 – 3600 rpm). The electrolyte is a basic solution of 0.1M KOH water solution.

sample	V <sub>oc</sub> 1600 rpm (V)	$J_k$ (mA cm <sup>-2</sup> )	MA <sub>Pt</sub> (mA mg <sup>-1</sup> )	MA <sub>total</sub> (mA mg <sup>-1</sup> )	
J.MPt	0.922	2.35	59.1	59.1	
Pt-CNT	0.935	2.67	94.6	94.6	
Pd-CNT	0.891		NA		
Co-CNT	0.654	2.70	NA	NA	
<u>Co@Pt</u>	0.886	2.32	0.13	14.9	
Pd@Pt	0.941	3.49	710.3	114.8	
Co@Pd	0.908	0.66	NA	9.3	
Co@Pd-Pt	0.937	2.28	715.8	120.2	

Table S3 Electrochemical performances of Co@Pd-Pt and control samples in LSV at 0.9 volt vs. RHE

7. Density functional theory model calculation on selectivity and reactivity of proposed local structure for oxygen adsorption via cross referencing results of structural characterizations

#### **Computational Details**

To evaluate the ORR activity of the NCs, density functional theory (DFT) calculations were carried out by using the Vienna Ab Initio Simulation Package (VASP). All the calculations were performed using a plane-wave basis with a cut-off kinetic energy of 420 eV and the projector augmented wave method<sup>5</sup>. The exchangecorrelation functional was treated by the generalized gradient approximations (GGA) in the parameterization of Perdew, Burke, and Ernzerhof (PBE)<sup>6</sup>. The structure of the Co@Pd-Pt NCs was modeled by a 4×4 slab containing 3 layers of Pd(111) atop 3 layers of Co(111) with the lattice constant of 3.907 Å (experimental result) and 3 Pt atoms positioned on the hcp-hollow sites of the top layer or replaced 3 Pd atoms of the top layer. We need to point out that the Co(111) in fcc phase is used to keep consistent with the observation from the XRD results. For comparison, 3 Pt atoms incorporated with 6 layers of Pd(111) and 6 layers of fcc-Co(111) were also constructed respectively. In this article, Pt atom was positioned at different sorption sites of the top layer for confirming the most stable atomic structure. We applied  $5 \times 5 \times 1$   $\Gamma$ -centered k-points to map the Brillouin-zone and an inter-slab vacuum spacing of 15 Å to avoid the interaction between the replicas of the slabs. The sensitivity of total energies for slab thickness, vacuum spacing, and kinetic energy cutoff were examined as well converged. All the relevant adsorbates and the upper most four layers of slabs were without symmetry restriction, while the bottom two layers were fixed to their calculated bulk position.

The adsorption energy  $(E_{ads})$  of a single oxygen atom adsorbed on the surfaces of interest is defined as  $E_{ads} = E(O-NCs) - 1/2E(O_2) - E(NCs)$ , where E(O-NCs) is the total energy of the entire system,  $E(O_2)$  is the energy of an oxygen molecule, and E(NCs) is the energy of the constructed slab. The negative values of  $E_{ads}$  refer to the oxygen adsorption in endothermic.



**Figure S5** Proposed local structure sites for oxygen adsorption (via cross referencing results of structural characterizations) and corresponding DFT calculations results on oxygen adsorption energy ( $E_{ads-O}$ ). Calculation models are built basing on local structure in Co@Pd interface, Co-Pt interface, and Pt decorated Co@Pd interface.

### **DFT** calculation results

Effects of nanostructure on oxygen adsorption energy are revealed by using DFT calculation. Models and results for DFT calculation are listed in Figure S5, where possible local structure in ternary (comprising Co, Pd, and Pt) and binary phase boundaries in Co-Pd core-shell interface and Co@Pd-Pt surface and only cases in optimized adsorption energy (hollow sites) are discussed. In Co-Pd core-shell interface, oxygen adsorbs in hollow sites of 3 Co atoms (in Co core surface, Co<sub>3</sub><sup>h</sup>), 3 Pd atoms (in Co core surface,  $Pd_3^h$ ), 2 Co atom + 1 Pd atom ( $Co_2Pd_1^h$ ), 1 Co atom + 2Pd atom  $(Co_1Pd_2^h)$ , and Co-Pt  $(Co_2Pt_1^h and Co_1Pt_2^h)$  sites in Co core surface. In Co@Pd-Pt surface, oxygen adsorbs in hollow sites of 3 Pt atoms (Pt<sub>3</sub><sup>h</sup>), 2 Pt atoms + 1 Pd atom (Pt<sub>2</sub>Pd<sub>1</sub><sup>h</sup>), 1 Pt atom + 2 Pd atoms (Pt<sub>1</sub>Pd<sub>2</sub><sup>h</sup>). As indicated, E<sub>ads-O</sub> is increased with number of Pd atoms in a hollow site in Co-Pd interface (Co3h (-2.62 eV) > $Pd_1Co_2^h(-2.47 \text{ eV}) > Pd_2Co_1^h(-1.62 \text{ eV}) > Pd_3^h(-0.93 \text{ eV}))$ . Such a trend indicates the Pd shielding and electronegative gradient (electron relocation) effects on weakening of O ads in NC surface; where substantially reduced E<sub>ads-O</sub> is found in pure Pd sites as compared to that of Pd rich sites. For cases of O adsorption in Co rich sites  $(Co_2Pd_1^h \text{ and } Co_3^h)$ ,  $E_{ads-O}$  is raised to a value higher than -2.47 eV indicating the formation of Co-O ionic bond (i.e., Co oxidation). Those characteristics reveal an easy oxidation of Co as consistently proved by absence of O adsorption peaks in CV sweeping curve of Co-CNT. For cases of Pt-Co sites in Co-Pd interface and Pt-Pd sites in Co@Pd-Pt surface, E<sub>ads-O</sub> possesses a similar trend to those are found in Co-Pd sites in Co-Pd interface. In pure Pt sites (Pt<sub>3</sub><sup>h</sup>) in Co-Pd interface and Co@Pd-Pt surface, E<sub>ads-O</sub> is determined to be -0.73eV and -0.97 eV, respectively. Notice that, E<sub>ads-O</sub> in Pd<sub>3</sub><sup>h</sup> and Pd<sub>3</sub><sup>h</sup> in Co surface is smaller than those in pure Pt and Pd surface implying an indirect electronegative dipole effect between O<sub>ads</sub> on Pd or Pt sites and Co crystal. In a meantime, Eads-O is substantially increased by 0.54 and 1.11 eV when O adsorption in Pt<sub>2</sub>Co<sub>1</sub><sup>h</sup> and Pt<sub>1</sub>Co<sub>2</sub><sup>h</sup> as compared to that of Pt<sub>3</sub><sup>h</sup> in Co surface. A large E<sub>ads-O</sub> difference between adsorption sites across different positions of calculating model implies a strong potential gradient that attracting O<sub>ads</sub> from weak to strong adsorption sites. In this circumstance, an easy oxidation so as to poor electrochemical durability of such a surface in O<sub>2</sub> reduction (which involving O<sub>2</sub> splitting in reaction steps) is expectable. For reducing E<sub>ads-O</sub> and potential gradient, model of tri-layer Co (111) facet capping with tri-layer Pd atom with a Pt<sub>3</sub> cluster in top layer is built. In such a model, E<sub>ads-O</sub> of Pt<sub>3</sub><sup>h</sup> site is smaller than that of O in pure Pd surface and E<sub>ads-O</sub> difference is substantially reduced by 0.29 to 1.26 eV as compared to that of Pt<sub>3</sub><sup>h</sup> in Co surface (from 0.54 - 1.66 eV to 0.25 - 0.4 eV).

# 8. XPS analysis determined surface compositions of NCs

Surface composition of experimental samples are determined by XPS analysis and results are summarized in Table S4. Accordingly, Pt is 46.9 at%, Pd is 55.1 at%, and Co is 3.9 at% in Co@Pt-Pd NC. Such a surface Co content is far lower from that of experimental design, however, is understandable by cross-referencing the results of Co K-edge XAS spectrum of Co@Pd-Pt in Figure S2. In these spectra, a strong radial spectrum extending to R > 2.2 Å with a k range of 2.4 to 11.1 Å<sup>-1</sup> and a strong edge step of 1.6 in fluorescence mode (If/I0). By comparing results of XPS and XAS, one can notice that Co atoms are majorly located in bury layer underneath (or capped by) Pd crystal. In the Co@Pd-Pt NC, Pt atoms are mainly decorated in surface region.

Sample	Pt chemical states			Pd chemical states		Co chemical states			Composition (%)			
Sampic	Pt0	Pt 2+	Pt 4+	Pd0	Pd 2+	Pd 4+	Со	Co 2+	Co 3+	Pt	Pd	Co
J.MPt	72.4	19.0	8.6	-	-	-				100	-	
Pt-CNT	73.7	18.1	8.1	-	-	-				100	-	
<b>Pd-CNT</b>	-	-	-	85.8	10.1	4.1				-	100	
Co-CNT							53.0	7.7	39.3			100
Co@Pt	82.5	13.0	4.5	-	-	-	51.6	9.2	39.2	36.3		63.7
Pd@Pt	75.4	16.7	7.9	87.7	8.3	4.0				34.4	65.6	
Co@Pd	-	-	-	93.4	6.6	0.00	60.3	0.00	39.7		97.1	2.9
Co@Pd-Pt	83.3	11.6	5.1	91.5	8.5	0.00	65.4	0.00	34.6	46.9	49.2	3.9

Table S4 XPS fitting results of experimental NCs

Reference

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