Electronic Supplementary Material (ESI) for Catalysis Science & Technology.

Supplementary Information

Atomistic Description of Cuboctahedral core-shell Pt_3Co Nanoparticles; Morphological Implications for Oxygen Reduction.

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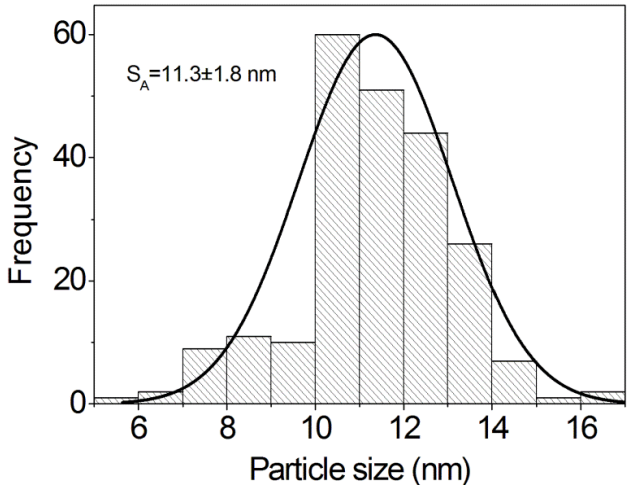

Figure S1. Size distribution of the cs-Pt_3Co nanoparticles.

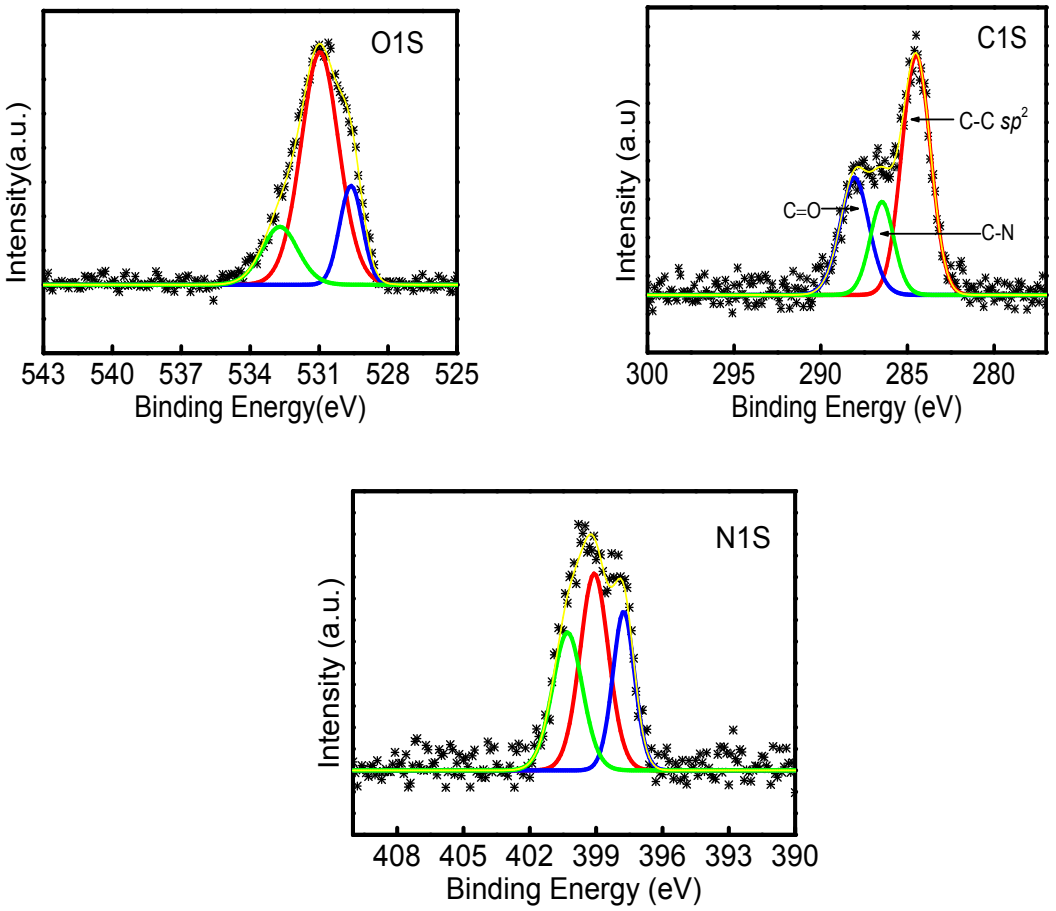

Figure S2. High-resolution XPS spectrum of C, O, and N in the cs-Pt_3Co nanocrystals

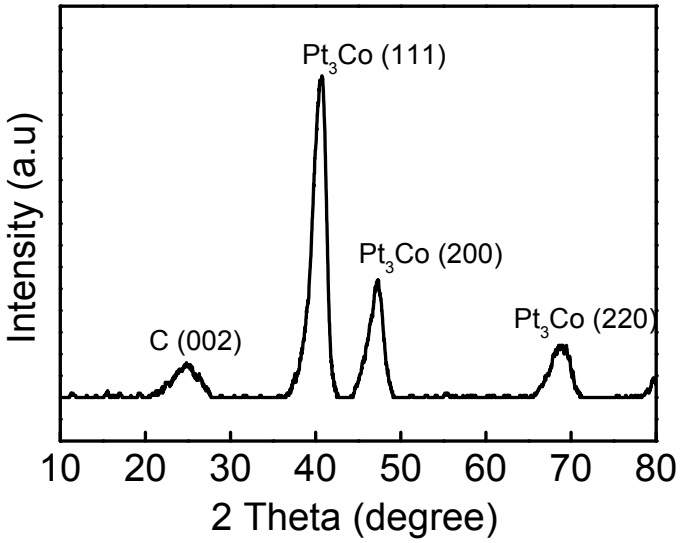

Figure S3. XRD pattern of the as-prepared cs-Pt_3Co catalyst decorated on Vulcan XC-72R

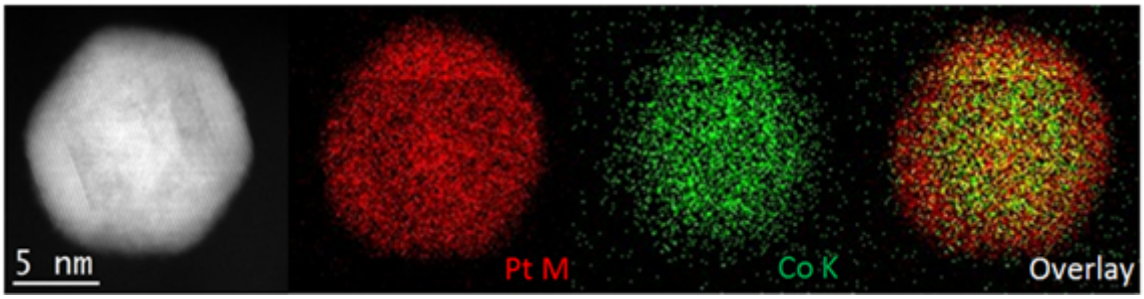

Table 1S Microarea analysis data from the EDS mapping profiles in Fig 1e-h							
Element	(keV)	Counts	Mass%	Error%	Atom%	Compound	Mass%Cation
Co K	6.924	2569.19	8.52	0.22	23.57		0.4528
Pt M	2.048	12489.44	91.48	0.05	76.43		1.0000
Total			100		100		

Table 2S Microarea analysis data corresponding to the above mapping profiles in Fig. S4							
Element	(keV)	Counts	Mass%	Error%	Atom%	Compound	Mass%Cation
Co K	6.924	16027.80	8.60	0.21	23.74		0.4528
Pt M	2.048	77177.53	91.40	0.05	76.26		1.0000
Total			100		100		

Figure S4. EDS analysis data of cs-Pt_3Co nanocrystals revealing Pt/Co atomic ratios of 3.2:1.

Considering an 11 nm truncated octahedral nanoparticle, it is then possible to estimate the number of layers (in this case 21 in total), and hence, the number of atoms in each layer by using the Equation 1 [T.P. Martin, Physics Reports, 273, 199–241 (1996)], where N_{total} is the number of atoms in the nanoparticle, and L is the number of layers.

$$N_{total} = 16L^3 - 33L^2 + 24L - 6 \qquad \text{Equation 1.}$$

Then based on the HRTEM observation, we classified the 6 outer layers as the nanoparticle's shell, the rest (15 layers) as the core. Out of these 6 shell layers, we also consider that the outer one is solely composed of Pt atoms (a condition needed to exhibit a high ORR performance). All these conditions, we first calculate the number of atoms in the shell with help of equation 1, and then by using equation 2 and expressing the Pt/Co ratio (from XPS) as in equation 3, it is possible to estimate the Pt content along the nanoparticle.

$$N_{shell} = N_{Shell,Co} + N_{Shell,Pt} \qquad \text{Equation 2.}$$

$$\frac{N_{Shell,Pt}}{N_{Shell,Co}} = 4.75 \qquad \text{Equation 3.}$$

Where "N_{Shell}" is the number of atoms at the shell, it can also be applied to the core or the whole nanoparticle. In this case, we obtain that the shell is composed of 83 At% of Pt, and since the top layer is 100% Pt, we then conclude that the rest of the shell (5 layers) contains just 78% of Pt. A similar procedure can be perform to estimate the Pt content at the core, resulting in 64 At%

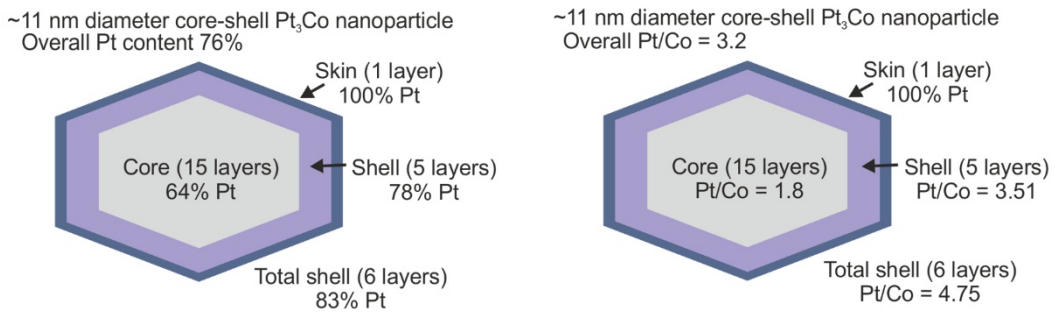

Figure S5. Description of Pt composition along the cs-Pt_3Co nanoparticle according to EDS, XPS, and the average particle size. Pt content is indicated by At% in the left side. Right side the Pt/Co ratio is indicated.

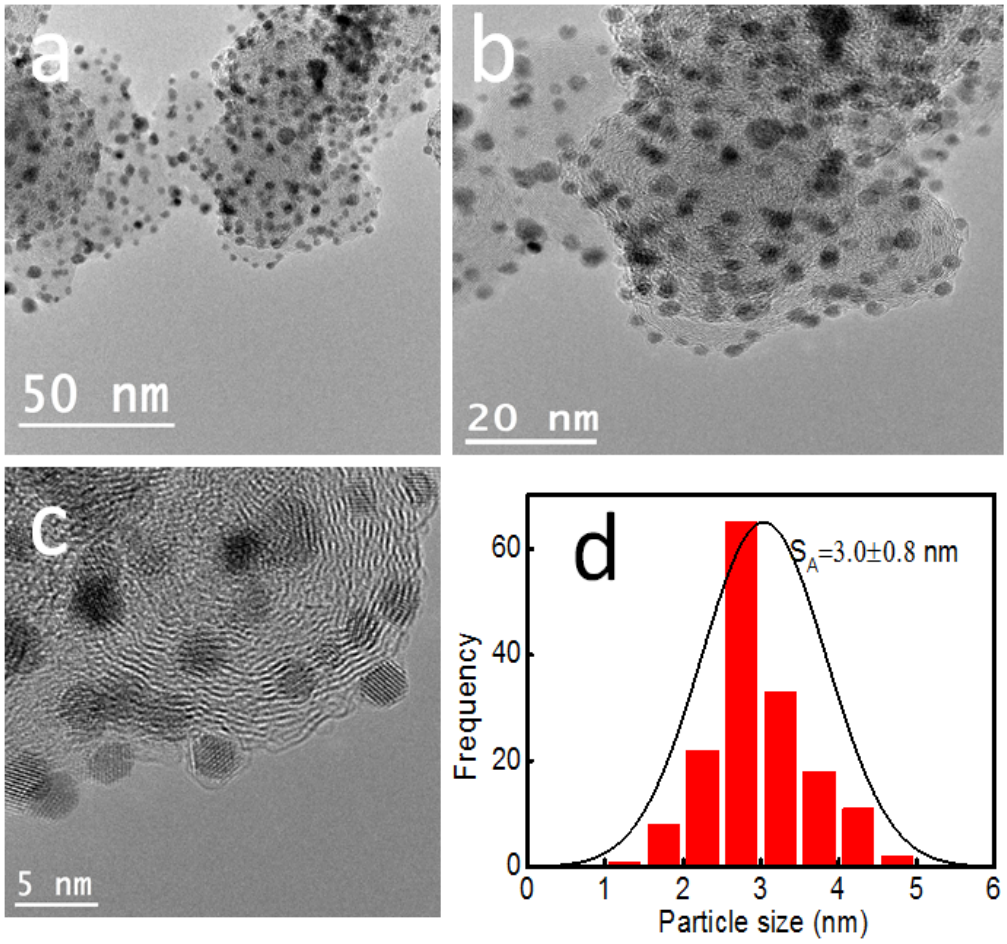

Figure S6. TEM images (a, b, and c) of sp-Pt_3Co/Vulcan in different magnification and their particle size distribution (d)

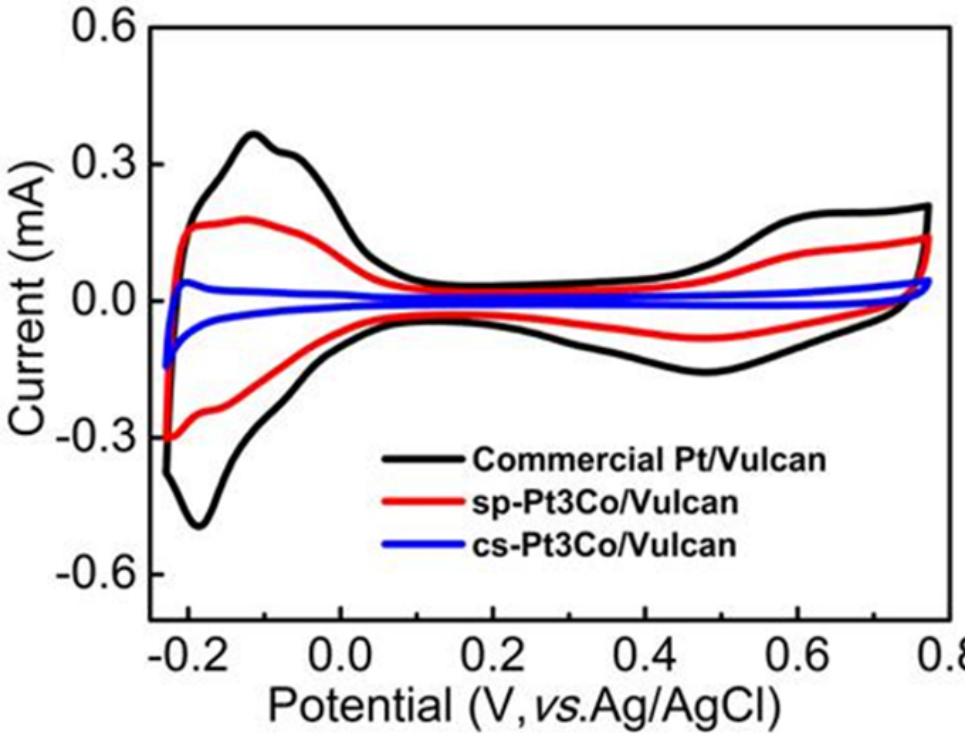

Figure S7. CVs of the different catalyst electrodes in argon-saturated 0.1 M $HClO_4$ solution at a scan rate of 0.05 V/s at room temperature.

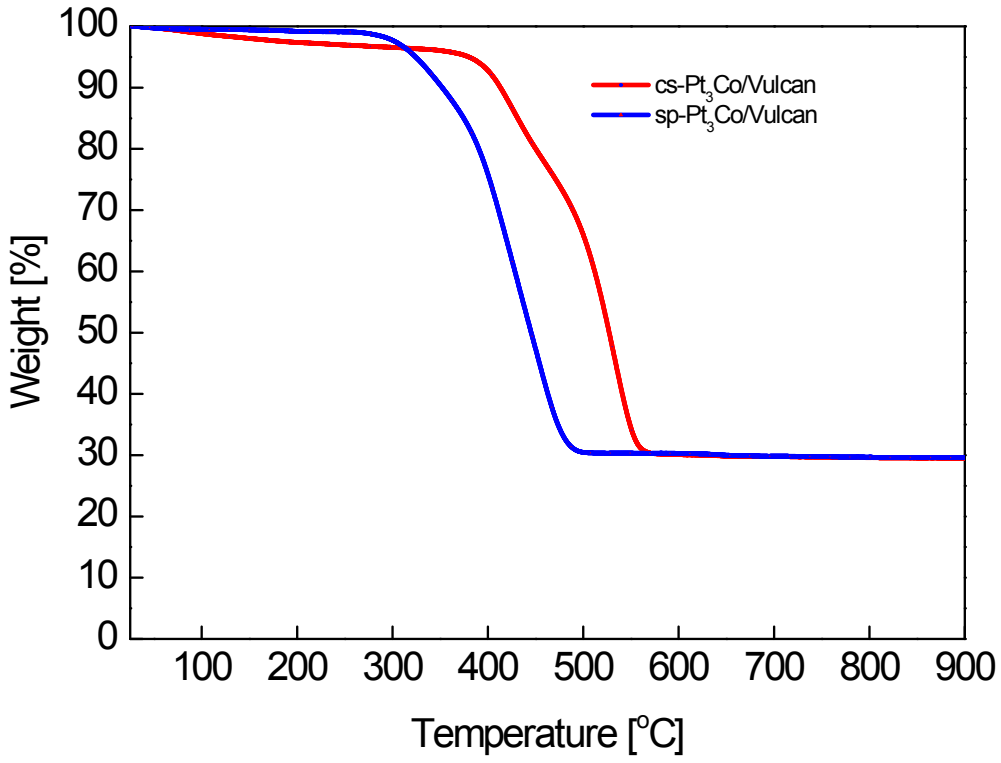

Figure S8. TGA analysis of the sp-Pt_3Co/Vulcan and cs-Pt_3Co/Vulcan is indicating that the Pt loading of sp- and cs-Pt_3Co catalysts is 30%.

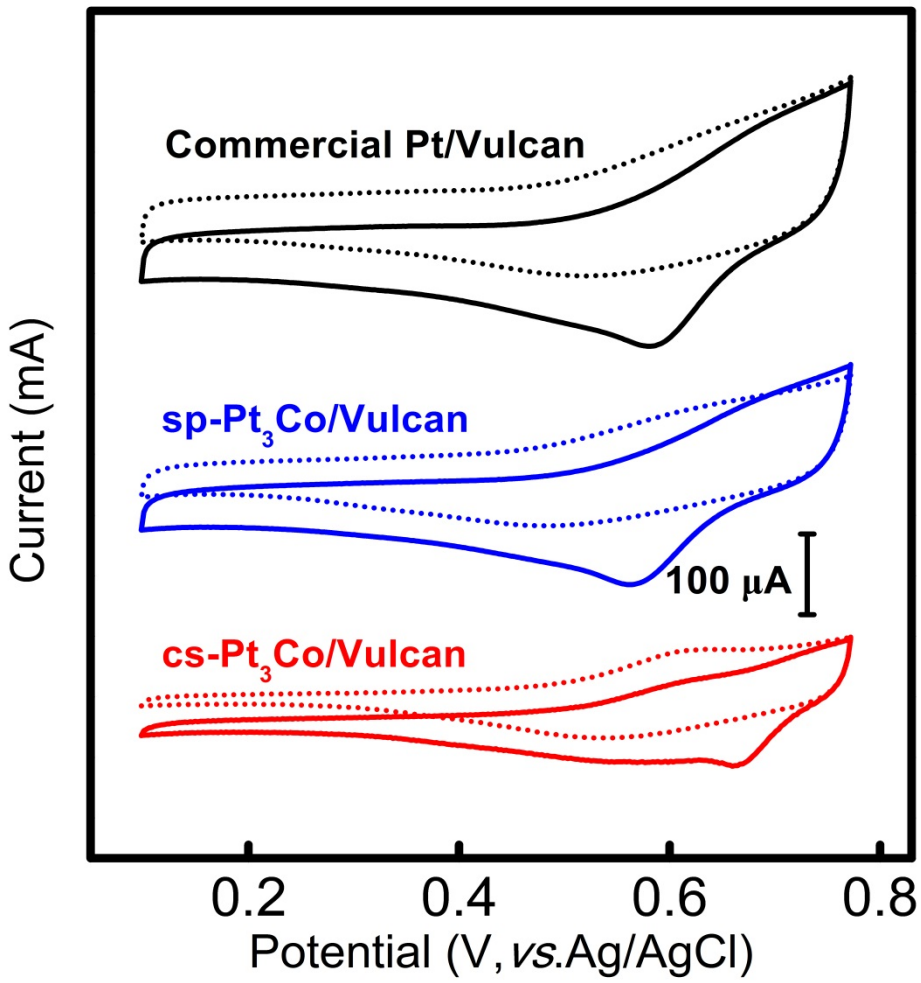

Figure S9 The CV Curves of Commercial Pt/Vulcan (black), sp-Pt_3Co/Vulcan and cs-Pt_3Co/Vulcan in argon (short dot line) and oxygen (solid line) saturated 0.1 M $HClO_4$ solution with scanning rate 50 mV/s. The ORR peak potential of cs-Pt_3Co/Vulcan is 0.664 V, which positively shifts around 100 mV compared to sp-Pt_3Co/Vulcan (0.568 V) and commercial Pt/Vulcan (0.583 V). The onset potential of cs-Pt_3Co/Vulcan is 0.75 V, while the onset potential of commercial Pt/Vulcan is 0.7 V and for sp-Pt_3Co/Vulcan it is 0.69 V.

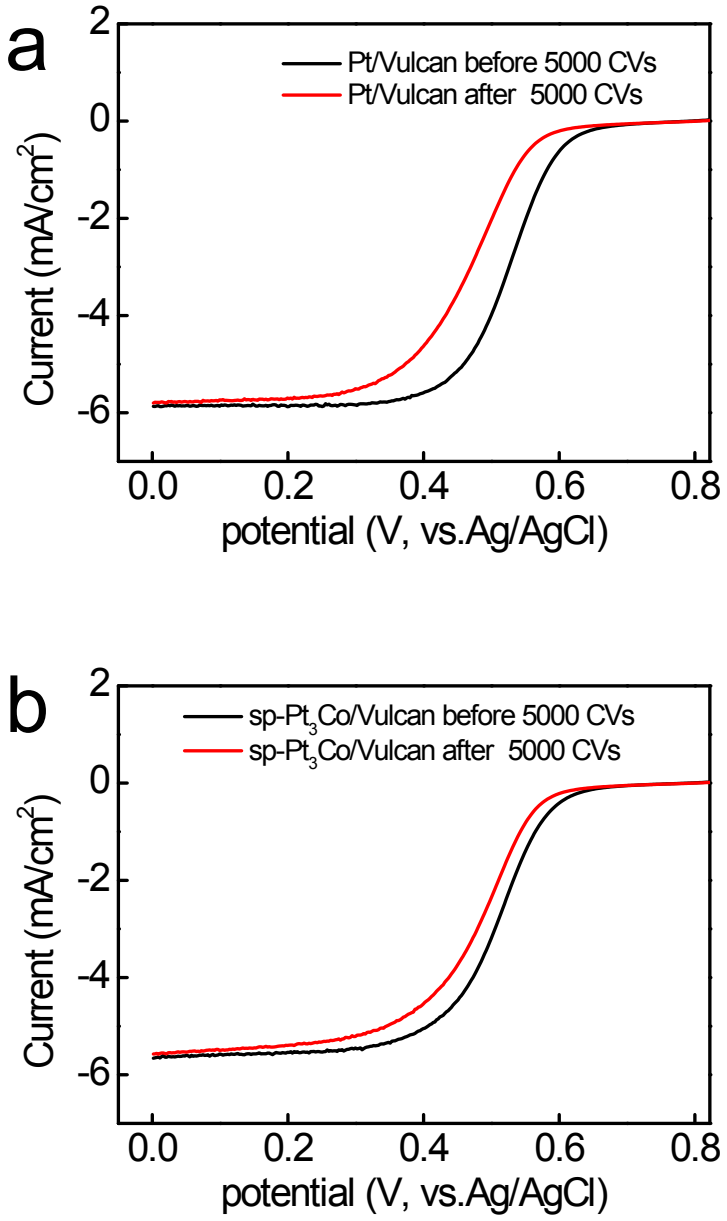

Figure S10 the polarization curves of Pt/Vulcan (a) and sp-Pt_3Co/Vulcan before (black) and after 5000 CVs in the sweep range 0.32-0.72 V in O_2-saturated 0.1 M $HClO_4$ solution. Rotating speed: 1600 r.p.m. scan rate: 0.05 V/s.

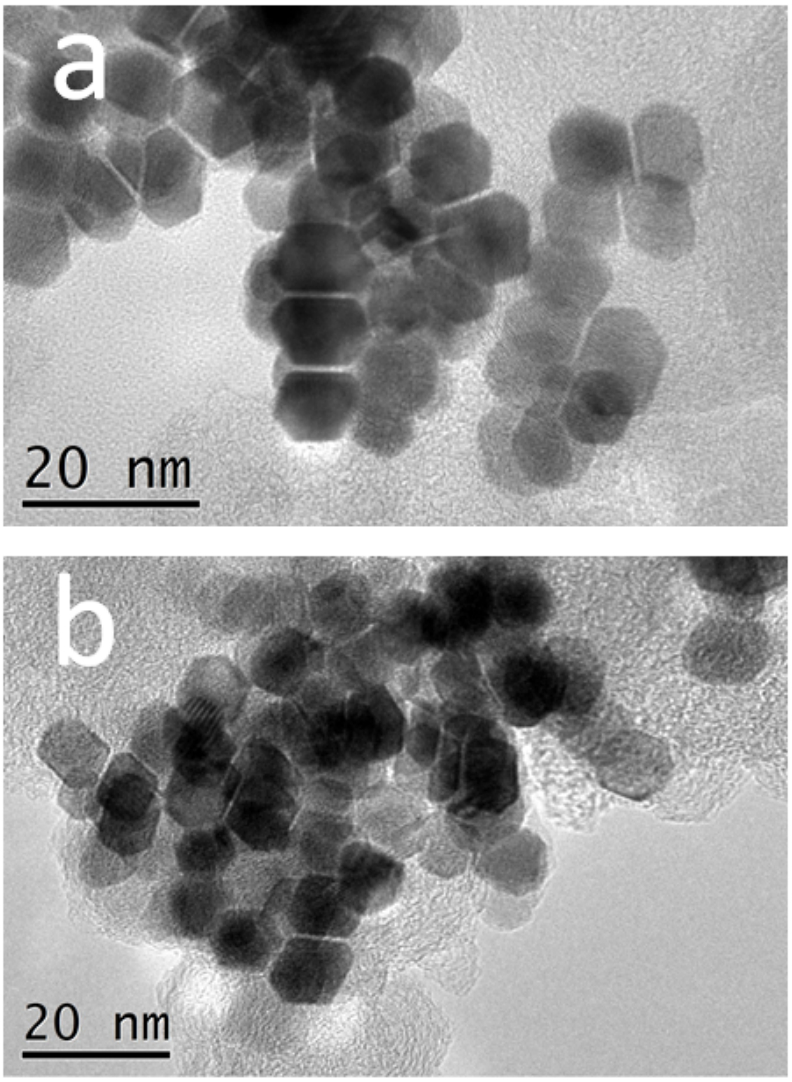

Figure S11. TEM images of cs-Pt_3Co decorated on Vulcan XC-72 support before (a) and after (b) 5000 cyclic voltammetry sweeps

Table 3S. Comparison of the current work with earlier reported results under similar conditions. The column of the half wave potential shift corresponds to the shift reported in the particular reports compared to their measurements on commercial Pt/C.

Catalyst	Pt loading (%)	Electrolyte	Specific activity at 0.9 V (mA/cm^2)	$\Delta U_{1/2}$[a] (mV)	Study by
Pt/C (Tanaka Kikinzoku Corporation)	28.2	0.1M $HClO_4$	0.19	~32	Koh et al. [1]
$PtCo_3$/C	27	0.1M $HClO_4$	0.57		
Pt/C	30	0.1M $HClO_4$	0.21		Srivastava et al.[2]
Pt_3Co/C	30	0.1M $HClO_4$	0.49	--	
Annealed Pt/C (TKK)	46	0.1M $HClO_4$	0.36		Chen et al.[3]
Annealed "Pt_3Co"/C	46	0.1M $HClO_4$	1.39	~26	
Acid-treated "Pt_3Co" /C	46	0.1M $HClO_4$	0.74	~29	
Pt/C (E-TEK)	40	0.5 M H_2SO_4	0.5	~40	Rao et al.[4]
Pt_3Co/Graphene	40	0.5 M H_2SO_4	1.4		
Pt/C	20	0.1M $HClO_4$	--	70	Wang et al.[5]
Pt_3Co/C-700	20	0.1M $HClO_4$	1.1		
Pt/C (BASF)	46	0.1M $HClO_4$	0.32		Guo et al.[6]
$Pt_{92}Co_8$ NWs/C (Ketjen carbon)	23.8	0.1M $HClO_4$	0.64	--	
Pt/Vulcan (Premetek, US)	30	0.1M $HClO_4$	0.24[b]	63	This paper
cs-Pt_3Co/Vulcan	30	0.1M $HClO_4$	1.44[b]		

[a] the potential at which the current reaches half its diffusion-limited value.
[b] calculated at 0.55 V vs. Ag/AgCl.

1. Koh, S., M.F. Toney, and P. Strasser, *Activity–stability relationships of ordered and disordered alloy phases of Pt3Co electrocatalysts for the oxygen reduction reaction (ORR).* Electrochimica Acta, 2007. **52**(8): p. 2765-2774.
2. Srivastava, R., et al., *Efficient oxygen reduction fuel cell electrocatalysis on voltammetrically dealloyed Pt–Cu–Co nanoparticles.* Angewandte Chemie International Edition, 2007. **46**(47): p. 8988-8991.
3. Chen, S., et al., *Enhanced Activity for Oxygen Reduction Reaction on "Pt3Co" Nanoparticles: Direct Evidence of Percolated and Sandwich-Segregation Structures.* Journal of the American Chemical Society, 2008. **130**(42): p. 13818-13819.
4. Rao, C.V., et al., *Synthesis and electrocatalytic oxygen reduction activity of graphene-supported Pt3Co and Pt3Cr alloy nanoparticles.* Carbon, 2011. **49**(3): p. 931-936.
5. Wang, D., et al., *Structurally ordered intermetallic platinum–cobalt core–shell nanoparticles with enhanced activity and stability as oxygen reduction electrocatalysts.* Nature materials, 2013. **12**(1): p. 81-87.
6. Guo, S., et al., *FePt and CoPt Nanowires as Efficient Catalysts for the Oxygen Reduction Reaction.* Angewandte Chemie International Edition, 2013. **52**(12): p. 3465-3468.

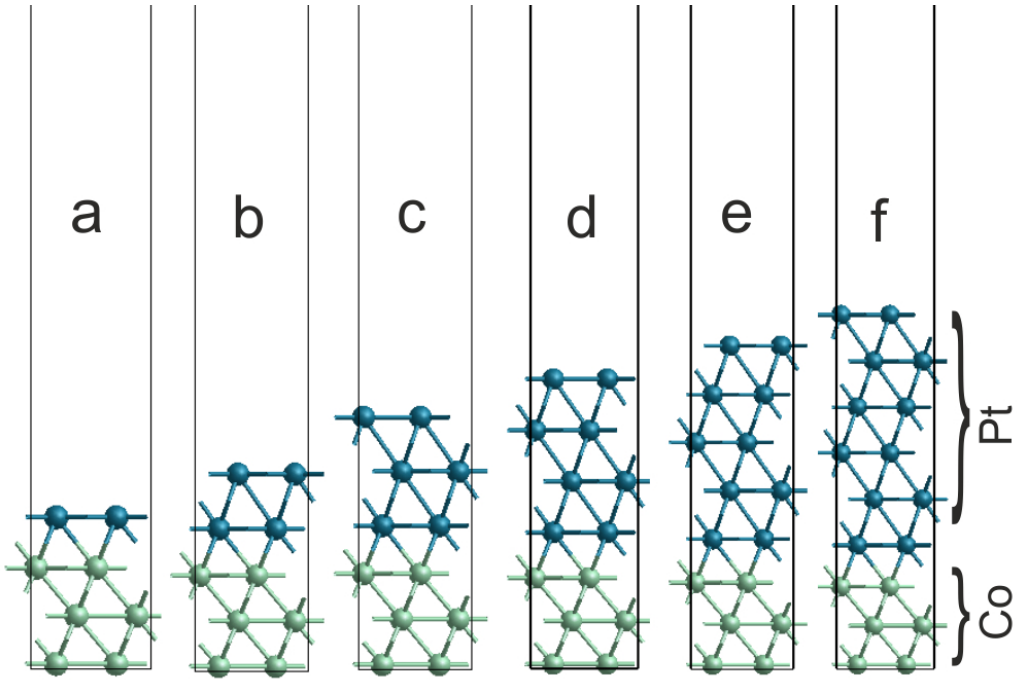

Figure S12 Pt-Co supercell with three bottom slabs as a cobalt core. In (a-f) systems with 1 up to 6 Pt slabs as a shell are shown.

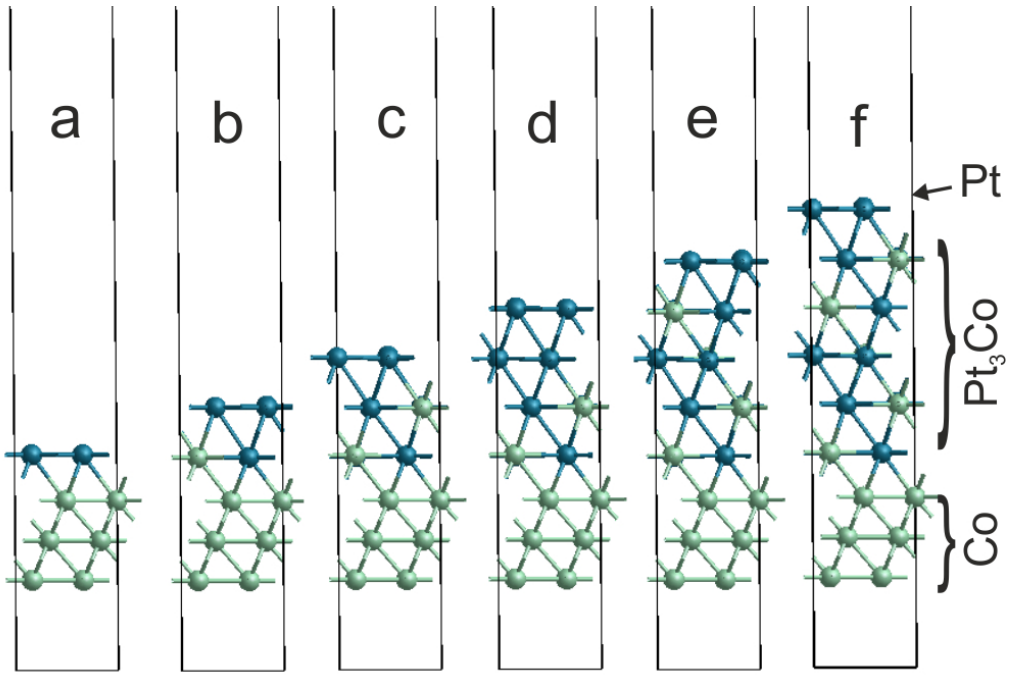

Figure S13 Pt_3Co supercell with three bottom slabs as a cobalt core, a Pt_3Co intermediate region (except in (a)), and a pure Pt monolayer at the top layer. (a) contains just Co and the Pt monolayer, while systems in (b-f) exhibit from 1 up to 5 Pt_3Co slabs as a shell, with their respective Pt monolayer at the top.

Table 4S. O-adsorption energy (ΔE_O), *d*-band center ($\varepsilon_d - \varepsilon_f$), and the ORR overpotential (η_{ORR}) obtained by DFT. The number in the system label indicates the number of shell-slabs. These values were used to create plots in Figure 4 in the main manuscript.

System label	**ΔE_O (eV)**	**ε_d - ε_f**	**η_{ORR}**
1-Pt-Co	1.98	-2.72	0.68
2-Pt-Co	1.75	-2.35	0.47
3-Pt-Co	1.61	-2.33	0.53
4-Pt-Co	1.56	-2.33	0.56
5-Pt-Co	1.56	-2.36	0.56
6-Pt-Co	1.55	-2.36	0.55
Pure Pt(111)	1.59	-2.38	0.55
1-Pt-Pt_3Co	2.19	-2.84	1.05
2-Pt-Pt_3Co	1.92	-2.55	0.56
3-Pt-Pt_3Co	1.87	-2.59	0.48
4-Pt-Pt_3Co	1.78	-2.59	0.43
5-Pt-Pt_3Co	1.83	-2.6	0.41
6-Pt-Pt_3Co	1.83	-2.61	0.40
Pure Pt-Pt_3Co (111)	1.82	-2.56	0.42
Pure Pt_3Co (111)	0.85	-	1.01