Supporting Information

Bimetallic Core-Based Cuboctahedral Core-Shell Nanocluster for Hydrogen Peroxide ($2e^-$ reduction) over Water ($4e^-$ reduction) Formation: Role of Core Metals

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Figure S1: (a) A (3 × 3) supercell of periodic AuCo@Pt(111) surface and (b) core atoms arrangements of $Au_{10}Co_9@Pt_{60}$ NC.

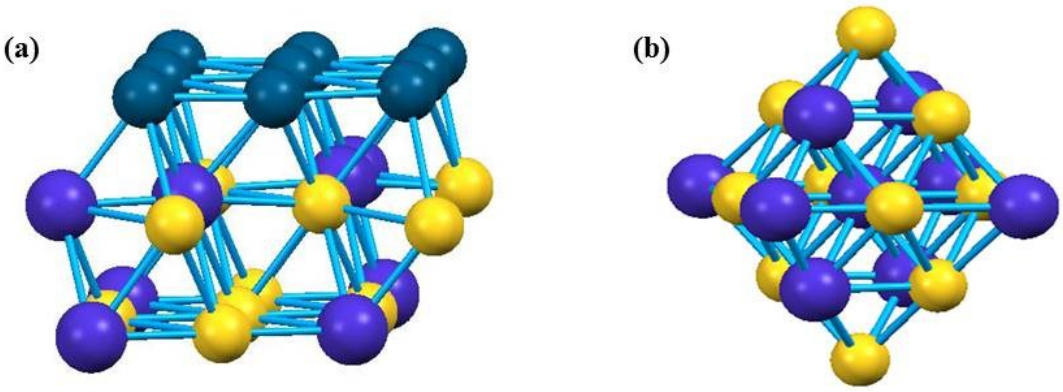
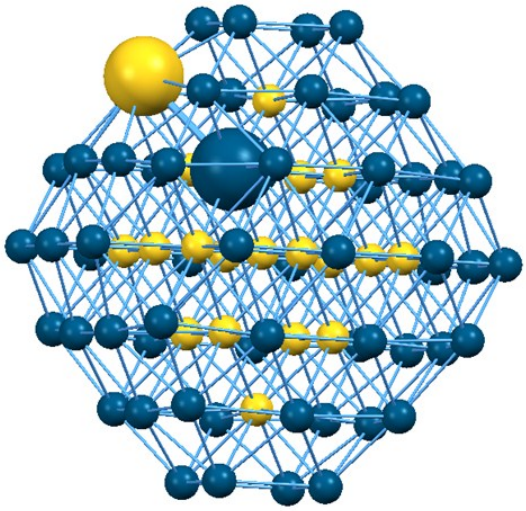
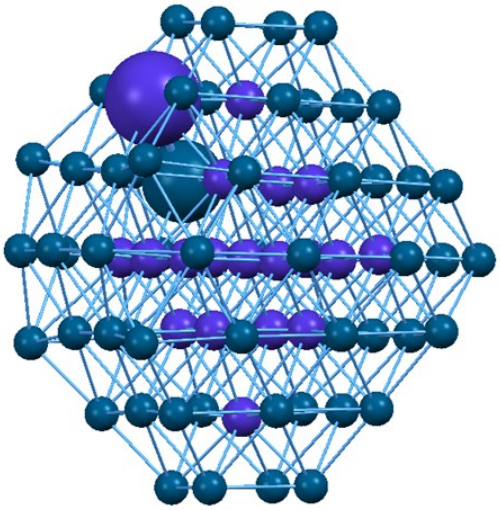


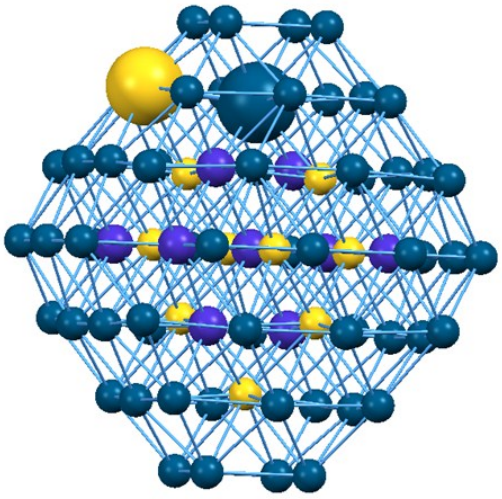
Figure S2: Optimized geometry and segregation energy of the NCs. The atoms with lager size represent the exchanged atoms.



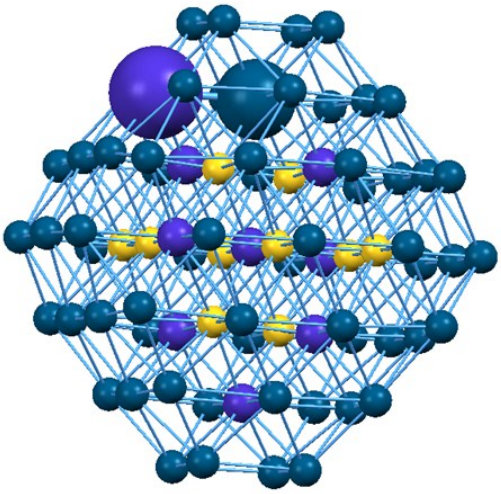
$Au_{18}Pt_1@Au_1Pt_{59}$



$Co_{18}Pt_1@Co_1Pt_{59}$



$Au_9Co_9Pt_1@Au_1Pt_{59}$



$Au_{10}Co_8Pt_1@Co_1Pt_{59}$

Test S1: Computational Details

Plane wave with a kinetic energy cut off of 470 eV is used to expand the electronic wave functions. A 22 × 22 × 22 $Å^3$ cubic supercell is used to optimize the NCs to rule out the possibility of interactions between the periodically repeated metal clusters. The Brillouin zone is sampled with a Gamma point (1×1×1) for clusters. The total energies of the NCs are improved in the range of 0.0001-0.002 eV if the k-point mesh set to 2 × 2 × 2. Therefore, we have used Gamma point for all the calculations to save the computational cost. For electronic structure calculations, a 2 × 2 × 2 k-point mesh is used. All the atoms of NCs are full relaxed during the structural relaxation. During relaxation of periodic surface, the bottom one layer is fixed and the top two layers are relaxed. A 12 Å of vacuum is used along the z-direction to avoid any periodic interactions. The Brillouin zone is sampled using a 3 × 3 × 1 k-point grid for the surface calculations. The convergence criteria for total energy and forces are set at 10^{-4} eV and <0.02 eV/Å, respectively. Spin-polarized calculations are performed for all the calculations. Six intermediate images are used in each CI-NEB pathway. Vibrational frequencies for the initial, transition and final states of the reactions are calculated and the transition states are confirmed by the presence of one imaginary frequency. Zero-point energy (ZPE) is calculated using the following equation:

$$\text{ZPE} = \sum_i 1/2h\upsilon_i$$

where h is the Planck constant and υ_i is the frequency of the i^{th} vibrational mode. The reaction free energies (ΔG) are calculated using the following equation:

$$\Delta G = \Delta E + \Delta ZPE - T\Delta S$$

where ΔE, ΔZPE and ΔS are the difference in total energies, zero-point energies and entropy between the product/TS and reactant. Gas phase entropy values have been taken from NIST

database.[1] The activation barriers and reaction free energies have been calculated in thermochemical way, whereas the free energy diagram has been plotted in electrochemical way. The forward (k_i) rate constants for all the elementary steps are calculated using the following equation:

$$k_i = \left(\frac{k_B T}{h}\right)\left(\frac{q_{TS}}{q_R}\right) e^{-\Delta G^{\ddagger}/k_B T}$$

where k_B is the Boltzmann constant, T is the temperature, h is the Plank constant. Here, q_{TS} and q_R are the vibrational partition functions for the transition state and reactant structures, respectively $and\ \Delta G^{\ddagger}$ is the Gibbs free energy barrier for the initial and final state of the elementary reaction. Bader charge[2] has been calculated using Henkelman programme.[3-4]

References:

[1] http://webbook.nist.gov/chemistry/

[2] R. F. W. Bader, *Oxford University Press: USA*, **1994.**

[3] G. Henkelman, A. Arnaldsson and H. Jonsson, *Comput. Mater. Sci.,* 2006, **36**, 354-360.

[4] E. Sanville, S. D. Kenny, R. Smith and G. Henkelman, *J. Comput. Chem.,* 2007, **28**, 899-908.

Figure S3: Adsorption behaviours of the intermediates on $Au_{10}Co_9@Pt_{60}$ NC: (a) $*O_2$, (b) *OOH, (c) *OH, (d) $*H_2O_2$, (e) $*H_2O$, (f) *O and (g) *H.

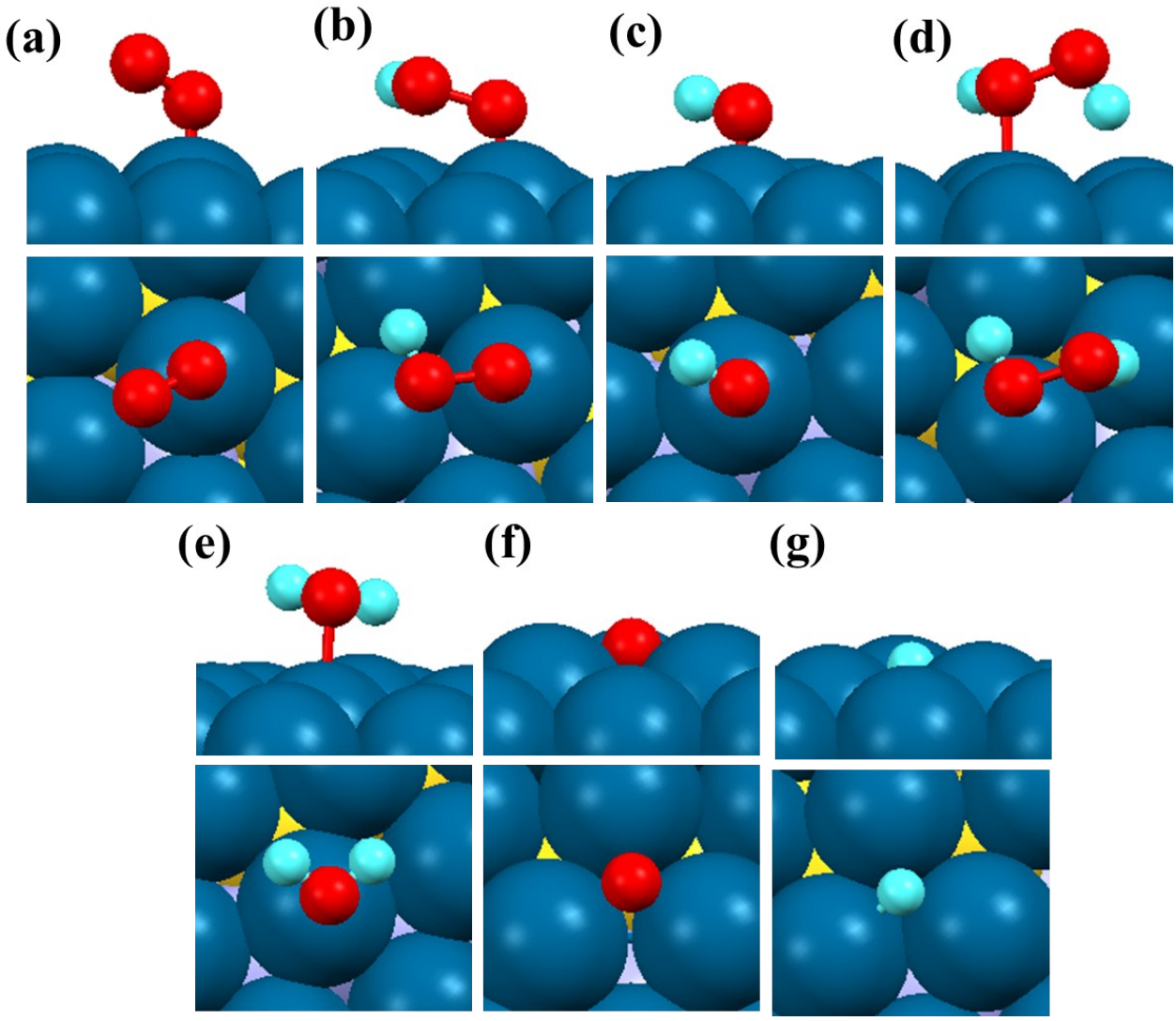


Table S1: Adsorption energies (in eV) of the reaction intermediates on $Au_{10}Co_9@Pt_{60}$ NC at edge and facet sites.

Adsorbed Species	**$Au_{10}Co_9@Pt_{60}$**	
	Edge	**Facet**
$*O_2$	-1.80 (b)	-0.22 (t)
*O	-4.86 (b)	-5.40 (f)
*OH	-2.57 (t)	-2.12 (t)
*OOH	-1.78 (b)	-1.12 (b)
$*H_2O_2$	-0.38 (b)	-0.28 (b)
$*H_2O$	-0.25 (t)	-0.22 (t)
*H	-2.91 (b)	-2.81 (f)
$*H_2$	-0.23 (t)	-

Table S2: Adsorption energies (in eV) of the reaction intermediates on $Au_9Co_{10}@Pt_{60}$ and $Au_{10}Co_9@Pt_{60}$ NC.

Adsorbed Species	**$Au_9Co_{10}@Pt_{60}$**	**$Au_{10}Co_9@Pt_{60}$**
$*O_2$	-0.23 (t)	-0.22 (t)
*O	-5.26 (f)	-5.40 (f)
*OH	-2.17 (t)	-2.12 (t)
*OOH	-1.18 (b)	-1.12 (b)
$*H_2O_2$	-0.27 (b)	-0.28 (b)
$*H_2O$	-0.17 (t)	-0.22 (t)

Table S3: Reaction free energies (ΔG in eV) and activation barriers ($\Delta G^{\ddagger}$ in eV) for the all-possible elementary reactions on the (111) facet of the $Co_{19}@Pt_{60}$, $Au_{19}@Pt_{60}$, $Au_{10}Co_{19}@Pt_{60}$ and Pt_{79} NCs.

Steps	**Elementary Reactions**	**$Au_{19}@Pt_{60}$**		**$Co_{19}@Pt_{60}$**		**$Au_{10}Co_{9}@Pt_{60}$**		**Pt_{79}**	
		ΔG	$\Delta G^{\ddagger}$	ΔG	$\Delta G^{\ddagger}$	ΔG	$\Delta G^{\ddagger}$	ΔG	$\Delta G^{\ddagger}$
1	$*O_2 \rightarrow *O + *O$	-2.81	0.76	-2.80	0.07	-2.27	0.06	-2.33	0.00
2	$*O_2 + *H \rightarrow *OOH$	-0.17	0.00	1.30	1.27	-0.21	0.12	-0.47	0.04
3	$*O + *H \rightarrow *OH$	0.49	1.02	-0.46	0.38	0.30	0.50	0.03	0.25
4	$*OOH \rightarrow *O + *OH$	-2.18	0.66	-3.35	0.11	-1.79	0.61	-1.92	0.00
5	$*OOH + *H \rightarrow *H_2O_2$	0.19	1.21	-0.23	0.95	-0.21	0.46	0.11	1.14
6	$*H_2O_2 \rightarrow *OH + *OH$	-1.46	0.21	-0.80	0.08	-0.97	0.20	-1.71	0.06
7	$*OH + *H \rightarrow *H_2O$	-0.06	0.39	-1.16	0.20	-0.76	0.12	-0.43	0.00

Table S4: Rate constants values for the elementary reactions at 300 K on different NCs.

Steps	Elementary reactions	$Au_{10}Co_9@Pt_{60}$	$Au_{19}@Pt_{60}$	$Co_{19}@Pt_{60}$	Pt_{79}
1	$*O_2 \xrightarrow{k_1} *O+*O$	6.29×10^{11}	2.61×10^{00}	4.35×10^{11}	8.66×10^{12}
2	$*O_2+*H \xrightarrow{k_2} *OOH$	6.63×10^{10}	6.08×10^{13}	4.07×10^{-09}	1.36×10^{12}
3	$*O+*H \xrightarrow{k_3} *OH$	1.13×10^{04}	2.57×10^{-05}	1.61×10^{06}	1.32×10^{08}
4	$*OOH \xrightarrow{k_4} *O+*OH$	4.82×10^{02}	6.13×10^{01}	9.06×10^{10}	7.92×10^{12}
5	$*H+*OOH \xrightarrow{k_5} *H_2O_2$	1.08×10^{05}	2.85×10^{-08}	7.43×10^{-04}	5.39×10^{-07}
6	$*H_2O_2 \xrightarrow{k_6} *OH + *OH$	2.93×10^{09}	2.09×10^{09}	3.83×10^{11}	8.73×10^{11}
7	$*H+*OH \xrightarrow{k_7} *H_2O$	6.20×10^{10}	1.76×10^{06}	3.38×10^{09}	1.67×10^{13}

Table S5: Reaction free energies (in eV) and activation barriers (in eV, parenthesis) on the edge and facet site of $Au_{10}Co_9@Pt_{60}$ NC.

Elementary steps	**$Au_{10}Co_9@Pt_{60}$**	
	Edge	**Facet**
$*O_2 \rightarrow *O + *O$	-1.57 (0.03)	-2.27 (0.06)
$*O_2 + *H \rightarrow *OOH$	0.47 (0.44)	-0.21 (0.12)
$*OOH \rightarrow *O + *OH$	-2.04 (-)	-1.79 (0.61)
$*OOH + *H \rightarrow *H_2O_2$	0.06 (0.24)	-0.21 (0.46)

Figure S4: Adsorption behaviors of the reaction intermediates ($*O_2$, *OOH and $*H_2O_2$) on $Au_9Co_9Pt_1@Au_1Pt_{59}$ NC

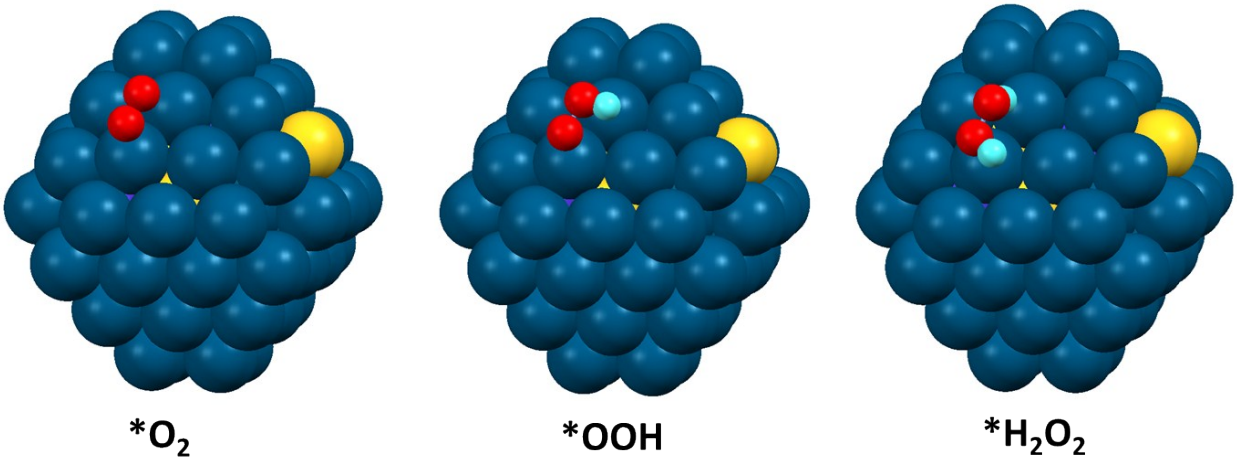


Table S6: Reaction free energies (in eV) and activation barriers (in eV) of two important H_2O_2 formation steps on the $Au_9Co_9Pt_1@Au_1Pt_{59}$ and $Au_{10}Co_9@Pt_{60}$ NC.

Nanoclusters	**$*O_2 + *H \rightarrow *OOH$**		**$*OOH + *H \rightarrow *H_2O_2$**	
	ΔG	$\Delta G^{\ddagger}$	ΔG	$\Delta G^{\ddagger}$
$Au_{10}Co_9@Pt_{60}$	-0.21	0.12	-0.21	0.46
$Au_9Co_9Pt_1@Au_1Pt_{59}$ (Au-segregated)	-0.26	0.11	-0.25	0.37

Table S7: Adsorption energies (in eV) of the reaction intermediates on periodic AuCo@Pt(111) surface and $Au_{10}Co_9@Pt_{60}$ NC.

Adsorbed Species	**Periodic AuCo@Pt(111) surface**	**$Au_{10}Co_9@Pt_{60}$**
$*O_2$	-0.11 (t)	-0.22 (t)
*O	-3.45 (f)	-5.40 (f)
*OH	-1.99 (t)	-2.12 (t)
*OOH	-0.88 (b)	-1.12 (b)
$*H_2O_2$	-0.22 (b)	-0.28 (b)
$*H_2O$	-0.15 (t)	-0.22 (t)
*H	-2.61 (f)	-2.81 (f)