Supporting Information

Origin of Enhanced Activities for CO Oxidation and O_2 Reaction over Composition-Optimized $Pd_{50}Cu_{50}$ Nanoalloy Catalysts

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Supporting information:

1. Tables:

Table S1. Adsorption energies (in eV) of O_2 on the Pd_{55}, $Pd_{43}Cu_{12}$, $Pd_{12}Cu_{43}$ and Cu_{55} nanoclusters (sites labeled adsorption sites are the final adsorption configurations, and sites labeled "NA." are unstable).

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Table S1. Adsorption energies (in eV) of O_2 on the Pd_{55}, $Pd_{43}Cu_{12}$, $Pd_{12}Cu_{43}$ and Cu_{55} nanoclusters (sites labeled adsorption sites are the final adsorption configurations, and sites labeled "NA." are unstable).

Clusters / Adsorption Site	Pd_{55}	$Pd_{43}Cu_{12}$	$Pd_{12}Cu_{43}$	Cu_{55}
B1	-1.239	-1.063	-0.868	-1.021
B2	-1.238	-0.930	-1.106	-1.266
H1	-0.574	-0.433	-0.396	-0.597
H2	-0.512	-0.462	-0.471	-0.458
T1	-1.566	-0.390	-0.622	-0.411
T2	-1.263	-0.399	-0.967	-0.283
T1-H1	B2	-1.125	-0.371	-1.199
T2-H1	-1.203	-0.896	B1-B1	B1-B2
T2-H2	-1.060	-0.924	-1.060	NA
B1-B1	B1-B2	-0.985	-1.137	-1.267
B1-B2	-1.187	-1.086	-0.915	-1.331
B2-B2	-1.119	-1.031	-1.040	NA

Table S2. Adsorption energies (in eV) of O_2 on the $Pd_{28}Cu_{27}$ nanocluster.

	B1	B2	B3	B4	B5	T1	T2	T3	T4	H1
O_2	-0750	-0.703	-0.935	-0.750	-0.700	-0.918	-0.247	-0.389	-0.412	T1
	H2	H3	T1-H1	T2-H1	T2-H2	T2-H3	T3-H2	T3-H3	T4-H2	T4-H3
	-0.027	T4	-0.775	-0.623	-0.796	NA	-0.440	-0.650	NA	NA
		B1-B1	B1-B2	B2-B3	B3-B3	B3-B4	B3-B5			
		-0.733	T2-H1	NA	NA	-0.592	NA			

Table S3. Adsorption energies (in eV) of CO on Pd_{55}, $Pd_{43}Cu_{12}$, $Pd_{12}Cu_{43}$ and Cu_{55} nanoclusters.

Clusters / Adsorption Site	Cu_{55}	$Cu_{43}Pd_{12}$	$Cu_{12}Pd_{43}$	Pd_{55}
B1	-0.934	-1.186	-1.878	-2.226
B2	-1.031	H1	H1	H1
H1	-1.065	-1.149	-2.096	-2.459
H2	-1.154	-0.840	-2.340	-2.294
T1	-1.055	-1.288	-1.100	-1.560
T2	-0.958	-0.828	-1.418	-2.156

Table S4. Adsorption energies (in eV) of CO on the $Pd_{28}Cu_{27}$ nanocluster.

sites	B1	B2	B3	B4	B5	H1	H2	H3	T1	T2	T3	T4
CO	-1.401	H1	-1.733	-1.727	B3	-1.409	-1.249	B5	-1.417	-0.848	-1.359	B5

Table S5. The numbers of d-electron of the surface Pd and Cu atom in the PdCu nanoalloys.

cluster	d-electron in surface Pd atom		d-electron in surface Cu atom	
	vertex	edge	vertex	edge
Pd_{55}	9.272	9.227		
$Pd_{43}Cu_{12}$	9.269	9.269		
$Pd_{27}Cu_{28}$	9.388	9.358		9.828
$Pd_{12}Cu_{43}$	9.488			9.846
Cu_{55}			9.868	9.858

Table S6. Adsorption energies (in eV) for the oxygen intermediates (O, OH, and OOH) involved in ORR on Pd_{55}, $Pd_{43}Cu_{12}$, $Pd_{12}Cu_{43}$ and Cu_{55} nanoclusters.

	Sites	Pd_{55}	$Pd_{43}Cu_{12}$	$Pd_{12}Cu_{43}$	Cu_{55}
O	B1	H1	-4.156	H1	H1
	B2	H1	H2	H1	H1
	H1	-4.808	-4.502	-4.969	-5.306
	H2	-4.530	-4.632	-5.064	-5.093
	T1	-3.527	-3.409	-3.382	-3.281
	T2	B1	B1	H1	H1
Average adsorption energy		-4.446	-4.247	-4.719	-4.933
OH	B1	-3.234	-2.921	-3.269	-3.392
	B2	H1	-2.854	H2	H1
	H1	-3.244	-2.823	-3.360	-3.504
	H2	-3.004	-2.930	-3.435	-3.394
	T1	-2.922	-2.650	-2.796	-2.974
	T2		-2.427	B1	H1
Average adsorption energy		-3.101	-2.904	-3.262	-3.376
OOH	B1	-1.601	-1.315	-1.315	-1.691
	B2	NA	NA	NA	NA
	T1-H1	NA	NA	NA	NA
	T2-H1	NA	NA	NA	NA
	T2-H2	NA	NA	NA	NA
Average adsorption energy		-1.601	-1.315	-1.315	-1.691

Table S7. Adsorption energies (in eV) for the oxygen intermediates (O, OH, and OOH) involved in ORR on the $Pd_{28}Cu_{27}$ nanocluster.

sites	B1	B2	B3	B4	B5	H1	H2	H3	T1	T2	T3	T4
O	-3.998	H2	H3	H3	-3.932	-3.932	-4.444	4.419	-4.320	-3.301	H3	B5
OH	-2.839	H2	H2	-2.975	-2.830	-2.952	-2.949	B4	-2.637	B1	B5	-2.660
sites	B1	B2	B3	B4	B5	T1-H1	T2-H1	T2-H2	T2-H3	T3-H2	T3-H3	T4-H3
OOH	-1.176	NA	NA	-1.277	-1.277	NA	-1.462	NA	NA	NA	NA	-1.168
Average adsorption energy										O	OH	OOH
										-4.099	-2.862	-1.272

(sites labeled adsorption sites are the final adsorption configurations, and sites labeled “NA.” are unstable)

2. Figures:

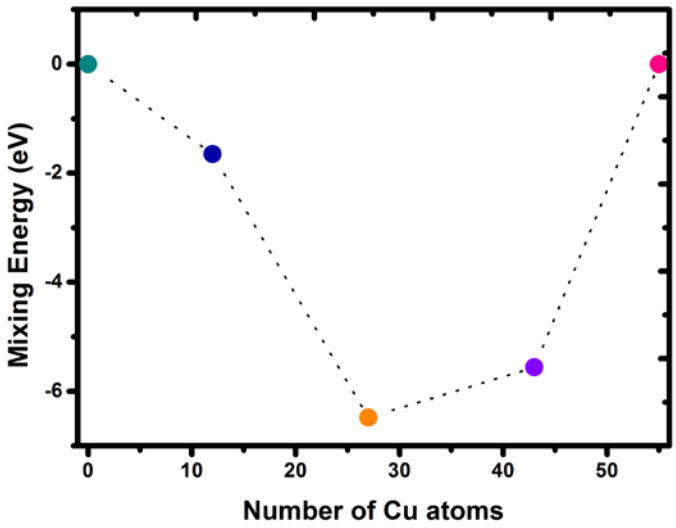


Figure S1. Plot of the mixing energies for 55-atom PdCu nanoalloys with icosahedral structure as a function of Cu concentration.

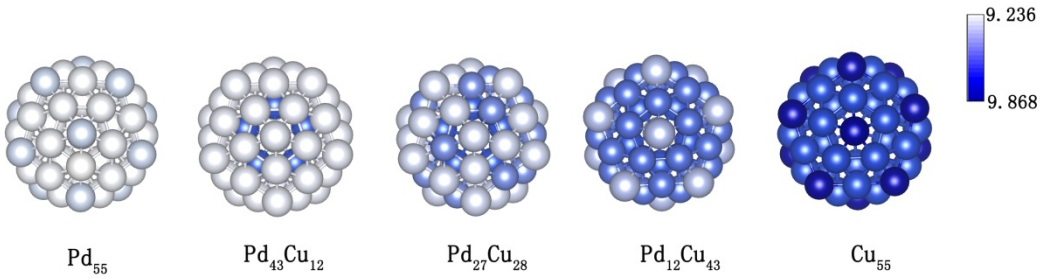


Figure S2. Polts of the number of d-electron in the surface Pd and Cu atom on PdCu nanoalloys. For Pd ($4d^9 5s^1$) atom, it has 9-electeon in its d orbit, where for Cu ($3d^{10}4s^1$) atom, it has 10-electron in our calculation (The pseudopotentials for Pd and Cu are Pd.pbe-nd-rrkjus.UPF and Cu.pbe-d-rrkjus.UPF, respectively.). For pure Pd and pure Cu clusters, the vertex atom can get electron from the edge atom. For PdCu alloy clusters, Pd atom can get electron from the Cu atom.

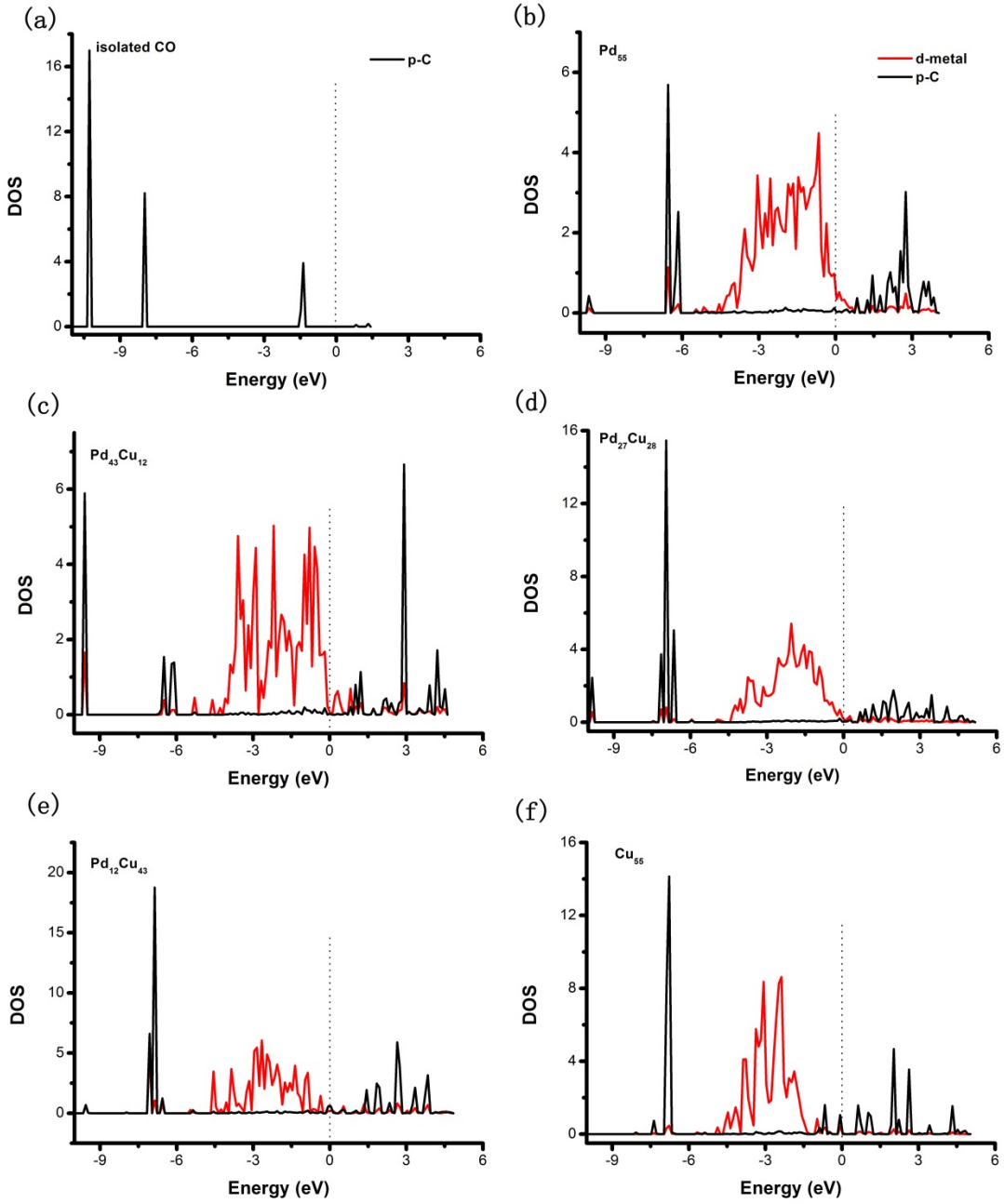
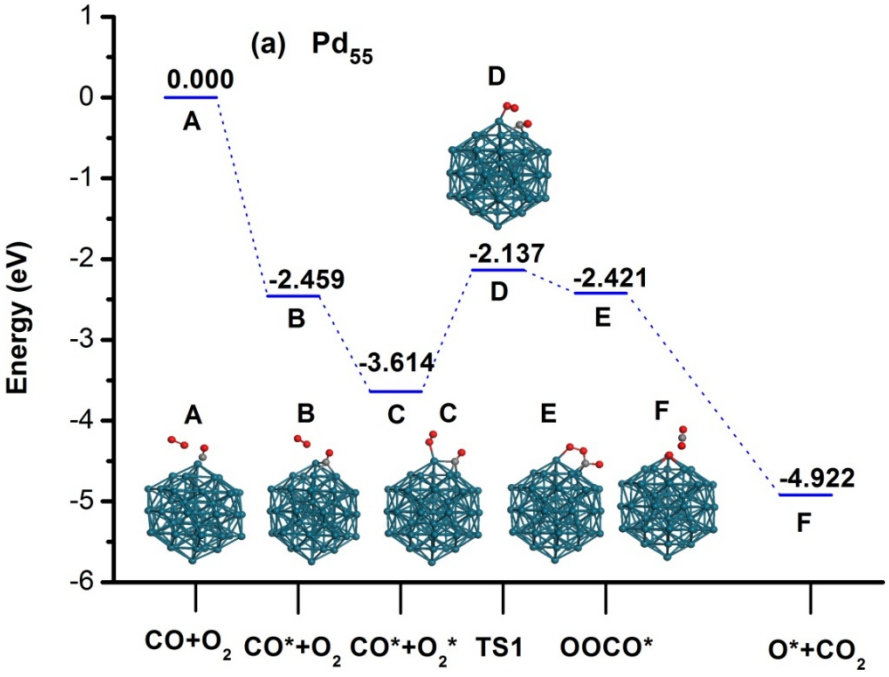
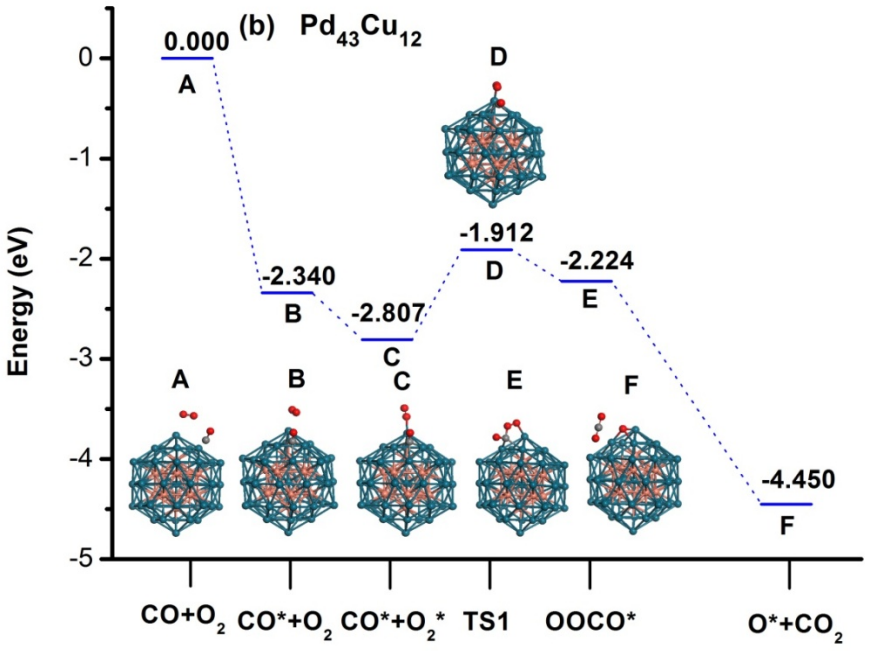


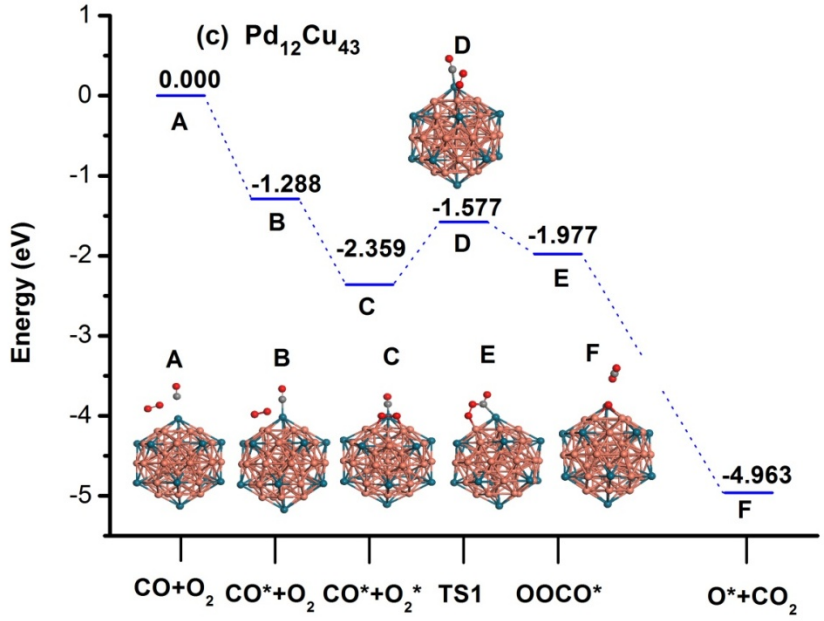
Figure S3. The partial density of states (PDOS) projected on the p-states of C atom of the isolated CO molecule (a); the PDOS projected on the d-states of the Pd or Cu atom and the p-states of the adatom C in the system for the adsorption of CO on (b) Pd_{55}, (c) $Pd_{43}Cu_{12}$, (d) $Pd_{27}Cu_{28}$, (e) $Pd_{12}Cu_{43}$, and (f) Cu_{55} nanoclusters at the most preferred CO adsorption configuration.


(a) Pd55
Energy (eV)
1
0
-1
-2
-3
-4
-5
-6
0.000
A
-2.459
B
-3.614
C
C
-2.137
D
D
-2.421
E
E
F
-4.922
F
A
B
CO+O2
CO*+O2
CO*+O2*
TS1
OOCO*
O*+CO2

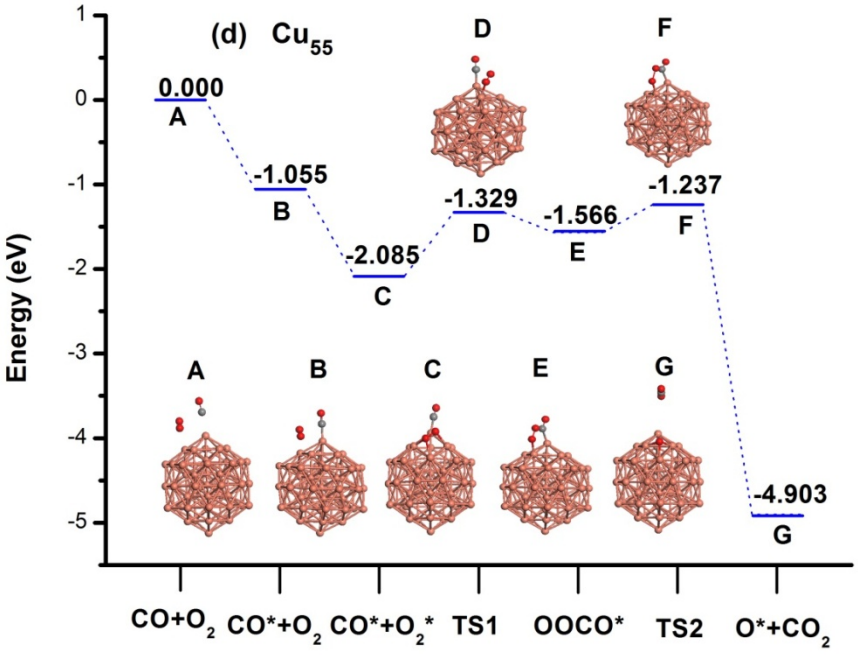
(a)


(b) Pd43Cu12
Energy (eV)
0
-1
-2
-3
-4
-5
0.000
A
-2.340
B
-2.807
C
D
-1.912
D
-2.224
E
E
F
-4.450
F
A
B
C
CO+O2
CO*+O2
CO*+O2*
TS1
OOCO*
O*+CO2

(b)



(c)



(d)

Figure S4. Potential energy profile and configurations for CO oxidation with the Langmuir–Hinshelwood (LH) mechanism on the (a) Pd_{55}, (b) $Pd_{43}Cu_{12}$, (c) $Pd_{12}Cu_{43}$, and (d) Cu_{55} nanoclusters.

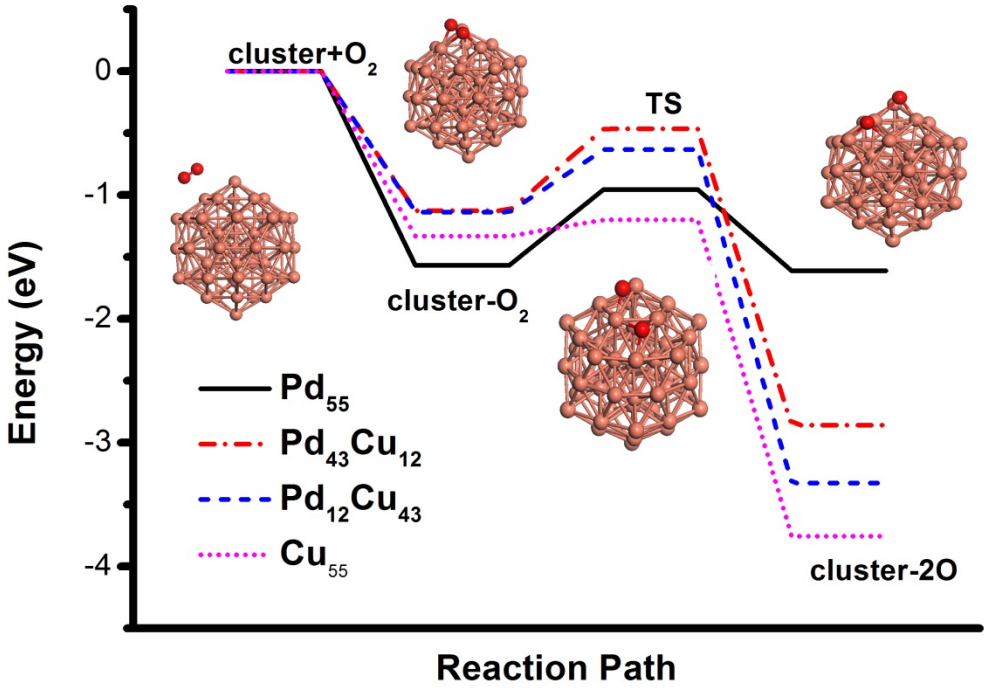


Figure S5. Plots of the reaction pathways for O_2 dissociation on the Pd_{55}, $Pd_{43}Cu_{12}$, $Pd_{12}Cu_{43}$, and Cu_{55} nanoclusters. TS denotes the transition state.