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

CO oxidation on Rh-doped Hexadecagold Clusters

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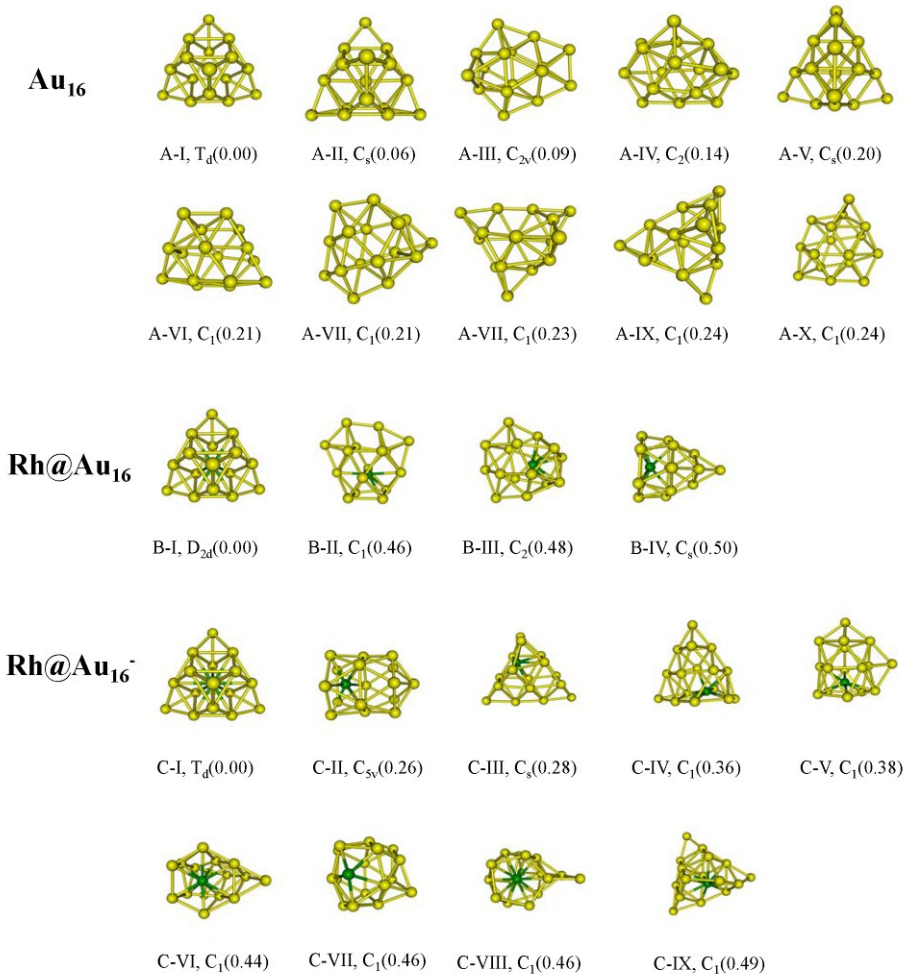

Figure S1. Structures of the candidates for the lowest-energy cluster of Au_{16}, neutral and anionic $Rh@Au_{16}$ clusters by genetic algorithm. The energy values (in eV) beneath each isomer are the relative energy with respect to the lowest-lying isomer calculated at the corresponding of PBE level of DFT calculations.

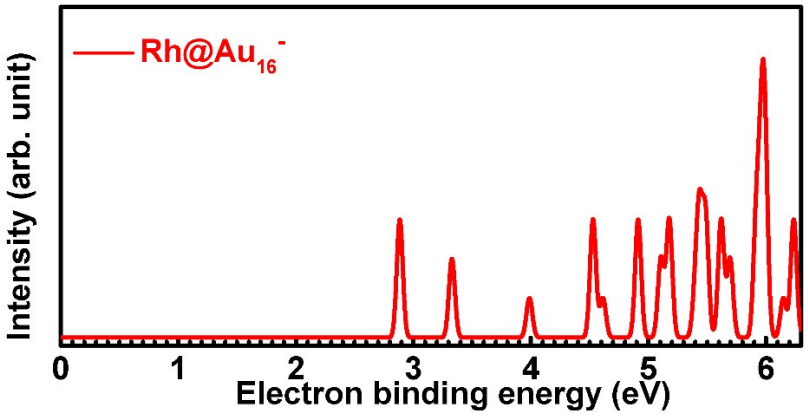

Figure S2. Calculated photoelectron spectra of $Rh@Au_{16}^-$ anionic cluster.

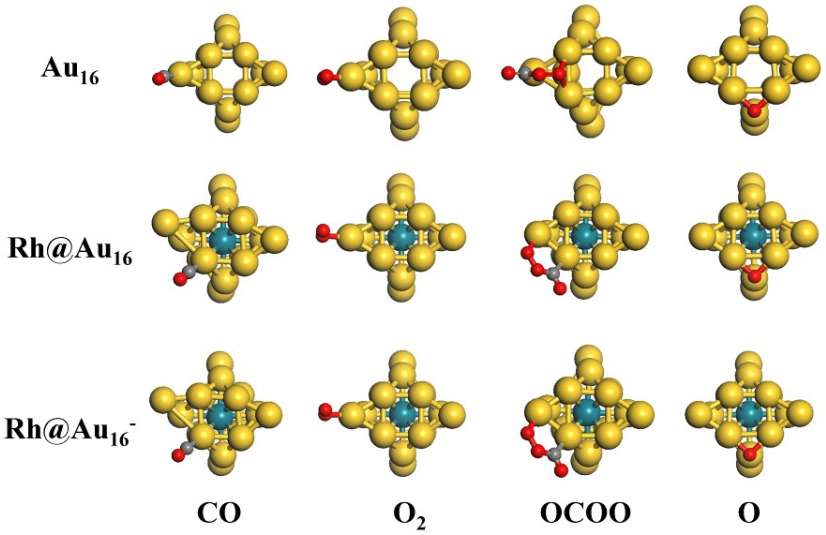

Figure S3. Optimized adsorption geometries involved in CO oxidation on Au_{16}, $Rh@Au_{16}$ and $Rh@Au_{16}^-$ clusters. Yellow, cyan, grey and red balls are Au, Rh, C and O atoms.

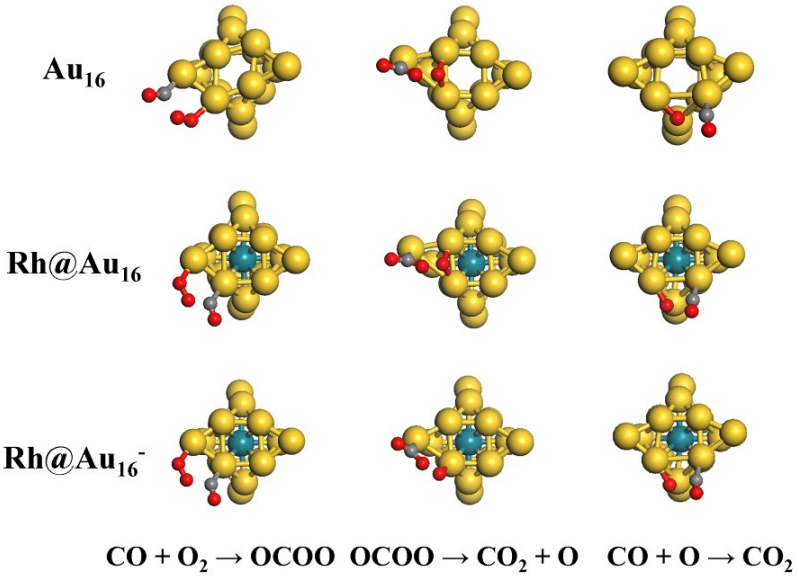

Figure S4. Optimized transition states for CO oxidation on Au_{16}, $Rh@Au_{16}$ and $Rh@Au_{16}^-$ clusters. Yellow, cyan, grey and red balls are Au, Rh, C and O atoms.

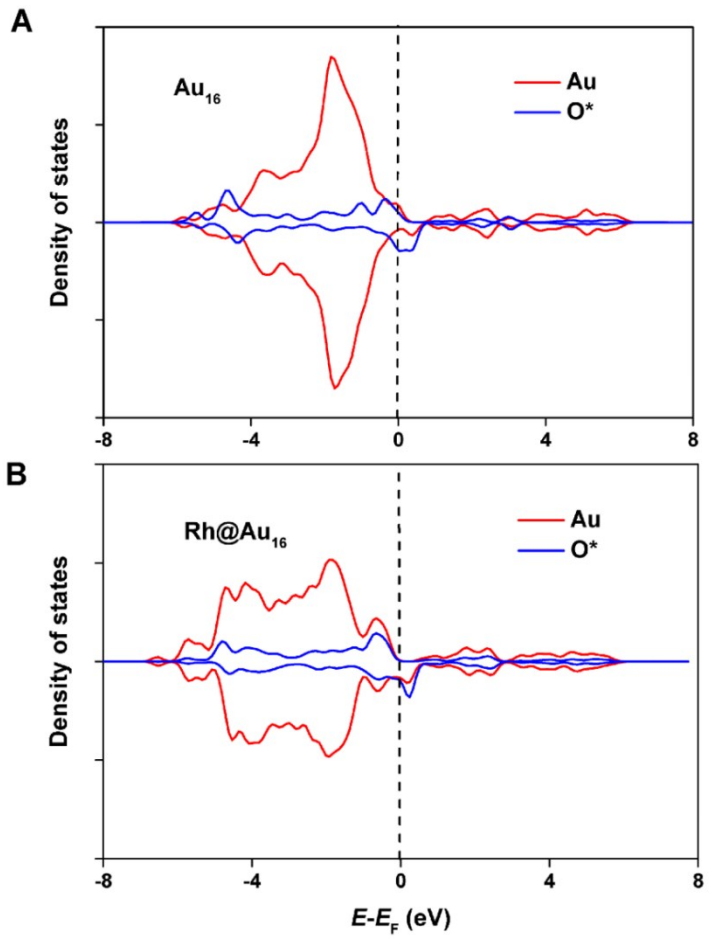

Figure S5. The projected density of states (PDOS) of the O* atom in the transition state on Au_{16} (A) and $Rh@Au_{16}$ (B) clusters. The blue and red lines are the PDOS for the adsorbed O* atom and the corresponding two Au atoms, respectively.

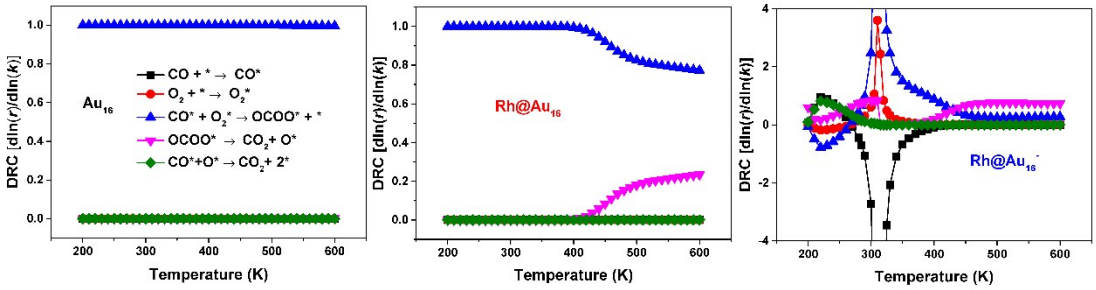

Figure S6. The degree of rate control (DRC) for CO oxidation as a function of the temperature (in K) on Au_{16}, $Rh@Au_{16}$ and $Rh@Au_{16}^-$ clusters.

Table S1. Calculated vibration frequency (in cm^{-1}) for Au_{16}, $Rh@Au_{16}$ and $Rh@Au_{16}^-$ clusters. There are 42 and 45 real frequencies for Au_{16} and Rh-doped Au_{16} clusters.

Au16							
14	14	14	18	18	18	35	35
44	44	44	58	58	58	60	60
60	68	68	68	84	84	84	85
85	86	99	99	99	101	109	109
111	111	111	147	147	147	173	173
173	188						
Rh@Au16							
22	28	31	32	36	36	38	38
42	45	51	56	56	57	57	59
60	71	72	72	76	76	79	79
81	82	83	83	86	102	103	104
104	104	109	134	138	138	150	150
152	173	173	175	178			
$Rh@Au_{16}^-$							
20	31	31	33	33	33	42	42
42	44	44	53	53	53	62	62
62	72	72	72	79	79	79	83
83	83	85	85	85	102	102	102
102	102	111	133	133	133	150	150
150	171	180	180	180			

Table S2. Calculated binding energies (in eV) of the intermediates involved in CO oxidation reaction on Au_{16}, $Rh@Au_{16}$ and $Rh@Au_{16}^-$ clusters. All the binding energies are calculated with respect to the corresponding gaseous free molecule except for OCOO with respect to $CO+O_2$ in the gas phase.

Cluster	CO	O	O_2	OCOO
Au_{16}	-0.70	-0.81	-0.14	-1.07
$Rh@Au_{16}$	-0.86	-0.46	-0.27	-1.03
$Rh@Au_{16}^-$	-0.85	-0.39	-0.34	-1.34

Table S3. Calculated elementary reaction barriers (E_f and E_b, in eV) and the distance (d^{TS}, in Å) between the two reacting fragments at the transition state involved in CO oxidation reaction on Au_{16}, $Rh@Au_{16}$ and $Rh@Au_{16}^-$ clusters. E_f and E_b are the forward and backward barriers, respectively.

Cluster	$CO + O_2 \rightarrow OCOO$			$OCOO \rightarrow CO_2 + O$			$CO + O \rightarrow CO_2$		
	E_f	E_b	d^{TS}	E_f	E_b	d^{TS}	E_f	E_b	d^{TS}
Au_{16}	0.45	0.68	1.85	0.39	3.27	1.85	0.61	2.24	2.82
$Rh@Au_{16}$	0.34	0.25	1.72	0.19	2.76	1.71	0.45	2.28	2.21
$Rh@Au_{16}^-$	0.17	0.32	1.99	0.37	2.56	1.78	0.33	2.23	2.26