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A collaborative diffusion mechanism of multiple atoms during Cu-Ag bimetal surface reconstruction

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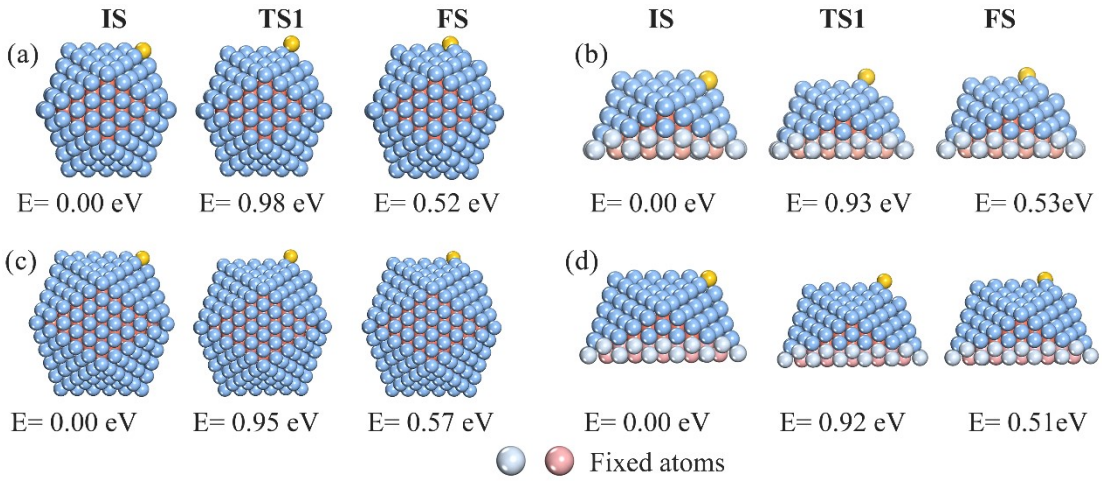

Fig. S1 The configuration and relative energy of direct outward diffusion of vertex atom. (a-b) $Cu_{147}@Ag_{162}$. (c-d) $Cu_{309}@Ag_{252}$.

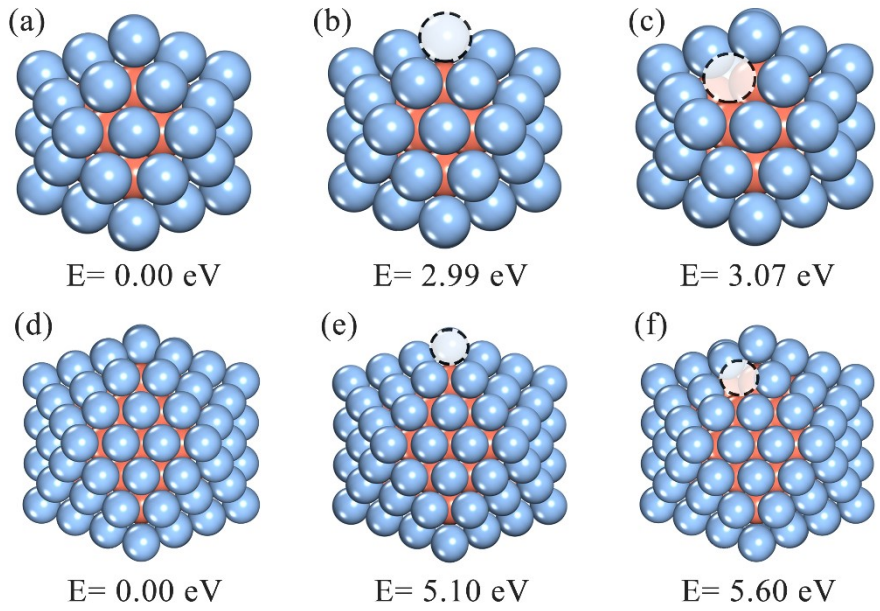

Fig. S2 The energy of (a) $Cu_{13}@Ag_{42}$, and $Cu_{13}@Ag_{41}$ with vacancy in (b) vertex site and (c) edge site. The energy of (d) $Cu_{55}@Ag_{92}$, and $Cu_{55}@Ag_{91}$ with vacancy in (e) vertex site and (f) edge site.

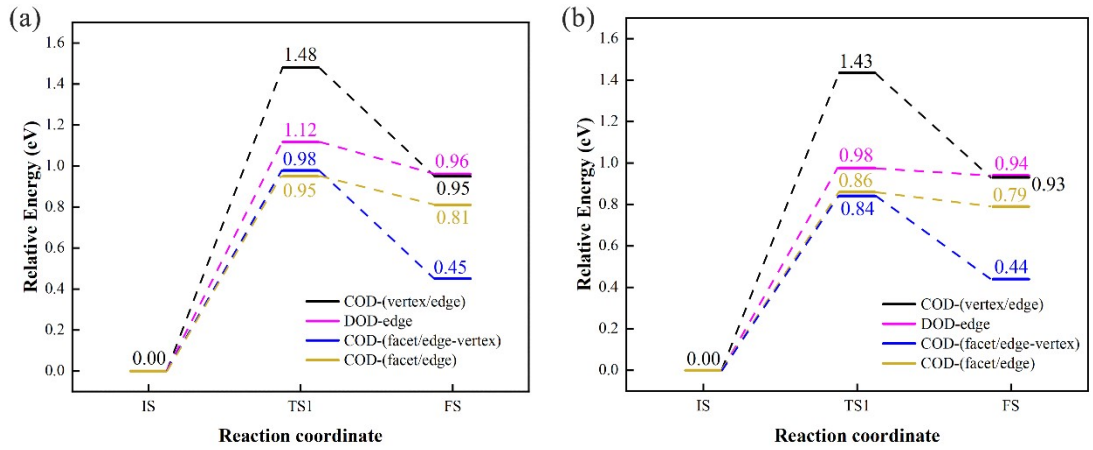

Fig. S3 Relative energy of surface diffusion of (a) $Cu_{147}@Ag_{162}$ and (b) $Cu_{309}@Ag_{252}$, direct outer diffusion (DOD) and collaborative outer diffusion (COD).

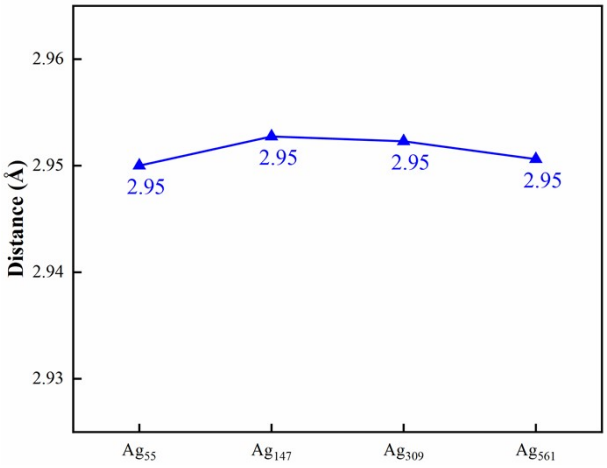

Fig. S4 The average surface Ag-Ag bond lengths for pure Ag NPs.

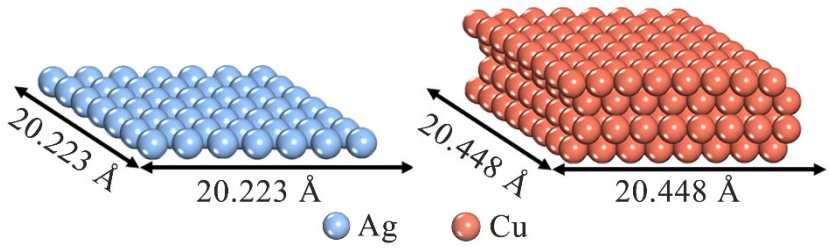

Fig. S5 Lattice parameter of Ag(111) and Cu(111) surface.

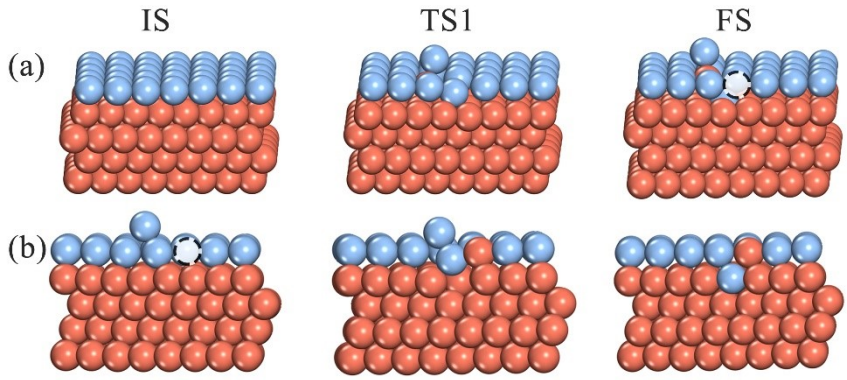

Fig. S6 (a) Directly inward diffusion process of surface Ag atom (DID-edge). (b) Collaborative inward diffusion process of surface Ag atom (CID-edge).

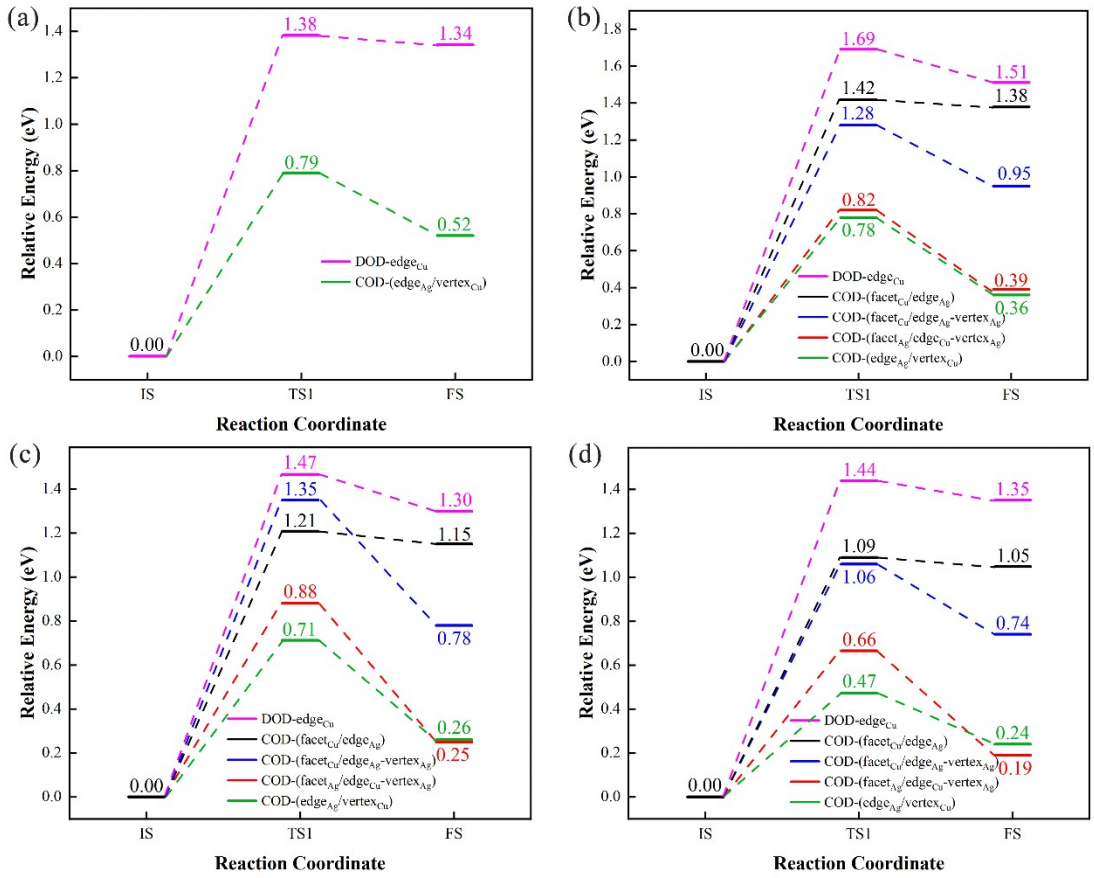

Fig. S7 Relative energy of outward diffusion of $Cu@AgCu_1$ NPs. (a) $Cu_{13}@Ag_{41}Cu_1$. (b) $Cu_{55}@Ag_{91}Cu_1$. (c) $Cu_{147}@Ag_{161}Cu_1$. (d) $Cu_{309}@Ag_{251}Cu_1$.

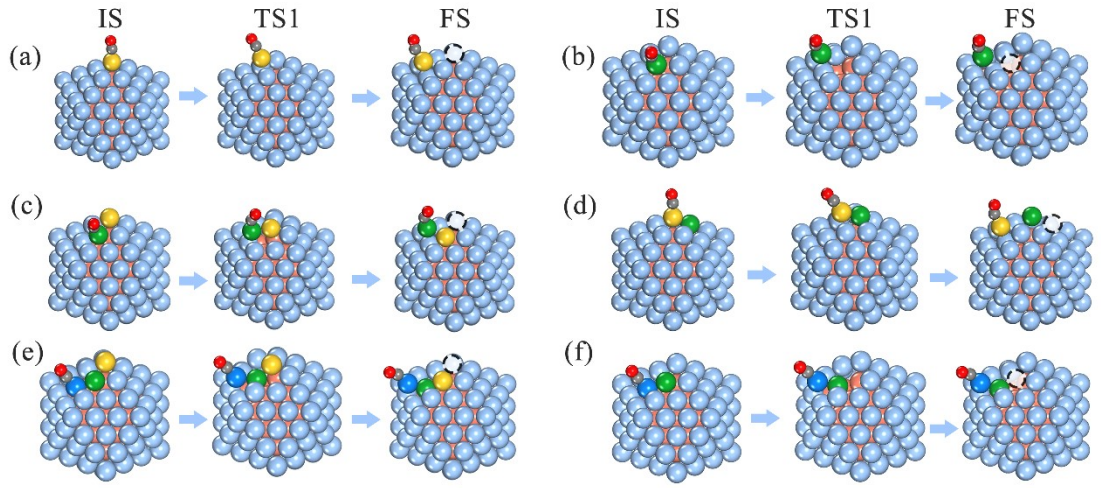

Fig. S8 Diffusion paths of $Cu_{55}@Ag_{92}(CO)_1$. (a) Directly outward diffusion of vertex atom, abbreviated as DOD-vertex$_{(Ag\text{-}CO)}$. (b) Directly outward diffusion of edge atom, abbreviated as DOD-edge$_{(Ag\text{-}CO)}$. (c) Outward diffusion of edge atom with collaborative diffusion of vertex atom, abbreviated as COD-(edge$_{(Ag\text{-}CO)}$/vertex). (d) Outward diffusion of vertex atom with collaborative diffusion of edge atom, abbreviated as COD-(vertex$_{(Ag\text{-}CO)}$/edge). (e) Outward diffusion of facet atom with collaborative diffusion of edge and vertex atom, abbreviated as COD-(facet$_{(Ag\text{-}CO)}$/edge-vertex). (f) Outward diffusion of facet atom with collaborative diffusion of edge atom, abbreviated as COD-(facet$_{(Ag\text{-}CO)}$/edge).

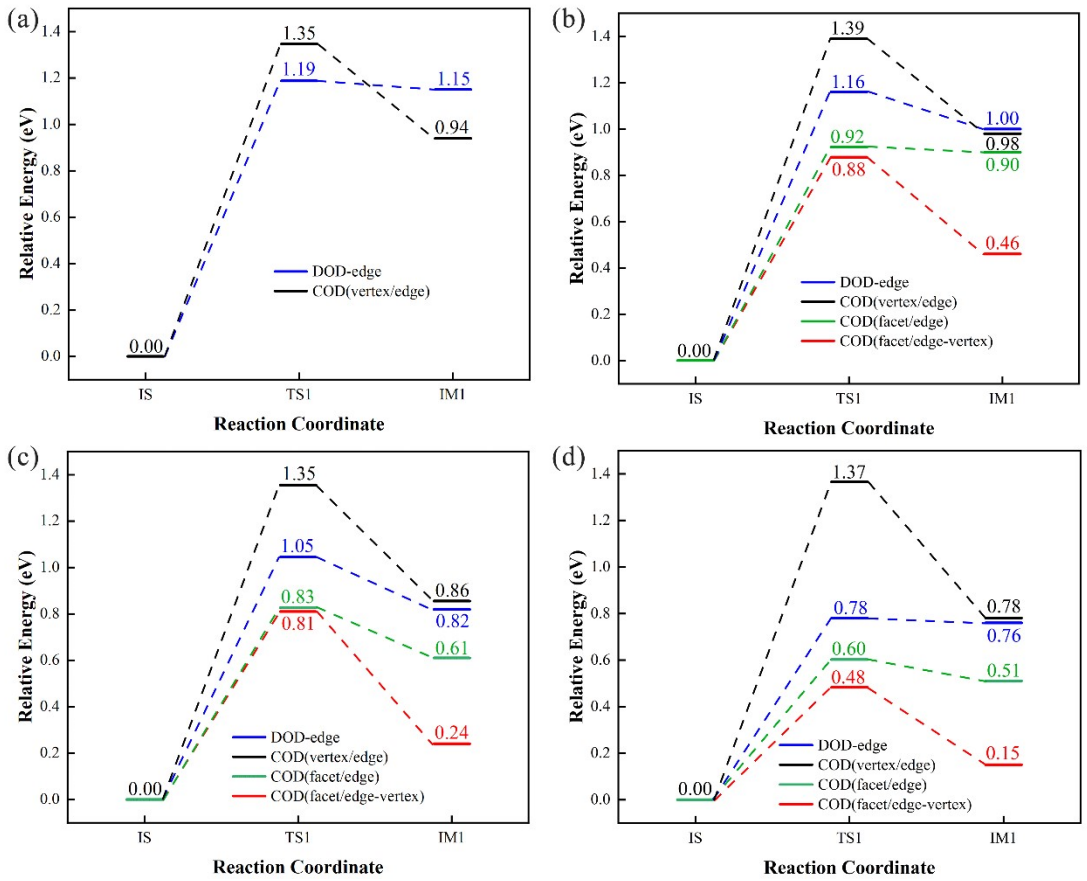

Fig. S9 Relative energy of outward diffusion in Cu@Ag NPs after one CO adsorbed. (a) $Cu_{13}@Ag_{42}(CO)_1$. (b) $Cu_{55}@Ag_{92}(CO)_1$. (c) $Cu_{147}@Ag_{162}(CO)_1$. (d) $Cu_{309}@Ag_{252}(CO)_1$.

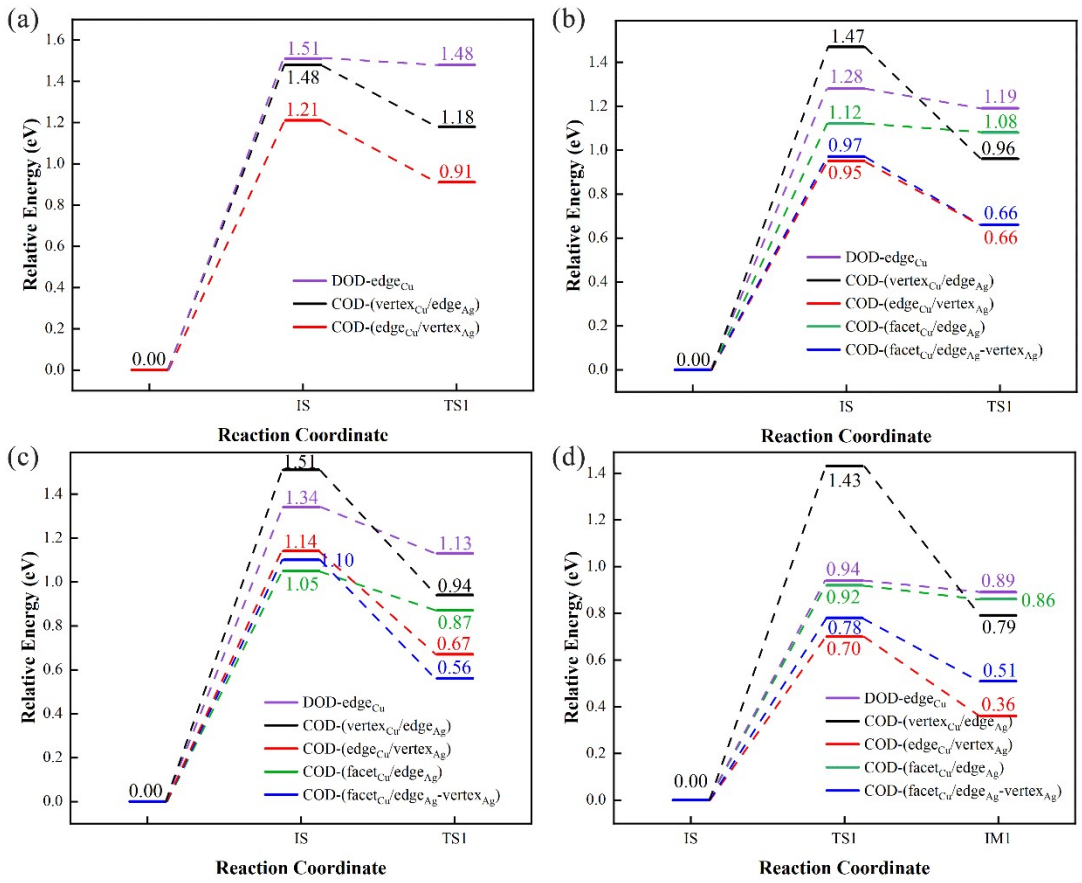

Fig. S10 Relative energy of outer diffusion in $Cu@AgCu_1$ NPs with one CO adsorbed. (a) $Cu_{13}@Ag_{41}Cu_1(CO)_1$. (b) $Cu_{55}@Ag_{91}Cu_1(CO)_1$. (c) $Cu_{147}@Ag_{161}Cu_1(CO)_1$. (d) $Cu_{309}@Ag_{251}Cu_1(CO)_1$.

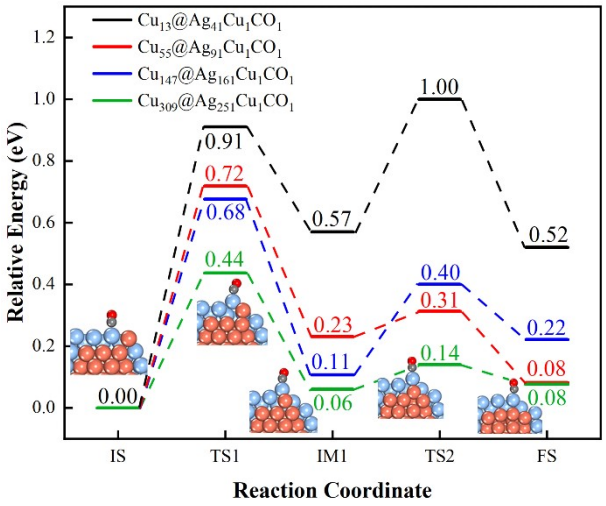

Fig. S11 Relative energy of outer diffusion of edge Ag atom with collaborative of vertex Cu atom (COD-edge$_{(Ag\text{-}CO)}$/vertex$_{Cu}$).

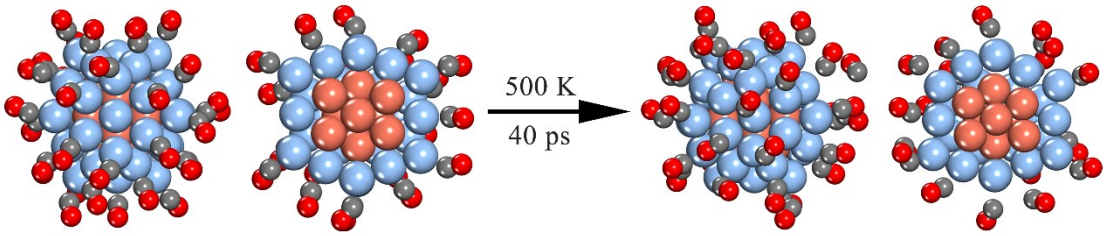

Fig. S12 Snapshots of icosahedral $Cu_{13}@Ag_{42}(CO)_{36}$ during AIMD simulation at 500 K.

Table S1 The adsorption energies of CO (in eV) in Cu@Ag NPs

	vertex	edge	facet
$Cu_{13}@Ag_{42}$_Ico	-1.27	-1.33	
$Cu_{55}@Ag_{92}$_Ico	-1.63	-1.57	-1.53
$Cu_{147}@Ag_{162}$_Ico	-1.10	-1.05	-0.98
$Cu_{309}@Ag_{252}$_Ico	-1.02	-0.92	-0.88

Table S2 The segregation energies (in eV) in Cu@Ag NPs

	Without CO[a]			One CO[b]		
	vertex	edge	facet	vertex	edge	facet
$Cu_{13}@Ag_{42}$_Ico	0.25	0.25		-0.25	-0.26	
$Cu_{55}@Ag_{92}$_Ico	0.13	0.01	0.01	-0.29	-0.43	-0.47
$Cu_{147}@Ag_{162}$_Ico	0.17	0.09	0.01	-0.34	-0.52	-0.53
$Cu_{309}@Ag_{252}$_Ico	0.14	0.04	-0.01	-0.37	-0.44	-0.59

[a]Segregation energies with one Cu atom segregating to surface. [b]Segregation energies with one Cu atom segregating to surface with one CO adsorbed.