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Nanostructuring Determines Poisoning: Tailoring CO Adsorption on PtCu Bimetallic Nanoparticles

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Fig. S1 Different studied CO adsorption sites exemplified on the Pt_{201} nanoparticle.

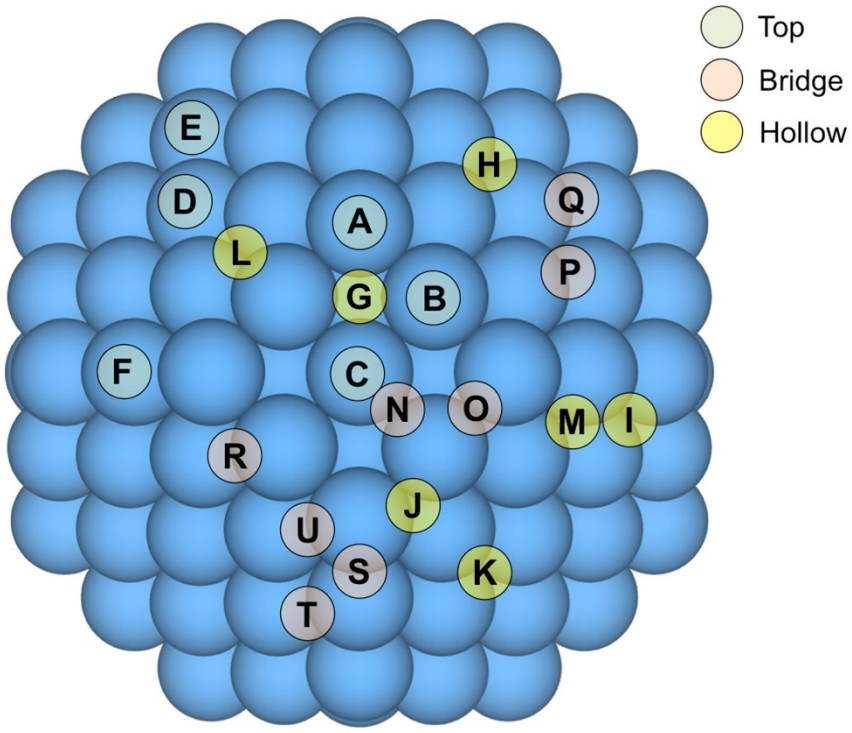

Table S1 Calculated adsorption energies, E_{ads}, given in eV, of CO molecule adsorbed through its O atom in various top positions of the nanoparticulate models **1**, **2**, **3**, and **5**. The adsorption sites and models are specified in Figs. S1 and Figure 2 of the main text. In model **5**, the O-end CO adsorption is explored on the exposed Cu atom.

Model / Site	A	B	C	D	F
1	~0	~0	~0	~0	~0
2	-0.01	-0.01	-0.01	~0	-0.01
3	-0.05	-0.05	-0.05	-0.04	-0.05
5	-0.03	-0.02	-0.01	-0.01	-0.02

Table S2 Adsorption energies, E_{ads}, in eV, for CO adsorbed in different bridge positions, see Fig. S1, of different models, see Fig. 2 in the main text.

Model / Site	N	O	P	Q	R	S	T	U
1	-1.97	-2.07	-1.94	-1.86	-1.73	-1.97	-1.75	-1.76
2	-0.77	→A	-0.60	→D	→I	→A	→I	→R
3	-1.67	-1.94	-1.15	-1.09	-1.22	-1.82	-1.40	-1.41
5	→P[b]	→B[a]	→E[a]	→E[a]	→U[b]	→A[a]	→A[a]	→R

[a] on Pt atom
[b] bridge between two Pt

Table S3 Adsorption energies, E_{ads}, in eV, for CO adsorbed in different hollow positions, see Fig. S1, of different models, see Fig. 2 in the main text.

Model / Site	G	H	I	J	K	L	M
1	-1.54	-1.78	→P	→P	-1.89	→T	→P
2	-0.80	-0.83	-0.69	-0.73	-0.68	→B	-0.67
3	-1.50	→S	→P	-1.23	-1.25	→O	-1.31
5	-1.64	→P[b]	→S[b]	→R[b]	→P[b]	→O[b]	→T[b]

[a] on Pt atom
[b] bridge between two Pt

S1 Electronic effects

The discussed seemingly counterintuitive CO adsorption strengthening can be understood using charge density difference (CDD) plots, see Fig. 5 of the main text, evaluating the donation/back-donation bonding mechanism, plus the corresponding Bader charge[1] data, see Tables S4 and S5. According to the Bader charges, the Pt corner atom completely surrounded at the surface by Cu atoms and having all subsurface Pt neighbours is negatively charged by -0.43 *e* due a charge transfer from its surface Cu neighbours, which contrasts with a significantly smaller negative charge of -0.11 *e* of the corner Pt atom in the Pt_{201} NP. Such accentuated negatively charged site favours attraction to it of the $C^{\delta+}$ CO atom. Figure 5 of the main text clearly shows a donation/back-donation mechanism on all Pt adsorption sites, and so, this excess charge is back-donated from Pt 5*d* states to the $2\pi^*$ CO orbital, contributing to a stronger binding. Finally, despite this charge transfer, the remaining charge of the corner Pt atom is still -0.13 *e*, serving as a Coulombic anchor to the $C^{\delta+}$ atom of the adsorbed CO molecule.

In the Pt_3 vacancy, CO bridges two rearranged surface Pt atoms, each with a negative charge of -0.15 *e*, different from a slightly positive charge of 0.07 *e* found in the Pt_3 vacancy in Pt_{201}. The conjunction of under-coordination and accumulation of electron charge is thus again the main origin of a stronger back-donation, resulting as well in a larger magnitude of the adsorption energy. Finally, the most undercoordinated Pt adatom on a (111) facet bears larger positive charge on the Pt_{201} NP, 0.26 *e*, than on the Cu@Pt NP, 0.18 *e*, thus weakening the CO adsorption in the former case.

Table S4 Bader charges, Q, in *e*, on metal atoms of **A** sites, see Fig. S1, of different models, see Fig. 2 of the main text, prior or after to CO adsorption, as well as on the adsorbed CO molecule. Surface (Sur) and subsurface (Sub) types of atoms are indicated. A distinction is made for surface, Q_{Sur}, and subsurface, Q_{Sub}, charges. CO adsorption energies E_{ads} (in eV) are also listed for convenience.

				Prior		After		
Model	E_{ads}	M_{Sur}	M_{Sub}	Q_{Sur}	Q_{Sub}	Q_{Sur}	Q_{Sub}	Q_{CO}
1	-2.08	Pt	Pt	-0.10	0.11	0.16	0.04	-0.16
2	-0.98	Cu	Cu	-0.06	0.06	0.20	0.02	-0.17
3	-1.67	Pt	Cu	-0.14	0.30	0.14	0.28	-0.16
5	-0.95	Cu	Cu	0.29	0.29	0.47	0.28	-0.13
6	-1.87	Pt	Cu	-0.54	0.21	-0.22	0.15	-0.18
7	-2.24	Pt	Pt	-0.44	-0.43	-0.13	-0.49	-0.19
8	-2.07	Pt	Cu	-0.09	0.29	0.18	-0.31	-0.17

Table S5. Bader charges, Q, in *e*, on Pt adatoms or Pt_3 vacancy sites of Pt_{201} (**model 1**) and $Cu_{79}@Pt_{119}$ (**model 3**) NPs prior and after CO adsorption, as well as on the CO molecule. Surface (Sur) and subsurface (Sub) types of atoms are indicated. A distinction is made for surface, Q_{Sur}, and subsurface, Q_{Sub}, charges. CO adsorption energies E_{ads} (in eV) are also listed for convenience.

Model	E_{ads}	M_{Sur}	M_{Sub}	Q_{Sur}	Q_{Sub}	Q_{Sur}	Q_{Sub}	Q_{CO}
1: Pt_3 vacancy	-1.20	Pt	Pt	0.07	-0.06	0.20	-0.05	-0.34
1: Pt adatom	-2.25	Pt	Pt	-0.01	-0.02	0.26	~0	-0.19
3: Pt_3 vacancy	-2.43	Pt	Cu	-0.15	0.22	0.06	0.12	-0.26
3: Pt adatom	-2.53	Pt	Pt	-0.02	-0.10	0.18	-0.14	-0.21

References

1 Bader, R. F. W. *Atoms in Molecules: a Quantum Theory*, Oxford University Press New York, 1990.