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Electronic Supplementary Information

Silver Residues As a Possible Key to Remarkable Oxidative Catalytic Activity of Nanoporous Gold

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The supplementary information includes

Tables with energetic and structural data of all studied adsorption complexes (Tables S1-S6)

Analysis of electronic structure in representative co-adsorbed systems

Cartesian coordinates of clean slab models and selected adsorption configurations as well as transition states (Tables S7, S8)

TABLE S1. Adsorption energies of CO on perfect and defective Au(332) and Au(321) surfaces

Model	Au coordination number	E_{ad}, eV
(1 × 3) Au(332) [a]	7	-0.65
(1 × 3) Au(332) with vacancies [a]	6	-0.75
(1 × 3) Au(332) with vacancies [a]	5	-0.88
(2 × 1) Au(321) [b]	6 and 8[c]	-0.45 to -0.62[d]
(2 × 1) Au(321) [b]	9	-0.16
(2 × 1) Au(321) [b]	6	-0.80
(2 × 1) Au(321) with vacancies [b]	5	-0.88
(2 × 1) Au(321) with displaced atoms [b]	5	-0.88

[a] Ref. 25. [b] This work. Models are shown in Fig. 2. [c] μ-CO. [d] Variation in E_{ad} due to the presence or absence of co-adsorbed end-on or μ-CO in the same unit cell.

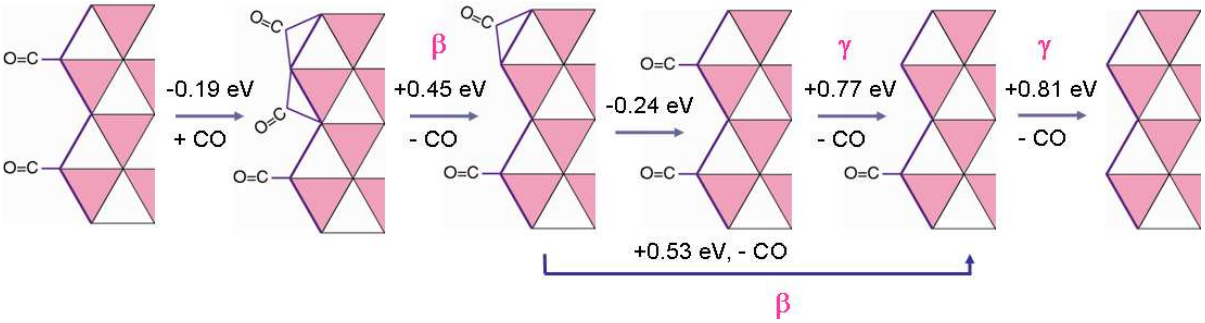

Figure S1. Schematic representation of the sequential CO desorption from the Au(321) surface saturated with CO (i.e. some of the CO adsorbed as μ-CO). This model offers an interpretation for two desorption peaks above 100 K (β and γ) observed in Ref. 27.

TABLE S2. Energetics[a] (eV) of O_2 dissociation on Au(321) surfaces with Ag impurities

Atomic positions replaced by Ag [b]	$E_{ad}(O_2)$ [c]	E_a [d]	ΔE [e]
none	-0.14	1.10	0.23
1′, 2	-0.31	1.20	0.19
1, 1′, 2	-0.34	1.29	0.13
1′, 2, 3	-0.32	1.08	0.05
1, 1′, 2, 5	-0.36	1.05	-0.05
1′, 2, 4, 5	-0.33	0.92	-0.14
1, 1′, 2, 3, 4, 5	-0.39	0.85	-0.34
1, 1′, 2, 2′, 3, 3′	-0.42	1.03	-0.05
1, 1′, 2, 2′, 3, 3′, 4, 5	-0.45	0.68	-0.37

[a]Calculated using (1 × 2) unit cell. [b] Numbering of surface atoms is defined in Fig. 1. [c]Adsorption energy of O_2 is calculated according to Eq. 2. [d]Activation energy: $E_a = E_{TS} - E_{\text{substrate-O}_2}$. [e]Change of energy: $\Delta E = E_{\text{substrate-O···O}} - E_{\text{substrate-O}_2}$.

TABLE S3. Adsorption energies (eV) and adsorption geometries (distances in pm) for atomic oxygen adsorbed on the Au(111) surface with and without Ag impurities

Model						
No. of Au atoms substituted by Ag[a]		Adsorption site of O	$E_{ad}(O)$[b]		*d*(O-Au)	*d*(O-Ag)
(2 × 2)	(3 × 3)		(2 × 2)	(3 × 3)	(2 × 2)	(2 × 2)
0 [0]	0 [0]	hcp	0.38		214 × 3	
0 [0]	0 [0]	fcc	0.14	0.07	213 × 3	
1 [25]	1 [11]	hcp	0.26		211 × 2	225
1 [25]	1 [11]	fcc	0.02	0.00	210 × 2	221
3 [75]	3 [33]	hcp	0.09			216 × 3
3 [75]	3 [33]	fcc	-0.11	-0.09		214 × 3
4 [100]		hcp	-0.21			216 × 3
4 [100]		fcc	-0.37			214 × 3

[a]One to four atoms in the topmost layer of a (2 × 2) or (3 × 3) unit cell were substituted by Ag. The substitution begins at that hollow site where O adsorbate resides, see also Fig. 7. Values in brackets are the corresponding surface concentrations of Ag in atom %. [b]Adsorption energies are calculated with respect to gaseous O_2 and the separated substrate according to Eq. 1.

TABLE S4. Adsorption energies (eV) and adsorption geometries (distances in pm) for CO adsorbed on the substituted Au(111) surface with preadsorbed atomic oxygen

Model			E_{ad}(CO)[b]		d(C-Au)	d(C-O)	d(O-Au)	d(O-Ag)
No. of Au atoms substituted by Ag[a]		Adsorption site of O						
(2 × 2)	(3 × 3)		(2 × 2)	(3 × 3)	(2 × 2)	(2 × 2)	(2 × 2)	(2 × 2)
0 [0]	0 [0]	hcp	-0.43		204	115	217 × 3	
0 [0]	0 [0]	fcc	-0.44	-0.37	204	115	215 × 2, 214	
1 [25]	1 [11]	hcp	-0.50		203	115	214 × 2	228
1 [25]	1 [11]	fcc	-0.49	-0.37	204	115	212 × 2	222
3 [75]	3 [33]	hcp	-0.66		202	115		218 × 3
3 [75]	3 [33]	fcc	-0.62	-0.41	203	115		216 × 3

[a]One or three atoms in the topmost layer of a (2 × 2) or (3 × 3) unit cell were substituted by Ag at that hollow site where O adsorbate resides. Values in brackets are the corresponding surface concentrations of Ag in atom %. [b]Adsorption energies are calculated with respect to free CO and the separated substrate with preadsorbed oxygen according to Eq. 3.

TABLE S5. Adsorption energies and adsorption geometries for atomic oxygen adsorbed on the Au(321) surface with Ag impurities

N(Ag)[a]	Adsorption site of O[a]	E_{ad}(O), eV[b]	Distances, pm	
			O-Au	O-Ag
None	h1 (II, hcp)	0.40[c] [0.42][c]	210, 210, 247	
None	h2/h4 (I, fcc)	-0.15[c] [-0.16][c]	214, 215, 218	
None	h3/h7 (II, fcc)	0.18[c] [0.14][c]	215, 215, 223	
None	h9/h10 (I, hcp)	0.04[c] [0.04][c]	211, 215, 222	
None	h5 (I, fcc)	0.07[c] [0.11][c]	209, 215, 233	
None	$b_{2\text{-}1'}$/ $b_{2'\text{-}1}$	0.07[c]	204, 205	
None	fh1/fh2 (I)	unstable		
2	h1 (II, hcp)	0.19	210, 216	223
2	h2 (I, fcc)	-0.22	210, 214	221
2	h7 (II, fcc)	0.06	212, 216	220
2	h5 (I, fcc)	-0.03	209, 223	221
2	h6 (III, fcc)	0.28	210, 218, 227	
2	h9 (I, hcp)	-0.13	209, 215	223
2	fh1 (I)	0.04	207, 223, 306	240
2	$b_{1\text{-}2}$	0.19	199	213
2	$b_{2\text{-}1'}$	0.08	199	212
2, 3′, 4 (h7)	h1 (II, hcp)	-0.23	208	219, 221
2, 3′, 4 (h7)	h2 (I, fcc)	-0.33	214, 212	220
2, 3′, 4 (h7)	h4 (I, fcc)	-0.20	211, 212	224
2, 3′, 4 (h7)	h7 (II, fcc)	-0.30		215, 216, 218
2, 3′, 4 (h7)	h9 (I, hcp)	-0.37	207	217, 222
2, 3, 4 (h1)	h1 (II, hcp)	0.00		215, 215, 218
2, 3, 4 (h1)	h2 (I, fcc)	-0.41	208	217, 220
2, 3, 4 (h1)	h3 (II, fcc)	0.04	211, 217	222
2, 3, 4 (h1)	h4 (I, fcc)	-0.09	215, 216, 217	
2, 3, 4 (h1)	h5 (I, fcc)	-0.15	210, 221	224
2, 3, 4 (h1)	h6 (III, fcc)	0.09	221	219, 222
2, 3, 4 (h1)	h7 (II, fcc)	-0.15	211	217, 221
2, 3, 4 (h1)	h9 (I, hcp)	-0.19	210, 214	222
2, 3, 4 (h1)	h10 (I, hcp)	-0.27	208, 212	232
2, 3, 4 (h1)	fh1 (I)	-0.11	204, 214, 218	218, 222
3, 4′, 5 (h8)	h2 (I, fcc)	-0.15	210, 213	226
3, 4′, 5 (h8)	h3 (II, fcc)	-0.13	210	219, 221
3, 4′, 5 (h8)	h6 (III, fcc)	0.15	213	226, 216
3, 4′, 5 (h8)	h8 (III, hcp)	-0.18	210	220, 232, 239
3, 4′, 5 (h8)	h10 (I, hcp)	-0.13	209, 212	230
3, 4′, 5 (h8)	fh2 (I)	-0.05	206, 219, 310	247

[a]N(Ag) stands for atomic positions replaced by Ag. Numbering of surface atoms and notations for O adsorption sites are defined in Figs. 1 and 11. [b]Adsorption energies are calculated with respect to gaseous O_2 and the separated substrate according to Eq. 1. [c]Calculated using a (1×1) unit cell. Values in brackets are from Ref. 42.

TABLE S6. Adsorption energies and adsorption geometries for CO adsorbed on the Au(321) surface with Ag impurities and co-adsorbed atomic oxygen

N(Ag)[a]	Adsorption site of O[a]	Adsorption site of CO	E_{ad}(CO), eV [b]	Distances, pm			
				C-Au	C-O	O-Au	O-Ag
Pure Au	none	1	-0.81 (-0.80 [c])	198	115		
Pure Au	h1 (II, hcp)	1/1′	-0.89 [c]	198	115	207, 210, 271	
Pure Au	h2/h4 (I, fcc)	1/1′	-0.97 [c]	189	115	197, 219, 224	
Pure Au	h3/h7 (II, fcc)	1/1′	-0.88 [c]	197	115	215, 215, 224	
Pure Au	h9/h10 (I, hcp)	1/1′	-1.03 [c]	189	115	197, 221, 227	
Pure Au	h5 (I, fcc)	1	-1.05 [c]	190	115	198, 216, 231	
Pure Au	fh1/fh2 (I)	1/1′	-1.10 [c,d]				
2	h1 (II, hcp)	1	-0.85 (-0.91 [c])	198	115	211, 217	222
2	h2 (I, fcc)	1	-1.01 (-0.95 [c])	189	115	197, 217	222
2′	h3 (II, fcc)	1	-0.88 (-0.90 [c])	198	115	212, 218	220
2′	h4 (I, fcc)	1	-0.81	197	115	210, 215	221
2	h5 (I, fcc)	1	-0.90				
2′	h10 (I, hcp)	1	-1.02	189	115	196, 222	225
2	fh1 (I)	1′	-0.89	190	116	196, 241, 296, 318	229
2	$b_{1\text{-}2}$	1′	-0.85	198	115	199	214
2, 3, 4 (h1)	h1 (II, hcp)	1	-0.87 (-0.89 [c])	198	115		214, 215, 219
2, 3, 4 (h1)	h2 (I, fcc)	1	-1.01 (-1.12 [c])	189	115	195	220, 221
2, 3, 4 (h1)	h2 (I, fcc)	1′	-0.80	198	115	203	217, 220
2, 3, 4 (h1)	h4 (I, fcc)	1	-0.81	198	115	216, 216, 218	
2, 3, 4 (h1)	h7 (II, fcc)	1′	-0.89	198	115	211	217, 222
2, 3, 4 (h1)	fh1 (I)	1′	-0.95	190	116	195, 309, 325	229, 232
2, 3, 4 (h1)	h2 (I, fcc) and h7 (II, fcc)	1′	-0.90	198	115	h2: 205 h7: 207	h2: 220, 224 h7: 220, 225

[a]N(Ag) stands for atomic positions replaced by Ag. Numbering of surface atoms and notations for O adsorption sites are defined in Figs. 1 and 11. [b]Adsorption energies are calculated with respect to free CO and the separated substrate with preadsorbed oxygen according to Eq. 3. [c]Calculated using a (1 × 1) unit cell. [d]Calculated with respect to O adsorbed at $b_{2\text{-}1'}$/ $b_{2'\text{-}1}$ because O adsorption at fh1/fh2 was found unstable.

Electronic structure. To elucidate the nature of binding in co-adsorbed systems described in the main text we examine the changes in the local density of states (LDOS) when O adsorbs near to CO at two representative sites of group I and group II. The LDOS were obtained for the adsorption complexes modeled using (1 × 1) surface unit cell.

Panel **a** of Fig. S2 shows the LDOS for a CO molecule adsorbed at a kink site of Au(321) without co-adsorbed oxygen. The bonding of CO to transition metal surfaces is dominated by an interaction of the 5σ HOMO and 2π* LUMO of CO with the metal d valence states.[1] The two sharp peaks on the left hand side are the 5σ and 1π orbitals of CO. The 5σ orbital is pushed down to low energies through interaction with the metal states and emerges on the left of 1π. The broad feature above the Fermi level, ε_F, originates from the interaction of the filled Au d levels with the unoccupied 2π*-orbitals of CO. Shifting some of the Au d density above the Fermi level results in a partial charge transfer from Au to CO. Concomitantly, the Au d band notably sharpens due to interaction with CO and shifts to low energies manifesting a rather strong coupling between the electronic states of the substrate and adsorbate consistent with a considerable adsorption energy of -0.80 eV.

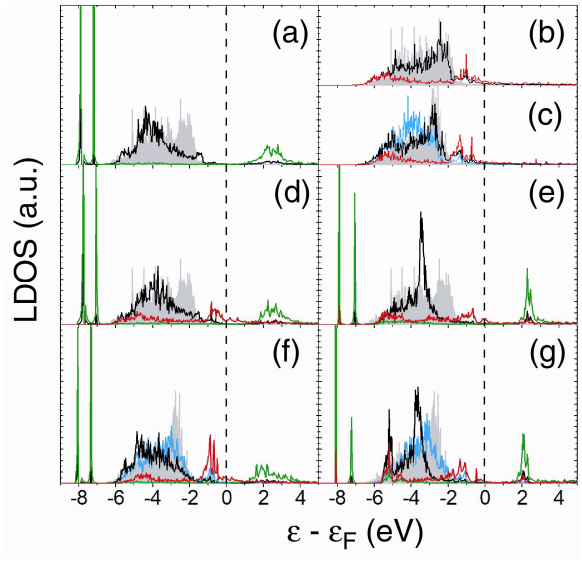

Figure S2. LDOS for Au(321) interacting with the adsorbates (a) CO, (b) O at h1, (d) CO and O at h3, (e) CO and O at h2. (c), (f) and (g) are analogous to (b), (d) and (e), respectively, but Ag replaces atoms in positions 2, 3, 4. Black, blue, green, and red lines represent the d states of Au (at position 1), d states of Ag (at position 2), sp states of CO, and sp states of O, respectively. Gray filled area shows the d states of Au (at position 1) for the corresponding surfaces without adsorbates.

Panel **b** shows the LDOS of an O atom adsorbed at the h2 site (group I) of Au(321). This is a representative example whereas the LDOS for other adsorption sites of O look quite similar. It is seen that the interaction of O sp states with the Au d states results in a bonding and antibonding combinations, corresponding to the two regions of high O derived LDOS on both sides of the Au d band. The

[1] Hammer, B.; Morikawa, Y.; Nørskov, J. K. *Phys. Rev. Lett.* **1996**, *76*, 2141.

antibonding states are largely occupied, which is reflected in only weak bonding between Au and O. For comparison, panel **c** contains the LDOS of an analogous adsorption complex on a silver contaminated surface, where three surface atoms at site h3 (and consequently at all the sites of group II due to translational symmetry) are replaced by Ag, corresponding to surface Ag content of 60%. Note that a replacement of less than three metal atoms in the unit cell by Ag did not produce notable changes in the LDOS plots. In panel **c** one can see some sharpening of the Au-O bonding and antibonding bands and a slight shift of the bonding states to lower energy reflected in a higher binding energy of oxygen on a surface with Ag patches, Table S5.

The LDOS of co-adsorbed CO at a kink site and O at a neighboring h3 site (group II) are shown in panel **d**. The overall picture is very similar to that for CO alone shown in panel **a**. The LDOS of the co-adsorbed O atom is similar to that given in panel **b**; although the antibonding Au–O states extend a bit more above the Fermi level. This change correlates with a slight increase in the adsorption strength of CO, by 0.08 eV, due to co-adsorption with O in this configuration as described in the previous section. Mind that no significant buildup of the Au d LDOS can be seen at the region of high O LDOS right above the Fermi level because the O atom adsorbed at an h3 site is not bound to the kink Au atom, whose LDOS is depicted.

In contrast, the co-adsorbed structure, where O is located in immediate vicinity of CO at an h2 site (group I) is characterized by the density of states, panel **e**, which is not just a superposition of those obtained for individually adsorbed CO and O. Particularly notable is the sharpening of the Au d band and of the $2\pi^*$ derived states of CO and Au, which is indicative of a more efficient orbital overlap as compared to individually adsorbed CO. A more efficient spatial orbital coupling is made possible through rather large displacements of the Au atoms along the step edge as pointed to above. Particularly notable is the coupling between the orbitals of co-adsorbed O with the 5σ and $2\pi^*$ CO derived states mediated by Au. Consequently, the adsorption energy of CO in this configuration increases in magnitude by 0.17 eV with respect to the case of individually adsorbed CO.

Panels **f** and **g** illustrate the changes in LDOS induced by a substitution of three surface atoms at site h3 with Ag. Panel **f** shows the LDOS for the co-adsorbed CO at a kink and O at h3 and panel **g** corresponds to the co-adsorption of O at h2 (analogous to the pure Au surface complexes whose LDOS are shown in panels **d** and **e**, respectively). Both plots look quite similar to those of their parent systems with no Ag

admixtures. The main difference is the notable sharpening of the O-Au and O-Ag bonding and antibonding states seen in both panels **e** and **f**. However, this difference is reflected mainly in the increased O adsorption energy but not that of CO. In the case of cooperative adsorption (**f**) also the binding energy of CO increases slightly, by 0.15 eV (Table S6), due to favorable coupling with O–Ag and O–Au states.

Table S7. Cartesian coordinates (in Å) of the atoms in the optimized clean Au(321) slabs. The uppermost seven atoms were allowed to relax, the remaining seven were kept fixed at the theoretical bulk-terminated geometry

(1x1) surface unit cell				**(2x1) surface unit cell**			
cell vectors:				**cell vectors:**			
5.110295633, 6.597363294, 15.612211042				10.220591266, 6.597363294, 15.612211042			
Element	X	Y	Z	X	Y	Z	X
Au	0	0	0	Au	0	0	0
Au	4.25856069	5.00787961	0.55757895	Au	5.11029563	0	0
Au	1.70341804	3.64209424	1.11515791	Au	4.25856069	5.00787961	0.55757895
Au	4.25857104	2.27630893	1.67273686	Au	9.36885632	5.00787961	0.55757895
Au	1.70342844	0.91052354	2.2303159	Au	1.70341804	3.64209424	1.11515791
Au	5.96198913	5.91840316	2.78789486	Au	6.81371367	3.64209424	1.11515791
Au	3.40684648	4.55261778	3.34547381	Au	4.25857104	2.27630893	1.67273686
Au	0.85995098	3.18537991	3.88889092	Au	9.36886667	2.27630893	1.67273686
Au	3.40223455	1.76080273	4.383051	Au	1.70342844	0.91052354	2.2303159
Au	0.74453712	0.33499756	5.10172952	Au	6.81372407	0.91052354	2.2303159
Au	5.03811829	5.41577868	5.72369485	Au	5.96198913	5.91840317	2.78789485
Au	2.49860905	4.10775907	6.16798162	Au	11.0722848	5.91840317	2.78789485
Au	5.06402636	2.70856224	6.5996618	Au	3.40684648	4.55261778	3.34547381
Au	2.5136929	1.43988246	6.99954632	Au	8.51714211	4.55261778	3.34547381
				Au	0.86734068	3.18125722	3.88989376
				Au	5.97763631	3.18125722	3.88989376
				Au	3.41507529	1.76742102	4.37891446
				Au	8.52537092	1.76742102	4.37891446
				Au	0.75507199	0.34229772	5.09817464
				Au	5.86536763	0.34229772	5.09817464
				Au	5.04838733	5.42332429	5.69870325
				Au	10.158683	5.42332429	5.69870325
				Au	2.5074324	4.11584697	6.1689434
				Au	7.61772803	4.11584697	6.1689434
				Au	5.06994772	2.71915001	6.60491625
				Au	10.1802434	2.71915001	6.60491625
				Au	2.52393337	1.45733569	6.99512193
				Au	7.63422901	1.45733569	6.99512193

Table S8. Cartesian coordinates (Å) of selected configurations. Only the coordinates of those atoms whose positions were relaxed are listed

Transition structures for O_2 dissociation on pure and Ag-substituted Au(321) [a]

Pure Au(321)				Ag at positions 1′, 2 [b]			
Element	X	Y	Z	Element	X	Y	Z
Au	11.0583723	3.16085951	3.9074049	Au	11.0234518	3.15019674	3.95336986
Au	5.94525557	3.19176547	3.89174207	Au	5.94268258	3.1843801	3.8772146
Au	3.38230813	1.76775263	4.42991265	Au	3.36200164	1.74618386	4.43256388
Au	8.48174412	1.78810903	4.40793186	Au	8.47852445	1.79143364	4.44518151
Au	0.82980731	0.31755532	4.99721117	Au	0.79041771	0.36595034	5.01924324
Au	5.87273296	0.42178452	5.07945985	Au	5.89969353	0.38584845	5.0844123
Au	5.07008892	5.44650648	5.69404653	Au	5.07960234	5.44756153	5.70418875
Au	10.1390085	5.44937509	5.59125047	Au	10.1464216	5.41599115	5.66166393
Au	2.55487548	4.03514373	6.13590057	Au	2.54446881	4.11348598	6.10000104
Au	7.54854049	4.17805123	6.1500801	Au	7.56739119	4.08577414	6.12239748
Au	5.0763432	2.75581466	6.68056268	Au	5.03348018	2.69307617	6.59422717
Au	2.68314537	1.40733575	7.16829963	Au	2.54869782	1.47882776	7.13731168
Au	7.48985349	1.57274359	7.15436863	Ag	7.51534362	1.44890168	7.17355584
Au	10.0894088	2.95976152	6.63227085	Ag	10.1395031	2.88630463	6.79232177
O	0.41436913	0.95768157	7.19790493	O	0.77591534	1.29652628	8.16240546
O	9.01454043	0.16590259	7.48436397	O	9.55252351	0.51081536	7.11586674

Ag at positions 1, 1′, 2 [b]				Ag at positions 1′, 2, 3 [b]			
Element	X	Y	Z	Element	X	Y	Z
Au	11.0317312	3.1449491	3.95892892	Au	11.0587469	3.17461099	3.9631752
Au	5.94552543	3.16892174	3.86365503	Au	5.94564751	3.18592216	3.87500991
Au	3.34387938	1.74773935	4.46571594	Au	3.3698503	1.78195503	4.44133328
Au	8.48386053	1.79601166	4.43359598	Au	8.49479909	1.80572961	4.42233232
Au	0.7953014	0.37399451	5.04788019	Au	0.80307612	0.39139303	5.00389664
Au	5.87745236	0.40021957	5.08728566	Au	5.90199716	0.39088901	5.07119757
Au	5.06994741	5.44952039	5.67475131	Au	5.08924434	5.44547382	5.66903134
Au	10.1393724	5.4027589	5.63079858	Au	10.1175892	5.38918795	5.61716513
Au	2.56427372	4.07928489	6.11278504	Au	7.56930165	4.07164436	6.13895894
Au	7.58509324	4.10192422	6.10900319	Au	5.08245055	2.68970544	6.59784521
Au	5.06678951	2.73471533	6.59214769	Au	2.61380429	1.49329727	7.13728806
Ag	2.56757723	1.42008523	7.20068811	Ag	2.54574615	4.1631332	6.19153199
Ag	7.51867351	1.46453646	7.15605557	Ag	7.61516034	1.38511618	7.13052345
Ag	10.1646397	2.90261985	6.81332359	Ag	10.1464265	2.87980885	6.79584233
O	0.660069	1.3685476	8.15357138	O	0.8166408	1.3019184	8.12985347
O	9.48196886	0.41827208	7.06210236	O	9.7235861	0.39205335	7.04456568

Table S8. Continued

Transition structures for O_2 dissociation on Ag-substituted Au(321) [a]

Ag at positions 1, 1′, 2, 5 [b]				Ag at positions 1, 1′, 4, 5 [b]			
Element	X	Y	Z	Element	X	Y	Z
Au	11.0423748	3.14179201	3.94331108	Au	11.0414977	3.16016004	3.93614498
Au	5.95174386	3.17025088	3.85754997	Au	5.94599185	3.17872592	3.87212194
Au	3.35516171	1.73262777	4.45716737	Au	3.38455042	1.72388485	4.42695718
Au	8.49175063	1.7954571	4.42617931	Au	8.49885024	1.78934404	4.43095892
Au	5.88884266	0.39104008	5.09280648	Au	5.93182812	0.35310544	5.08694645
Au	5.08086474	5.43101203	5.65054966	Au	5.11060552	5.40409474	5.68819966
Au	10.1458245	5.38016999	5.60628132	Au	7.61143062	4.04576986	6.10947623
Au	2.58221934	4.04390277	6.08730754	Au	5.08490398	2.64942427	6.59996138
Au	7.60356616	4.08412715	6.11447556	Au	2.59031905	4.04663154	6.06643704
Au	5.09668176	2.72723524	6.58939194	Au	2.63894053	1.41790682	7.15588718
Ag	0.79245591	0.3963921	5.10865611	Ag	0.81352256	0.37308113	5.06892365
Ag	2.65202946	1.39502139	7.21002592	Ag	10.1969193	5.39694473	5.63984883
Ag	7.54395827	1.4489912	7.15108722	Ag	7.56160011	1.40451738	7.16387201
Ag	10.195546	2.90163295	6.8141628	Ag	10.1920218	2.83375023	6.74124512
O	0.69998824	1.29129195	8.04687229	O	0.83393782	1.22533982	8.10948212
O	9.47078438	0.35755577	7.04043152	O	9.58925393	0.48526042	7.06201299

Ag at positions 1, 1′, 2, 3, 4, 5 [b]				Ag at positions 1, 1′, 2, 2′, 3, 3′ [b]			
Element	X	Y	Z	Element	X	Y	Z
Au	0.85136748	3.1814309	3.95321067	Au	0.8736409	3.19703566	3.95263819
Au	5.94330329	3.16986861	3.85269205	Au	5.95257059	3.17344037	3.90933341
Au	3.35116078	1.77028471	4.47052084	Au	3.40962813	1.81037418	4.51102812
Au	8.49883215	1.81373758	4.41007872	Au	8.49716456	1.82205428	4.42779476
Au	5.8925471	0.38629451	5.0832396	Au	5.92696728	0.43299548	5.10882933
Au	5.08421785	5.42485536	5.62893389	Au	5.14572118	5.43784794	5.60531022
Au	7.60157271	4.07144647	6.10915072	Au	0.86356656	0.45147043	4.91994914
Au	5.11648805	2.70584733	6.58144592	Au	10.0831259	5.38635895	5.57078637
Ag	0.80433067	0.4142029	5.0629434	Ag	7.60443741	4.07445399	6.15084852
Ag	10.1354032	5.39708039	5.57573234	Ag	5.12325346	2.67465671	6.66156523
Ag	2.56461777	4.1025955	6.17364241	Ag	2.63767702	4.0771104	6.22384556
Ag	2.65969971	1.38975696	7.1941462	Ag	2.45851014	1.32046727	7.17013228
Ag	7.61773911	1.38523169	7.12331528	Ag	7.7917811	1.34321163	7.13507316
Ag	10.1576308	2.85817124	6.7350069	Ag	10.2049948	2.87907116	6.722424
O	0.71516566	1.33716701	8.07435908	O	0.36876747	1.16912413	7.96912467
O	9.62996593	0.30705833	7.00677305	O	11.8319756	6.03852486	6.8377582

Table S8. Continued

Transition structures for O2 dissociation on Ag-substituted Au(321) a

Ag at positions 1, 1′, 2, 2′, 3, 3′, 4, 5 [b]

Element	X	Y	Z
Au	0.87954863	3.17689497	3.93673539
Au	5.94627143	3.16400758	3.90111353
Au	3.40792205	1.77159105	4.51513892
Au	8.50110753	1.82227483	4.421926
Au	5.95712794	0.39946891	5.1258796
Au	5.17235821	5.40624772	5.59729442
Ag	10.1264276	5.3699218	5.53751662
Ag	0.83685354	0.41782465	4.97107413
Ag	2.6646478	4.01200955	6.20454786
Ag	7.6335821	4.03767913	6.14117133
Ag	5.14965872	2.62690988	6.65714633
Ag	2.49357494	1.25654865	7.17862414
Ag	7.85388632	1.30265926	7.13532279
Ag	10.2384655	2.82310109	6.66137416
O	0.40413186	1.11119438	7.89750339
O	1.60543333	5.84432803	6.8613397

O adsorption, Ag at position 2 [a,b]

O at h1 [b]				**O at h2 [b]**			
Element	X	Element	X	Element	X	Element	X
Au	0.87303014	Au	0.87303014	Au	0.87303014	Au	0.87303014
Au	5.98732539	Au	5.98732539	Au	5.98732539	Au	5.98732539
Au	3.462614	Au	3.462614	Au	3.462614	Au	3.462614
Au	8.50907741	Au	8.50907741	Au	8.50907741	Au	8.50907741
Au	0.75588517	Au	0.75588517	Au	0.75588517	Au	0.75588517
Au	5.91926587	Au	5.91926587	Au	5.91926587	Au	5.91926587
Au	5.02001836	Au	5.02001836	Au	5.02001836	Au	5.02001836
Au	10.190469	Au	10.190469	Au	10.190469	Au	10.190469
Au	2.50271453	Au	2.50271453	Au	2.50271453	Au	2.50271453
Au	7.85262748	Au	7.85262748	Au	7.85262748	Au	7.85262748
Au	2.43414322	Au	2.43414322	Au	2.43414322	Au	2.43414322
Au	7.7485679	Au	7.7485679	Au	7.7485679	Au	7.7485679
Au	10.2172247	Au	10.2172247	Au	10.2172247	Au	10.2172247
Ag	5.06470731	Ag	5.06470731	Ag	5.06470731	Ag	5.06470731
O	5.92949331	O	5.92949331	O	5.92949331	O	5.92949331

Table S8. Continued

O adsorption, Ag at position 2′ [a,b]

O at h3 [b]

Element	X	Y	Z
Au	11.068893	3.22150884	3.94048049
Au	6.02147563	3.18151225	3.94190586
Au	3.39782944	1.78864149	4.3773972
Au	8.58081103	1.81471264	4.40371262
Au	0.84874692	0.39441502	5.07258636
Au	5.8804682	0.36585938	5.0084422
Au	5.04931319	5.43091204	5.63904495
Au	10.3337163	5.55006206	5.69560421
Au	2.57417192	4.08012227	6.1475307
Au	7.46044949	4.19090416	6.31707955
Au	5.04351903	2.73643772	6.65661691
Au	2.64385063	1.4057347	7.0604555
Au	7.5281529	1.45714992	6.96490867
Ag	10.2645606	2.53308097	6.7201277
O	9.3366904	4.45742155	7.26361264

O at h5 [b]

Element	X	Y	Z
Au	11.063409	3.16211888	3.94908414
Au	5.98192728	3.17112484	3.88656029
Au	3.41446101	1.77000795	4.40402109
Au	8.54263634	1.79114008	4.41034356
Au	0.78346266	0.3188299	5.06408747
Au	5.8968839	0.37040633	5.06374919
Au	5.12666381	5.42402935	5.65473406
Au	10.1619735	5.4011781	5.67665739
Au	2.55793718	4.08497803	6.12060009
Au	7.64611792	4.11563811	6.18317361
Au	5.15399135	2.77236455	6.65989973
Au	2.82368095	1.50832288	7.12956362
Au	7.60427285	1.40477837	7.02453549
Ag	10.1440275	2.8104576	6.76334806
O	0.83877222	0.85650804	7.23005407

O at h10 [b]

Element	X	Y	Z
Au	11.0566773	3.18592751	3.96751272
Au	6.02798861	3.21478199	3.94550484
Au	3.41898732	1.82177096	4.367253
Au	8.52440656	1.82132286	4.41885905
Au	0.75692005	0.44109486	5.09866177
Au	5.86386769	0.34842398	5.03259617
Au	5.04645053	5.50965293	5.65639886
Au	10.1657378	5.47703203	5.6410579
Au	2.50082054	4.20322258	6.15775186
Au	7.57854367	4.47201038	6.6062741
Au	5.01783745	2.86208266	6.60443832
Au	2.56235221	1.52656387	6.99262036
Au	7.43270174	1.38554201	6.98400724
Ag	10.2272651	2.81074004	6.76519394
O	8.35001027	2.98892712	7.95516935

O at fh2 [b]

Element	X	Y	Z
Au	11.0141506	3.20607184	3.99078459
Au	5.96292994	3.16914583	3.88971521
Au	3.39405778	1.8028189	4.37443549
Au	8.50308781	1.74674428	4.41027051
Au	0.86861337	0.33338439	5.014336
Au	5.91566333	0.36784466	5.05160807
Au	5.11437304	5.42834345	5.66895333
Au	10.2793899	5.3313066	5.81900614
Au	2.57930799	4.0736426	6.176485
Au	7.66109191	4.11686221	6.08715599
Au	5.05511311	2.76806808	6.64858623
Au	2.61340155	1.39501905	7.02093893
Au	7.39070746	1.55018191	7.12578636
Ag	10.1892663	2.51271855	6.71686771
O	9.13072093	0.46283071	7.36678734

Table S8. Continued

O adsorption, Ag at position 2′ [a,b]							
O at $b_{1'-2'}$ [b]				O at $b_{1-2'}$ [b]			
Element	X	Y	Z	Element	X	Y	Z
Au	11.0626667	3.16392539	3.98240867	Au	0.84485455	3.15525667	3.98435746
Au	5.9743852	3.18792915	3.86782068	Au	5.98150141	3.15943993	3.87844115
Au	3.39553702	1.74498014	4.41649526	Au	3.40361171	1.774529	4.37369464
Au	8.55501056	1.80107882	4.43299908	Au	8.54180257	1.76724601	4.44305522
Au	0.7834113	0.39605346	5.07147308	Au	0.78505579	0.37445119	5.09772919
Au	5.87963956	0.3422198	5.05667117	Au	5.89605782	0.37199175	5.10433802
Au	5.09468347	5.48663201	5.72703903	Au	5.07662959	5.41875267	5.67375659
Au	10.1766585	5.40932653	5.6674971	Au	10.1924912	5.39558792	5.64430732
Au	2.55921386	4.17608466	6.10765887	Au	2.54766713	4.12452185	6.16512672
Au	7.6257592	4.09007468	6.15200025	Au	7.63915243	4.08947332	6.08894373
Au	5.09175452	2.75443427	6.55274672	Au	5.08235618	2.72859907	6.58574043
Au	2.58142967	1.49467942	7.06843224	Au	2.61227101	1.42314085	7.00533591
Au	7.55125766	1.38361322	7.01491022	Au	7.53451162	1.38469055	7.0837398
Ag	10.0592668	2.75772025	6.86969695	Ag	10.2995303	2.75912554	6.82705234
O	1.19541048	2.07233032	8.36859455	O	9.08770858	1.77551857	8.26014122

O adsorption, Ag at positions 2, 3, 4 [a,b]							
O at h2 [b]				O at h10 [b]			
Element	X	Y	Z	Element	X	Y	Z
Au	0.85909368	3.17770431	3.86570317	Au	0.86064597	3.15015279	3.93883481
Au	5.99282647	3.22367033	3.97721193	Au	6.0199303	3.22381511	3.97822548
Au	3.47607292	1.8112052	4.42856553	Au	3.45834822	1.80193123	4.3904443
Au	8.50187184	1.81391674	4.4003975	Au	8.5281453	1.83188446	4.41035356
Au	0.7829419	0.34462518	5.05148436	Au	0.77760438	0.39984275	5.0708366
Au	5.92747052	0.38442116	5.0292952	Au	5.88536099	0.33342102	5.04858649
Au	10.2232551	5.42685502	5.65539454	Au	10.1890847	5.45860554	5.57805221
Au	2.52420139	4.0922362	6.12602146	Au	2.54396867	4.14485345	6.12380027
Au	2.46356594	1.41332727	7.02031515	Au	2.52164874	1.45688051	7.00218395
Au	7.71900679	1.24426423	7.03969775	Au	7.51487355	1.31862161	6.98702555
Au	10.2127503	2.70196049	6.55913064	Au	10.3114943	2.84673478	6.75803099
Ag	5.07268402	5.45097009	5.63166698	Ag	5.06653055	5.45290618	5.6510289
Ag	7.71116026	4.22945154	6.29775216	Ag	7.65038726	4.23590746	6.37956829
Ag	4.98256766	2.68688718	6.74478581	Ag	5.03932808	2.71953688	6.64402355
O	6.83490957	2.94643494	7.85362075	O	8.57151748	2.82094952	7.96800457

Table S8. Continued

O adsorption, Ag at positions 2, 3′, 4 [a,b]							
O at h2 [b]				O at h9 [b]			
Element	X	Y	Z	Element	X	Y	Z
Au	0.87381044	3.19750521	3.87828691	Au	8.51714211	4.55261778	3.34547381
Au	5.98265383	3.20504384	3.97541994	Au	0.9287225	3.21892304	3.95631843
Au	3.45938872	1.81919094	4.42998031	Au	5.94958087	3.17648737	3.96946327
Au	8.51172902	1.81183685	4.39115962	Au	3.42209857	1.81959344	4.42819795
Au	0.78136905	0.33964111	5.05255942	Au	8.53921249	1.80284809	4.36204432
Au	5.93622106	0.39463039	5.0217631	Au	0.76566258	0.32148022	5.05937363
Au	10.2309172	5.42122625	5.64573469	Au	5.88368051	0.40702183	5.07968909
Au	7.71038823	4.26120881	6.27190437	Au	10.17276	5.45875925	5.65569203
Au	2.44995156	1.39760828	7.02017644	Au	7.63285332	4.15099288	6.14355875
Au	7.74961803	1.22875788	7.04104711	Au	2.31860268	1.40042783	6.98848814
Au	10.2050672	2.69763572	6.56127704	Au	7.68338687	1.4541158	6.9913128
Ag	5.09332819	5.44619198	5.62450299	Au	10.1210505	2.80362148	6.6016253
Ag	2.53188046	4.10018822	6.1673665	Ag	5.06167577	5.45865899	5.62652026
Ag	4.98502182	2.62472056	6.72305853	Ag	2.48372774	4.3939073	6.63992476
O	6.86952621	3.00680286	7.79121145	Ag	5.15244562	2.75880351	6.75634367

CO + O coadsorption, Ag at position 2 [a,b]							
O at h1, CO at 1 [b]				O at h2, CO at 1 [b]			
Element	X	Y	Z	Element	X	Y	Z
Au	0.86225796	3.17163429	3.86219879	Au	0.8709456	3.13748344	3.86797074
Au	5.97105314	3.23237863	3.94645901	Au	5.99768926	3.19428384	3.96786228
Au	3.43971077	1.78564256	4.41080641	Au	3.48939701	1.81407653	4.40886999
Au	8.46945683	1.82662033	4.49564367	Au	8.4655328	1.78264459	4.52648225
Au	0.79208185	0.40572114	5.02510033	Au	0.74921084	0.38530802	5.06237252
Au	5.94860767	0.4566339	5.07064663	Au	5.96440773	0.42796557	5.06593941
Au	5.05694346	5.58120831	5.74034758	Au	5.08537809	5.4825474	5.61119137
Au	10.2231981	5.47466068	5.57789956	Au	10.1992431	5.4818587	5.57224108
Au	2.51738848	4.1703061	6.12288303	Au	2.54777481	4.15531785	6.14590757
Au	7.83247739	4.22620784	6.34477974	Au	7.75372421	4.20381258	6.16174536
Au	2.42248133	1.53140997	7.05879389	Au	2.47140129	1.4511929	6.98498219
Au	7.79389798	1.40503521	7.14622775	Au	8.15162792	1.89180316	8.48139258
Au	10.2448833	2.814859	6.60544059	Au	10.2479093	2.81363235	6.57794831
Ag	5.00185329	2.66292277	6.66467915	Ag	5.01667486	2.69233087	6.69876767
C	7.47165229	1.11816932	9.07558183	C	9.30697138	0.61172956	9.25390935
O	7.3539361	0.92540279	10.2034924	O	11.6865078	6.19796333	9.75687276
O	6.01354715	4.50481462	7.36917341	O	6.8300047	3.20413414	7.87867567

Table S8. Continued

CO + O coadsorption, Ag at position 2 [a,b]							
	O at h5, CO at 1 [b]				TS for O shift from h1 to h2, CO at 1 [b]		
Element	X	Y	Z	Element	X	Y	Z
Au	0.8629592	3.14645589	3.86717082	Au	0.86261734	3.16783987	3.85999678
Au	5.96549356	3.17305057	3.93900927	Au	5.97112126	3.21548631	3.95334937
Au	3.46331321	1.80101263	4.40486081	Au	3.44590008	1.79047127	4.4151991
Au	8.47631196	1.74827248	4.49681825	Au	8.47243594	1.79782949	4.48794991
Au	0.76905652	0.38731838	5.04857928	Au	0.77504219	0.36603973	5.04394746
Au	5.96623853	0.34288186	5.06475085	Au	5.93181456	0.46014674	5.08225314
Au	5.07106955	5.48696278	5.64221792	Au	5.08261714	5.47703866	5.66232631
Au	10.203088	5.44480989	5.62231449	Au	10.2156423	5.43412597	5.57031513
Au	2.51322147	4.17404415	6.1756179	Au	2.5233733	4.13720313	6.14726454
Au	7.65272656	4.03239171	6.10281421	Au	7.78150172	4.22605335	6.21536324
Au	10.1961691	2.80153307	6.56779039	Au	2.45284429	1.41316384	7.02611435
Au	2.45979029	1.48032696	6.99022134	Au	7.81572008	1.35095414	7.13504895
Au	7.86247549	1.35571281	8.00950521	Au	10.2681211	2.76173124	6.59282106
Ag	4.99923843	2.92450031	6.74017219	Ag	4.94307209	2.6900735	6.68858179
C	9.38867958	1.45486921	9.14086471	C	7.49903935	1.05454502	9.06959369
O	10.2214408	1.45748545	9.94182709	O	7.35669947	0.84974137	10.1908589
O	6.08631084	1.07840085	7.21754198	O	6.39242435	3.8994672	7.68426801

CO + O coadsorption, Ag at position 2′ [a,b]							
	O at h3, CO at 1 [b]				O at h4, CO at 1 [b]		
Element	X	Y	Z	Element	X	Y	Z
Au	11.0547068	3.18010696	3.92049248	Au	11.0724237	3.18759865	3.9523431
Au	6.015231	3.1919898	3.90331884	Au	5.97466812	3.18997086	3.85027922
Au	3.39661379	1.7801104	4.36740938	Au	3.39329771	1.80672975	4.38796302
Au	8.52198865	1.79309055	4.51716585	Au	8.50983479	1.77268965	4.52948383
Au	0.84423899	0.38822534	5.08376556	Au	0.80433314	0.41272317	5.03949332
Au	5.93012044	0.40591635	5.03633379	Au	5.91282885	0.38372981	5.09710026
Au	5.09032185	5.44940334	5.62657754	Au	5.13786006	5.45834663	5.64940653
Au	10.3229763	5.4859196	5.6210516	Au	10.1726136	5.43486992	5.61624151
Au	2.60371499	4.08719682	6.12906428	Au	2.59819534	4.29006032	6.26082606
Au	7.50265312	4.11584432	6.2259758	Au	7.64218588	4.08539552	6.12073791
Au	5.07229126	2.73517732	6.58637626	Au	5.11202084	2.74691659	6.52697021
Au	2.68009673	1.40901419	7.05508106	Au	2.66386776	1.26399648	7.03854885
Au	7.59730345	1.37487192	7.14422996	Au	7.61054471	1.35964949	7.16252888
Ag	10.3371383	2.55879691	6.71561952	Ag	10.145771	2.73378314	6.71541518
C	7.63601187	0.95205574	9.07456806	C	7.59964259	1.15793555	9.1268829
O	7.62188246	0.67602003	10.1904409	O	7.5850353	1.05418463	10.2730977
O	9.33076781	4.44281357	7.25292649	O	1.82331333	3.02751691	7.81765371

Table S8. Continued

CO + O coadsorption, Ag at position 2′ [a,b]

O at h10, CO at 1 [b]				O at fh2, CO at 1 [b]			
Element	X	Y	Z	Element	X	Y	Z
Au	0.84494062	3.10646034	3.94341422	Au	11.0401971	3.18174431	3.96646967
Au	6.02984769	3.1708863	3.90856514	Au	5.97352135	3.16896243	3.87843479
Au	3.46268297	1.7767504	4.38234844	Au	3.4217991	1.7761091	4.37424584
Au	8.51200386	1.74329953	4.5455308	Au	8.4759991	1.75318963	4.44838676
Au	0.79181557	0.3893327	5.12872093	Au	0.83066846	0.36827466	5.02017445
Au	5.9959665	0.40676291	5.0989265	Au	5.95547766	0.39475642	5.11099877
Au	5.11922477	5.4625628	5.62965127	Au	5.10895994	5.46133543	5.69599014
Au	10.2214589	5.41405328	5.55503864	Au	10.1800091	5.41303958	5.71768144
Au	2.55819874	4.13628329	6.13570575	Au	2.51376473	4.14180315	6.16071382
Au	7.61628858	4.11228279	6.15569105	Au	7.62355789	4.0549606	6.07712577
Au	5.10615455	2.74480659	6.600839	Au	5.07296082	2.75771949	6.56557398
Au	2.62541404	1.46511726	7.00768424	Au	2.57172143	1.4704746	6.99895722
Au	7.21846921	2.00437335	8.61615414	Au	7.33742134	1.63393262	8.24917887
Ag	10.2736646	2.72929549	6.72831016	Ag	10.1525029	2.65842036	6.68960081
C	6.0709779	0.7098574	9.37651678	C	6.02058613	2.25047451	9.47233747
O	7.09805998	6.29114689	9.86976726	O	5.28015994	2.59004675	10.2914937
O	8.53233215	3.32990035	8.01562794	O	8.83251555	0.87121186	7.24658438

O at $b_{1'-2'}$, CO at 1 [b]				TS for O shift from h3 to h10, CO at 1 [b]			
Element	X	Y	Z	Element	X	Y	Z
Au	11.0245276	3.14060605	3.964877	Au	11.0494664	3.15790613	3.9358461
Au	5.96735289	3.19782481	3.85362199	Au	6.03173212	3.18784089	3.91361465
Au	3.38347316	1.74641983	4.41648901	Au	3.41578622	1.78817586	4.36906146
Au	8.47995063	1.7637988	4.54219998	Au	8.52467204	1.75692287	4.55247183
Au	0.77299902	0.40581055	5.06144306	Au	0.80540964	0.38392889	5.11530798
Au	5.91252339	0.39347087	5.10376439	Au	5.9507425	0.39692726	5.06946722
Au	5.10418961	5.51751955	5.72166745	Au	5.09778191	5.44791011	5.60307293
Au	10.1643327	5.40540971	5.63238969	Au	10.2389108	5.40894632	5.63360493
Au	2.54665918	4.19409212	6.0846344	Au	2.57831487	4.11724842	6.13976904
Au	7.61091236	4.08321727	6.12101641	Au	7.52253271	4.13411623	6.22060859
Au	5.07327968	2.78470079	6.51982109	Au	5.0651914	2.73526722	6.59827077
Au	2.58104693	1.53112462	7.08525585	Au	2.66277988	1.4121175	7.02871227
Au	7.56160922	1.34115986	7.18820508	Au	7.6678286	1.35065922	7.18326246
Ag	10.1134918	2.81084763	6.81993319	Ag	10.3615966	2.64360934	6.75749636
C	7.69803161	1.12533559	9.15245312	C	7.33143784	0.66205013	9.01660271
O	7.77091627	1.00244398	10.2925525	O	7.07935803	0.22024091	10.0458859
O	1.09569025	1.92120826	8.35191628	O	8.82534392	3.73799959	7.77163099

Table S8. Continued

CO + O coadsorption, Ag at positions 2, 3, 4 [a,b]							
O at h1, CO at 1 [b]				O at h2, CO at 1 [b]			
Element	X	Y	Z	Element	X	Y	Z
Au	0.85548229	3.15796201	3.85868531	Au	0.86092825	3.1327093	3.8662026
Au	5.96191629	3.24092169	3.93925439	Au	6.00495264	3.21399431	3.96973888
Au	3.4394273	1.76753362	4.41997928	Au	3.50283955	1.81534146	4.42246711
Au	8.46626384	1.82592402	4.48911569	Au	8.4711155	1.78862433	4.52018707
Au	0.8056779	0.38538635	5.0363332	Au	0.76167844	0.38149193	5.06587051
Au	5.95576063	0.45144268	5.04430904	Au	5.98408303	0.4253101	5.0436673
Au	10.211317	5.44943219	5.56940196	Au	10.1910502	5.46707651	5.56451689
Au	2.49632721	4.14614664	6.0947571	Au	2.53462099	4.14644147	6.11888088
Au	2.42102966	1.5090937	7.06750494	Au	2.46076253	1.46707254	7.0033368
Au	7.77715454	1.35876428	7.12685823	Au	10.2234577	2.79323	6.56800502
Au	10.2212296	2.77723839	6.59378159	Au	8.09725575	1.9639081	8.50434952
Ag	5.0997947	5.5504208	5.76509003	Ag	5.08815766	5.48628194	5.60513123
Ag	7.77319834	4.20064929	6.29012428	Ag	7.72906637	4.18931922	6.17797623
Ag	4.98409973	2.65620114	6.65501084	Ag	5.01998355	2.64738725	6.70232176
C	7.4741201	1.1811645	9.07271848	C	9.28595293	0.70418445	9.26152821
O	7.37377401	1.05734154	10.2117653	O	11.6765466	6.29436811	9.75619022
O	5.96477662	4.40288378	7.42419137	O	6.74668368	3.24500754	7.92250612

O at h2, CO at 1′ [b]				O at h4, CO at 1 [b]			
Element	X	Y	Z	Element	X	Y	Z
Au	0.85703183	3.19319282	3.84081781	Au	0.86217808	3.18164432	3.91437895
Au	5.96383635	3.2089855	3.94761315	Au	5.98226543	3.202554	3.9090474
Au	3.40427462	1.76842906	4.53305675	Au	3.42745729	1.80463164	4.40508154
Au	8.49424665	1.8166287	4.38994927	Au	8.49242985	1.80005778	4.52746875
Au	0.82404473	0.39011409	5.08590886	Au	0.82757807	0.40969588	5.01422942
Au	5.91495532	0.40506086	5.02320951	Au	5.92093095	0.38721468	5.07708736
Au	10.2446596	5.47607945	5.64563484	Au	10.1919396	5.43752023	5.58065402
Au	2.51948666	4.09838127	6.091725	Au	2.6032161	4.2543458	6.17160834
Au	2.47904456	1.40074857	7.16118095	Au	2.63796494	1.23099496	7.03763757
Au	7.7150375	1.27774141	7.03251387	Au	7.65821213	1.33087098	7.14545537
Au	10.2023298	2.74663415	6.50895672	Au	10.1345829	2.69167804	6.65463329
Ag	5.07512364	5.44148423	5.61681838	Ag	5.15141732	5.42969399	5.61075071
Ag	7.71671658	4.25568548	6.27745494	Ag	7.66874104	4.1028498	6.15940069
Ag	5.01943947	2.73012323	6.70093999	Ag	5.08356859	2.69793648	6.59345826
C	2.47496379	1.3012218	9.13846092	C	7.4357358	1.16097623	9.10066885
O	2.45185526	1.36067113	10.2878152	O	7.35834312	1.0552151	10.2451284
O	6.84807558	2.98827331	7.84985228	O	1.72853824	3.05179586	7.76182589

Table S8. Continued

CO + O coadsorption, Ag at positions 2, 3, 4 [a,b]

O at h7, CO at 1′ [b]

Element	X	Y	Z
Au	0.92045604	3.19642932	3.9166433
Au	5.94626143	3.19758689	3.92272045
Au	3.41766616	1.78827337	4.5269945
Au	8.50831308	1.80332598	4.36789797
Au	0.82956334	0.41754526	5.02718097
Au	5.95002629	0.38927066	5.07452333
Au	10.2024097	5.43709711	5.60327118
Au	2.39818521	4.15404982	6.27670762
Au	2.4799476	1.38483152	7.14163205
Au	7.78714792	1.39487024	7.04150708
Au	10.1794826	2.74045282	6.58723662
Ag	5.16493656	5.47200676	5.61430358
Ag	7.69742417	4.10122811	6.14809232
Ag	5.21596644	2.54684859	6.70669885
C	2.54121531	0.89806751	9.056678
O	2.55703022	0.5744913	10.1595055
O	4.22119594	4.38477795	7.30662554

O at fh1, CO at 1′ [b]

Element	X	Y	Z
Au	0.85653474	3.15794907	3.87593905
Au	5.93762786	3.22421148	4.00769311
Au	3.38608224	1.75594108	4.42726295
Au	8.53180005	1.79177666	4.37946115
Au	0.86380714	0.38060006	5.081568
Au	5.97912191	0.35404413	4.9918338
Au	10.2595309	5.41566074	5.66334769
Au	2.54273991	4.02117656	6.05506385
Au	2.2147742	1.45534614	8.29097408
Au	7.71106271	1.40953975	6.99627573
Au	10.2296502	2.7032568	6.58796268
Ag	5.10291221	5.44510815	5.77947498
Ag	7.68523866	4.10412102	6.17482105
Ag	5.02731054	2.54793295	6.66171071
C	0.84304625	1.99864781	9.48517942
O	10.2932694	2.28065154	10.299766
O	3.76386542	0.75827955	7.33083867

O at h2, O at h7, CO at 1′ [b]

Element	X	Y	Z
Au	0.90128813	3.19631485	3.88855788
Au	5.95466945	3.20493309	3.94964093
Au	3.4164139	1.81536616	4.55233531
Au	8.48548557	1.820489	4.37353761
Au	0.82282283	0.38992508	5.01365577
Au	5.94283745	0.4111119	5.04175239
Au	10.2372919	5.43580942	5.60001225
Au	2.38231517	4.08386733	6.27392743
Au	2.47938576	1.33118155	7.16491608
Au	7.82937348	1.21650381	7.05019087
Au	10.1947078	2.67414088	6.52723037
Ag	5.1647532	5.47418153	5.5757651
Ag	7.74282426	4.20928754	6.24826334
Ag	5.13722868	2.5471612	6.76904432
C	2.49572199	0.78070078	9.06784363
O	2.50139804	0.42648001	10.1605221
O	4.14957308	4.50050668	7.27120425
O	7.04356818	2.91530693	7.88737561

[a] Calculated using the (2×1) surface unit cell. [b] For labeling of atom positions see main text, Figs. 1 and 11.