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1 Golden Single-atomic-site Platinum Electrocatalysts

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22 Keywords: gold, platinum, colloidal synthesis, single-atomic site, alloy bonding, electrocatalysis,
23 formic acid oxidation

24

Abstract

25
26 Bimetallic nanoparticles with tailored structure constitute a desirable model system for catalysts,
27 as crucial factors such as geometric and electronic effects can be readily controlled by tailoring
28 the structure and alloy bonding of the catalytic site. Herein, we report a facile colloidal method to
29 prepare a series of platinum-gold (PtAu) nanoparticles with tailored surface structures and
30 particle diameters on the order of 7 nm. Samples with low Pt content, particularly Pt₄Au₉₆,
31 exhibited unprecedented electrocatalytic activity for the oxidation of formic acid. A high forward
32 current density of 3.77 A·mg_{Pt}⁻¹ was observed for Pt₄Au₉₆, a value two orders of magnitude
33 greater than those observed for core-shell-structured Pt₇₈Au₂₂ and a commercial Pt nanocatalyst.
34 Extensive structural characterization and theoretical DFT simulations of the best-performing
35 catalysts revealed densely packed single-atom Pt surface sites surrounded by Au atoms,
36 suggesting that their superior catalytic activity and selectivity could be attributed to the unique
37 structural and alloy bonding properties of these single-atomic-site catalysts.

38

39

40 Platinum (Pt) has a long history of use in catalysis, due primarily to its high activity in a
41 wide range of chemical reactions.¹ However, it faces major obstacles in some reactions,
42 including the problem of carbon monoxide (CO) poisoning in the formic acid oxidation (FAO)
43 reaction.² Due to the very strong binding affinity of CO at Pt surfaces, exposure to even small
44 quantities of CO can gradually poison (*i.e.*, deactivate) a Pt catalyst.³ In recent years, it has
45 become common to alloy Pt with other metals in order to modify its catalytic properties;⁴⁻⁷ thus,
46 it seems reasonable this approach could also be used to address the issue of CO poisoning and
47 enhance the performance of such Pt catalysts.^{8,9} Recent advances in nanoparticle synthesis have
48 allowed for the preparation of bimetallic nanocatalysts with increasingly well-defined alloy
49 structures.¹⁰⁻¹³ An important quality of these bimetallic nanoparticles is that the interaction
50 between atoms of different metals at the nanoparticle surface can result in significantly enhanced
51 catalytic activity due to both geometric and electronic effects.¹⁴⁻¹⁶ By definition, these alloy
52 interactions occur at the boundaries between domains of the two metals; thus, any catalytic
53 enhancement effect should also be maximized by increasing the degree of intermetallic mixing at
54 the nanoparticle surface.¹⁶ A very interesting and little-researched limit to this mixing is found in
55 single-Pt-site catalysis in an alloy nanoparticle system, wherein distinct geometric and electronic
56 effects set it apart from other phase-segregated surface nanostructures via the so-called
57 “ensemble effect” theory.¹⁷⁻²¹

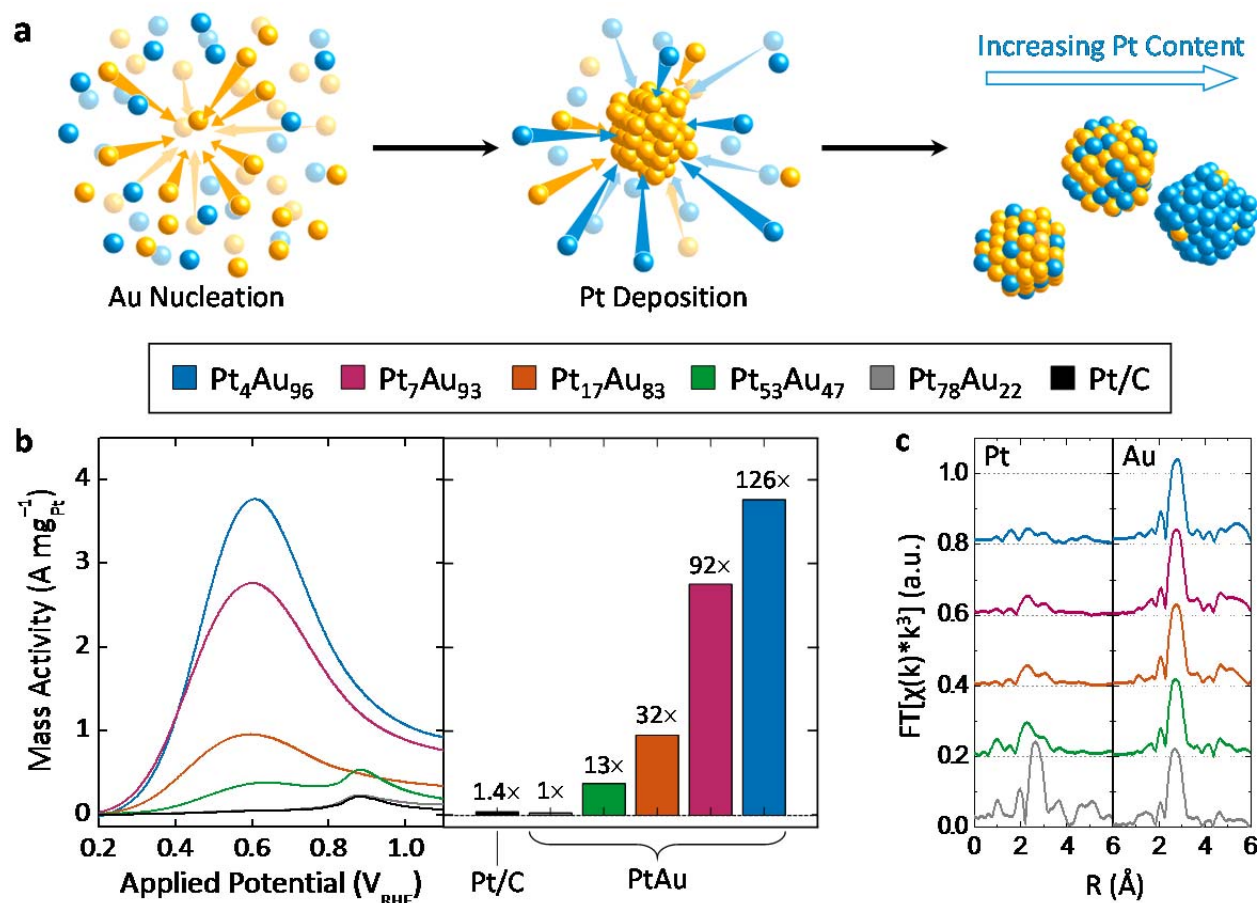
58 Herein is presented a series of colloidal bimetallic PtAu nanoparticles, obtained via a
59 facile solution-phase synthesis, that feature stable single-atomic Pt catalytic sites with high FAO
60 activity. Electrocatalytic measurements reveal a remarkable enhancement in activity that is
61 highly dependent on the PtAu composition of the sample. Characterization of such materials is
62 very challenging, as Pt and Au have nearly identical atomic numbers. Nonetheless, we
63 demonstrate that convincing conclusions can be achieved through the use of several
64 complementary techniques, including X-ray absorption spectroscopy (XAS), X-ray
65 photoelectron spectroscopy (XPS), energy dispersive X-ray spectroscopy (EDX), high-angle
66 annular dark-field scanning transmission electron microscopy (HAADF-STEM), and
67 electrochemical measurements, with each offering its own insights into the structure of the
68 subject material. The results of this structural characterization, together with density functional
69 theory (DFT) modeling, demonstrate that it is not only elemental composition that dictates the

70 electrocatalytic activity of the PtAu nanoparticles, but that the local bonding environment of
71 single-atomic-site Pt surface atoms plays the most critical role.

72 The bimetallic PtAu nanoparticles used in this study were prepared from stock solutions
73 of Pt and Au chloride precursor salts using a colloidal synthetic method adapted from that of
74 Chen *et al.*¹⁶ This synthetic procedure and a complete set of the PtAu samples with
75 systematically varied compositions from 4% Pt to 96% Pt are provided in Supplementary Fig. 1.
76 An illustration of nanoparticle formation from ions in solution is shown in Fig. 1a. Of particular
77 importance was the replacement of the CO reducing agent/co-ligand (used in the original
78 synthesis) with ethylene glycol (EG), such that the PtAu nanoparticles were prepared in a CO-
79 free environment. Following synthesis, these nanoparticles were deposited onto a carbon powder
80 support material in preparation for catalytic activity testing. Transmission electron microscopy
81 (TEM) was employed to confirm successful sample preparation (see Supplementary Fig. 2), and
82 inductively coupled plasma optical emission spectroscopy (ICP-OES) was used to measure
83 relative elemental compositions and mass loadings (see Supplementary Table 1). TEM results
84 confirmed a high degree of nanoparticle dispersion and uniformity, with observed mean particle
85 diameters of *ca.* 7 nm for all samples, and ICP-OES measurements revealed an average mass
86 loading of 11 ± 2 wt% for the carbon-supported samples. The measured elemental compositions
87 from ICP-OES (*i.e.*, Pt₇₈Au₂₂, Pt₅₃Au₄₇, Pt₁₇Au₈₃, Pt₇Au₉₃, and Pt₄Au₉₆) corresponded closely to
88 the nominal concentrations of Pt and Au used during synthesis, and are hereafter used to
89 distinguish between PtAu samples.

90 CV analysis yielded a very interesting result regarding the specific electrocatalytic
91 activities of the PtAu nanoparticles. As can be seen from the magnitude of the Pt-mass-
92 normalized current peaks at *ca.* 0.6 V_{RHE} in the anodic sweeps (see Fig. 1b), the highest activities
93 were observed for those samples containing the least Pt. The most active sample, Pt₄Au₉₆,
94 exhibited activity greater than that of the commercial Pt/C catalyst and least-active PtAu
95 nanoparticle sample by up to two orders of magnitude (*i.e.*, 126 times greater than Pt₇₈Au₂₂, and
96 90 times greater than Pt/C). A strong correlation was observed between low FAO peak currents
97 and the presence of a significant peak at *ca.* 0.85 V_{RHE} in the CV plot. This secondary peak arises
98 from the electrochemical oxidation of adsorbed CO molecules, which are well known to poison
99 the surface of Pt and suppress its catalytic activity.²² The absence of such a peak in the CV plots
100 of those PtAu nanoparticles containing the least Pt suggests that resistance to CO poisoning may

101 play a significant role in their enhanced catalytic activity. It should be noted that characterization
 102 of pure Au nanoparticles, prepared according to the same protocol, revealed no measurable
 103 activity in the FAO reaction (see Supplementary Fig. 3).
 104



105
 106 **Fig. 1 | Synthesis, reactivity and EXAFS of catalysts.** **a**, Illustration of nanoparticle formation via reduction of
 107 solvated ions. **b**, Pt mass-normalized anodic sweeps obtained from PtAu nanoparticle catalysts in electrolyte
 108 containing 0.1 M concentrations of both $HClO_4$ and $HCOOH$, with peak currents graphed for comparison. The data
 109 acquired from a commercial Pt/C catalyst is included to provide additional context. **c**, Plotted FT-EXAFS spectra
 110 obtained from Pt and Au L_3 -edge absorption spectra of PtAu nanoparticles, illustrating the drastic under-
 111 coordination of Pt atoms in low-Pt-content samples such as Pt_7Au_{93} and Pt_4Au_{96} .
 112

113 In order to gain a structural perspective on this activity enhancement, FT-EXAFS
 114 analysis was performed on the PtAu nanoparticles at the Pt and Au L_3 absorption edges, shown
 115 in Fig. 1c. Detailed information regarding the local Pt and Au bonding environments in each
 116 sample was obtained by fitting these spectra (see Supplementary Fig. 4), resulting in the
 117 structural parameter values shown in Table 1. Observed trends in coordination number and bond
 118 length values are also presented graphically in Supplementary Fig. 5. While the scattering paths

119 involving Pt and Au atoms were too similar to produce separable peaks in the FT-EXAFS
 120 spectrum (see Supplementary Fig. 6 for a topographical illustration), this similarity made it
 121 possible to treat scattering from both Pt and Au as a single path (denoted Pt–M and Au–M for the
 122 Pt and Au L₃-edges, respectively). Analysis of the resulting bond lengths suggested that Pt atoms
 123 in Pt₇Au₉₃ and Pt₄Au₉₆, the most highly active PtAu samples, were present almost exclusively as
 124 single-atom sites surrounded by atoms of Au. This observation is based on the close agreement
 125 between the measured Pt–M bond lengths (2.82 Å) and the expected bimetallic bond length of
 126 2.822 Å for a homogenous PtAu alloy, as calculated from experimental Pt–Pt and Au–Au bond
 127 lengths in pure Pt and Au nanoparticles (see Supplementary Table 2). Further evidence for the
 128 single-atom structure of Pt in these two samples is provided via HAADF-STEM,
 129 electrochemistry and XPS valence band analyses. It is notable that a similar Pt–M bond distance
 130 was also observed for Pt₁₇Au₈₃; however, its Pt–M coordination number (CN) is identical to that
 131 of the core-shell structured nanoparticles (Pt₅₃Au₄₇ and Pt₇₈Au₂₂) and considerably higher than
 132 the single-atom Pt samples. These results indicate that Pt₁₇Au₈₃ exhibits a mixed structure
 133 containing both single-atom and few-atom Pt cluster regions, with more of them located within
 134 the core of the nanoparticle. Additional support for this conclusion is provided by the particularly
 135 large Debye-Waller coefficient (σ^2) value obtained for Pt₁₇Au₈₃, indicating that there is greater
 136 variation among the Pt–M bond lengths due to significant contributions from both Pt–Pt and Pt–
 137 Au bonds. Further evidence will also be provided in the electrochemical and valence band
 138 studies.

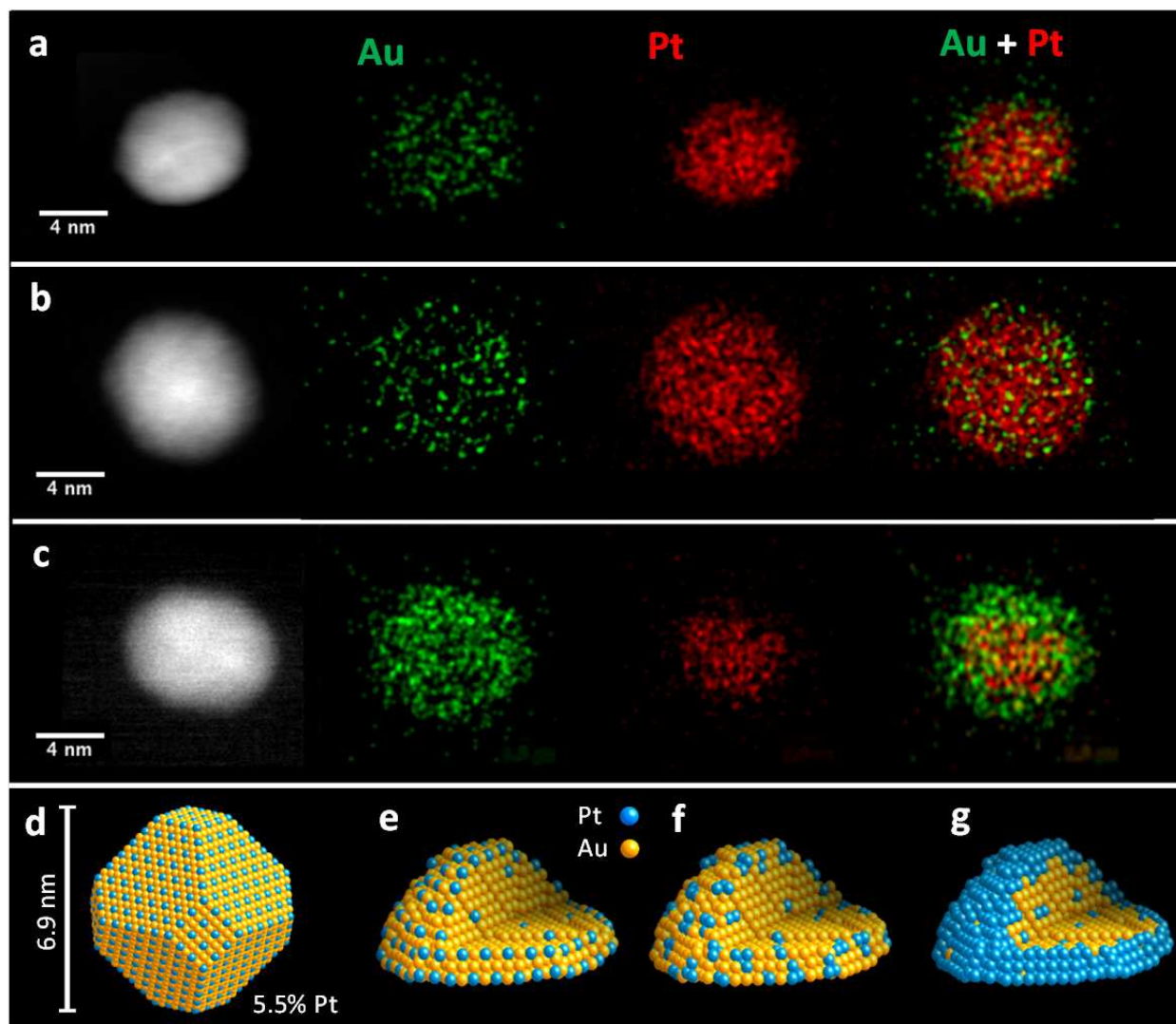
139 **Table 1 | Structural parameter values for PtAu nanoparticles.**

Sample	Pt–M				Au–M			
	CN (atoms)	R (Å)	σ^2 (10 ⁻³ Å ²)	ΔE_0 (eV)	CN (atoms)	R (Å)	σ^2 (10 ⁻³ Å ²)	ΔE_0 (eV)
Pt ₁₀₀ Au ₀	11.1(5)	2.772(1)	2.1(2)	3.9(4)	-----	-----	-----	-----
Pt ₇₈ Au ₂₂	9(1)	2.776(4)	2.6(6)	3(1)	12(1)	2.839(4)	4.3(6)	0(1)
Pt ₅₃ Au ₄₇	9(2)	2.776(8)	3(2)	2(1)	12.1(9)	2.851(3)	4.2(4)	2.3(7)
Pt ₁₇ Au ₈₃	9(1)	2.818(5)	8(1)	2.8(8)	11.6(9)	2.861(3)	3.6(4)	2.6(7)
Pt ₇ Au ₉₃	7.4(9)	2.813(5)	6(1)	2.6(8)	12(1)	2.862(4)	3.4(5)	2(1)
Pt ₄ Au ₉₆	5(2)	2.82(2)	4(3)	3(3)	11.0(8)	2.871(2)	3.1(3)	3.4(6)
Pt ₀ Au ₁₀₀	-----	-----	-----	-----	12.0(4)	2.872(1)	3.4(2)	2.7(3)

These parameter values were obtained by fitting the respective Pt and Au L₃-edge FT-EXAFS spectra of each nanoparticle sample. Numbers in parenthesis indicate the uncertainty (1 σ) in the last digit of the corresponding value.

140 EXAFS analysis of local CNs revealed that Pt atoms were under-coordinated in the PtAu
141 nanoparticles, especially those bearing highly active single-atom sites. CNs for the Pt–M
142 scattering path ranged from 9 nearest neighbours in Pt₇₈Au₂₂ to just 5 in Pt₄Au₉₆, standing in
143 stark contrast with the CN of 11 observed for pure Pt nanoparticles synthesized using the same
144 method. Combined with Au–M CNs on the order of 11 to 12 nearest neighbours, this evidence
145 strongly suggests an Au-core/PtAu shell nanoparticle structure, with Pt predominantly located at
146 surface sites. Furthermore, Pt concentrations measured using surface-sensitive X-ray
147 photoelectron spectroscopy (XPS) were consistently greater than those obtained using bulk-
148 sensitive ICP-OES (see Supplementary Fig. 7), providing convincing evidence of Pt surface-
149 enrichment in all PtAu nanoparticle samples. The very low CNs observed for Pt₇Au₉₃ and
150 Pt₄Au₉₆ (7 and 5, respectively) further indicate that Pt should be predominantly found on the
151 particle surface with high-level surface roughness, including edge and corner sites.¹² X-ray
152 absorption near edge structure (XANES) analysis of samples (see Supplementary Fig. 8) further
153 confirmed the metallic nature of both Pt and Au in these nanoparticles, and provided support for
154 the presence of single-atom Pt sites via a positive binding energy shift and increased white line
155 breadth (both indicative of increasingly isolated Pt atoms²³). This high degree of direct Pt–Au
156 interaction was also observed in the XPS data, which featured a negative shift of the Pt 4f
157 electron binding energies of Pt₁₇Au₈₃ and Pt₄Au₉₆ (as was shown in Supplementary Fig. 7). In
158 contrast to the extensive Pt–Au mixing in those samples with a low Pt content, Pt₅₃Au₄₇ and
159 Pt₇₈Au₂₂ exhibited predominantly Pt–Pt bonding, reflecting their more complete Au-core/Pt-shell
160 structures.

161 The emerging picture of these nanoparticles as containing Pt preferentially located at the
162 surface of Au cores is consistent with real space imaging of these nanoparticles using atomic
163 resolution high angle annular dark field scanning transmission electron microscopy (HAADF-
164 STEM) and elemental imaging using spatially resolved energy dispersive X-ray (EDX)
165 spectroscopy (see Fig. 2a-c). In order to prevent beam damage to these nanoparticles, electron
166 beam intensity was minimized during EDX spectroscopy measurements, which resulted in low
167 X-ray counting statistics; nonetheless, there is strong evidence for Au signal originating

169
170

171 **Fig. 2 | HAADF-STEM images and structural models.** **a, b, c,** STEM/EDX mapping images of individual particles
 172 from $\text{Pt}_4\text{Au}_{96}$ and $\text{Pt}_7\text{Au}_{93}$ single-atom Pt, and $\text{Pt}_{78}\text{Au}_{22}$ core-shell samples, respectively. **d,** Structural model of an
 173 ideal, truncated octahedral nanoparticle with optimal single-atomic site coverage. Though strictly not
 174 representative of the nanoparticles synthesized herein, this model provides a reasonable estimate of the upper
 175 concentration limit for such single-atom Pt sites. **e, f, g,** Models depicting the proposed evolution of PtAu surface
 176 structures from single-atom Pt sites to few-atom Pt clusters to a complete Pt shell, respectively, as a result of
 177 increased Pt content.

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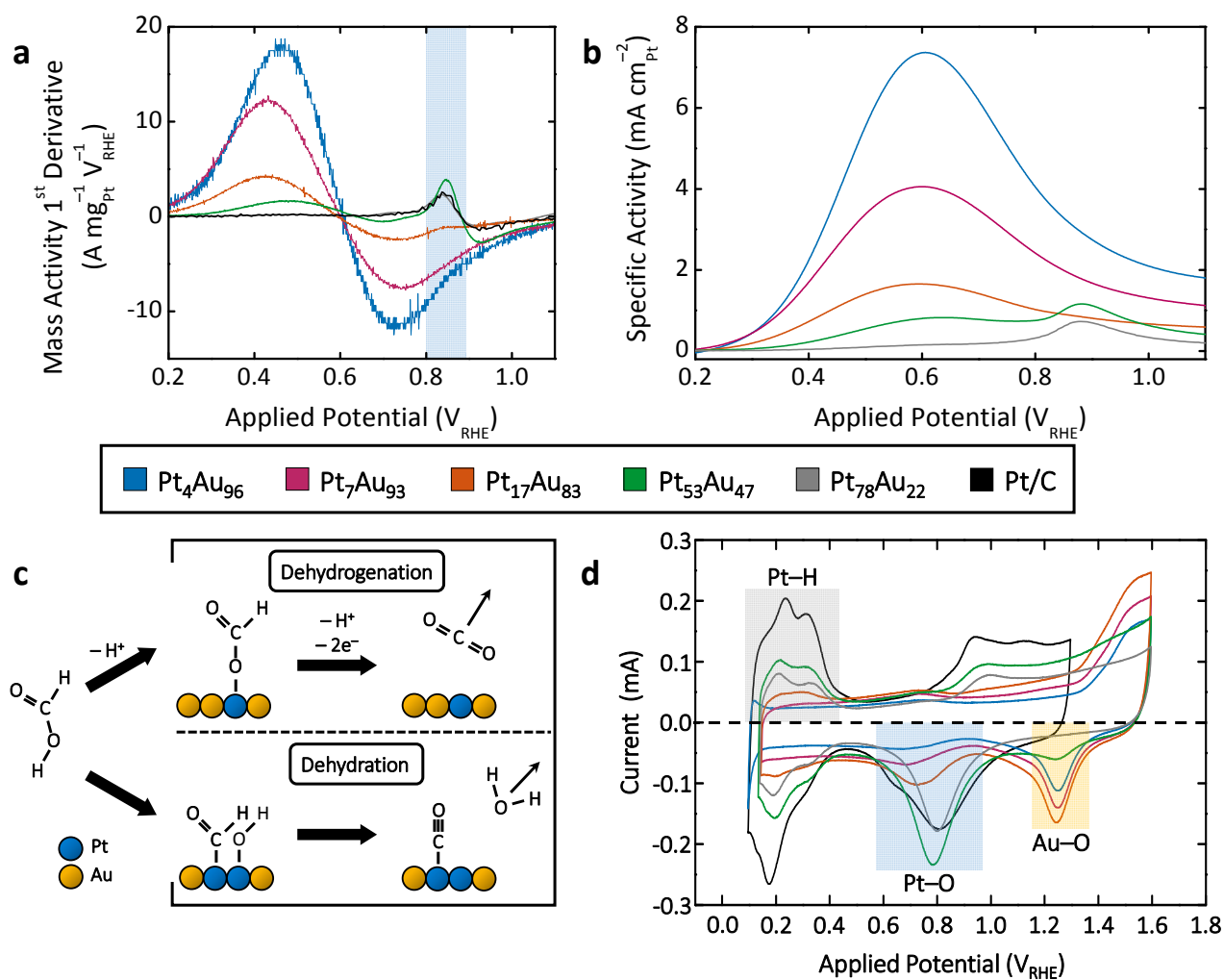
179 mainly from the cores of nanoparticles, with the Pt signal being more diffuse and slightly
 180 enhanced at the particle edges. This effect can also be illustrated by comparing the overlay EDX
 181 maps of representative particles shown in Fig.2a-c. It is noteworthy that similar control over
 182 surface structure generally requires two or more sequential steps during synthesis, as Pt and Au
 183 are capable of forming homogeneous alloys.^{23–26} The ability to achieve these complex surface

184 morphologies in a single reaction step likely stems from a combination of factors, including
185 sequential reduction (due to the more negative reduction potential of Au relative to Pt) and
186 preferential coordination of stabilizing amine ligands to surface Pt sites rather than Au sites.^{27,28}
187 The significantly greater adsorption energy of the oleylamine ligand molecules at surface Pt sites
188 can contribute to the preferential Au-core/Pt-shell structure of the PtAu nanoparticles, as it
189 results in greater stabilization and limits further deposition of Au atoms, thereby resulting in a Pt-
190 enriched surface.

191 The observation of a Pt-rich surface is consistent with a single-atom Pt surface structure.
192 For an ideal truncated octahedral nanoparticle (see Fig. 2d), maximum surface coverage by
193 single-atomic sites (*i.e.*, with no co-adjacent Pt atoms) is achieved with a Pt content of 5.5%.
194 While atomic-scale HAADF-STEM images suggest that the PtAu nanoparticles synthesized
195 herein are predominantly polycrystalline, this single-crystalline estimate serves as a reasonable
196 upper concentration limit at which exclusively single-atom Pt sites are able to exist, and suggests
197 that Pt₄Au₉₆ and Pt₇Au₉₃ could reasonably exhibit such a surface morphology.

198 Based on the available information, the PtAu samples can now be categorized in terms of
199 their surface structure: Au with single-atom Pt sites (Pt₇Au₉₃ and Pt₄Au₉₆), Au with single-atom
200 and few-atom Pt sites (Pt₁₇Au₈₃), and Au-core/Pt-shell (Pt₇₈Au₂₂ and Pt₅₃Au₄₇). This gradual
201 change from single-atomic to near-complete shell coverage in these PtAu/C nanocatalysts is
202 illustrated in Fig. 2e-g. Additional support for the proposed surface structures of the
203 nanoparticles can be found in the detailed analysis of their electrocatalytic performance
204 presented in Fig. 3. The disappearing peak at *ca.* 0.85 V_{RHE} in Fig. 1b is more clearly shown in
205 the first-derivative plots of Pt mass activity in Fig. 3a. Such peak intensity was completely absent
206 in both the Pt₇Au₉₃ and Pt₄Au₉₆ samples (as is more clearly illustrated in Supplementary Fig. 9),
207 and was markedly reduced in Pt₁₇Au₈₃. These electrochemical results offer another piece of
208 evidence for the Pt single-atom structure in Pt₇Au₉₃ and Pt₄Au₉₆. As is illustrated in Fig. 3c, the
209 existence of adjacent Pt surface sites will produce a CO poisoning peak in the first derivative
210 voltammogram, whereas the single-atom Pt geometry of the catalyst surface will encourage the
211 CO₂ formation via the dehydrogenation mechanism. Moreover, the small CO first derivative
212 peak for Pt₁₇Au₈₃ in Fig. 3a illustrates the existence of some smaller, cluster-like Pt domains in
213 this sample. Fig. 3b shows that a similar trend in specific activity is observed when normalizing
214 FAO anodic sweep voltammograms by the electrochemically active surface area (ECSA) of Pt,

215 indicating again that the observed increase in activity was not simply due to an increased
 216 proportion of Pt surface sites in those samples with lower Pt content. Both Pt₇Au₉₃ and Pt₄Au₉₆
 217 exhibited very similar peak intensities when the anodic sweeps were normalized by the
 218 combined ECSAs of Pt and Au, suggesting that they shared a similar surface structure in addition
 219 to their mutual resistance to CO poisoning. Finally, normalization of electrocatalytic
 220 performance by total metal catalyst mass resulted in a trade-off between reduced surface
 221 poisoning by CO and the number of available Pt catalytic sites (see Supplementary Fig. 10).



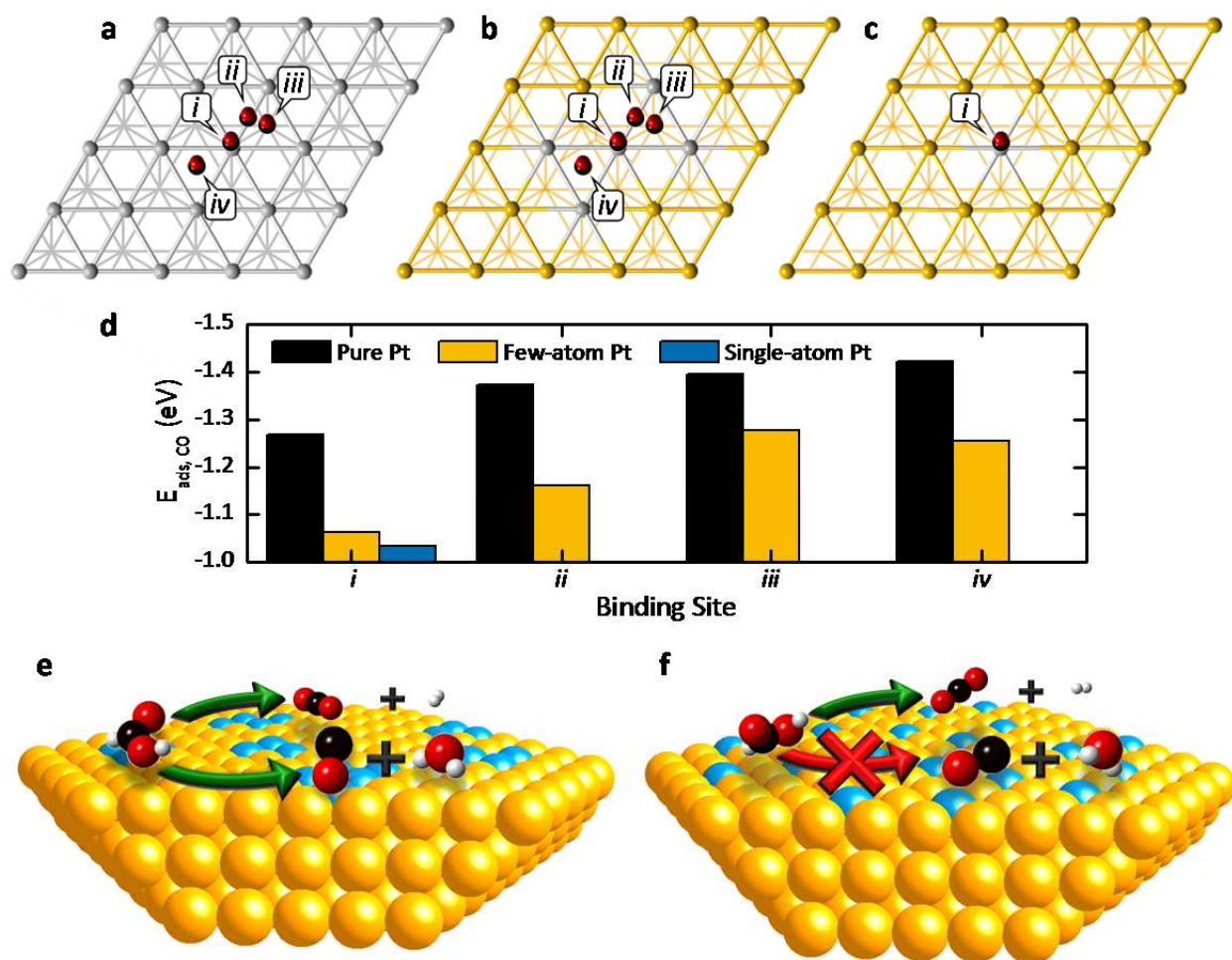
222
 223 **Fig. 3 | Further electrochemical analysis.** **a**, First-derivative of Pt mass-normalized FAO voltammograms
 224 presented in Fig. 1a. The blue box highlights the sensitivity of the first-derivative peak at ca. 0.85 V_{RHE} to the Pt
 225 surface structure. **b**, FAO anodic sweep voltammograms obtained from PtAu nanoparticle and commercial Pt/C
 226 catalyst samples, as normalized by the electrochemically active surface area of Pt. These voltammograms were
 227 also obtained using a sweep rate of 10 mV·s⁻¹ and an electrolyte containing 0.1 M concentrations of both HClO₄
 228 and HCOOH. **c**, Schematic illustration of the dehydrogenation and dehydration mechanisms of FAO reactions on
 229 PtAu surfaces. **d**, Cyclic voltammograms from PtAu nanocatalysts (shown at full amplitude) and commercial Pt
 230 nanocatalysts (shown at half amplitude to facilitate comparison) acquired in 0.1 M HClO₄ with a sweep rate of 100
 231 mV·s⁻¹.

232

233 This structure is experimentally supported by the behaviour of distinct Au–O adlayer
234 formation on the exposed Au surfaces, as revealed by CV measurements under non-catalytic
235 conditions (see Fig. 3d). Regions of interest include the positive Pt–H desorption peaks
236 highlighted from *ca.* 0.1 to 0.4 V_{RHE} , and the negative Pt–O and Au–O adlayer removal peaks
237 highlighted from 0.55 to 0.95 V_{RHE} and from 1.15 to 1.35 V_{RHE} , respectively. As expected from
238 the relative compositions, the areas of the Pt–O and Au–O adlayer removal peaks revealed a
239 gradual transition from a pure Pt surface in Pt₇₈Au₂₂ (indicative of its Au-core/Pt-shell structure)
240 to the predominantly Au surface decorated with Pt in Pt₄Au₉₆. In addition to a steady reduction
241 of Pt–H peak area, a significant negative shift of the Pt–O adlayer removal peak was observed
242 with decreasing Pt content; this shift reached a maximum of *ca.* 0.1 V_{RHE} in Pt₄Au₉₆, revealing
243 markedly strengthened Pt–O adsorption, likely due to the increasingly lowered coordination
244 numbers of Pt atoms in these samples. This observation provides strong evidence for the
245 thorough mixing of Pt and Au at the surface of samples with low Pt content, resulting in a
246 relatively even distribution of Pt across the predominantly Au surface. The less-drastic shift of
247 the Au–O adlayer desorption peak relative to that of Pt–O can be explained by the fact that any
248 charge transfer effects involve up to 9 Au atoms per Pt atom, depending on the relative
249 composition of the sample.

250 Given that CO poisoning has a drastic impact on the measured activity of Pt-based FAO
251 catalysts, DFT calculations were performed to study the adsorption properties of CO at single-
252 atom, few-atom, and pure Pt surfaces (see Fig. 4a-c). The (111) surface is selected in our DFT
253 calculations since the (111) sites are the most abundant surface sites in regular colloidal Au and
254 Pt nanoparticles. Multiple adsorption sites for CO exist at pure and few-atom Pt surfaces (in
255 order of increasing adsorption energy: apical, bridging, hcp hollow, and fcc hollow), whereas
256 only a single site (apical) was found to be significant for the single-atom Pt surface. The results
257 of these calculations indicate that CO adsorption is weakened at all adsorption sites on both few-
258 atom and single-atom Pt surfaces relative to bulk Pt (see Fig. 4d and Supplementary Table 3).
259 Adsorption energies of CO at apical sites, for example, are reduced from –1.268 eV on bulk Pt to
260 –1.063 and –1.032 eV on few-atom and single-atom surfaces, respectively. This finding is in line
261 with the observed enhancement in FAO activity, rationalized via a weakening of the typically
262 too-strong CO adsorption on Pt (as per the Sabatier Principal).^{29,30} While this weakened CO

263 adsorption is consistent with the observed activity enhancement, however, it is generally
 264 recognized that the availability of adjacent adsorption sites also makes a significant contribution
 265 to FAO activity.⁷ It is worthwhile to note that the PtAu nanoparticles also show significant
 266 retention of activity as shown by both chronoamperometric measurements performed at 0.55
 267 V_{RHE} and repeated cycling between 0.1 and 1.1 V_{RHE} (Supplementary Fig. 11). These results
 268 further indicate the fairly good stability of the alloy-based single-atom catalysts, with the latter
 269 demonstrating that high activity (> 70% of the initial value) can be retained even after 1,500
 270 successive rounds of potential cycling.

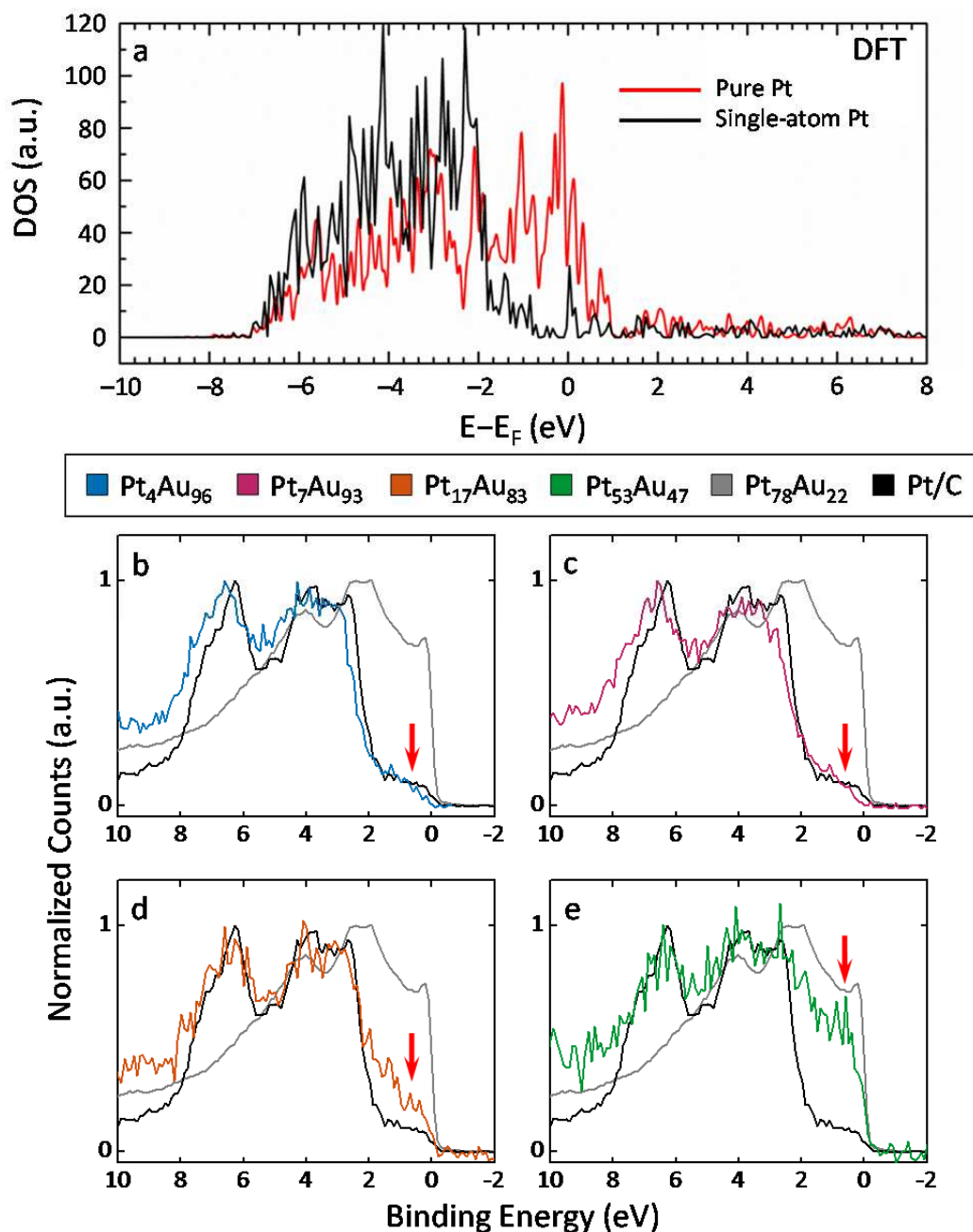


271
 272 **Fig. 4 | DFT-calculated binding of CO at PtAu surfaces.** **a, b, c,** Illustration of CO adsorption modes on model (111)
 273 lattices of pure, few-atom, and single-atomic Pt surfaces, respectively, including apical (*i*), bridging (*ii*), hcp hollow
 274 (*iii*), and fcc hollow (*iv*) coordination sites. **d,** Calculated adsorption energies for the indicated CO adsorption sites.
 275 **e, f,** Predominant FAO reaction pathways on few-atom (or greater) and single-atom Pt surfaces, highlighting the
 276 selectivity achieved via the ensemble effect.
 277

278 While a number of possible pathways exist for the oxidation of formic acid at Pt surfaces,
279 the dehydrogenation and dehydration pathways tend to predominate, overall (see Fig. 4e).³⁰ The
280 former pathway is responsible for the majority of the observed FAO activity of Pt, the latter is a
281 major concern, as it leads to the formation of adsorbed CO species at Pt sites and blocks them
282 from participating in future reaction steps. Due to its large impact on catalytic activity, surface
283 morphology also plays a large role in determining which of these two reaction pathways will
284 predominate. Both DFT calculations³¹ and experimental evidence³² support this observation,
285 indicating that only one Pt adsorption site is required for formic acid dehydrogenation, whereas
286 the indirect dehydration pathway requires a greater number of adjacent atoms. This so-called
287 “ensemble effect” strongly discourages the detrimental indirect reaction, leaving the direct
288 dehydrogenation reaction as the primary reaction pathway (see Fig. **Error! Reference source**
289 **not found.**4f). Thus, the formation of isolated single-atom catalytic sites can be linked to the
290 remarkable activity increases observed in these PtAu nanocatalysts.

291 Valence band analysis was also performed on the PtAu/C nanocatalyst using both DFT
292 density of states (DOS) calculations and XPS measurements to better understand the electronic
293 effect of alloy formation on catalytic activity. The DFT DOS results in Fig. 5a predict a drastic
294 reduction of intensity near the Fermi level (*i.e.*, 0 eV) for the single-atomic PtAu surface relative
295 to the pure Pt surface. Tellingly, in the XPS valence band measurements shown in Fig. 5b-e, the
296 near-Fermi level DOS (*i.e.*, -2 to 0 eV) is also found to be very sensitive to the local structural
297 environment of Pt. The two samples bearing single-atom Pt sites, Pt₄Au₉₆ and Pt₇Au₉₃, show the
298 lowest DOS intensity in the near-Fermi level region, being virtually identical to the pure Au
299 surface. In contrast, a pronounced increase in DOS intensity near the Fermi level is observed for
300 the few-atom-cluster Pt sample, Pt₁₇Au₈₃. Finally, when a more complete Pt shell is formed at the
301 Au nanoparticle surface in Pt₅₃Au₄₇, the near-Fermi level DOS becomes higher still and its
302 intensity begins to approach that of the pure Pt surface.

303 The aforementioned results indicate that samples containing larger amounts of Pt
304 demonstrate much more pronounced Pt character in their valence bands, resulting in increased
305 DOS intensities near the Fermi level. For single-atom Pt surfaces, however, no such Pt–Pt
306 bonding exists and the overall DOS is determined by the predominant Au–Au bonding. Thus, the
307 low DOS intensities observed near the Fermi level of single-atom Pt surfaces arises from the
308 large number of Au atoms relative to Pt. When Pt–Pt bonds begin to appear, as occurs in the few-



310
 311 **Fig. 5 | Calculated and experimental DOS.** a, Calculated DFT density of states (DOS) plots corresponding to the
 312 pure and single-atom Pt surfaces used to calculate CO adsorption energies in Fig. 4a-d. b, c, d, e, XPS valence band
 313 spectra of Pt₄Au₉₆, Pt₇Au₉₃, Pt₁₇Au₈₃, and, Pt₅₃Au₄₇ samples compared against those of Pt and Au foil references.
 314 Red arrows indicate the near-Fermi level region, wherein samples containing single-atom Pt sites show
 315 considerable difference from those containing few-atom cluster and core-shell Pt surfaces.
 316

317 atom Pt clusters of Pt₁₇Au₈₃, the DOS intensity of the near-Fermi level increases
318 considerably. These results are in good agreement with previous observations that DOS intensity
319 near the Fermi level is determined primarily by chemical bonding between like nearest neighbor
320 atoms.³³ This means that the identical near-Fermi level DOS intensities observed for Pt₄Au₉₆,
321 Pt₇Au₉₃, and the bulk Au reference prove, again, the single-atomic Pt structure for these two
322 PtAu nanoparticle samples. Furthermore, the valence band structure of PtAu nanoparticle
323 samples is also closely linked to their catalytic performance. Due to relativistic effects, the d-
324 orbitals of Au are higher in energy, and the valence s-orbital lower, than would typically be
325 expected, resulting in a shift of electron density from the former to the latter. As a result, Au
326 atoms are less able to accept σ -donated electrons and engage in π back-donation to adsorbed CO
327 molecules, weakening CO adsorption energies on these surfaces as was shown previously in Fig.
328 4.

329 In conclusion, bimetallic PtAu nanoparticles with extraordinary electrocatalytic FAO
330 activity have been synthesized using a facile and easily tuneable colloidal method. By
331 employing a comprehensive suite of structural characterization techniques, these PtAu
332 nanocatalysts were identified as having distinct Au-core/Pt-shell, few-atom Pt cluster, or single-
333 atom Pt surface structures, dictated by their relative elemental compositions. Structural
334 characterization revealed a high surface density of low-coordinate, single-atom Pt sites in
335 Pt₇Au₉₃ and Pt₄Au₉₆, which, according to the ensemble effect theory, prevented these catalysts
336 from self-poisoning via CO generation at their surfaces. Thus, the observed orders-of-magnitude
337 increase in Pt mass-normalized FAO activity for the best-performing PtAu nanocatalyst (single-
338 atomic Pt₄Au₉₆) relative to the poorest (core-shell Pt₇₈Au₂₂ and commercial Pt) is readily
339 explained in terms of surface structure and alloy bonding. DFT calculations further supported
340 these results by revealing weakened adsorption of CO to few-atom and single-atom Pt surfaces
341 as a result of both electronic effects arising from Pt-Au bonding interactions and the formation of
342 discrete single-atom Pt catalytic sites (*i.e.*, the ensemble effect). Unlike many other published
343 syntheses, only a single-step colloidal method was required to achieve a high degree of control
344 over surface structure and alloy bonding, and a very high surface packing density of single-atom
345 catalytic sites up to 7% can be achieved. As a result, the excellent electrocatalytic activity of
346 these PtAu nanoparticles represents remarkable progress in the development of single-atomic-

347 site Pt catalysis, with their exceptional selectivity enabling the use of highly active Pt to perform
348 reactions typically prohibited by CO poisoning.

349

350 **Methods**

351 Methods, including statements of data availability and any associated accession codes and references, are available
352 at <https://doi.org/10.1038>

353

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447

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461 corrected (S)TEM operating at 200keV.

462

463 **Author contributions**

464 P.N.D synthesized all samples, conducted the XAS experiments and analysis, performed some of
465 the electrochemical and TEM studies, and wrote the manuscript. P.Z. designed the project,
466 coordinated the whole process of the work, and supervised P.N.D. to conduct this research.
467 Z.Y.L. and J.Y. performed the HAADF-STEM measurements and image analysis. C.P.D.
468 performed the electrochemical experiments under the supervision of S.C. V.F. conducted the
469 DFT calculations under the supervision of D.J. X.Z contributed to the TEM measurements under
470 the supervision of N.Z. A.A. and Z.A. also contributed to part of the TEM measurements. T.R.
471 performed some of the XPS measurements at the Canadian Light Source.

472

473 **Competing Financial Interests**

474 The authors declare no competing financial interests.

475

476 **Additional information**

477 Supplementary information is available for this paper at <https://doi.org/10.1038>

478

479 **Methods**

480 **Materials.** Dihydrogen hexachloroplatinate ($\text{H}_2\text{PtCl}_6 \cdot 6\text{H}_2\text{O}$, 99.9 %), hydrogen tetrachloroaurate
481 ($\text{HAuCl}_4 \cdot 3\text{H}_2\text{O}$, 99.9 %), ethylene glycol (EG, 99+ %), and HiSPEC 3000 carbon-supported Pt
482 catalyst (Pt/C, ≤ 500 ppm impurities) were purchased from Alfa Aesar. Oleylamine (OAm, C18-
483 content 80-90 %) and formic acid (HCOOH , 99 %) were purchased from Acros Organics.
484 Vulcan XC-72 carbon powder was purchased from Cabot. Nafion® 117 Solution (Nafion, 5 %) and *n*-butylamine (BuNH_2 , 99.5 %) were purchased from Sigma Aldrich. Perchloric acid
485 (HClO_4 , 70 %) was purchased from Fisher Scientific. Ethanol used in cyclic voltammetry
486

487 experiments (EtOH, 96 %) was purchased from J.T. Baker. All reagents and solvents were used
488 as received, without further purification.

489 **Synthesis of PtAu Nanoparticles.** PtAu nanoparticles were prepared from stock solutions of Pt
490 and Au chloride precursor salts, with nominal compositions of 10, 25, 50, and 75 atom% Pt
491 being selected by controlling the ratio of precursors used. In a typical synthesis, 72.5 mg
492 $\text{H}_2\text{PtCl}_6 \cdot 6\text{H}_2\text{O}$ and 55.1 mg $\text{HAuCl}_4 \cdot 3\text{H}_2\text{O}$ were each dissolved in 70 mL of OAm through a
493 combination of ultrasonication and manual mixing to obtain metal precursor stock solutions.
494 Appropriate volumes of these Pt and Au stock solutions (prepared in OAm) were then added to a
495 100 mL round-bottom flask to give the desired Pt-to-Au ratio with a total volume of 20 mL. An
496 additional 20 mL of EG was then added while mixing vigorously using a magnetic stirrer. The
497 resulting mixture was subsequently bubbled with $\text{N}_{2(\text{g})}$ for several minutes in order to remove
498 dissolved $\text{O}_{2(\text{g})}$ from solution. Each mixture was then placed in a 180 °C oil bath, sealed, and
499 allowed to react for 1 h. Once the reaction was complete, flask was removed from heat and
500 allowed to cool to room temperature while still sealed under a $\text{N}_{2(\text{g})}$ atmosphere. Due to the large
501 excess of reducing agents employed in this reaction (OAm and EG, also functioning as solvents),
502 all Pt^{4+} and Au^{3+} species can reasonably be assumed to have been reduced to a zero-valent state.
503 In order to purify the product nanoparticles, each sample was divided amongst several 30 mL
504 polypropylene centrifuge tubes. The nanoparticles were precipitated via addition of two to three
505 volume equivalents of EtOH, and then isolated by centrifuging the resulting suspension (at 6,000
506 RPM for 5 min) and decanting the supernatant. The precipitated nanoparticles were then
507 redispersed in hexanes via brief ultrasonication and shaking before being again precipitated and
508 centrifuged. After this second centrifugation cycle, the purified nanoparticles were redispersed in
509 hexanes and centrifuged once more to remove any insoluble material.

510 **Deposition of PtAu Nanoparticles onto XC-72 Carbon Powder.** Following purification, the
511 nanoparticle samples were deposited onto an XC-72 carbon powder support material via ligand
512 exchange-induced destabilization. A nanoparticle loading of 20 wt% (by total mass of Pt and Au)
513 was selected in order to allow for better comparison with the commercial Pt/C catalyst (HiSPEC
514 3000, 20 wt% Pt) used as a reference material for electrocatalytic testing. For each sample, four
515 mass equivalents of XC-72 powder (assuming a theoretical yield of 100 % for each nanoparticle
516 sample) were added to 15 mL of BuNH_2 and thoroughly dispersed via ultrasonication. Each
517 purified nanoparticle sample was then precipitated using EtOH and isolated via centrifugation

518 and decantation. The isolated nanoparticle material was redispersed and extracted from the
519 centrifuge tube using ultrasonication and successive aliquots of the previously prepared XC-
520 72/BuNH₂ suspension. This final mixture was then allowed to stir magnetically for 24 h in order
521 to allow the ligand exchange and nanoparticle deposition to occur gradually. Finally, the post-
522 deposition PtAu nanoparticle materials were isolated once more via EtOH addition and
523 centrifugation (at 12,000 RPM for 20 min) and allowed to dry in air.

524 **Transmission Electron Microscopy.** Bright field TEM imaging of the samples was performed
525 both prior to and following deposition onto the XC-72 carbon support. In preparation for
526 analysis, each sample was dispersed in *ca.* 200 μ L EtOH via sonication and drop-cast onto
527 Formvar-coated copper TEM grids. Unsupported PtAu nanoparticle samples were imaged using
528 a JEOL JEM-2100F transmission electron microscope operated at a 200 kV accelerating voltage.
529 PtAu nanoparticle samples supported on XC-72 carbon powder were imaged using a Tecnai F-30
530 transmission electron microscope operated at a 300 kV accelerating voltage. Size distributions
531 and mean particle diameters of the nanoparticles were measured and calculated using
532 MacBiophotonics ImageJ software³⁴ using several representative images from each sample.
533 HAADF and EDX mapping measurements were performed at the University of Birmingham
534 (UK) using a JEOL 2100F scanning transmission electron microscope with a CEOS aberration-
535 corrector. A JEOL annular dark field detector was used for HAADF imaging and a Bruker
536 XFlash 4030 silicon drift detector was used for EDX mapping of the PtAu nanoparticle samples.
537 During the EDX mapping, the HAADF-STEM images were monitored to check for possible
538 beam-induced structure changes of the atomic structure. EDX data presented are from only those
539 nanoparticles that did not show any visible structural changes.

540 **X-ray Absorption Spectroscopy.** XAS measurements were performed using the Sector 20-BM
541 beamline of the Advanced Photon Source at Argonne National Laboratory in Argonne, IL. The
542 end-station was equipped with a double-crystal Si(111) monochromator for wavelength
543 selection, which was detuned to 80 % in order to help reject higher harmonics of the desired
544 energy; a toroidal focusing mirror was also employed to further enhance harmonic rejection.
545 Gas-ionization detectors were used to measure the absorption spectra of Pt and Au foil reference
546 materials; however, data acquisition from the bimetallic nanoparticles was complicated by
547 overlap between the spectra obtained at the Pt and Au L₃-edges (occurring at 11,562.76 eV and
548 11,919.70 eV, respectively³⁵). This challenge was addressed by employing a 12-element Ge

549 fluorescence detector to collect data from the bimetallic PtAu nanoparticles. Although there also
550 exists overlap between the Pt and Au L_{α} emission peaks centered at 9,442.3 eV and 9,713.3 eV,
551 respectively³⁶), nearly all of the interfering signal could be filtered out by excluding the
552 overlapping energy region between the two (as depicted in Supplementary Fig. 12). While
553 excluding this region also resulted in a reduction of fluorescence intensity, the loss was largely
554 offset by the greater sensitivity of the fluorescence detector relative to standard absorption
555 detectors. As a result, useable spectra were obtained for all samples through the use of this
556 method. In order to compensate for the greater amount of noise present in the fluorescence data,
557 PtAu nanoparticle samples were held at 90 ± 1 K during measurement in order to enhance
558 EXAFS signal intensity by suppressing thermal vibrations in the material. Full details regarding
559 the data ranges (“k-range” and “R-range”) used to obtain and fit the FT-EXAFS spectra are
560 presented in the Supporting Information (Supplementary Table 4). Data processing and fitting
561 were performed using WinXAS³⁷ and Analyzer v0.1 software, with scattering paths generated by
562 FEFF8³⁸. S_0^2 values for Pt and Au (both equal to 0.93) were obtained by fitting a metallic
563 reference foil of same element. A bulk, homogeneous PtAu alloy structural model was used to
564 calculate the Pt–M and Au–M scattering paths used in FT-EXAFS fitting. A single metal-metal
565 scattering path was used in fitting the FT-EXAFS data because insufficient degrees of freedom
566 were available to include separate Pt and Au scattering paths; the Pt–M and Au–M fitting values
567 reported herein thus represent averages of the Pt–Pt/Pt–Au and Au–Au/Au–Pt contributions.

568 **X-ray Photoelectron Spectroscopy.** X-ray photoelectron spectroscopy (XPS) measurements
569 were performed at Canadian Light Source in Saskatoon, Canada, using an excitation energy of
570 3,000 eV at the SXRMB beamline and an excitation energy of 300 eV at the SGM beamline.
571 PtAu/C nanocatalyst samples were prepared by spreading the powder onto conductive, double-
572 sided carbon tape, which was then affixed to a copper sample holder. Many scans of each sample
573 were averaged together in order to obtain higher signal-to-noise ratios. Relative PtAu
574 compositions were determined from peak areas obtained by fitting the Pt and Au 4f peaks using
575 Au^0/Au^+ and Pt^0/Pt^{2+} contributions in conjunction with empirically derived atomic sensitivity
576 factors.³⁹ Splitting between $4f_{5/2}$ and $4f_{7/2}$ peaks was set based upon data obtained from the
577 NIST X-ray Photoelectron Spectroscopy Database.⁴⁰ Full-width at half-maximum values for the
578 $4f_{5/2}$ and $4f_{7/2}$ peaks within each contribution were correlated to be equal, and relative area ratios
579 were correlated such that $area(4f_{7/2}):area(4f_{5/2}) = 4:3$. XPS valence band spectra were collected

580 using an excitation energy of 3,000 eV and normalized by setting the valence band maximum
581 equal to unity.

582 **Cyclic Voltammetry.** Cyclic voltammetry was performed using a CHI 710 electrochemical
583 work station with a three-electrode setup, including a polished glassy carbon working electrode
584 (rotating disc electrode), a Ag/AgCl reference electrode, and a Pt sheet counter electrode. A
585 solution of 0.1 M perchloric acid was used as the supporting electrolyte, with the addition of 0.1
586 M formic acid during FAO activity measurements. Catalyst “ink” suspensions were prepared by
587 dispersing the carbon-supported PtAu material in EtOH via ultrasonication to obtain a final
588 catalyst concentration of $1 \mu\text{g}\cdot\mu\text{L}^{-1}$. A volume of the Nafion solution equal to 1 % the volume of
589 added EtOH was then added and sonicated for a further 15 min to complete the preparation. For
590 ORR testing, 20 μL of the catalyst ink were drop-cast onto the glassy carbon electrode surface
591 and allowed to dry completely. A 3 μL volume of a diluted Nafion solution (20 % v/v in EtOH)
592 was then deposited onto the dried catalyst layer in order to help improve its physical stability and
593 electrical conductivity. The electrode surface was allowed to dry completely prior to
594 electrochemical testing. After purging the electrolyte solution with ultrahigh purity $\text{N}_{2(\text{g})}$, CV
595 measurements were performed. Pt electrochemically active surface areas (ECSAs) were
596 calculated from the integrated region beneath the H-desorption peaks in each voltammograms,
597 whereas Au ECSAs were estimated from the integrated area of the Au–O adlayer removal peak.
598 **DFT Calculations.** DFT calculations were performed using Vienna *ab initio* package (VASP)
599 software. The revised Perdew-Burke-Erzerhof (RPBE) form of the generalized-gradient
600 approximation (GGA) was chosen for electron exchange and correlation in order to correct for
601 the over-binding of small molecules at transition metal surfaces observed using the standard
602 Perdew-Burke-Erzerhof approach. Although DFT-RPBE tends to overstabilize the hollow and
603 bridge sites over the atop site for CO adsorption on Pt(111), the adsorption energies on these
604 sites are quite close (within 0.10 eV) and in good agreement with the experimental value.⁴¹ The
605 electron-core interaction was described using the projector-augmented wave method (PAW). A
606 kinetic energy cutoff of 450 eV was used for the planewaves, and the Brillouin zone was
607 sampled using a $3\times 3\times 1$ Monkhorst-Pack scheme. The surface model slab was created using a
608 4×4 supercell of the Pt/Au unit cell, with four atomic layers and a 15 Å unit cell. Adsorption
609 energies were calculated using the following equation:

610
$$E_{\text{ads}} = E_{\text{surface+adsorbate}} - (E_{\text{surface}} + E_{\text{adsorbate}})$$

611 wherein the energy of the adsorbate, $E_{adsorbate}$, was computed by placing the CO adsorbate
612 molecule in a 10 Å wide cubic cell vacuum to prevent intermolecular interactions resulting from
613 the periodic boundary conditions.

614

615 **Data availability.**

616 The data supporting the results of this work are available from the authors on reasonable
617 requests.

618