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1 Revisited mechanisms for glucose electrooxidation at platinum and gold 2 nanoparticles

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10 **Abstract**

11 *The electrooxidation of glucose on gold (Au) and platinum (Pt) nanoparticles (NPs) is*
12 *investigated in alkaline medium by cyclic voltammetry after chronoamperometry at*
13 *different potentials (+0.100 V, +0.200 V and +0.400 V vs the reversible hydrogen*
14 *electrode, RHE), in situ Fourier transform infrared spectroscopy and differential*
15 *electrochemical mass spectrometry measurements. We show that glucose can*
16 *adsorb on both metallic Au and Pt surfaces at low potentials, but that the adsorbed*
17 *species are different: hydrogen atoms, carbon monoxide (CO), lactones and*
18 *gluconate species on Pt-NPs, and only hydrogen atoms and gluconate species on*
19 *Au-NPs. On Pt-NPs, the first oxidation peak between +0.050 V vs RHE and +0.250 V*
20 *vs RHE is due to glucose adsorption and hydrogen atoms oxidation into protons (H⁺),*
21 *whereas the second electrochemical feature between +0.250 V vs RHE and +0.800*
22 *V vs RHE is due to the oxidation of glucose into lactone, gluconate and of adsorbed*
23 *CO into carbon dioxide (CO₂). For Au-NPs, adsorbed hydrogen atoms are not*
24 *oxidized into H⁺ but transformed into molecular hydrogen H₂, and glucose is*
25 *adsorbed as gluconate species that are desorbed into gluconates for potentials*
26 *higher than +0.300 V vs RHE.*

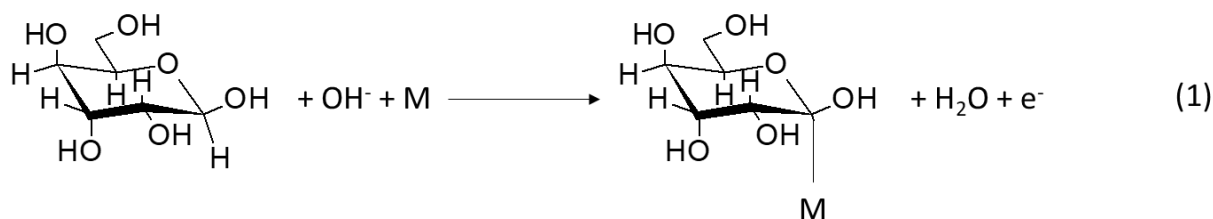
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28 **Keywords:** Glucose, Electrooxidation, Gold, Platinum, *in situ* Fourier transform
29 infrared spectroscopy, Differential electrochemical mass spectrometry, Reaction
30 mechanism.

31 **1. Introduction**

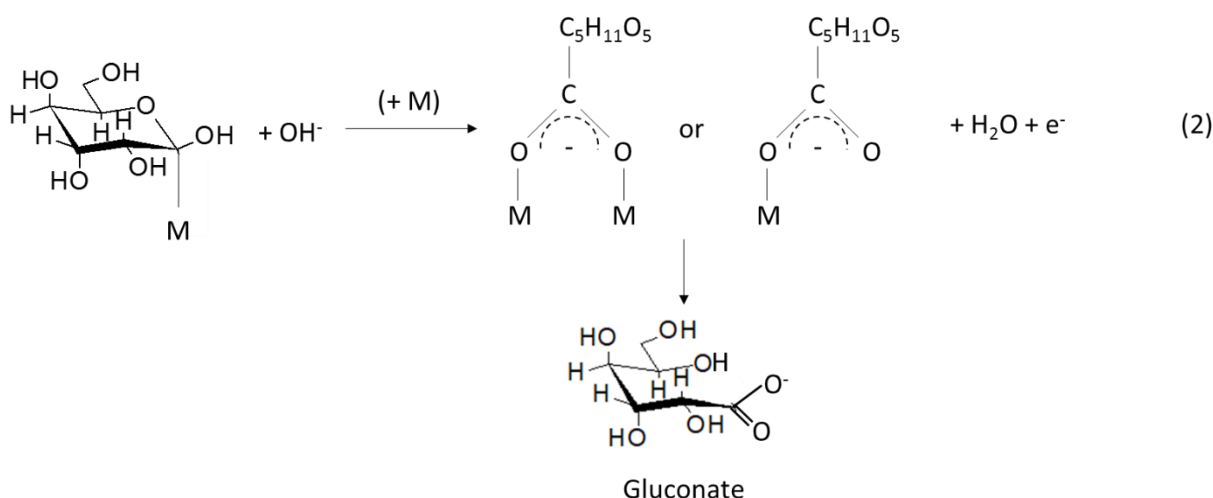
32 The increasing demand for energy and raw materials and the depletion of the fossil
33 fuel resources [1] have made the use of substantial alternative resources mandatory.
34 Non-edible lignocellulosic biomass issued from agriculture residues, grass and
35 forests represents annually more than 12 billion tons [2]. Therefore, it is then
36 considered as a rich renewable hydrogen and carbon reservoir to harvest both
37 energy and chemicals [3]. Non-edible lignocellulosic biomass is composed of around
38 20% lignin, 30–45% cellulose (linear crystalline polymers of glucose units [4]) and
39 20–50% hemicellulose (branched polymers of mainly xylose and glucose [5]),
40 depending on the feedstock [4]. Therefore, hydrolysates after lignocellulosic
41 pretreatments to separate lignin from cellulose and hemicellulose [6] contain more
42 than 50 mol. % of glucose; glucose accounts then for more than 40 % of the whole
43 lignocellulosic biomass (lignin accounting for ca. 20 %), which represents a very huge
44 quantity of raw materials for production of chemicals. Noteworthy, electroreforming of
45 glucose in an electrolysis cell can produce high value-added chemicals at the anode
46 together with pure hydrogen at the cathode [7,8]. In this context, unveiling the
47 oxidation mechanism of glucose (considered as a model molecule) is of paramount
48 importance and will further allow developing active and selective catalysts in view of
49 the production of value-added compounds, such as gluconic acid, at high conversion
50 rate and selectivity.

51 The electrooxidation of glucose in alkaline media has been extensively studied on
52 bulk platinum (Pt) and gold (Au) [9-14], because of their high activity. The mechanism
53 generally accepted on both metal surfaces involves the adsorption of glucose on a
54 metallic Pt or Au site (M) through the anomeric function according to the following
55 reaction (1):



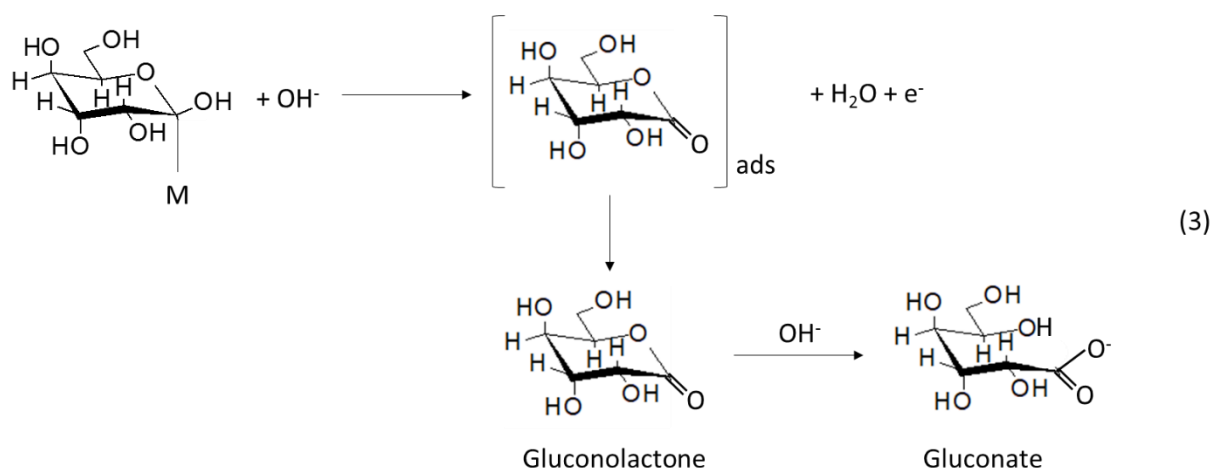
56

57 followed by an attack of the C-M bond by a hydroxyl anion in solution to produce
 58 weakly bonded gluconate species that later desorb in the electrolyte according to the
 59 reaction scheme (2):



60

61 A second mechanism was proposed for potential higher than +0.600 V vs RHE on Pt
 62 [9] and as an alternative path on Au [13]. It consists of the oxidation of the adsorbed
 63 dehydrogenated glucose species into δ -gluconolactone. After desorption, δ -
 64 gluconolactone is hydrolyzed in the presence of a hydroxyl anion in the electrolyte
 65 into gluconate, according to reaction scheme (3):



66

67 However, considering that Pt proved to be extremely non-selective compared to Au

68 at low electrode potentials and that the cyclic voltammograms recorded on both

69 materials differ dramatically in terms of shapes and oxidation waves/peaks potentials,

70 one may find very surprising that similar mechanisms are proposed (and accepted)

71 for the glucose oxidation reaction (GOR) on both Pt and Au [9,13,14]. In our view,

72 these experimental features rather suggest the existence of electrocatalyst-

73 dependent glucose oxidation mechanisms.

74 The present contribution aims at going beyond these uncertainties by providing new

75 insights into the adsorption modes of glucose, the intermediates and the final

76 products formed both as a function Pt or Au surfaces and of the electrode potentials

77 to propose mechanisms of the GOR on Pt and Au nanoparticles (Pt-NPs and Au-

78 NPs). The knowledge of the reaction mechanisms is paramount important because it

79 is mandatory to be able to design very active catalysts with great selectivity towards

80 the desired product. To our knowledge, it is the first time that the herein-employed

81 complementary analyses are performed to obtain important information allowing

82 proposing different GOR processes according to the catalytic material and the

83 electrode potential. These analyses consist of (i) cyclic voltammograms recorded

84 after chronoamperometry at different potentials to verify the poisoning of the

85 surfaces, (ii) spectra from *in situ* Fourier transform infrared spectroscopy (*in situ*
86 FTIRS) to determine intermediates/products formed at the electrode/electrolyte
87 interface and (iii) differential electrochemical mass spectrometry (DEMS)
88 measurements to determine volatile compounds formed.

89 **2. Experimental**

90 **Materials.** Hexachloroplatinic acid hexahydrate ($\text{H}_2\text{PtCl}_6 \cdot 6 \text{H}_2\text{O}$) and
91 tetrachloroauric acid trihydrate ($\text{HAuCl}_4 \cdot 3 \text{H}_2\text{O}$), both 99.99% in purity, were
92 purchased from Alfa Aesar, polyethylene glycol dodecyl ether (Brij[®] L4), acetone
93 (Chomasolv[®], 99.8% in purity), sodium borohydride (NaBH_4 , Reagent Plus, 99% in
94 purity), NaOH (semiconductor grade, 99.99% in purity), glucose (99% in purity) and
95 Nafion 5 wt.% in aliphatic alcohols from Sigma-Aldrich, and n-heptane (99% in purity)
96 from Acros Organics. A Milli-Q-Millipore system was used to provide ultra-high purity
97 water (18.2 M Ω cm, < 2 ppb Total Organic Carbon).

98 All chemicals were used as received, except the carbon powder (Vulcan XC72 from
99 Cabot Corp., further called C), which was heat-treated at 673 K under N₂ atmosphere
100 (U-quality from Air Liquide) for 4 hours to remove adsorbed impurities.

101 **Synthesis and characterization of carbon-supported catalysts**

102 The protocol of the water-in-oil route for the synthesis of Pt-NPs/C and Au-NPs/C
103 catalysts was described elsewhere, as well as the characterization methods to
104 determine the metal loading, the particle and the crystallite sizes [7,10,15]. The
105 results are given in Table 1.

106

107

108

109

110 **Table 1.** Characterization data for the Pt/C and Au/C catalysts prepared by a water-in-oil
 111 route: metal loading, W , from thermogravimetric analysis (TGA), cell parameter, a , and mean
 112 crystallite size, L_v , from X-ray diffraction (XRD) measurements, mean particle size, d_{TEM} , from
 113 transmission electron microscopy (TEM) and electrochemical surface area, $ECSA$, from
 114 cyclic voltammetry measurements.

	$W / \text{wt.}\%$	$a / \text{\AA}$	L_v / nm	d_{TEM}	$ECSA / \text{m}^2 \text{g}^{-1}$
Pt-NPs/C	39.0	3.916	3.5	5.2	41
Au-NPs/C	35.4	4.047	4.4	6.8	14

115 **Electrochemical measurements.** Chronoamperometry (CA) and cyclic
 116 voltammograms (CV) were recorded at 293 K in a three-electrode cell using a
 117 Voltalab PGZ402 potentiostat (Radiometer Analytical). The reference electrode was a
 118 home-made reversible hydrogen electrode (RHE), the counter electrode was a 3 cm²
 119 geometric surface area glassy carbon plate, and the working electrode consisted of a
 120 100 $\mu\text{g}_{\text{metal}} \text{cm}^{-2}$ catalytic layer deposited on a 0.071 cm² geometric surface area
 121 glassy carbon disc. The electrolyte consisted of a N₂-purged 0.10 mol L⁻¹ NaOH
 122 aqueous solution for catalyst characterization, to which 0.10 mol L⁻¹ of glucose was
 123 added for electrooxidation measurements. More experimental details are given
 124 elsewhere [7,10,15].

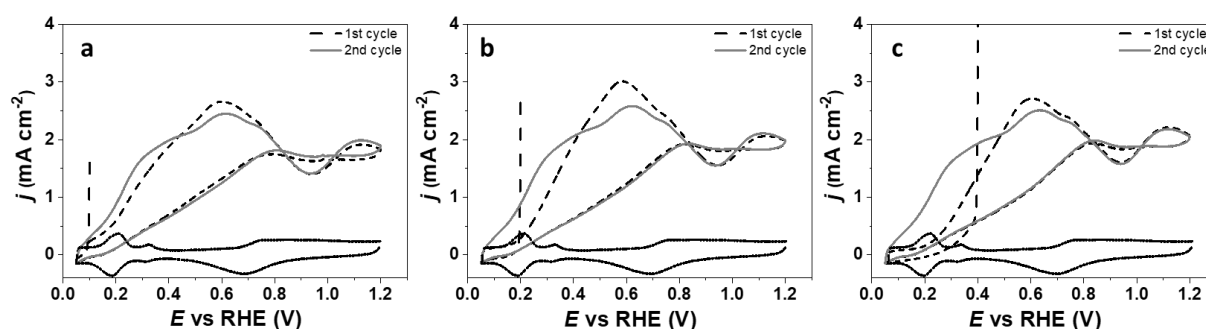
125 **In situ FTIR spectroscopy.** FTIRS measurements were performed using a Bruker
 126 IFS 66 FTIR spectrometer modified for beam reflection on the electrode surface. The
 127 incident angle and the spectral resolution were 65° and 4 cm⁻¹, respectively. Detailed
 128 experimental conditions can be found elsewhere [16,17]. 512 interferograms
 129 recorded for 35 s during the linear voltammetry at 0.001 V s⁻¹ carried out in a 0.10
 130 mol L⁻¹ NaOH + 0.10 mol L⁻¹ glucose electrolyte were averaged every 0.050 V from
 131 +0.050 to +1.200 V vs RHE. Spectra were normalized considering the averaged one
 132 recorded at +0.050 V vs RHE as the reference. By this way, negative absorption
 133 bands correspond to the formation of species and positive absorption bands to the
 134 consumption of species at the electrode surface [7,10].

135 **Differential electrochemical mass spectrometry measurements (DEMS).** A
136 Pfeiffer Vacuum QMG 220 M1 quadrupole mass spectrometer was used for on-line
137 differential electrochemical mass spectrometry measurements. The description of the
138 method can be found elsewhere [18-20]. The current vs potential curves were
139 recorded simultaneously with the mass intensity vs potential curves, for selected
140 values of m/z (mass/charge) ionic signals (here $m/z = 2$ for dihydrogen detection and
141 $m/z = 44$ for carbon dioxide detection have been particularly surveyed). The working
142 electrodes were prepared in the form a Pt or Au nanoporous layer (0.28 cm^2 area, 50
143 nm +/- 10 nm average thickness), obtained by sputtering onto a porous
144 polytetrafluoroethylene (PTFE) membrane (pore size $0.02 \text{ }\mu\text{m}$, thickness $20 \text{ }\mu\text{m}$,
145 Cobetter filtration[®]), which serves as interface between the electrochemical cell and
146 the high vacuum chamber of the mass spectrometer. The Pt/PTFE or Au/PTFE
147 working electrode (WE) were connected to a VMP2Z potentiostat (Biologic[®]) via a
148 ring-shaped Au (for an Au WE) or Pt (for a Pt WE) current collector. The counter
149 electrode (CE, Pt grid) was located near the surface of the electrolyte, as far as
150 possible from the working electrode to avoid any interference with the H_2 bubbles that
151 can be formed at the CE when the glucose oxidation reaction proceeds on the WE.
152 The electrochemical measurements were first performed in 0.01 L of 0.10 mol L^{-1}
153 NaOH supporting electrolyte to determine the $m/z = 2$ and $m/z = 44$ signal baselines.
154 A $171 \text{ }\mu\text{L}$ aliquot of 0.595 mol L^{-1} glucose in 0.10 mol L^{-1} NaOH solution was added at
155 open circuit potential (ocp) conditions to reach 0.010 mol L^{-1} glucose, the changes of
156 potential and m/z signals being measured concomitantly. The amounts of evolved H_2
157 and CO_2 were measured during a CV (0.010 V s^{-1}) of glucose oxidation reaction from
158 the ocp to $+0.050 \text{ V}$ vs RHE as lower potential limit and $+1.500 \text{ V}$ vs RHE as upper
159 potential limit.

160

161 3. Results

162 The mechanism generally proposed for the electrooxidation of glucose at Pt and Au
163 surfaces involves the adsorption of glucose as the first step. To test this hypothesis,
164 chronoamperometry (CA) were performed at different electrode potentials until a
165 stable current density was reached. The CAs were followed by CVs recorded in the
166 negative scan direction from the CA potential to +0.050 V vs RHE and then between
167 +0.050 V vs RHE and +1.200 V vs RHE (Figs. 1 and 2 for Pt-NPs/C and Au-NPs/C,
168 respectively). For clarity reasons, only the first and second CVs are represented in
169 Figs. 1 and 2, because additional CVs perfectly superimposed with the second one.

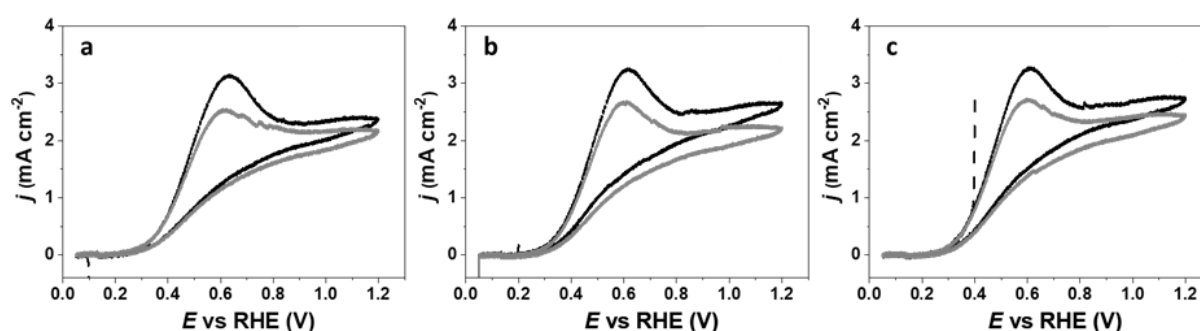


170

171 **Fig. 1** CV of the Pt-NPs/C electrode in 0.1 mol L⁻¹ NaOH electrolyte (plain black line);
172 CA performed at (a) +0.100 V vs RHE, (b) +0.200 V vs RHE and (c) +0.400 V vs
173 RHE followed by a first CV (dotted black line), and a second CV (plain gray line)
174 recorded in N₂-purged 0.10 mol L⁻¹ NaOH electrolyte in the presence of 0.10 mol L⁻¹
175 glucose at a Pt-NPs/C electrode. Scan rate = 0.005 V s⁻¹, T = 293 K.

176 On a Pt-NPs/C electrode (Fig. 1), two oxidation waves, the first one between +0.050
177 V and +0.200 V vs RHE and the second one between +0.200 V and +0.500 V vs
178 RHE, and an oxidation peak at ca. +0.600 V vs RHE can be seen in the potential
179 range from +0.050 to +0.800 V vs RHE. These electrochemical features were already
180 observed by Beden *et al.* [9] on a bulk Pt surface, although with different relative
181 intensities compared to those reported for Pt-NPs/C. After the CA at +0.100 V vs
182 RHE, the first CV is slightly shifted towards higher potentials compared to the second

183 one, but all features are still visible between +0.050 and +0.800 V vs RHE, indicating
184 that the surface is only slightly covered by adsorbed species. When the CA potential
185 is increased, the oxidation wave of the first CV is delayed toward more positive
186 potentials compared with the second one, which seems to indicate either that there
187 are more adsorbed species on the Pt surface or that they are more strongly
188 adsorbed, or even that the adsorbed species are not the same according to the CA
189 potential.

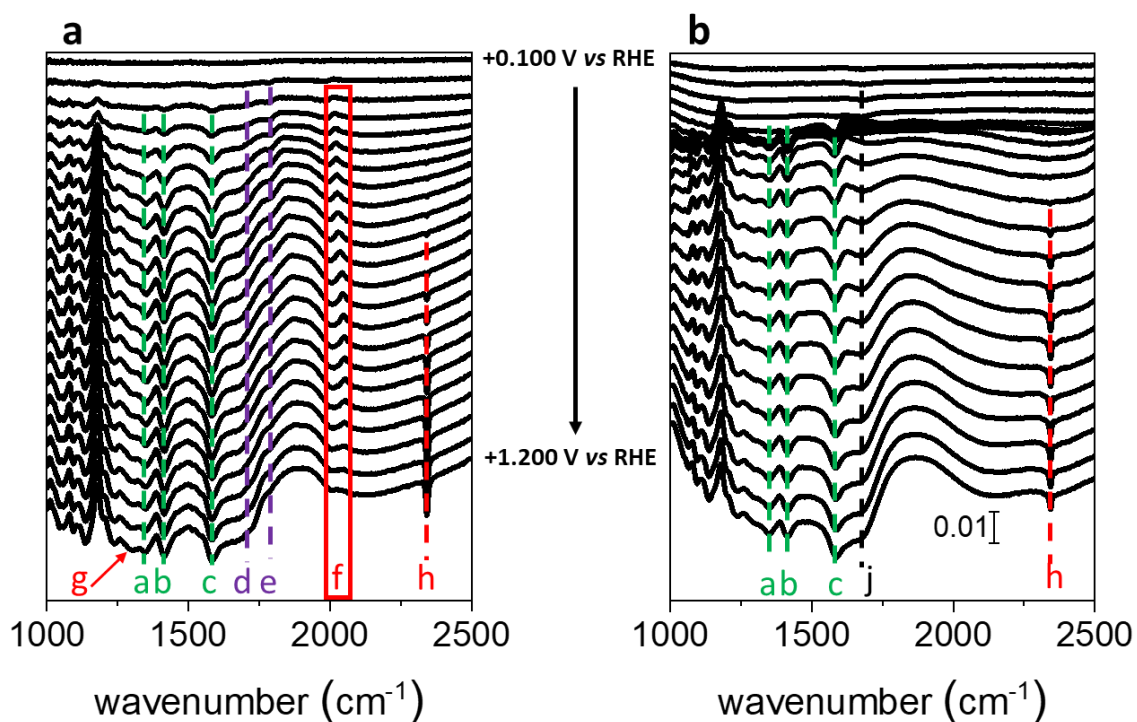


190

191 **Fig. 2** Cyclic voltammograms recorded in N_2 -purged 0.10 mol L^{-1} NaOH electrolyte at
192 an Au-NPs/C electrode in the presence of 0.10 mol L^{-1} glucose (black line for the first
193 cycle and grey line for the second one), after chronoamperometry (black dotted line)
194 at (a) +0.100 V vs RHE, (b) +0.200 V vs RHE and (c) +0.400 V vs RHE; scan rate =
195 0.005 V s^{-1} , $T = 293 \text{ K}$

196 In the case of an Au-NPs/C electrode (Fig. 2), the first CVs recorded after CA at
197 different potentials display an onset potential at ca. +0.300 V vs RHE, a peak current
198 at ca. 0.600 V vs RHE and a diffusion plateau from +0.800 V vs RHE. Such behavior
199 was already observed for bulk CO oxidation on Pt-based catalyst and is typical of
200 strong poisoning of the surface by adsorbed species at low potentials [21] and
201 limitation by diffusion in the plateau region. The adsorption of glucose on metallic
202 gold has already been described in the literature [9,13]. The peak current density as
203 well as the current densities in the plateau region between +0.800 and +1.200 V vs
204 RHE are higher than those for the second stable cycle. The higher peak current
205 density of the first cycle suggests that more species are adsorbed on Au surface

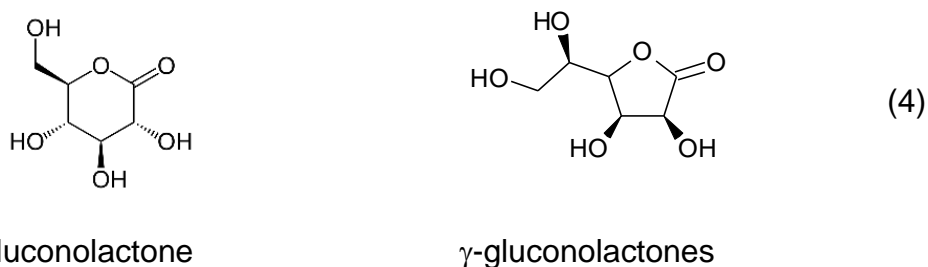
206 during all CAs at constant potential than during linear potential variation for the
 207 second cycle. However, conversely to the case of the Pt-NPs/C electrode, where the
 208 great dependence of the shape of the first CV on the CA potential was explained in
 209 terms of changes in amount of adsorbed species on the Pt surface or in their
 210 adsorption strength, or in their nature, the similarity in the case of the Au-NPs/C
 211 electrode of CV shapes and achieved current densities whatever the CA potential
 212 speaks rather towards invariance of the nature of the adsorbates and of their
 213 coverage on the Au-NPs/C electrode. Taken together, the results also point towards
 214 different initial steps of glucose oxidation at Au-NPs and Pt-NPs surface.
 215 Fourier transform infrared (FTIR) spectra were recorded at Pt-NPs/C and Au-NPs/C
 216 electrodes during a linear scan voltammetry (LSV) at 0.001 V s^{-1} in 0.10 mol L^{-1}
 217 $\text{NaOH} + 0.10 \text{ mol L}^{-1}$ glucose aqueous electrolyte (Fig. 3).



218
 219 **Fig. 3** Fourier transform infrared spectra recorded every 0.050 V during 0.10 mol L^{-1}
 220 glucose electrooxidation in 0.10 mol L^{-1} NaOH electrolyte from $+0.100 \text{ V}$ to $+1.200 \text{ V}$
 221 vs RHE on (a) Pt-NPs/C and (b) Au-NPs/C catalysts. Scan rate: 0.001 V s^{-1} ,
 222 resolution 4 cm^{-1} , $T = 293 \text{ K}$. Vertical scale: $\Delta R/R$

223 Fig. 3a displays the spectra recorded from +0.100 V to +1.200 V vs RHE on a Pt-
224 NPs/C electrode. A negative IR band located 1581 cm^{-1} is visible starting from
225 +0.150 V vs RHE. Simultaneously, IR bands appear in the $1340\text{ cm}^{-1} - 1420\text{ cm}^{-1}$
226 wavelength region. The negative bands are located at 1346 cm^{-1} and 1415 cm^{-1} , and
227 a positive one at 1388 cm^{-1} . The spectrum of glucose recorded in alkaline solution
228 (supporting information, SI 1) shows a weak band at ca. 1363 cm^{-1} , that could
229 translate into a positive band during glucose consumption. However, looking closely
230 at the positive band height, it always reaches the same value as that of the baseline
231 at ca. 1500 cm^{-1} . This is even more obvious when looking at the *in-situ* IR spectra
232 recorded on $\text{Pt}_9\text{Bi}_1/\text{C}$ catalyst during glucose electrooxidation [10], where both
233 negative bands display high intensities. Moreover, the *in situ* infrared spectra of
234 methylglucoside (supporting information, SI 2) display two negative bands
235 corresponding to the formation of carboxylate species in the same wavenumber
236 region as for glucose oxidation ($1340 - 1420\text{ cm}^{-1}$), without the positive one between
237 those two negative bands. At last, the bands at 1415 cm^{-1} (band b) and at 1581 cm^{-1}
238 (band c) were assigned to the formation of gluconate ($\nu_{\text{sym.}}$ and $\nu_{\text{asym.}}$ O-C-O,
239 respectively) and the one at 1346 cm^{-1} (band a) attributed to the $\delta(\text{CH}_2)$ mode of
240 gluconate or gluconolactone by Beden *et al.* [9]. But it is possible that a small positive
241 band related to glucose consumption exists in the spectra, together with the two
242 negative bands already attributed by Beden *et al.* [9]. The intensities of these three
243 negative bands increase with an increase in the electrode potential. Gluconate is
244 then formed at low electrode potential at a Pt-NPs/C electrode. The absorption band
245 in the $2000\text{ to }2100\text{ cm}^{-1}$ wavenumber range (band f) appearing from +0.150 V vs
246 RHE is assigned to the formation of linearly adsorbed CO (CO_{ads}) [22,23]. This band
247 appears positive from +0.200 V vs RHE, shifts by $51.5\text{ cm}^{-1}\text{ V}^{-1}$ (not linearly) towards

248 lower wavenumbers between +0.200 V and +0.750 V vs RHE and stabilizes at 2052
 249 cm^{-1} at higher potentials. This result suggests that CO_{ads} species are formed at
 250 potentials lower than +0.200 V vs RHE and progressively depleted from the surface
 251 as the potential is increased. The red shift of the signal may correspond to a
 252 decrease of the CO surface coverage upon increasing potentials, sign of progressive
 253 consumption of the CO_{ads} species formed at low potential. The small band g (pointed
 254 by an arrow) and the band h, located at 1304 cm^{-1} and 2343 cm^{-1} , respectively, are
 255 compatible with the formation of hydrogenocarbonate ions (HCO_3^-) [24] from ca.
 256 +0.250 V vs RHE and CO_2 [25] for potentials higher than +0.500 V vs RHE on Pt-
 257 NPs/C electrode. Another interesting band (band e) at 1785 cm^{-1} , in the carbonyl
 258 region, can be attributed to the formation of γ -gluconolactone ($\nu_{\text{C=O}}$) [9] and is
 259 detected negative from +0.150 V vs RHE. A shoulder (band d) around 1720 cm^{-1} ,
 260 that could be attributed to $\nu_{\text{C=O}}$ of δ -gluconolactone [9] is detected at high potentials
 261 (but the band exists already form ca. +0.150 / +0.200 V vs RHE). Chemical structures
 262 of δ - and γ -gluconolactones are given in scheme (4):

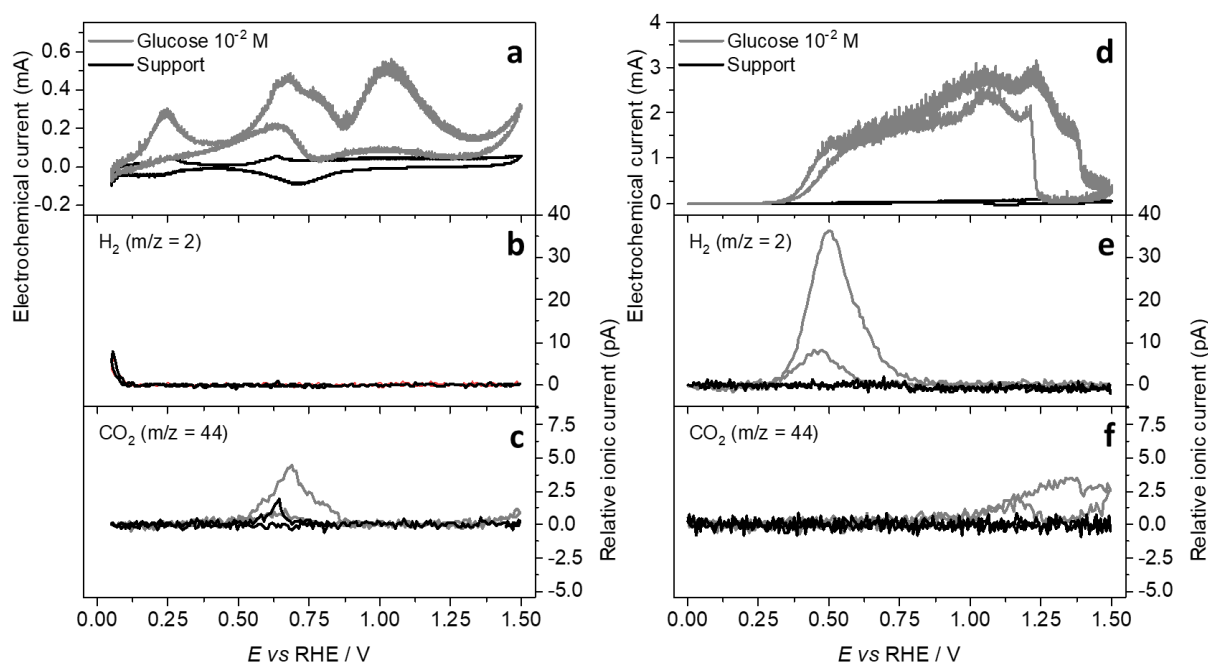


267 Importantly, the bands characteristic of such species do not appear for the oxidation
 268 of methylglucoside on a Pt-NPs/C electrode, i.e. when the anomeric function of
 269 glucose is protected by a methyl group, and when the C6 primary alcohol is oxidized
 270 (supporting information, SI 2) [10]. Their presence in Fig. 3a is strong evidence that
 271 the anomeric function was oxidized and that gluconolactones did form from very low
 272 electrode potentials at the Pt-NPs/C electrode.

273 IR spectra recorded at an Au-NPs/C electrode from +0.100 V to +1.200 V vs RHE
274 (Fig. 3b) display the same a, b and c absorption bands as those observed at Pt-
275 NPs/C in the wavenumber range from 1000 to 1650 cm^{-1} , but their intensity increases
276 for potentials higher than +0.350 V vs RHE, suggesting that gluconate is continuously
277 formed on Au/C electrode for potential higher than +0.300 V vs RHE. Now,
278 comparing the IR spectra recorded on Au-NPs/C and on Pt-NPs/C, three bands are
279 missing for the Au surfaces: the shoulder at ca. 1720 cm^{-1} and the band at 1785 cm^{-1}
280 related to the formation of gluconolactone, and the band at ca. 2050 cm^{-1} related to
281 the formation of CO_{ads} . This confirms the hypothesis made from the results of Fig. 1,
282 Pt and Au surfaces are likely not covered by same species for the early stage of
283 glucose oxidation, and Au-NPs/C catalyst does not produce lactone conversely to Pt-
284 NPs/C catalyst. The pseudo-band j observed at ca. 1680 cm^{-1} cannot be attributed to
285 any carbonyl function and is likely due to the growth of the positive interfacial water
286 band at ca. 1640 cm^{-1} [26].

287 DEMS measurements were performed at $m/z = 2$ and $m/z = 44$ to detect the
288 formation of dihydrogen, H_2 , and/or of carbon dioxide, CO_2 , as a function of the
289 electrode potential (Fig. 4). To avoid any possible signal perturbation due to carbon
290 support oxidation into CO_2 at potentials higher than +0.207 V vs the normal hydrogen
291 electrode (NHE) [27], DEMS experiments were carried out on unsupported sputtered
292 Pt-NPs and Au-NPs (i.e., in the absence of any carbon support that would render
293 uncertain the CO_2 origin from the GOR or from the oxidation of the carbon support).
294 In the case of 0.010 mol L^{-1} glucose electrooxidation on Pt-NPs, little H_2 is detected,
295 but only for potentials lower than +0.100 V vs RHE (Fig. 4B, grey line hidden by the
296 blank experiment), between +0.050 V and +0.075 V vs RHE. The formation of H_2 at
297 so low potentials is more likely due to the hydrogen evolution reaction (HER) from the

298 water electrochemical reduction than to glucose adsorption and this hypothesis was
 299 confirmed by a blank experiment in 0.10 mol L⁻¹ NaOH (black line in Fig. 4b). Note
 300 that similar results were observed during borohydride oxidation [18]. CO₂ is detected
 301 over the potential range from ca. +0.450 V vs RHE to +0.900 V vs RHE (Fig. 4c), in
 302 the potential region that corresponds to the third oxidation process in CVs of Fig. 4a
 303 and Fig. 1, and where IR spectra (Fig. 3a) indicate a strong shift of the CO_{ads} band
 304 towards lower wavenumber values due to lowering of the CO_{ads} surface coverage. In
 305 the case of 0.010 mol L⁻¹ glucose electrooxidation on Au-NPs (Fig. 4d), H₂ is
 306 detected as soon as glucose is added in the electrolyte at the ocp (supporting
 307 information, SI2), and then a large peak with high intensity is recorded in the potential
 308 range from +0.300 V to +0.900 V vs RHE (Fig. 4e), that corresponds to the first
 309 oxidation peak in CVs of Fig. 4d and Fig. 2. This H₂ production is also witnessed in
 310 the backward cycle (although in smaller extent), which demonstrates that it originates
 311 from the glucose oxidation mechanism and not from pre-adsorbed species formed at
 312 low potentials. For higher potentials, only CO₂ is detected in the course of the
 313 glucose electrooxidation reaction (Fig. 4f).

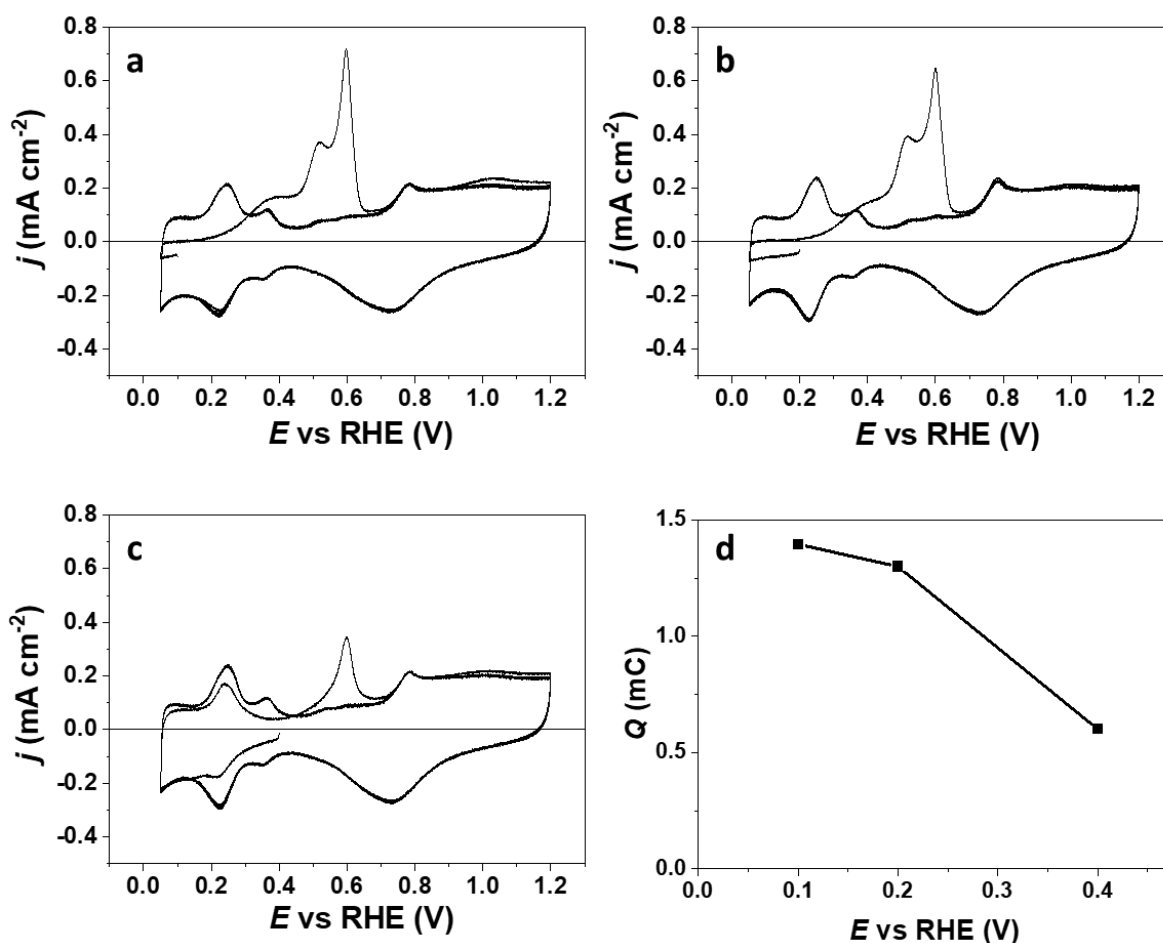


314

315 **Figure 4.** CVs of 0.10 mol L⁻¹ glucose oxidation in 0.10 mol L⁻¹ NaOH electrolyte on
316 (a) sputtered Pt-NPs and (d) sputtered Au-NPs; DEMS measurement performed at
317 $m/z = 2$ for the electrooxidation of 0.010 mol L⁻¹ glucose oxidation in 0.10 mol L⁻¹
318 NaOH electrolyte on (b) sputtered Pt-NPs and (e) sputtered Au-NPs; DEMS
319 measurement performed at $m/z = 44$ for the electrooxidation of 0.010 mol L⁻¹ glucose
320 oxidation in 0.10 mol L⁻¹ NaOH electrolyte on (d) sputtered Pt-NPs and (f) sputtered
321 Au-NPs. Scan rate: 0.010 V s⁻¹, $T = 293$ K.

322 **4. Discussion**

323 The sequential CAs and CVs displayed in Fig. 1 provide clear evidence that CO_{ads} is
324 formed at potentials lower than +0.200 V vs RHE on Pt-NPs/C. This hypothesis is
325 further supported by CO stripping measurements (Fig. 5) showing that the charge
326 involved in the oxidation of the CO_{ads} layer (i.e., the coverage with adsorbed CO at
327 the Pt-NPs/C surface) decreases with an increase of the CO adsorption potential,
328 from ca. 0.14 mC cm⁻², to ca. 0.13 mC cm⁻² and to 0.06 mC cm⁻² for CO adsorption at
329 +0.100 V, +0.200 V and +0.400 V vs RHE, respectively (Fig. 5d). Additionally, the
330 results indicate that adsorbed CO molecules are partly oxidized at $E > +0.200$ V vs
331 RHE.



332
 333 **Fig. 5** CO stripping measurements recorded in N₂-purged 0.10 mol L⁻¹ NaOH electrolyte at a
 334 Pt-NPs/C electrode after 20 min chronoamperometry at (a) +0.100 V vs RHE, (b) +0.200 V
 335 vs RHE and (c) +0.400 V vs RHE (scan rate = 0.005 V s⁻¹, $T = 293$ K). (d) Charge density
 336 under the CO stripping peak as a function of the CO adsorption potential

337 Nevertheless, the lower CO_{ads} coverage achieved upon glucose dissociation and
 338 dehydrogenation at +0.400 V vs RHE is unlikely to account for the positive shifts of
 339 both the onset potential and the oxidation wave on Pt-NPs/C. Rather, we postulate
 340 that other species are co-adsorbed on the Pt surface, and the IR spectroscopy
 341 measurements of Fig. 3a suggest δ - and γ -gluconolactones as possible candidates.
 342 Also, as no H₂ formation was detected by DEMS measurements on Pt-NPs (while
 343 current is detected in this potential region by voltammetry), one can infer that
 344 adsorbed hydrogen is oxidized into protons on the Pt surface. Based on these
 345 results, the following mechanism is proposed for the adsorption of glucose on Pt-

346 NPs/C at $E \leq +0.200$ V vs RHE, corresponding to the first voltammetric feature of the
347 second cycles in Fig. 1:



351 This mechanism is in line with that proposed by Beden *et al.* [9] on bulk Pt.
352 Interestingly, it may be noticed that the formation of lactones (IR measurements, Fig.
353 3a) coincides with the onset of the second electrochemical feature of the second
354 cycle in Fig. 1, at ca. +0.150/+0.200 V vs RHE. According to equation (3), the
355 formation of lactones (from the first aldose adsorbed specie) involves the attack by a
356 hydroxyl anion (OH^-). Strmcnik *et al.* [28] reported that OH species could adsorb on
357 low-coordinated Pt atoms in alkaline media, which can help for the formation of
358 lactone on Pt-NPs. But the formation of lactone on Pt-NPs could also proceeds via an
359 Eley-Rideal mechanism, similar to that for the oxidation of adsorbed CO_{ads} [29].
360 Moreover, as the position of the IR absorption bands assigned to lactone does not
361 change with potential, lactone species are likely in solution or very weakly adsorbed
362 to the Pt surface, and therefore can desorb to be hydrolyzed into gluconate in the
363 electrolyte (equation (4)). As no CO_{ads} and no lactones are produced during the
364 electrooxidation of methylglucoside on Pt-NPs/C (supporting information, SI 2) [10],
365 we propose that CO_{ads} species form, at least partially, from the carbonyl function of
366 lactones.

367 For potentials higher than +0.450 V vs RHE, Pt adsorbs OH^- species (OH_{ads}) in
368 alkaline electrolyte [30], hence a Langmuir-Hinshelwood mechanism likely
369 accelerates the oxidation of adsorbed lactones into gluconate and adsorbed CO into
370 CO_2 . As the three IR adsorption bands located at 1346 cm^{-1} (band a), 1415 cm^{-1}

371 (band b) and 1581 cm^{-1} (band c) in Fig. 3a assigned to the formation of gluconate
372 appear at $E > +0.150\text{ V vs RHE}$, and because their position is independent on the
373 electrode potential, the parallel formation of weakly adsorbed gluconate-like species
374 (equation (2)) to produce gluconate by the mechanisms proposed above cannot be
375 discarded.

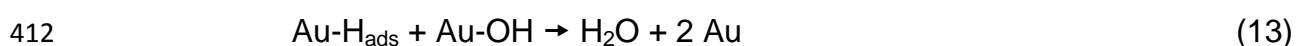
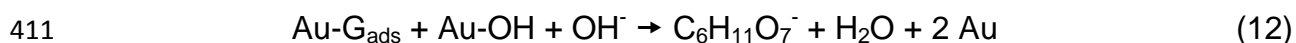
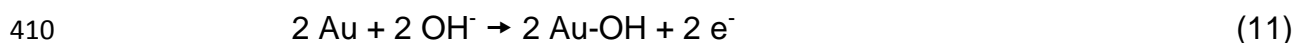
376 The CVs recorded after CAs at different potentials ($+0.100\text{ V}$, $+0.200\text{ V}$ and $+0.400\text{ V}$
377 vs RHE) on Au-NPs/C catalyst indicate that some species are adsorbed at the
378 metallic surface, but in contrast to Pt-NPs/C where CO_{ads} and lactones are
379 concomitantly formed, none of these species is detected during the glucose oxidation
380 on Au-NPs/C (Fig. 3b). Indeed, Au does not adsorb OH species at $E <$
381 $+0.300/+0.400\text{ V vs RHE}$ [31]. In the low potential region from $+0.050\text{ V}$ to $+0.300\text{ V}$
382 vs RHE, the same first step as on Pt-NPs/C (equations (5) and (6)) can occur on
383 metallic Au-NPs/C (equations (8) and (9)). For potentials comprised between $+0.300$
384 V and $+0.900\text{ V vs RHE}$ corresponding to the first oxidation peaks in CVs, the DEMS
385 measurements clearly indicate that H_2 is formed on Au-NPs, not on Pt-NPs. As
386 atomic H can adsorb on metallic Au surface in the presence of organic species [32],
387 and as DFT calculations have shown that H_{ads} at metallic Au surface are less stable
388 than free H_2 [33], we postulate that adsorbed H atoms diffuse on the metallic Au
389 surface and combine to produce hydrogen molecules (equation (10)) [34], similarly to
390 what happens during the electrooxidation of borohydride at Au electrode [20]. For
391 potential lower than $+0.300\text{ V vs RHE}$, the DEMS measurements indicate that
392 glucose adsorbs on and blocks the metallic Au surface, producing too few H_2 to be
393 detected during the CV (the whole baseline of the $m/z = 2$ is raised in presence of
394 glucose; the transient signal of H_2 production, was however detected during the
395 glucose addition steps at ocp (supplementary information, SI 3)). For potentials

396 comprised between +0.300 V vs RHE and +0.900 V vs RHE, the competition
 397 between glucose and OH⁻ adsorption likely leads to the coexistence of metallic Au
 398 and Au-OH patches at the surface of NPs (this hypothesis is supported by the IR
 399 baseline perturbation that starts around +0.350 V – +0.400 V vs RHE and the
 400 formation of the positive band at ca. 1640 cm⁻¹ in Fig. 3b). Therefore, it may be
 401 postulated that glucose adsorbs on the metallic sites of the Au surface while the Au-
 402 OH surface species oxidize adsorbed species into gluconate and water via a
 403 Langmuir-Hinshelwood mechanism. The following mechanism is then proposed for
 404 Au-NPs:

405 - For +0.050 V < E < +0.900 V vs RHE



409 - from +0.300 V vs RHE to +0.900 V vs RHE



413 The first step of this mechanism (equation (8)) agrees with former propositions of
 414 Beden *et al.* [9], Pasta *et al.* [13,35], and Adzic *et al.* [36]. This mechanism explains
 415 why an oxidation current peak/wave is observed at low potentials on Pt-NPs (Fig. 1)
 416 and not on Au-NPs (Fig. 2). As no gluconolactone was detected by IR measurements
 417 (Fig. 3b) in the 1640 cm⁻¹ to 1800 cm⁻¹ wavenumber range, the reaction process
 418 described in reaction scheme (2) seems thus to be favored on Au-NPs/C compared
 419 to Pt-NPs/C. In addition, our results suggest that adsorbed lactone are not formed on
 420 Au-NPs/C, conversely to what was proposed by Pasta *et al.* [13] and Adzic *et al.* [36].

421 For potentials higher than +0.900 V vs RHE, CO₂ is detected both by *situ* FTIRS and
422 DEMS on Au-NPs, indicating that the mechanism is more complex, owing to the
423 ability of Au to break the C-C bond and to produce C1 to C6 oxidized species. At
424 such high overpotentials, the glucose oxidation mechanism is also unclear on Pt-
425 NPs.

426 **5. Conclusion**

427 In conclusion, by combining cyclic voltammetry, *in situ* FTIRS and DEMS results, we
428 have brought new insights into the glucose oxidation mechanisms on Pt and Au
429 nanoparticles. We provided spectrometric evidence that different species are
430 adsorbed on Pt-NPs and Au-NPs, hence different mechanisms are involved. In
431 particular, lactones seem to be (at least some of) the adsorbed intermediates during
432 the oxidation of glucose into gluconate on Pt-NPs, whereas only adsorbed gluconate
433 species are formed on Au-NPs. The proposed glucose oxidation mechanisms
434 account for the difference in electrocatalytic behavior between Pt-NPs and Au-NPs,
435 and particularly for the lower onset potential of glucose electrooxidation observed on
436 Pt-NPs than on Au-NPs. Because the knowledge of the reaction mechanisms is a
437 prerequisite for the development of more selective and more active electrocatalysts,
438 the findings described in the present contribution are of paramount importance
439 concerning the selective electrooxidation of glucose into values added compounds,
440 and that of aldoses in general.

441 Pt-NPs led to poor selectivity whatever the electrode potential, whereas Au-NPs have
442 shown high selectivity towards gluconate +0.300 V < E < +0.800 V vs RHE.
443 Moreover, Au-NPs are less prone to poisoning by strong adsorbed species such as
444 CO_{ads}. In addition, DEMS evidenced hydrogen evolution on gold in the same
445 electrode potential range, with the maximum of production coinciding with the first

446 current peak of glucose oxidation into gluconate around +0.500 – + 0.600 V vs RHE.
447 The electrocatalytic behavior of gold could then help to integrate electrochemical
448 methods in biorefinery by demonstrating high activity and selectivity, and lower
449 energy cost. Indeed, electrochemical reactors often consist of divided cells separated
450 by an ionic conductive separator allowing biomass oxidation reaction into value
451 added compounds at the anode and either hydrogen production [7,10] or reduction
452 reaction of biomass molecules into value added compounds (paired electrochemical
453 processes) [37, 38] at the cathode. The production of valuable compounds at both
454 electrodes allows decreasing the total energy cost [39]. Using gold at the anode of a
455 glucose electroreforming reactor [40], as an example, will lead to the simultaneous
456 production of two valuable compounds, hydrogen and gluconate, at the anode and of
457 one valuable compound, hydrogen, at the cathode of the reactor, i.e. twice more
458 hydrogen per glucose molecule oxidized into gluconate than in conventional systems.
459 Of course, gold is an expensive strategical metal, but its amount in catalysts can
460 certainly be lowered keeping its properties by material engineering.

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473 **Statements**

474 The authors declare that they have no known competing financial interests or
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477 **References**

- 478 [1] X. Pang, C. Jia, K. Zhang, M. Li, Y. Wang, J. Peng , B. Li, J. Chen, The depth limit
479 for the formation and occurrence of fossil fuel resources, Earth System Science
480 Data, (2020). <https://doi.org/10.5194/essd-2019-72>
- 481 [2] N. Dahmen, I. Lewandowski, S. Zibek, A. Weidtmann, GCB Bioenerg. (2019).
482 <https://doi.org/10.1111/gcbb.12586>
- 483 [3] C. Dollé, N. Neha, C. Coutanceau, Curr. Op. Electrochem. (2022).
484 <https://doi.org/10.1016/j.coelec.2021.100841>
- 485 [4] E. Taarning, C. M. Osmundsen, X. Yang, B. Voss, S. I. Andersen, C. H.
486 Christensen, Energy Environ. Sci. (2011). <https://doi.org/10.1039/c004518g>
- 487 [5] V. B. Agbor, N. Cicek, R. Sparling, A. Berlin, D. B. Levin, Biotechnol. Adv. (2011).
488 <https://doi.org/10.1016/j.biotechadv.2011.05.005>
- 489 [6] T. Rafaïdeen, S. Baranton, C. Coutanceau, ChemElectroChem (2022).
490 <https://doi.org/10.1002/celec.202101575>
- 491 [7] T. Rafaïdeen, S. Baranton, C. Coutanceau, Appl. Catal. B: Env. (2019).
492 <https://doi.org/10.1016/j.apcatb.2018.11.006>
- 493 [8] W. J. Liu, Z. Xu, D. Zhao, X.-Q. Pan, H.-C. Li, X. Hu, Z.-Y. Fan, W.-K. Wang, G.-
494 H. Zhao, S. Jin, G. W. Huber, H.-Q. Yu, Nature Comm. (2020).
495 <https://doi.org/10.1038/s41467-019-14157-3>

- 496 [9] B. Beden, F. Largeaud, K. B. Kokoh, C. Lamy, *Electrochim. Acta.* (1996).
497 [https://doi.org/10.1016/0013-4686\(95\)00359-2](https://doi.org/10.1016/0013-4686(95)00359-2)
- 498 [10] N. Neha, S. R. B. Kouamé, T. Rafaïdeen, S. Baranton, C. Coutanceau,
499 *Electrocatalysis* (2021). <https://doi.org/10.1007/s12678-020-00586-y>
- 500 [11] G. Moggia, T. Kenis, N. Daems, T. Breugelmans. *ChemElectroChem* (2020).
501 <https://doi.org/10.1002/celec.201901960>
- 502 [12] Nicolas Schlegel, Gustav K.H. Wiberg, Matthias Arenz. On the electrooxidation
503 of glucose on gold: Towards an electrochemical glucaric acid production as value-
504 added chemical. *Electrochimica acta* (2022).
505 <https://doi.org/10.1016/j.electacta.2022.140023>
- 506 [13] M. Pasta, F. La Mantia, Y. Cui, *Electrochim. Acta* (2010).
507 <https://doi.org/10.1016/j.electacta.2010.04.069>
- 508 [14] Y. B. Vassilyev, O. A. Khazova, N. N. Nikolaeva, *J. Electroanal. Chem. Interfac.*
509 *Electrochem.* (1985). [https://doi.org/10.1016/0022-0728\(85\)85085-3](https://doi.org/10.1016/0022-0728(85)85085-3)
- 510 [15] B. S. R. Kouamé, S. Baranton, P. Brault, C. Canaff, W. Chamorro-Coral, A.
511 Caillard, K. De Oliveira Vigier, C. Coutanceau, *Electrochim. Acta* (2020).
512 <https://doi.org/10.1016/j.electacta.2019.135161>
- 513 [16] B. Beden, C. Lamy, in *Spectroelectrochemistry: theory and practice*, ed. By R. J.
514 Gale (Plenum Press, New York, 1988) pp 189–261.
515 https://doi.org/10.1007/978-1-4613-0985-7_5
- 516 [17] A. Kabbabi, R. Faure, R. Durand, B. Beden, F. Hahn, J.M. Léger, C. Lamy, *J.*
517 *Electroanal. Chem.* (1998). [https://doi.org/10.1016/S0022-0728\(97\)00558-5](https://doi.org/10.1016/S0022-0728(97)00558-5)
- 518 [18] G. Braesch, A. Bonnefont, V. Martin, E. R. Savinova, M. Chatenet, *Electrochim.*
519 *Acta* (2018). <https://doi.org/10.1016/j.electacta.2018.04.068>

- 520 [19] R. Ianniello, V. M. Schmidt, Berichte der Bunsen-Gesellschaft Physical
521 Chemistry Chemical Physics (1995). <https://doi.org/10.1002/bbpc.19950990114>
- 522 [20] M. B. Molina Concha, M. Chatenet, F. H. B. Lima, E. A. Ticianelli, Electrochim.
523 Acta (2013). <https://doi.org/10.1016/j.electacta.2012.11.027>
- 524 [21] W.T. Napporn, J.-M. Léger, C. Lamy. J. Electroanal. Chem. (1996).
525 [https://doi.org/10.1016/0022-0728\(96\)04543-3](https://doi.org/10.1016/0022-0728(96)04543-3)
- 526 [22] A. Couto, A. Rincon, M. C. Perez, C. Gutierrez, Electrochim. Acta (2001).
527 [https://doi.org/10.1016/S0013-4686\(00\)00714-3](https://doi.org/10.1016/S0013-4686(00)00714-3)
- 528 [23] T. Elgayyar, R. Atwi, A. Tuel, F. C. Meunier, Catal. Today (2021).
529 <https://doi.org/10.1016/j.cattod.2021.01.009>
- 530 [24] C. Lafforgue, F. Maillard, V. Martin, L. Dubau, M. Chatenet, ACS Catal. (2019).
531 <https://doi.org/10.1021/acscatal.9b00439>
- 532 [25] L. Dubau, F. Hahn, C. Coutanceau, J.-M. Léger, C. Lamy, J. Electroanal. Chem.
533 (2003). [https://doi.org/10.1016/S0022-0728\(03\)00308-5](https://doi.org/10.1016/S0022-0728(03)00308-5)
- 534 [26] A. Rodes, E. Pastor, T. Iwasita, J. Electroanal. Chem. (1994).
535 [https://doi.org/10.1016/0022-0728\(94\)03585-7](https://doi.org/10.1016/0022-0728(94)03585-7)
- 536 [27] L. Castanheira, W. O. Silva, F. H. B. Lima, A. Crisci, L. Dubau, F. Maillard, ACS
537 Catal. (2015). <https://doi.org/10.1021/cs501973j>
- 538 [28] D. Strmcnik, M. Uchimura, C. Wang, R. Subbaraman, N. Danilovic, D. van der
539 Vliet, A. P. Paulikas, V. R. Stamenkovic, N. M. Markovic. Nat Chem. (2013).
540 <https://doi.org/10.1038/nchem.1574>
- 541 [29] P. Urchaga, S. Baranton, C. Coutanceau, G. Jerkiewicz, Langmuir (2012).
542 <https://doi.org/10.1021/la302388p>
- 543 [30] S. Kusano, D. Matsumura, K. Ishii, H. Tanaka, J. I. Mizuki, Nanomaterials
544 (2019). <https://doi.org/10.3390/nano9040642>

- 545 [31] B. Beden, I. Cetin, A. Kahyaoglu, D. Takky, C. Lamy, J. Catal. (1987).
546 [https://doi.org/10.1016/0021-9517\(87\)90334-4](https://doi.org/10.1016/0021-9517(87)90334-4)
- 547 [32] N. Arjona, G. Trejo, J. Ledesma-García, L. G. Arriaga, M. Guerra-Balcázar, RSC
548 Adv. (2016). <https://doi.org/10.1039/C5RA23780G>
- 549 [33] S. A. C. Carabineiro, B. E. Nieuwenhuys, Gold Bull. (2009).
550 <https://doi.org/10.1007/BF03214951>
- 551 [34] W. Watkins, Y. Borensztein, Phys. Chem. Chem. Phy. (2017).
552 <https://doi.org/10.1039/C7CP04843B>
- 553 [35] M. Pasta, R. Ruffo, E. Falletta, C. M. Mari, C. Della Pina, Gold Bull. (2010).
554 <https://doi.org/10.1007/BF03214967>
- 555 [36] R. R. Adzic, M. W. Hsiao, E. B. Yeager, J. Electroanal. Chem. Inter.
556 Electrochem. (1989). [https://doi.org/10.1016/0022-0728\(89\)87164-5](https://doi.org/10.1016/0022-0728(89)87164-5)
- 557 [37] K. Park, P. N. Pintauro, M. M. Baizer, K. Nobe. J. Electrochem. Soc. 132, (1985).
558 <https://doi.org/10.1149/1.2114229>
- 559 [38] Y. Cao, J. Knijff, A. Delparish, M. F. N. D'Angelo, T. Noël. ChemSusChem 14
560 (2021). <https://doi.org/10.1002/cssc.202002833>
- 561 [39] Y. Kwon, K. J. P. Schouten, J. C. van der Waal, E. de Jong, M. T. M. Koper.
562 ACS Catal. 6 (2016). <https://doi.org/10.1021/acscatal.6b01861>
- 563 [40] C. Lamy, C. Coutanceau, S. Baranton. in Hydrogen and Fuel cells primers, ed.
564 By B. Pollet (Elsevier, Amsterdam, 2020) pp 82-106.
565 <https://doi.org/10.1016/B978-0-12-821500-5.00001-1>