

Mechanistic study of an immobilised molecular electrocatalyst by in-situ gap plasmon assisted spectro-electrochemistry

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Abstract

Immobilised first-row transition metal complexes are potential low-cost electrocatalysts for selective CO₂ conversion to produce renewable fuels. Mechanistic understanding of their function is vital for the development of next-generation catalysts, though poor surface sensitivity of many techniques makes this challenging. Here, a nickel bis(terpyridine) complex is introduced as a CO₂ reduction electrocatalyst in a unique electrode geometry, sandwiched by thiol anchoring moieties between two gold surfaces. Gap-plasmon-assisted surface-enhanced Raman scattering spectroscopy coupled with density functional theory calculations reveals the nature of the anchoring group plays a pivotal role in the catalytic mechanism by eliminating ligand loss. Our *in-situ* spectro-electrochemical measurement enables the detection of as few as 8 molecules undergoing redox transformations in the individual plasmonic hot-spots, together with the calibration of electrical fields *via* vibrational Stark effects. This advance allows rapid exploration of non-resonant redox reactions at the few-molecule level and provides scope for future mechanistic studies of single-molecules.

30 **Introduction**

31 Understanding interface organisation and charge transport between materials and molecules is a major
32 issue plaguing the systematic development of photocatalysis, electrochemistry, and molecular
33 electronics. An emerging tool for interfacial studies exploits plasmonic gaps constructed from metallic
34 nanostructures,¹ which confine optical fields far below the diffraction limit to create a highly localised
35 surface probe with enhanced spectroscopic sensitivity and selectivity. One such plasmonic gap
36 approach is tip-enhanced Raman spectroscopy (TERS), which has been used to observe redox active
37 molecules responding to electrochemical potential.^{2,3} However, the major challenge of reliable
38 fabrication and availability of suitable probes,⁴ as well as probe degradation,⁵ has precluded widespread
39 utilisation of TERS. By contrast, although surface-enhanced Raman scattering (SERS)⁶⁻⁸ at roughened
40 surfaces is easy to implement, it is limited by poor control over surface morphologies that alter
41 electrochemical and spectroscopic behaviours.⁹ The high precision of gap-plasmon-assisted SERS
42 (introduced below), which uses metal nanoparticles on an electrode surface, is thus becoming a valuable
43 tool in studying real-time *in-situ* redox processes.¹⁰

44 While electron transfer at the surface of nanoparticles has been studied electrochemically,¹¹⁻¹³
45 plasmonic nano-gaps enable *in-situ* observation of both oxidised and reduced species through SERS.
46 The high signal-to-noise ratios eliminate the need for electronically resonant enhancement, which is
47 typically susceptible to bleaching over time. These vibrational spectroscopies serve as powerful tools
48 to study catalysis as they provide structural fingerprint information about the catalyst. Of particular
49 interest are immobilised systems,^{14,15} where molecular catalysts are anchored to surfaces.
50 Understanding these systems is important for designing industrially-relevant catalysts, by enhancing
51 performance through improved electron transfer dynamics,^{16,17} tuning the redox mechanisms, and
52 improving the long-term stability of catalysts *via* facile recovery and separation from products.¹⁸

53 In this work, we perform gap-plasmon-assisted SERS coupled with electrochemistry to study the CO₂
54 reduction catalyst [Ni(2,2':6',2''-terpyridine-4'-thiol)₂](BF₄)₂ (**Ni(tpyS)**)₂.¹⁹ While bis(terpyridine)
55 complexes of cobalt and nickel have been previously used for electrocatalytic CO₂ reduction,¹⁹⁻²¹ no

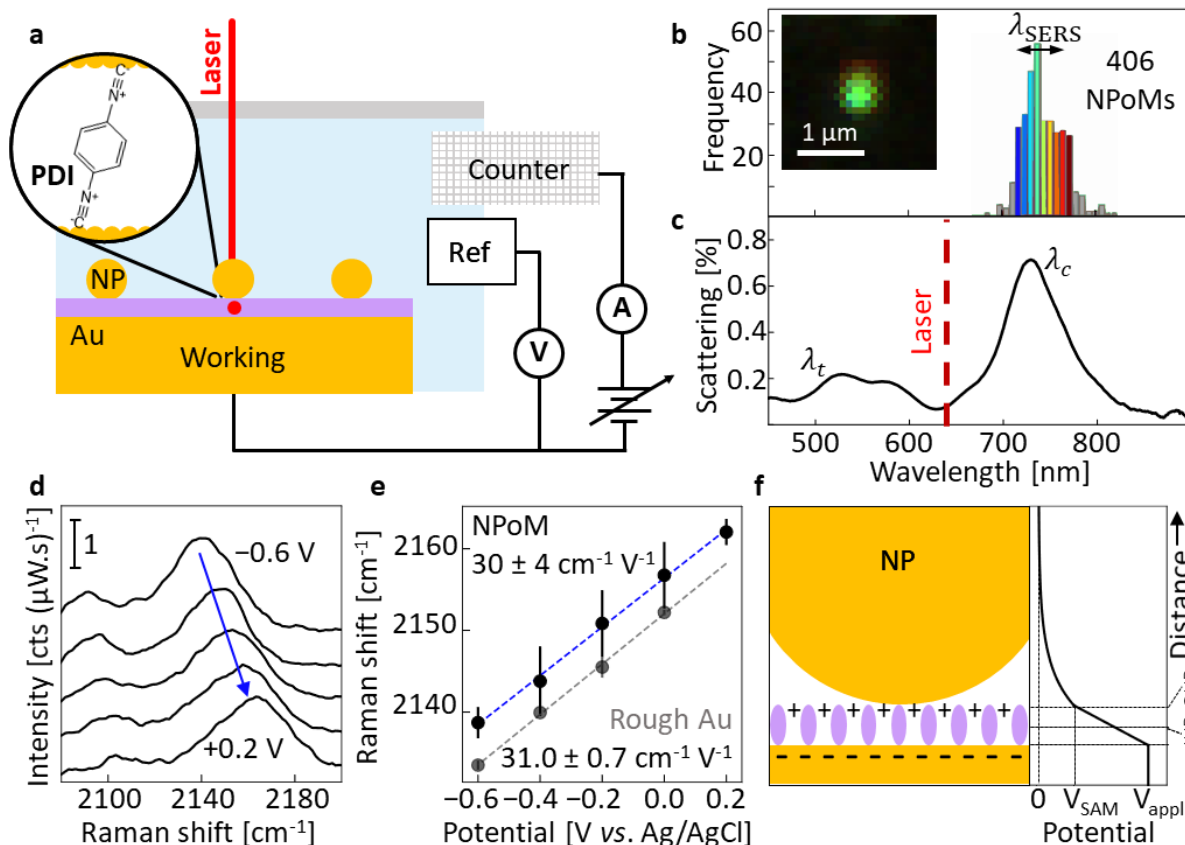
56 mechanistic studies have been performed in a sandwich geometry with a highly confined volume. The
57 nickel-centred complex is chosen in this study due to its excellent selectivity for CO₂ reduction towards
58 CO over hydrogen evolution.¹⁹⁻²¹ Using *in-situ* SERS between two gold surfaces we are able to
59 characterise the spectro-electrochemical behaviour, resolving changes in chemical bonding and
60 identifying the catalytic reaction mechanism. Comparing experimental SERS spectra with density
61 functional theory (DFT) calculations of Ni(tpyS)₂ shows the first electron transferred during reduction
62 weakens the Au-S bonds, while the electronic environment of the metal centre changes less, confirming
63 that the nature of the anchoring group plays a pivotal role in the catalytic mechanism. Electrode design
64 such as confined environments²² and layered geometries^{23,24} advance the catalysis by enhancing
65 nanoscale mass transport and electrode dynamics compared to conventional electrodes. We utilise a
66 single-site sandwiched electrode geometry with a molecular catalyst. Compared to the conventional
67 system with solution-phase nickel catalysts,^{19,20} this electrode geometry with adsorbed catalyst is likely
68 to change the reaction mechanism as it allows the gained electron from reduction to delocalise over the
69 Au-S anchoring unit, inhibits ligand loss and preserves catalyst integrity. This work gives unique
70 insights into material-molecule hybrid catalysis by going beyond prior work on redox-inactive biphenyl
71 monolayers where changes in molecule polarizability are induced electrochemically,²⁵ or tracking
72 resonant molecules when they enter and leave electronically-active states during redox transitions.²⁶

73 **Results**

74 **Gap-plasmon-assisted spectro-electrochemical assembly.** Gap plasmon cavities have extremely
75 small mode volumes (< 50 nm³) with high optical field enhancements (>500) that strongly amplify the
76 Raman scattering of molecules in the gap by >10⁹. To construct the nanoparticle-on-mirror (NPoM)
77 plasmonic cavities used here, planar gold substrates are functionalised with a self-assembled monolayer
78 (SAM, see Methods). Gold nanoparticles (AuNPs) are then drop-cast on top of the monolayer (**Fig. 1a**),
79 sandwiching the active molecules in the nano-gap. The advantage of this geometry is that the gold
80 mirror conveniently forms one electrode of the cell (**Fig.1a**). Dark-field scattering spectra (**Fig. 1b,c**)
81 on each NPoM characterise the monolayer quality in the gap. These scattering spectra show transverse
82 ($\lambda_t \sim 530$ nm) and coupled ($\lambda_c \sim 700$ nm) modes in the NPoM nanocavities. The coupled plasmon at λ_c

83 arises from the interaction of the nanoparticle with its image charges in the mirror below, tightly
84 confining the plasmonic hot spot underneath the NPoM.^{1,27} The position of λ_c strongly depends on the
85 properties of the gap spacer, including its thickness (d) and effective refractive index (n_g).²⁸ Using
86 automated tracking microscopy,²⁹ dark-field scattering spectra are observed for many hundreds of
87 individual NPoMs across the sample surface. Real-time spectro-electrochemical measurements are
88 achieved by incorporating NPoM samples into a 3D-printed cell. SERS spectra are recorded by
89 illuminating individual NPoMs with a continuous wave laser at wavelength $\lambda_l = 633$ nm, with
90 electrochemical potential applied simultaneously to the gold substrate using a 3-electrode configuration.

91 **Electric field calibration by vibrational Stark effect.** The electrochemical control of the applied
92 potential in the nano-gap was first probed with SERS from a calibration molecule, PDI (1,4-phenylene
93 diisocyanide) (**Fig. 1a**). Scattering spectra for PDI monolayers are measured from automated tracking
94 of >400 NPoMs (**Fig. 1b**). These give near-identical coupled modes at $\lambda_c = 739 \pm 22$ nm (**Fig. 1c**),
95 indicating a highly consistent monolayer over the gold substrate (standard error matches variation in
96 nanoparticle size and shape³⁰). Modelling the coupled mode resonance²⁸ gives $n_{g,\text{PDI}} = 1.4$ and $d_{\text{PDI}} =$
97 1 nm, which is consistent with the thickness expected for a monolayer in which the molecules bind to
98 the substrate in a near-vertical rather than flat orientation. SERS spectra for PDI in NPoMs (**Fig. 1d**)
99 are recorded at potentials ranging from -0.6 to $+0.2$ V (vs. Ag/AgCl) in a N_2 -saturated aqueous solution
100 with a 0.1 M KCl supporting electrolyte. In this electrochemically inert range for PDI (Supplementary
101 **Fig. 1**), the SERS band near 2130 cm^{-1} shows a significant blue-shift as positive potential is applied,
102 shifting linearly at $30 \pm 4\text{ cm}^{-1}\text{ V}^{-1}$ (**Fig. 1e**, black). This is consistent with the stretching mode for
103 isocyanide ($\text{N}\equiv\text{C}$) bound to the gold surface³¹. For comparison, SERS spectra for PDI at
104 electrochemically roughened gold surfaces are recorded and analysed (**Fig. 1e**, grey) in the same
105 conditions, where $\nu(\text{N}\equiv\text{C})$ shifts by $31 \pm 1\text{ cm}^{-1}\text{ V}^{-1}$.

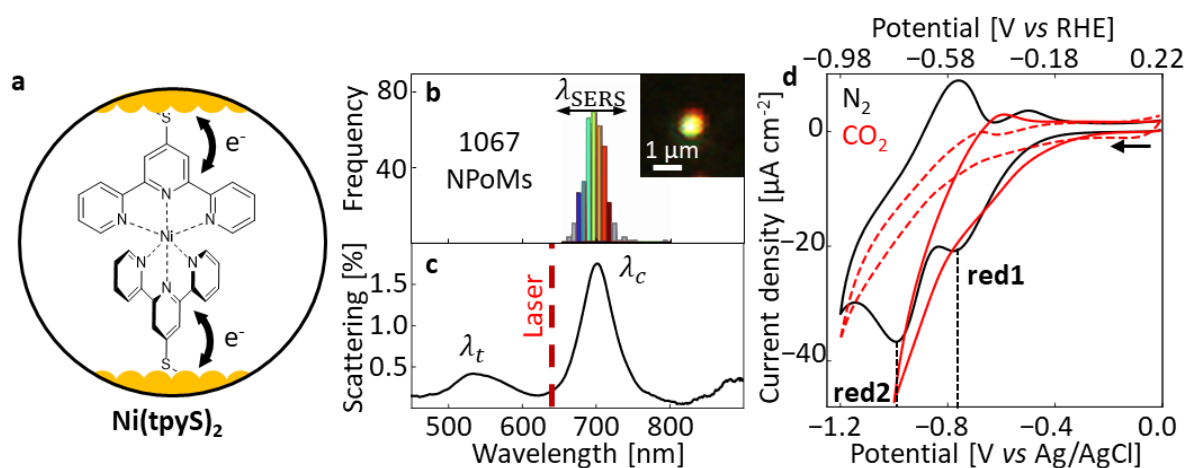


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107 **Fig. 1 | Electric field calibration in nanoparticle-on-mirror (NPoM).** a, NPoM geometry in spectro-electrochemical cell
 108 using three electrodes: gold mirror working electrode, platinum counter electrode and 3 M KCl Ag/AgCl reference electrode.
 109 Inset: PDI molecule. b, Histogram of plasmon coupled mode positions. Inset shows spatial dark field image of single 80 nm
 110 diameter NPoM. c, Dark-field scattering spectra for PDI monolayer in NPoM. d, SERS spectra for PDI in gold nano-gap in
 111 aqueous solution with 0.1 M KCl and saturated with N₂, showing $\nu(\text{N}\equiv\text{C})$ region at different bias. e, Potential-dependent
 112 $\nu(\text{N}\equiv\text{C})$. Black: NPoMs, grey: roughened gold surface. Error bars refer to standard deviation, $n = 50$ measurements for NPoM,
 113 $n = 80$ measurements for roughened gold. f, Model of electrical double layer in NPoM and potential drop across the gap.

114 These SERS shifts arise from the vibrational Stark effect (VSE),^{31–33} where the vibrational energies of
 115 chemical bonds are perturbed by an electric field. The Stark shift versus potential, known as the Stark
 116 tuning rate, enables direct measurement of the potential gradient at the electrode. Our measurements
 117 provide direct evidence that the electrochemical potential gradient (*i.e.* electric field) at the NPoM
 118 surface of a SAM is identical to that found at a roughened electrode surface of a SAM. While electron
 119 tunnelling has been reported across NPoM plasmonic gaps, the electron transfer process at the interface
 120 between the SAM and this sandwiched electrode geometry remains unclear.^{12,13} To address this
 121 question, a model of the electrical double layer^{31,34} for the NPoM junction (**Fig. 1f**) is developed here.
 122 As the SAM is adsorbed on the gold substrate, the electrical centre of the monolayer is the Inner
 123 Helmholtz Plane (IHP). Solvated ions from the supporting electrolyte approach the SAM by diffusion,

124 and the position of these nearest ions is the Outer Helmholtz Plane (OHP), roughly corresponding to
 125 the length of molecules ($d = 1$ nm). Following the double layer capacitive (non-Faradaic) charging, the
 126 potential drops rapidly within the OHP. Faradaic electron transfer takes place readily between the gold
 127 substrate and the monolayer (as observed below). This electron transfer process is similar to the case
 128 when no nanoparticle is on top of the SAM, implying that electron tunnelling is not the only path across
 129 the gaps, otherwise the VSE should not be observed. In fact, the electron tunnelling is less efficient due
 130 to the 1 nm barrier width³⁵ and hence an electron transfer process through the SAM dominates
 131 (Supplementary Fig. 2).

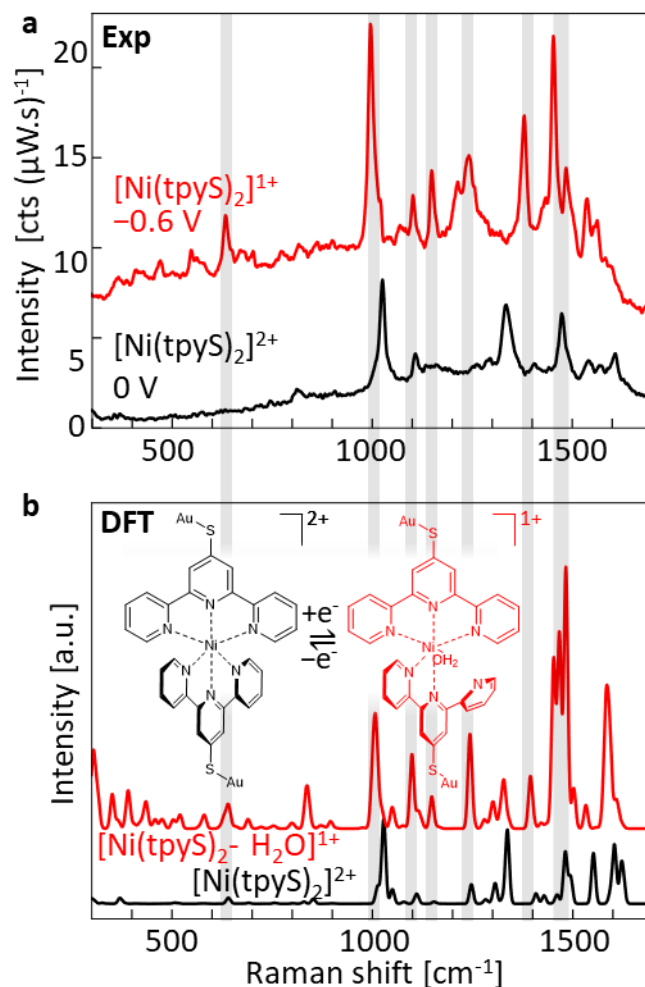


132
 133 **Fig. 2 | Dark-field scattering spectroscopy and electrochemistry for Ni(tpyS)₂.** **a**, Ni(tpyS)₂ in nanoparticle-on-mirror
 134 (NPoM) geometry. **b**, Histogram of plasmon coupled mode positions. Inset shows spatial image of single 60 nm diameter
 135 NPoM. **c**, Scattering spectra for Ni(tpyS)₂ monolayer in NPoM. **d**, Cyclic voltammograms for NPoMs with (solid lines) or
 136 without (dashed line) Ni(tpyS)₂ monolayer in pH 3.8 aqueous solution supported with 0.1 M KCl and saturated with N₂ (black)
 137 or CO₂ (red). Scan rate = 100 mV s⁻¹.

138 **Spectro-electrochemical studies of immobilised Ni(tpyS)₂.** Using Ni(tpyS)₂ in the nano-gap (**Fig. 2a**)
 139 allows tracking of redox and catalytic reactions. Scattering spectra for Ni(tpyS)₂ monolayer measured
 140 from >1000 NPoMs (**Figs. 2b,c**) shows the coupled mode at $\lambda_c = 696 \pm 15$ nm, confirming the
 141 monolayer is uniform with $n_{g, Ni(tpyS)_2} = 1.4$ and $d_{Ni(tpyS)_2} = 1.5$ nm. A dark field image (Supplementary
 142 **Fig. 3**) demonstrates nanoparticle distribution. Cyclic voltammetry (CV) for Ni(tpyS)₂ NPoMs is first
 143 recorded in a N₂-saturated pH 3.8 aqueous solution supported with 0.1 M KCl, from 0 to -1.2 V (vs
 144 Ag/AgCl) and back to 0 V (**Fig. 2d**, black). Two reductive waves are observed: **red1** at $E_p = -0.76$ V
 145 and **red2** at $E_p = -0.99$ V, corresponding to the first and second reduction of Ni(tpyS)₂.^{19,20} These

146 electrochemical responses are markedly different from the voltammogram when no nanoparticle is on
147 top of the Au-Ni(tpyS)₂ monolayer (Supplementary Fig. 4, blue). In the absence of AuNPs, the lack of
148 oxidative waves indicates the redox process is chemically irreversible. This may in part be due to the
149 loss of one tpyS ligand. While in the NPoM construct, the presence of two oxidative waves supports a
150 chemically reversible process, confirming preservation of the tpyS ligand coordinated to the nickel
151 centre. Voltammetric features of Ni(tpyS)₂ are significantly clearer, indicating that the voltammogram
152 is dominated by the molecules underneath the nanoparticles, rather than the exposed monolayer. As a
153 result, the CV directly measures conditions in the gap. More importantly, while a broad peak at -0.86
154 V is observed in the absence of the nanoparticle on top (Supplementary Fig. 4, blue), the presence of
155 nanoparticles shows a well-defined reductive peak shifting by ~+0.1 V (Supplementary Fig. 4, black).
156 This can be explained by the reduction of the monolayer becoming thermodynamically more
157 favourable, due to stabilisation of the reduced radical species *via* adsorption by the nanoparticle on top
158 (Supplementary Fig. 4d).³⁶ The nanoparticle further stabilises the adsorbed system by withdrawing
159 electron density from the monolayer, making reduction easier. This stabilisation is not molecule
160 specific, as for PDI the $\nu(\text{N}\equiv\text{C})$ shifts by $\sim-5\text{ cm}^{-1}$ in NPoMs vs. a rough gold electrode (Fig. 1e). NPoM
161 plasmonic cavities thus significantly enhance interfacial electron transfer.

162 The CV for CO₂ catalytic reduction is recorded in a CO₂-saturated solution with Ni(tpyS)₂ NPoMs (Fig.
163 2d, red solid line), and compared with CO₂ reduction on the gold substrate without Ni(tpyS)₂ monolayer
164 in the same solution (Fig. 2d, red dashed line). Comparison of these shows over 2-fold increased current
165 density with the onset potential shifting to $\sim-0.52\text{ V}$, illustrating that the electrocatalytic CO₂ reduction
166 is mediated by Ni(tpyS)₂ NPoMs before proton reduction on gold.²⁵



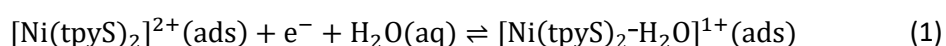
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168 **Fig. 3 | Surface-enhanced Raman spectroscopy (SERS) and density functional theory (DFT) calculations for Ni(tpyS)₂.**
 169 **a**, Experimental SERS spectra of Ni(tpyS)₂ in nanoparticle-on-mirror (NPoM) at 0 V (black) and -0.6 V (red, difference
 170 spectrum) vs Ag/AgCl in pH 3.8 aqueous solution supported with 0.1 M KCl and saturated with N₂. Additional bands
 171 appearing at -0.6 V are highlighted in grey. **b**, DFT calculations for [Ni(tpyS)₂]²⁺ and [Ni(tpyS)₂-H₂O]¹⁺.

172 SERS is now used to explore chemical bonding changes. SERS spectra (**Fig. 3a**) are recorded for the
 173 reduced state ([Ni(tpyS)₂]¹⁺, -0.6 V) and oxidised state ([Ni(tpyS)₂]²⁺, 0 V vs. Ag/AgCl, according
 174 to the CV in **Fig. 2d**). To avoid proton reduction²⁵ which forms bubbles disrupting the optical
 175 measurements, potentials are kept at -0.6 V to observe Ni(tpyS)₂ in the first reduced state only.
 176 Comparison of these spectra shows that during reduction, the SERS background increases and several
 177 spectral bands emerge (highlighted in grey). Despite attenuation and scattering from the spectro-
 178 electrochemical cell, SERS signals exceed 10 cts (μW.s)⁻¹ with a high signal-to-noise ratio. While
 179 Ni(tpyS)₂ is electronically non-resonant at λ_i = 633 nm (Supplementary **Fig. 5** shows no
 180 absorption/emission at λ_i, which is essential to correctly measure electrochemical performance), the

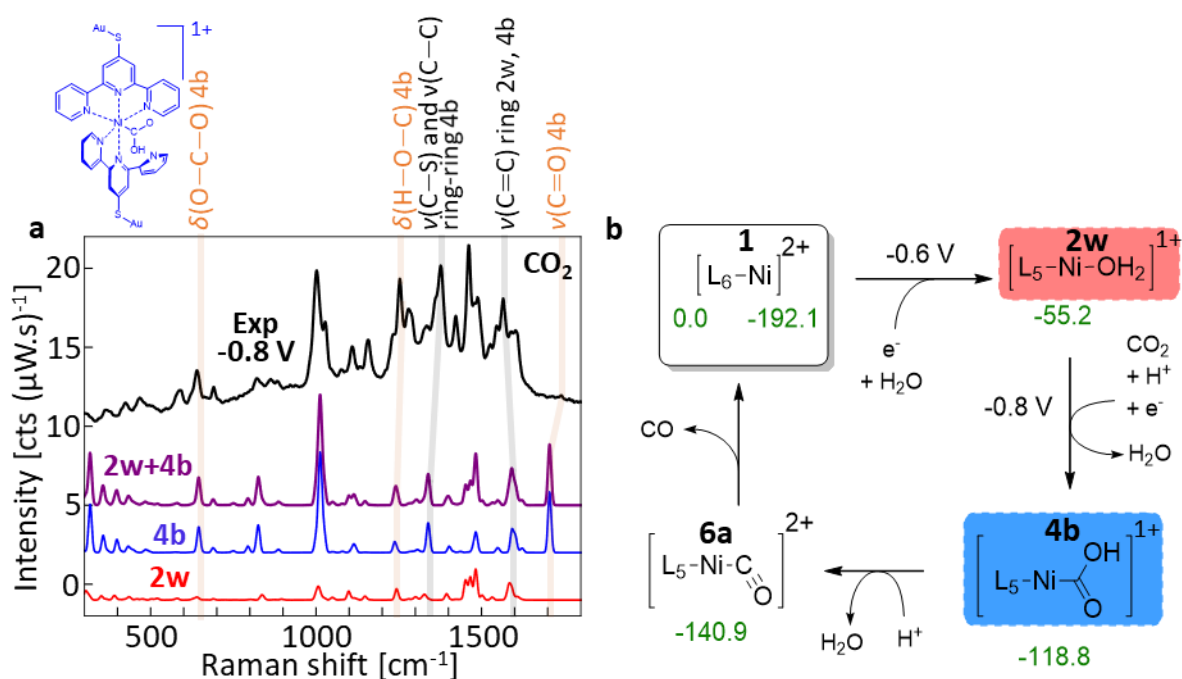
181 near-resonant plasmonic mode at 696 nm strongly enhances the SERS (**Fig. 2c**). Similar measurements
182 for **Ni(tpyS)₂** on an electrochemically roughened gold substrate (Supplementary **Fig. 6**) show spectral
183 changes in the reduced **[Ni(tpyS)₂]¹⁺** state, though with broader, less defined SERS bands with an
184 order of magnitude lower intensity.

185 DFT calculations are performed to simulate the SERS responses for **Ni(tpyS)₂** in different redox states.
186 Comparison of computational spectra with experimental SERS for **[Ni(tpyS)₂]²⁺** (black lines **Figs.**
187 **3a,b**) shows excellent agreement. We consider several possible reduction products for bis(terpyridine)
188 complexes involving different mechanisms including those in refs. ^{19,21}. The calculated Raman spectra
189 (Supplementary **Fig. 7**) shows that **[Ni(tpyS)₂-H₂O]¹⁺** involving a one electron reduction of the ligand
190 and an addition of a water molecule to the nickel coordination gives the best agreement with
191 experiments (red lines in **Fig. 3**). The spectral bands are labelled with relevant vibrational modes and
192 discussed in Supplementary **Fig. 8** and Supplementary Note 1. Further DFT calculations considering
193 effects of the electrical double layer on the polarization of dipoles (Supplementary **Fig. 9**) shows the
194 same spectral matching results with calculations from isotropic and unpolarized environments. The first
195 reduction process **red1** (**Fig. 2d**) is thus identified as the electron transfer step:



196 The reduction process for the dissolved non-thiolated catalyst, **[Ni(2,2':6',2''-terpyridine)₂](BF₄)₂**
197 (**Ni(tpy)₂**), has been suggested to accompany the loss of one terpyridine ligand to form an active
198 mono(terpyridine) complex.¹⁹ With the unique sandwiched electrode geometry and thiolated catalyst
199 here, mono(terpyridine)-nickel complex was not observed in our spectra (Supplementary **Fig. 7**).
200 Instead, the calculated charge distribution shows the single electron gained from reduction is not
201 localised at the metal centre and instead perturbs the Au-S bond (Supplementary **Fig. 10**). This is
202 consistent with the reported electrochemistry for the nickel-centred bis(terpyridine) complexes, where
203 ligand-based redox dominates²⁰ due to the relative stability of **Ni²⁺ d⁸** outer shell electron configuration.

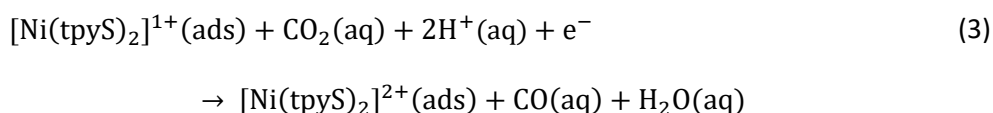
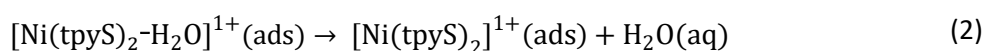
204 In addition to weakening the Au-S bond, DFT also shows that bond orders for the coordination bonds
 205 are affected (Supplementary **Table 1**). The axial Ni-N bonds on both tpyS ligands are strengthened, but
 206 the equatorial Ni-N bonds are weakened during reduction. Since partial ligand exchange is
 207 thermodynamically favourable when the complex is reduced, solvent access to the nickel centre for
 208 coordination is proposed. This is confirmed by comparison of calculated and experimental spectra of
 209 the reduced state by a discrete implementation of the earth mover's algorithm (Supplementary Note 2),
 210 whereby we find a significant improvement in spectral agreement when including a coordinated water
 211 molecule (Supplementary **Fig. 7**). Since the complexes are octahedral, at least one of the existing
 212 coordination bonds must be broken to allow CO₂ binding to the metal centre for subsequent catalytic
 213 reduction. Our experiments and computations strongly support this reaction is realised through the
 214 breaking of a single Ni-N bond followed by rotation of a pyridine unit from one tpyS ligand.
 215 (Supplementary **Fig. 7**).



216

217 **Fig. 4 | Ni(tpyS)₂ catalysed CO₂ reduction.** **a**, Experimental SERS of Ni(tpyS)₂ averaged from different nanoparticle-on-
 218 mirror (NPoM)s in CO₂-saturated pH 3.8 aqueous solution at -0.8 V and DFT calculated best-matched purple spectrum. The
 219 latter is from linear combination of the red and blue spectra, corresponding to their colour-shaded intermediates respectively
 220 in **b**. Grey bars highlight matching spectral bands between experiments and calculations. Vibrational modes relevant to CO₂
 221 reduction are highlighted in orange. More vibrational modes are shown in Supplementary **Figs. 8** and **15**. **b**, Proposed catalytic
 222 cycle of Ni(tpyS)₂ mediated CO₂ reduction. Relative Gibbs free energies (kcal mol⁻¹) are displayed in green. Shaded
 223 intermediates are spectroscopically verified. L_n represents tpyS ligands forming *n* Ni-N bonds. [L₆-Ni]²⁺ = [Ni(tpyS)₂]²⁺, [L₅-
 224 Ni-H₂O]¹⁺ = [Ni(tpyS)₂-H₂O]¹⁺.

225 **Mechanistic studies of Ni(tpyS)₂ mediated CO₂ reduction.** Performing SERS in the presence of CO₂,
226 several new spectral modes emerge (**Fig. 4a**, black). Gibbs energies (Supplementary **Table 3** and
227 Supplementary **Fig. 11**) and Raman spectra (Supplementary **Fig. 12**) were calculated for 22 different
228 reaction intermediates (Supplementary Note 3, Supplementary Table 2). Experimental SERS
229 measurements were compared with DFT calculated single and combined spectra obtained as a mixture
230 of two or three intermediates (Supplementary **Fig. 13** and Supplementary **Table 4**). In calculations, the
231 effect of electron transfer was estimated based on the measured half-cell potentials. The catalytic
232 2H⁺/2e⁻ reduction of CO₂ overall is:



233 Where eq. (2) illustrates the creation of a vacant site on [Ni(tpyS)₂]¹⁺ as H₂O dissociates. We have
234 explored the possible intermediates for a different order of electron and proton transfer steps
235 (Supplementary **Table 2**). Only spectra from the most feasible structures according to calculated Gibbs
236 and electronic energies were used for spectral matches (Supplementary **Fig. 12**). Deprotonated carboxyl
237 groups bound to the nickel centre have been reported as intermediates in bis(terpyridine) complexes
238 catalysing CO₂ reduction.^{19,37} We performed geometry optimizations for structures where we removed
239 the proton covalently bonded to the CO₂ (Supplementary **Fig. 14**). Most of these calculations show CO₂
240 detachment from the complex. For the only successfully converged structure, the reaction relative free
241 energy for deprotonation was calculated as +10 kcal mol⁻¹, hence the intermediate is less stable when
242 deprotonated. This free energy can be interpreted as a pK_a of 7.3 while the experiments are performed
243 at pH 3.8, confirming the carboxyl group is protonated. Further calculations find pK_a of the pendant
244 pyridyl group as -9.3 for [Ni(tpyS)₂-H₂O]¹⁺, which is not equivalent to the free unsubstituted ligand in
245 solution³⁸ (see Supplementary **Table 5**, Supplementary Note 4). Despite the similarity of the molecules
246 to those in the literature, bis(terpyridine) ligands have been used as homogeneous systems where a

247 terpyridine has been proposed to dissociate after its first reduction. Our work is performed in a confined
248 environment with two Au-S anchoring points imposing electronic and steric constraints on the system,
249 giving distinctive pK_a and intermediates.

250 The best spectral match in CO_2 conditions (**Fig. 4a**, purple) is a linear combination of two different
251 species (**Fig. 4a**, red and blue) that correspond to the shaded intermediates in **Fig. 4b**. Vibrational modes
252 of these intermediates are assigned and discussed in Supplementary Note 5 and Supplementary **Figs. 8**
253 and **15**. $\nu(\text{C}=\text{O})$ is low intensity and absent from some NPoMs, due to weak enhancement when $\text{C}=\text{O}$
254 is near perpendicular to the gap optical field (in the DFT unpolarized excitations are used). We find
255 (Supplementary **Table 4**) 75% of the spectral contribution is from $[\text{L}_5\text{-Ni-OH}_2]^{1+}$ (see full structure in
256 **Fig. 3b**, red), and 25% is from $[\text{L}_5\text{-Ni-COOH}]^{1+}$ (see full structure in **Fig. 4a**, blue). Using the size of
257 individual nanostructures and single molecules, the number of molecules in the plasmonic hotspot can
258 be estimated geometrically as 32 (see Supplementary Note 6). Combining these numbers, we are able
259 to detect and identify ~ 8 molecules undergoing catalytic turnover optically. Consecutive SERS spectra
260 with real-time chronoamperometry (Supplementary **Fig. 6**) show more stochastic behaviour of
261 reduction onset for NPoM samples compared with electrochemically roughened gold, as is expected for
262 the few-molecule regime.

263 A catalytic cycle is proposed (**Fig. 4b**) based on combined spectroscopic and computational results.
264 Following the initial reduction and Ni-N bond breaking, the water coordinated species $[\text{L}_5\text{-Ni-OH}_2]^{1+}$
265 is formed. The water molecule is highly labile and creates a vacant site on the nickel centre as it
266 dissociates. After the second reduction step, the nickel centre is sufficiently nucleophilic to attack the
267 CO_2 carbon atom, forming CO as the catalytic product. **Fig. 16** and Supplementary Note 7 contain
268 further discussion.

269 **Conclusions**

270 We have introduced an electrode geometry for *in-situ* spectro-electrochemical SERS measurement with
271 excellent signal-to-noise ratios owing to gap-plasmon enhancements. We spectroscopically track the

272 redox transitions of as few as 8 molecules, showing that single molecular catalyst spectroscopy is within
273 reach. The electrochemical properties of the nanoparticle-on-mirror (NPoM) electrode are compared
274 with the standard roughened gold electrode *via* the vibrational Stark effect, finding that NPoM is a
275 promising electrode geometry for surface bound species. Utilising this electrode, we probe the
276 electrocatalytic mechanism of CO₂ reduction by the molecular catalyst, **Ni(tpyS)₂**. Through virtual
277 screening of intermediates in combination with SERS, we identify a reaction pathway that involves an
278 anchoring group-based intermediate species, emphasising that the nature of the anchoring group can
279 play a pivotal role for surface-bound catalysis. This electrode geometry successfully tunes the catalytic
280 reaction mechanism by preventing ligand loss and hence facilitates facile recovery of catalyst.

281 **Methods**

282 **Assembly of Ni(tpyS)₂**. All chemicals were purchased from Sigma-Aldrich unless stated otherwise, at
283 the highest purity available and used as received. **Ni(tpyS)₂** is the abbreviation for [Ni(2,2':6',2''-
284 terpyridine-4'-thiol)₂](BF₄)₂. It was assembled by a previously reported procedure.¹⁹ 2,2':6',2''-
285 terpyridine-4'-thiol (tpyS) was purchased from HetCat (Switzerland) and Ni(BF₄)₂.6H₂O was purchased
286 from Acros Organics.

287 **Electrode preparation.** Gold electrodes were fabricated by the template-stripping method as reported
288 elsewhere³⁹. **Ni(tpyS)₂** SAMs were formed by immersing gold electrodes in a 1 mM **Ni(tpyS)₂**
289 acetonitrile solution for 22 hours, rinsing with acetonitrile and drying with compressed N₂. Standard
290 gold nanoparticles (AuNPs) in a citrate buffer were purchased from BBI solutions³⁰ (60 nm, 80 nm)
291 with reported morphology¹⁰. AuNPs were deposited by drop-casting AuNP solution onto the sample for
292 20 s, rinsing with distilled water and drying with compressed N₂. Electrochemically roughened gold
293 electrodes were made using an established oxidation and reduction cycling method⁴⁰. Gold films were
294 immersed in 0.1 M KCl and potentiostatted at -0.6 V vs Ag/AgCl for 10 s, then swept to 1.1 V and held
295 at this potential for 2 s. The samples were swept back to -0.6 V and these steps were repeated 25 times.
296 **Ni(tpyS)₂** monolayer was formed as above.

297 **Spectro-electrochemical cell.** A specially designed three-electrode 3D-printed cell is used for all
298 spectro-electrochemical measurements. NPoM samples are used as working electrode, a platinum mesh
299 (Alfa Aesar) as counter electrode, and Ag/AgCl (3 M KCl, eDAQ ET072, Green Leaf Scientific) as
300 reference electrode. The cell is closed by a $25 \times 25 \times 0.2$ mm glass cover slip. Sample to coverslip
301 distance is approximately 0.3 mm to allow high NA collection of SERS scattering. Electrochemical
302 measurements were recorded on a CompactStat (Ivium Technologies) or an Autolab PGSTAT204
303 (Metrohm).

304 **SERS collection.** SERS measurements were recorded on a modified Olympus BX51 coupled to a 633
305 nm laser set at powers below $100 \mu\text{W}$. Excitation and collection were through an Olympus
306 MPLFLN100xBD NA0.9 objective. Spectra were recorded by an Andor camera coupled to a Triax 320
307 spectrometer.

308 **Dark-field scattering spectroscopy.** Dark field spectroscopy was performed on a modified Olympus
309 BX51 coupled to an incoherent white light source. Excitation and collection were through a 0.8 NA
310 Olympus LWD BF/DF objective. Spectra were recorded on a fibre-coupled OceanOptics QE65000.
311 Automated scans were performed by a Python particle tracking code.²⁹ A standard diffuser was used as
312 a reference to normalise white light scattering.

313 **UV/Vis collection.** UV-Vis spectra were recorded on a Cary 50 (Varian) with a quartz UV-Visible
314 cuvette (Fisher).

315 **DFT calculations.** Absorbed **Ni(tpyS)₂** molecules were modelled as thiol groups anchored to single
316 gold atoms on both ends. DFT from a single Au atom shows an excellent match with the experimental
317 SERS⁴¹ at a much lower computational cost comparing to DFT from large Au clusters,^{17,31} and is
318 sufficient to describe any charge transfer to the molecules. Although Ni(II) can form square planar and
319 tetrahedral complexes, bis(terpyridine) ligands form strong octahedral coordination due to steric
320 considerations.⁴² DFT optimization performed for $[\text{Ni}(\text{tpyS})_2]^{2+}$ gives a clear preference for the
321 tetrahedral rather than square planar by a relative free energy of $-24.4 \text{ kcal mol}^{-1}$. Both literature and

322 DFT optimization thus confirm this geometry. Geometry optimizations and frequency calculations were
323 performed with B3LYP⁴³ hybrid functional and def2SVP basis set including core potentials as
324 implemented in Gaussian09 Revision E.⁴⁴ Non-covalent interactions were corrected using Grimme's
325 dispersion correction version 3 with Becke-Johnson damping.⁴⁵ Charge distribution and bond indices
326 were calculated using the natural bond analysis (NBO) package.^{46,47} Free energies were estimated based
327 on single point electronic energies calculated with def2TZVPP⁴⁸ basis set, thermal corrections obtained
328 using RRHO approximation, solvent correction was incorporated with PCM solvation using SMD
329 parametrisation.⁴⁹ Stability of the wave functions were ensured in all cases. Free energy corrections
330 were introduced for both reduction steps as $\Delta G = eV$, cost of protonation was calculated for the pH of
331 3.8 based on the experimental free energy of a solvated proton.⁵⁰ Computational spectra were scaled by
332 a factor of 0.978 to match with experiment. More details on the matching are available in Supplementary
333 Note 2.

334 **Data availability**

335 The data that support the findings of this study are available from the University of Cambridge data
336 repository at DOI: 10.17863/CAM.60379.

337 **Code availability**

338 The code for spectral matching using the Earth Mover's algorithm is available from the University of
339 Cambridge data repository at DOI: 10.17863/CAM.60379.

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468 **Author contributions**

469 D.W., Q.L., E.Reisner and J.J.B. conceived the research and developed the experiments. D.B., T.F. and
470 E.Rosta carried out density functional theory calculations and provided input on catalytic interpretation.
471 A.W. and E.Reisner provided input on interpretation of electrochemical and catalytic results. J.G.
472 helped with spectral analysis. C.R. helped with synthesis of **Ni(tpyS)₂**. D.W., Q.L., D.B., T.F. and J.J.B.
473 analysed the data and wrote the manuscript with input from all authors.

474 **Competing interests**

475 The authors declare no competing interests.

476 **Additional information**

477 **Supplementary information** is available for the following files: UV-Vis spectra, dark-field image,
478 additional cyclic voltammograms, dark-field scattering spectra, SERS spectra, and DFT calculations in
479 pdf file; and the atomic coordinates of the optimised models are provided in Supplementary Data 1.