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.
**Introduction**

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

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

In this work, we perform gap-plasmon-assisted SERS coupled with electrochemistry to study the CO\(_2\) reduction catalyst \([\text{Ni}(2,2':6',2''-\text{terpyridine}-4''\text{-thiol})_2](\text{BF}_4)_2\) (Ni(tpyS)\(_2\)).\(^19\) While bis(terpyridine) complexes of cobalt and nickel have been previously used for electrocatalytic CO\(_2\) reduction,\(^19-21\) no
mechanistic studies have been performed in a sandwich geometry with a highly confined volume. The nickel-centred complex is chosen in this study due to its excellent selectivity for CO$_2$ reduction towards CO over hydrogen evolution.$^{19-21}$ Using *in-situ* SERS between two gold surfaces we are able to characterise the spectro-electrochemical behaviour, resolving changes in chemical bonding and identifying the catalytic reaction mechanism. Comparing experimental SERS spectra with density functional theory (DFT) calculations of Ni(tpyS)$_2$ shows the first electron transferred during reduction weakens the Au-S bonds, while the electronic environment of the metal centre changes less, confirming that the nature of the anchoring group plays a pivotal role in the catalytic mechanism. Electrode design such as confined environments$^{22}$ and layered geometries$^{23,24}$ advance the catalysis by enhancing nanoscale mass transport and electrode dynamics compared to conventional electrodes. We utilise a single-site sandwiched electrode geometry with a molecular catalyst. Compared to the conventional system with solution-phase nickel catalysts,$^{19,20}$ this electrode geometry with adsorbed catalyst is likely to change the reaction mechanism as it allows the gained electron from reduction to delocalise over the Au-S anchoring unit, inhibits ligand loss and preserves catalyst integrity. This work gives unique insights into material-molecule hybrid catalysis by going beyond prior work on redox-inactive biphenyl monolayers where changes in molecule polarizability are induced electrochemically,$^{25}$ or tracking resonant molecules when they enter and leave electronically-active states during redox transitions.$^{26}$

**Results**

**Gap-plasmon-assisted spectro-electrochemical assembly.** Gap plasmon cavities have extremely small mode volumes (< 50 nm$^3$) with high optical field enhancements (>500) that strongly amplify the Raman scattering of molecules in the gap by >10$^9$. To construct the nanoparticle-on-mirror (NPoM) plasmonic cavities used here, planar gold substrates are functionalised with a self-assembled monolayer (SAM, see Methods). Gold nanoparticles (AuNPs) are then drop-cast on top of the monolayer (**Fig. 1a**), sandwiching the active molecules in the nano-gap. The advantage of this geometry is that the gold mirror conveniently forms one electrode of the cell (**Fig. 1a**). Dark-field scattering spectra (**Fig. 1b,c**) on each NPoM characterise the monolayer quality in the gap. These scattering spectra show transverse ($\lambda_c$~530 nm) and coupled ($\lambda_c$~700 nm) modes in the NPoM nanocavities. The coupled plasmon at $\lambda_c$
arises from the interaction of the nanoparticle with its image charges in the mirror below, tightly
confining the plasmonic hot spot underneath the NPoM.\textsuperscript{1,27} The position of $\lambda_c$ strongly depends on the
properties of the gap spacer, including its thickness ($d$) and effective refractive index ($n_g$).\textsuperscript{28} Using
automated tracking microscopy,\textsuperscript{29} dark-field scattering spectra are observed for many hundreds of
individual NPoMs across the sample surface. Real-time spectro-electrochemical measurements are
achieved by incorporating NPoM samples into a 3D-printed cell. SERS spectra are recorded by
illuminating individual NPoMs with a continuous wave laser at wavelength $\lambda_l = 633$ nm, with
electrochemical potential applied simultaneously to the gold substrate using a 3-electrode configuration.

**Electric field calibration by vibrational Stark effect.** The electrochemical control of the applied
potential in the nano-gap was first probed with SERS from a calibration molecule, PDI (1,4-phenylene
diisocyanide) (Fig. 1a). Scattering spectra for PDI monolayers are measured from automated tracking
of >400 NPoMs (Fig. 1b). These give near-identical coupled modes at $\lambda_c = 739 \pm 22$ nm (Fig. 1c),
indicating a highly consistent monolayer over the gold substrate (standard error matches variation in
nanoparticle size and shape\textsuperscript{30}). Modelling the coupled mode resonance\textsuperscript{28} gives $n_{g,\text{PDI}} = 1.4$ and $d_{\text{PDI}} =
1$ nm, which is consistent with the thickness expected for a monolayer in which the molecules bind to
the substrate in a near-vertical rather than flat orientation. SERS spectra for PDI in NPoMs (Fig. 1d)
are recorded at potentials ranging from $-0.6$ to $+0.2$ V (vs. Ag/AgCl) in a $\text{N}_2$-saturated aqueous solution
with a 0.1 M KCl supporting electrolyte. In this electrochemically inert range for PDI (Supplementary
Fig. 1), the SERS band near 2130 cm\textsuperscript{-1} shows a significant blue-shift as positive potential is applied,
shifting linearly at 30 ± 4 cm\textsuperscript{-1} V\textsuperscript{-1} (Fig. 1e, black). This is consistent with the stretching mode for
isocyanide ($\text{N}≡\text{C}$) bound to the gold surface\textsuperscript{31}. For comparison, SERS spectra for PDI at
electrochemically roughened gold surfaces are recorded and analysed (Fig. 1e, grey) in the same
conditions, where $\nu(\text{N}≡\text{C})$ shifts by 31 ± 1 cm\textsuperscript{-1} V\textsuperscript{-1}. 

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

These SERS shifts arise from the vibrational Stark effect (VSE),\textsuperscript{31–33} where the vibrational energies of chemical bonds are perturbed by an electric field. The Stark shift versus potential, known as the Stark tuning rate, enables direct measurement of the potential gradient at the electrode. Our measurements provide direct evidence that the electrochemical potential gradient (\textit{i.e.} electric field) at the NPoM surface of a SAM is identical to that found at a roughened electrode surface of a SAM. While electron tunnelling has been reported across NPoM plasmonic gaps, the electron transfer process at the interface between the SAM and this sandwiched electrode geometry remains unclear.\textsuperscript{12,13} To address this question, a model of the electrical double layer\textsuperscript{31,34} for the NPoM junction (Fig. 1f) is developed here. As the SAM is adsorbed on the gold substrate, the electrical centre of the monolayer is the Inner Helmholtz Plane (IHP). Solvated ions from the supporting electrolyte approach the SAM by diffusion,
and the position of these nearest ions is the Outer Helmholtz Plane (OHP), roughly corresponding to the length of molecules ($d = 1$ nm). Following the double layer capacitive (non-Faradaic) charging, the potential drops rapidly within the OHP. Faradaic electron transfer takes place readily between the gold substrate and the monolayer (as observed below). This electron transfer process is similar to the case when no nanoparticle is on top of the SAM, implying that electron tunnelling is not the only path across the gaps, otherwise the VSE should not be observed. In fact, the electron tunnelling is less efficient due to the 1 nm barrier width and hence an electron transfer process through the SAM dominates (Supplementary Fig. 2).

![Fig. 2](image_url)

**Fig. 2** | Dark-field scattering spectroscopy and electrochemistry for Ni(tpyS)$_2$. **a**, Ni(tpyS)$_2$ in nanoparticle-on-mirror (NPoM) geometry. **b**, Histogram of plasmon coupled mode positions. Inset shows spatial image of single 60 nm diameter NPoM. **c**, Scattering spectra for Ni(tpyS)$_2$ monolayer in NPoM. **d**, Cyclic voltammograms for NPoMs with (solid lines) or without (dashed line) Ni(tpyS)$_2$ monolayer in pH 3.8 aqueous solution supported with 0.1 M KCl and saturated with N$_2$ (black) or CO$_2$ (red). Scan rate = 100 mV s$^{-1}$.

**Spectro-electrochemical studies of immobilised Ni(tpyS)$_2$**. Using Ni(tpyS)$_2$ in the nano-gap (Fig. 2a) allows tracking of redox and catalytic reactions. Scattering spectra for Ni(tpyS)$_2$ monolayer measured from >1000 NPoMs (Figs. 2b,c) shows the coupled mode at $\lambda_c = 696 \pm 15$ nm, confirming the monolayer is uniform with $n_g\text{Ni(tpyS)}_2 = 1.4$ and $d\text{Ni(tpyS)}_2 = 1.5$ nm. A dark field image (Supplementary Fig. 3) demonstrates nanoparticle distribution. Cyclic voltammetry (CV) for Ni(tpyS)$_2$ NPoMs is first recorded in a N$_2$-saturated pH 3.8 aqueous solution supported with 0.1 M KCl, from 0 to $-1.2$ V (vs Ag/AgCl) and back to 0 V (Fig. 2d, black). Two reductive waves are observed: red1 at $E_p = -0.76$ V and red2 at $E_p = -0.99$ V, corresponding to the first and second reduction of Ni(tpyS)$_2$.$^{19,20}$
electrochemical responses are markedly different from the voltammogram when no nanoparticle is on top of the Au-Ni(tpyS)_2 monolayer (Supplementary Fig. 4, blue). In the absence of AuNPs, the lack of oxidative waves indicates the redox process is chemically irreversible. This may in part be due to the loss of one tpyS ligand. While in the NPoM construct, the presence of two oxidative waves supports a chemically reversible process, confirming preservation of the tpyS ligand coordinated to the nickel centre. Voltammetric features of Ni(tpyS)_2 are significantly clearer, indicating that the voltammogram is dominated by the molecules underneath the nanoparticles, rather than the exposed monolayer. As a result, the CV directly measures conditions in the gap. More importantly, while a broad peak at ~0.86 V is observed in the absence of the nanoparticle on top (Supplementary Fig. 4, blue), the presence of nanoparticles shows a well-defined reductive peak shifting by ~+0.1 V (Supplementary Fig. 4, black). This can be explained by the reduction of the monolayer becoming thermodynamically more favourable, due to stabilisation of the reduced radical species via adsorption by the nanoparticle on top (Supplementary Fig. 4d).^{36} The nanoparticle further stabilises the adsorbed system by withdrawing electron density from the monolayer, making reduction easier. This stabilisation is not molecule specific, as for PDI the ν(N≡C) shifts by ~−5 cm\(^{-1}\) in NPoMs vs. a rough gold electrode (Fig. 1e). NPoM plasmonic cavities thus significantly enhance interfacial electron transfer.

The CV for CO\(_2\) catalytic reduction is recorded in a CO\(_2\)-saturated solution with Ni(tpyS)_2 NPoMs (Fig. 2d, red solid line), and compared with CO\(_2\) reduction on the gold substrate without Ni(tpyS)_2 monolayer in the same solution (Fig. 2d, red dashed line). Comparison of these shows over 2-fold increased current density with the onset potential shifting to ~−0.52 V, illustrating that the electrocatalytic CO\(_2\) reduction is mediated by Ni(tpyS)_2 NPoMs before proton reduction on gold.\(^{25}\)
Fig. 3 | Surface-enhanced Raman spectroscopy (SERS) and density functional theory (DFT) calculations for Ni(tpyS)₂.

(a) Experimental SERS spectra of Ni(tpyS)₂ in nanoparticle-on-mirror (NPoM) at 0 V (black) and −0.6 V (red, difference spectrum) vs Ag/AgCl in pH 3.8 aqueous solution supported with 0.1 M KCl and saturated with N₂. Additional bands appearing at −0.6 V are highlighted in grey.

(b) DFT calculations for [Ni(tpyS)₂]²⁺ and [Ni(tpyS)₂-H₂O]¹⁺.

SERS is now used to explore chemical bonding changes. SERS spectra (Fig. 3a) are recorded for the reduced state ([Ni(tpyS)₂]¹⁺, −0.6 V) and oxidised state ([Ni(tpyS)₂]²⁺, 0 V vs. Ag/AgCl, according to the CV in Fig. 2d). To avoid proton reduction which forms bubbles disrupting the optical measurements, potentials are kept at −0.6 V to observe Ni(tpyS)₂ in the first reduced state only.

Comparison of these spectra shows that during reduction, the SERS background increases and several spectral bands emerge (highlighted in grey). Despite attenuation and scattering from the spectro-electrochemical cell, SERS signals exceed 10 cts (µW.s)⁻¹ with a high signal-to-noise ratio. While Ni(tpyS)₂ is electronically non-resonant at λᵢ = 633 nm (Supplementary Fig. 5 shows no absorption/emission at λᵢ, which is essential to correctly measure electrochemical performance), the
near-resonant plasmonic mode at 696 nm strongly enhances the SERS (Fig. 2c). Similar measurements for Ni(tpyS)$_2$ on an electrochemically roughened gold substrate (Supplementary Fig. 6) show spectral changes in the reduced [Ni(tpyS)$_2$]$^{1+}$ state, though with broader, less defined SERS bands with an order of magnitude lower intensity.

DFT calculations are performed to simulate the SERS responses for Ni(tpyS)$_2$ in different redox states. Comparison of computational spectra with experimental SERS for [Ni(tpyS)$_2$]$^{2+}$ (black lines Figs. 3a,b) shows excellent agreement. We consider several possible reduction products for bis(terpyridine) complexes involving different mechanisms including those in refs. 19,21. The calculated Raman spectra (Supplementary Fig. 7) shows that [Ni(tpyS)$_2$·H$_2$O]$^{1+}$ involving a one electron reduction of the ligand and an addition of a water molecule to the nickel coordination gives the best agreement with experiments (red lines in Fig. 3). The spectral bands are labelled with relevant vibrational modes and discussed in Supplementary Fig. 8 and Supplementary Note 1. Further DFT calculations considering effects of the electrical double layer on the polarization of dipoles (Supplementary Fig. 9) shows the same spectral matching results with calculations from isotropic and unpolarized environments. The first reduction process red1 (Fig. 2d) is thus identified as the electron transfer step:

$$\text{[Ni(tpyS)$_2$]}^{2+}(\text{ads}) + e^- + \text{H}_2\text{O(aq)} \rightleftharpoons \text{[Ni(tpyS)$_2$·H$_2$O]}^{1+}(\text{ads})$$  \hspace{1cm} (1)

The reduction process for the dissolved non-thiolated catalyst, [Ni(2,2’:6’,2”-terpyridine)$_2$](BF$_4$)$_2$ (Ni(tpy)$_2$)$_2$, has been suggested to accompany the loss of one terpyridine ligand to form an active mono(terpyridine) complex.\textsuperscript{19} With the unique sandwiched electrode geometry and thiolated catalyst here, mono(terpyridine)-nickel complex was not observed in our spectra (Supplementary Fig. 7). Instead, the calculated charge distribution shows the single electron gained from reduction is not localised at the metal centre and instead perturbs the Au-S bond (Supplementary Fig. 10). This is consistent with the reported electrochemistry for the nickel-centred bis(terpyridine) complexes, where ligand-based redox dominates\textsuperscript{20} due to the relative stability of Ni$^{2+}$ d\textsuperscript{8} outer shell electron configuration.
In addition to weakening the Au-S bond, DFT also shows that bond orders for the coordination bonds are affected (Supplementary Table 1). The axial Ni-N bonds on both tpyS ligands are strengthened, but the equatorial Ni-N bonds are weakened during reduction. Since partial ligand exchange is thermodynamically favourable when the complex is reduced, solvent access to the nickel centre for coordination is proposed. This is confirmed by comparison of calculated and experimental spectra of the reduced state by a discrete implementation of the earth mover’s algorithm (Supplementary Note 2), whereby we find a significant improvement in spectral agreement when including a coordinated water molecule (Supplementary Fig. 7). Since the complexes are octahedral, at least one of the existing coordination bonds must be broken to allow CO₂ binding to the metal centre for subsequent catalytic reduction. Our experiments and computations strongly support this reaction is realised through the breaking of a single Ni-N bond followed by rotation of a pyridine unit from one tpyS ligand. (Supplementary Fig. 7).

**Fig. 4** Ni(tpyS)₂ catalysed CO₂ reduction. a, Experimental SERS of Ni(tpyS)₂ averaged from different nanoparticle-on-mirror (NPoM)is in CO₂-saturated pH 3.8 aqueous solution at −0.8 V and DFT calculated best-matched purple spectrum. The latter is from linear combination of the red and blue spectra, corresponding to their colour-shaded intermediates respectively in b. Grey bars highlight matching spectral bands between experiments and calculations. Vibrational modes relevant to CO₂ reduction are highlighted in orange. More vibrational modes are shown in Supplementary Figs. 8 and 15. b, Proposed catalytic cycle of Ni(tpyS)₉ mediated CO₂ reduction. Relative Gibbs free energies (kcal mol⁻¹) are displayed in green. Shaded intermediates are spectroscopically verified. Lₙ represents tpyS ligands forming n Ni-N bonds. [L₅-Ni][²⁺ = [Ni(tpyS)₂]²⁺, [L₅-Ni-H₂O][⁺ = [Ni(tpyS)₂]-H₂O][⁺].

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Mechanistic studies of Ni(tpyS)$_2$ mediated CO$_2$ reduction. Performing SERS in the presence of CO$_2$, several new spectral modes emerge (Fig. 4a, black). Gibbs energies (Supplementary Table 3 and Supplementary Fig. 11) and Raman spectra (Supplementary Fig. 12) were calculated for 22 different reaction intermediates (Supplementary Note 3, Supplementary Table 2). Experimental SERS measurements were compared with DFT calculated single and combined spectra obtained as a mixture of two or three intermediates (Supplementary Fig. 13 and Supplementary Table 4). In calculations, the effect of electron transfer was estimated based on the measured half-cell potentials. The catalytic 2H$^+/2e^-$ reduction of CO$_2$ overall is:

$$[\text{Ni(tpyS)}_{2}\text{-H}_2\text{O}]^{1+}(\text{ads}) \rightarrow [\text{Ni(tpyS)}_{2}]^{1+}(\text{ads}) + \text{H}_2\text{O(aq)} \quad (2)$$

$$[\text{Ni(tpyS)}_{2}]^{1+}(\text{ads}) + \text{CO}_2(\text{aq}) + 2\text{H}^+(\text{aq}) + e^- \rightarrow [\text{Ni(tpyS)}_{2}]^{2+}(\text{ads}) + \text{CO(aq)} + \text{H}_2\text{O(aq)} \quad (3)$$

Where eq. (2) illustrates the creation of a vacant site on [Ni(tpyS)$_2$]$^{1+}$ as H$_2$O dissociates. We have explored the possible intermediates for a different order of electron and proton transfer steps (Supplementary Table 2). Only spectra from the most feasible structures according to calculated Gibbs and electronic energies were used for spectral matches (Supplementary Fig. 12). Deprotonated carboxyl groups bound to the nickel centre have been reported as intermediates in bis(terpyridine) complexes catalysing CO$_2$ reduction.$^{19,37}$ We performed geometry optimizations for structures where we removed the proton covalently bonded to the CO$_2$ (Supplementary Fig. 14). Most of these calculations show CO$_2$ detachment from the complex. For the only successfully converged structure, the reaction relative free energy for deprotonation was calculated as $+10$ kcal mol$^{-1}$, hence the intermediate is less stable when deprotonated. This free energy can be interpreted as a $pK_a$ of 7.3 while the experiments are performed at pH 3.8, confirming the carboxyl group is protonated. Further calculations find $pK_a$ of the pendant pyridyl group as $-9.3$ for [Ni(tpyS)$_2$-H$_2$O]$^{1+}$, which is not equivalent to the free unsubstituted ligand in solution$^{38}$ (see Supplementary Table 5, Supplementary Note 4). Despite the similarity of the molecules to those in the literature, bis(terpyridine) ligands have been used as homogeneous systems where a
terpyridine has been proposed to dissociate after its first reduction. Our work is performed in a confined environment with two Au-S anchoring points imposing electronic and steric constraints on the system, giving distinctive pK_{a} and intermediates.

The best spectral match in CO\textsubscript{2} conditions (Fig. 4a, purple) is a linear combination of two different species (Fig. 4a, red and blue) that correspond to the shaded intermediates in Fig. 4b. Vibrational modes of these intermediates are assigned and discussed in Supplementary Note 5 and Supplementary Figs. 8 and 15. ν(C=O) is low intensity and absent from some NPoMs, due to weak enhancement when C=O is near perpendicular to the gap optical field (in the DFT unpolarized excitations are used). We find (Supplementary Table 4) 75% of the spectral contribution is from [L\textsubscript{5}-Ni-OH\textsubscript{2}]\textsuperscript{1+} (see full structure in Fig. 3b, red), and 25% is from [L\textsubscript{5}-Ni-COOH]\textsuperscript{1+} (see full structure in Fig. 4a, blue). Using the size of individual nanostructures and single molecules, the number of molecules in the plasmonic hotspot can be estimated geometrically as 32 (see Supplementary Note 6). Combining these numbers, we are able to detect and identify ~8 molecules undergoing catalytic turnover optically. Consecutive SERS spectra with real-time chronoamperometry (Supplementary Fig. 6) show more stochastic behaviour of reduction onset for NPoM samples compared with electrochemically roughened gold, as is expected for the few-molecule regime.

A catalytic cycle is proposed (Fig. 4b) based on combined spectroscopic and computational results. Following the initial reduction and Ni-N bond breaking, the water coordinated species [L\textsubscript{5}-Ni-OH\textsubscript{2}]\textsuperscript{1+} is formed. The water molecule is highly labile and creates a vacant site on the nickel centre as it dissociates. After the second reduction step, the nickel centre is sufficiently nucleophilic to attack the CO\textsubscript{2} carbon atom, forming CO as the catalytic product. Fig. 16 and Supplementary Note 7 contain further discussion.

Conclusions

We have introduced an electrode geometry for in-situ spectro-electrochemical SERS measurement with excellent signal-to-noise ratios owing to gap-plasmon enhancements. We spectroscopically track the
redox transitions of as few as 8 molecules, showing that single molecular catalyst spectroscopy is within reach. The electrochemical properties of the nanoparticle-on-mirror (NPoM) electrode are compared with the standard roughened gold electrode via the vibrational Stark effect, finding that NPoM is a promising electrode geometry for surface bound species. Utilising this electrode, we probe the electrocatalytic mechanism of CO$_2$ reduction by the molecular catalyst, Ni(tpyS)$_2$. Through virtual screening of intermediates in combination with SERS, we identify a reaction pathway that involves an anchoring group-based intermediate species, emphasising that the nature of the anchoring group can play a pivotal role for surface-bound catalysis. This electrode geometry successfully tunes the catalytic reaction mechanism by preventing ligand loss and hence facilitates facile recovery of catalyst.

**Methods**

Assembly of Ni(tpyS)$_2$. All chemicals were purchased from Sigma-Aldrich unless stated otherwise, at the highest purity available and used as received. Ni(tpyS)$_2$ is the abbreviation for [Ni(2,2′:6′,2″-terpyridine-4′-thiol)$_2$(BF$_4$)$_2$. It was assembled by a previously reported procedure.$^{19}$ 2,2′:6′,2″-terpyridine-4′-thiol (tpyS) was purchased from HetCat (Switzerland) and Ni(BF$_4$)$_2$.6H$_2$O was purchased from Acros Organics.

Electrode preparation. Gold electrodes were fabricated by the template-stripping method as reported elsewhere.$^{39}$ Ni(tpyS)$_2$ SAMs were formed by immersing gold electrodes in a 1 mM Ni(tpyS)$_2$ acetonitrile solution for 22 hours, rinsing with acetonitrile and drying with compressed N$_2$. Standard gold nanoparticles (AuNPs) in a citrate buffer were purchased from BBI solutions$^{30}$ (60 nm, 80 nm) with reported morphology.$^{10}$ AuNPs were deposited by drop-casting AuNP solution onto the sample for 20 s, rinsing with distilled water and drying with compressed N$_2$. Electrochemically roughened gold electrodes were made using an established oxidation and reduction cycling method.$^{40}$ Gold films were 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 at this potential for 2 s. The samples were swept back to -0.6 V and these steps were repeated 25 times. Ni(tpyS)$_2$ monolayer was formed as above.
Spectro-electrochemical cell. A specially designed three-electrode 3D-printed cell is used for all spectro-electrochemical measurements. NPoM samples are used as working electrode, a platinum mesh (Alfa Aesar) as counter electrode, and Ag/AgCl (3 M KCl, eDAQ ET072, Green Leaf Scientific) as reference electrode. The cell is closed by a 25 × 25 × 0.2 mm glass cover slip. Sample to coverslip distance is approximately 0.3 mm to allow high NA collection of SERS scattering. Electrochemical measurements were recorded on a CompactStat (Ivium Technologies) or an Autolab PGSTAT204 (Metrohm).

SERS collection. SERS measurements were recorded on a modified Olympus BX51 coupled to a 633 nm laser set at powers below 100 μW. Excitation and collection were through an Olympus MPLFLN100xBD NA0.9 objective. Spectra were recorded by an Andor camera coupled to a Triax 320 spectrometer.

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

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

DFT calculations. Absorbed Ni(tpyS)₂ molecules were modelled as thiol groups anchored to single gold atoms on both ends. DFT from a single Au atom shows an excellent match with the experimental SERS at a much lower computational cost comparing to DFT from large Au clusters, and is sufficient to describe any charge transfer to the molecules. Although Ni(II) can form square planar and tetrahedral complexes, bis(terpyridine) ligands form strong octahedral coordination due to steric considerations. DFT optimization performed for [Ni(tpyS)₂]³⁺ gives a clear preference for the tetrahedral rather than square planar by a relative free energy of -24.4 kcal mol⁻¹. Both literature and
DFT optimization thus confirm this geometry. Geometry optimizations and frequency calculations were performed with B3LYP\textsuperscript{43} hybrid functional and def2SVP basis set including core potentials as implemented in Gaussian09 Revision E.\textsuperscript{44} Non-covalent interactions were corrected using Grimme’s dispersion correction version 3 with Becke-Johnson dumping.\textsuperscript{45} Charge distribution and bond indices were calculated using the natural bond analysis (NBO) package.\textsuperscript{46,47} Free energies were estimated based on single point electronic energies calculated with def2TZVPP\textsuperscript{48} basis set, thermal corrections obtained using RRHO approximation, solvent correction was incorporated with PCM solvation using SMD parametrisation.\textsuperscript{49} Stability of the wave functions were ensured in all cases. Free energy corrections were introduced for both reduction steps as $\Delta G=\text{eV}$, cost of protonation was calculated for the pH of 3.8 based on the experimental free energy of a solvated proton.\textsuperscript{50} Computational spectra were scaled by a factor of 0.978 to match with experiment. More details on the matching are available in Supplementary Note 2.

**Data availability**

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

**Code availability**

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

We thank G. Di Martino for support with spectro-electrochemical cell design, thank B. de Nijs for support with Raman facilities, and thank D.-B. Grys for support with understanding on polarized and unpolarized DFT. We acknowledge funding from the EPSRC (EP/L027151/1, EP/R013012/1, and Cambridge NanoDTC EP/L015978/1 to D.W. and C.R.), and the ERC (Project No. 757850 BioNet to D.B. and T.F.). We are grateful to the UK Materials and Molecular Modelling Hub for computational resources, which is partially funded by EPSRC (EP/P020194/1). The authors acknowledge use of the research computing facility at King’s College London, Rosalind (https://rosalind.kcl.ac.uk).

Author contributions

D.W., Q.L., E.Reisner and J.J.B. conceived the research and developed the experiments. D.B., T.F. and E.Rosta carried out density functional theory calculations and provided input on catalytic interpretation. A.W. and E.Reisner provided input on interpretation of electrochemical and catalytic results. J.G. 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. analysed the data and wrote the manuscript with input from all authors.

Competing interests

The authors declare no competing interests.

Additional information

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