

## Mechanistic insights into electrocatalytic reactions provided by SERS

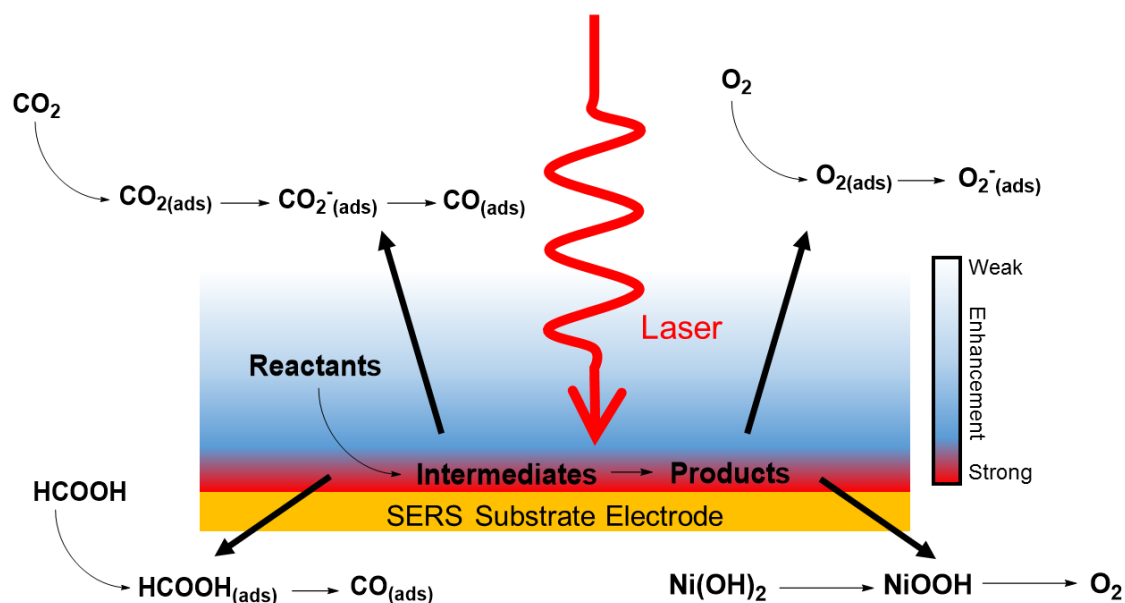
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### Abstract

*In situ* vibrational spectroscopy can provide molecular level mechanistic insights missing from purely electrochemical measurements. Surface enhanced Raman spectroscopy (SERS) is a particularly promising method and is employed in aqueous and non-aqueous studies of a variety of electrode reactions. Enhancement of the weak Raman signal is achieved by structuring the electrode surface or by use of SERS probes. This review article highlights the recent use of SERS to study several important electrode reactions; oxygen reduction and evolution, carbon monoxide oxidation and carbon dioxide reduction, and the electrocatalytic oxidation of small organic molecules such as formic acid.



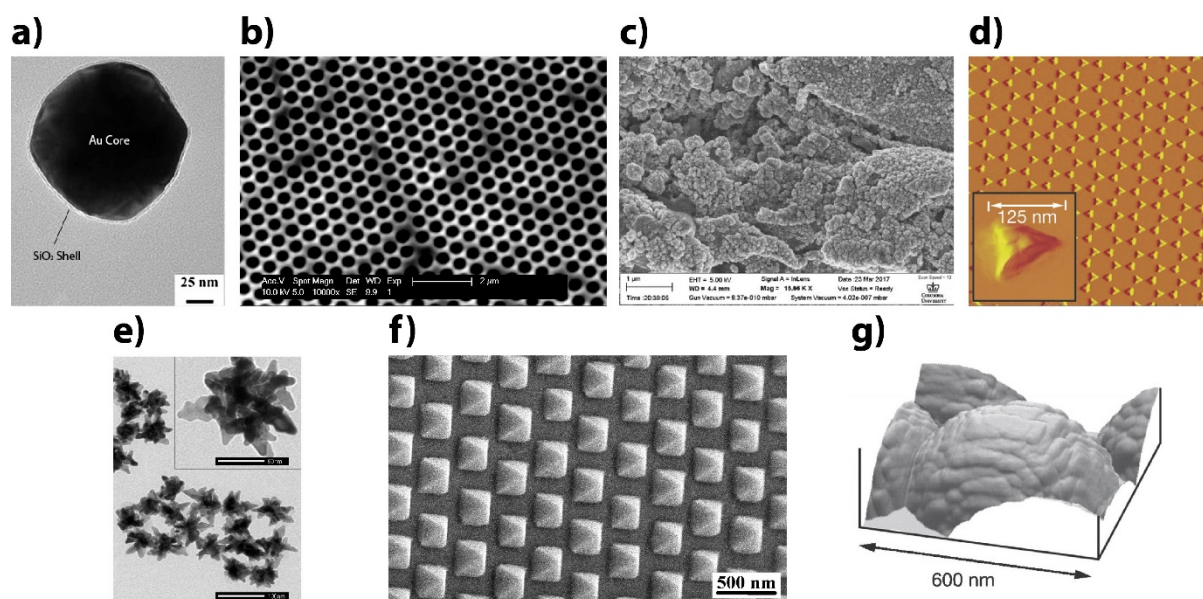
**Figure 1:** A schematic diagram of the study of electrochemical reaction mechanisms using SERS depicting the reactions covered in this review. The SERS substrate electrode must be structured in a manner to provide the SERS enhancement (see Figure 2) and the reactants, intermediates, and products detected must be located in the region in which the enhancement of the Raman signal is strong for effective detection.

## Introduction

Surface enhanced Raman spectroscopy (SERS)<sup>1</sup> was discovered in the 1970s in an experiment that sought to characterise species adsorbed on or near electrode surfaces during electrochemical reactions<sup>2</sup>. The enhancement observed with a roughened Ag electrode<sup>3</sup> was orders of magnitude greater than that expected and was later attributed to electromagnetic<sup>4</sup> and chemical<sup>5</sup> effects, with the former now understood to provide most of the typically 10<sup>6</sup>-fold enhancement. In the many years since the initial discovery there have been over 19,000 SERS papers published, most of which describe the development of new or improved SERS substrates<sup>6</sup>, further study of the SERS mechanism<sup>7</sup>, and the development of advanced SERS techniques, such as tip-enhanced Raman spectroscopy (TERS), as evidenced by the two most recent Faraday Discussions on SERS<sup>8,9</sup> and some of the reviews published in this journal<sup>10,11,12</sup>.

SERS offers several advantages over other vibrational spectroscopic probes of electrode surfaces such as FTIR. The enhancement is strongest for molecules at or on the surface of substrate<sup>13,14</sup> and the metal-adsorbate vibrations are readily observed, whereas these would be in the far-infrared region for IR studies, where the strong absorbance by the solvent obscures the rather weak signals, causing experimental difficulties<sup>15</sup>. Water and many other solvents used in electrochemistry do not have strong Raman signals and thus thin-layer cells with micron-scale pathlengths are not necessary. Additionally, molecules such as O<sub>2</sub> can be observed by Raman making SERS particularly useful in the study of the oxygen reduction and evolution reactions, as will be illustrated later in this review.

SERS substrates have advanced considerably from the highly roughened/disordered metal surfaces characteristic of the original discovery, although such highly disordered surfaces are still used, as understanding of the role of plasmonics and the (optical) electric field strength in achieving the enhancement improved. This understanding has enabled the design of nanostructured substrates in which the plasmons are focussed (e.g. sharp tips<sup>16</sup> or dendrites<sup>17</sup>) or confined (e.g. sphere segment voids/SSV<sup>18,19,20</sup>) as well as the development of SERS probes (e.g. shell isolated nanoparticles/SHIN<sup>21,22,23</sup>) that can be used to study non-SERS active surfaces as depicted in Figure 2a. All of which have been employed to study electrode reactions.



**Figure 2:** A selection of SERS substrates: a) Au@SiO<sub>2</sub> SHINERS particles<sup>24</sup>, b) Au sphere segment voids (original image), c) roughened Cu<sup>30</sup>, d) Au nanotriangles<sup>16</sup>, e) Au nanostars<sup>17</sup>, f) Au nanopyramids<sup>25</sup> and g) Ag film-over-nanospheres<sup>16</sup>. Adapted with permission from original content authors.

Alongside these developments in SERS substrates, there has been improved understanding that the structure of electrode surfaces can affect the outcome of electrode reactions through the study of single crystal surfaces and nanoparticles. Thus, it may be inappropriate to assume that the structure of the SERS substrate (roughened or otherwise intentionally nanostructured) can be treated as an insignificant parameter. The use of SHIN particles provides a means of achieving enhancement on non-active surfaces such as smooth single crystal metal surfaces<sup>23</sup> or highly absorbing (black electrode) surfaces such as glassy carbon (GC)<sup>26</sup>. However, casting SHIN particles on an electrode surface may also cause a perturbation to the reaction by restricting mass transport.

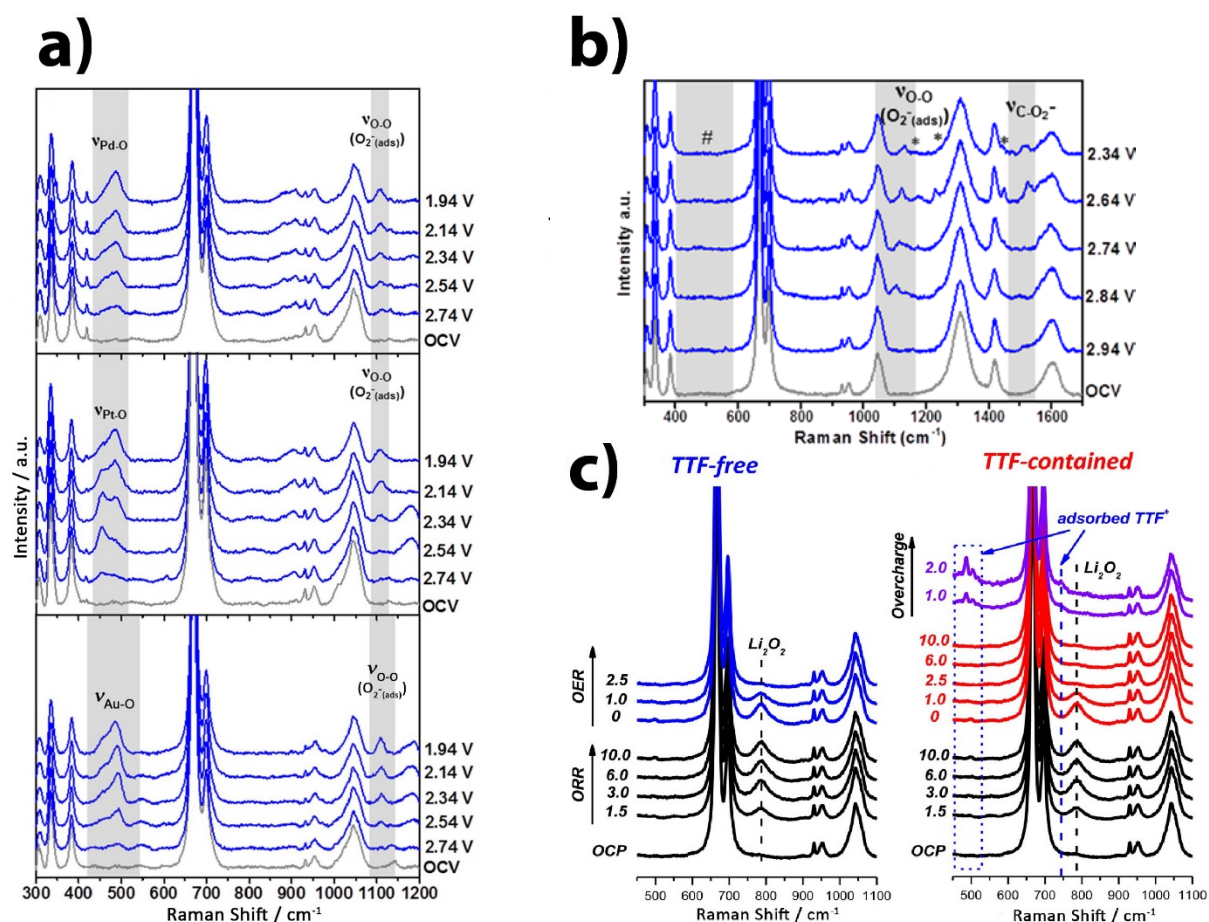
In this brief review we present some of the most recent SERS studies of electrode reactions to highlight the mechanistic understanding that can be achieved and encourage further use of SERS to study electrode reactions. In doing so, note is made of where the authors have ensured that, at least some, of the electrochemical data that is presented is obtained using the same electrodes as those used for the SERS measurements.

### Oxygen electrochemistry

The electrochemical reactions of oxygen are both technologically important (fuel cells, water electrolyzers, air-batteries, etc.) and well suited to study by SERS as the species involved are Raman active. In particular, the SERS has proved useful in the study of the oxygen reduction reaction (ORR) in the aprotic solvents used in lithium-air (oxygen) batteries, which

may be a promising power source for electric vehicles if the barriers such as low cycle life and the formation of undesirable byproducts can be overcome.

Galloway and Hardwick<sup>26</sup> employed SHIN particles to study the ORR in DMSO at smooth Au, Pt, Pd, and GC and in acetonitrile at GC electrode surfaces, showing that the SHINERS method was useful at each of these electrode surfaces. In DMSO they showed that the interaction of the superoxide  $O_2^-$  intermediate with the electrode surface was dependent on the nature of that surface as suggested by the cyclic voltammetric results obtained for electrodes in DMSO that were free of the SHIN particles, the lack of any effects of SHIN particles on the voltammograms for the GC surface are shown in the supporting information of their paper. The SHINERS results suggest that  $O_2^-$  lies flat on Pt at more positive potentials, switching to an end-on orientation as the potential is made more negative, whilst the end-on orientation is preferred at all potentials for Au and Pd, as evidenced by metal oxide peaks observed between 400 and 550  $cm^{-1}$  (Figure 3a). In contrast, no peaks were observed for the metal metal oxide interaction at GC and only peaks attributed to  $O_2^-$  in solution and weakly interacting with the GC surface were observed. Other peaks were observed at GC attributed to  $HO_2$  and  $LiO_2$ , the latter observed in the presence of 0.5 mol  $dm^{-3}$   $LiClO_4$  (Figure 3b).  $LiO_2$  can decompose to produce  $Li_2O_2$ , which is insulating and is, thus, an undesirable byproduct. Qiao and Ye<sup>27</sup> used SERS at sputtered Au electrodes, employed for both the electrochemical and Raman measurements, to investigate the use of tetrathiafulvalene (TTF) as a redox mediator, designed to facilitate the oxidation of  $Li_2O_2$  during the oxygen evolution reaction (OER) in DMSO and thus improve the cycle life of the Li- $O_2$  battery. Their results showed that at the Au electrode the  $TTF^+$  ions produced were mainly consumed by the oxidative decomposition of  $LiO_2$  during ORR/OER cycles in contrast to the desired action (Figure 3c). In contrast, at porous carbon electrodes, for which they were unable to obtain SERS, the *ex situ* Raman data supported TTF mediated oxidation of  $Li_2O_2$ , but also showed that the excess  $TTF^+$  formed during round trip ORR/OER cycles correlated with the amount of a  $Li_2CO_3$  byproduct, which similarly suggested that TTF would not be a good redox mediator at this surface. The insights provided by SERS in both of these studies are highly valuable, enabling identification of byproducts and furthering understanding of the dependence of their interaction with the electrode surface on the nature of that surface.



**Figure 3:** In situ SERS spectra of a) the ORR with SHIN's on the surface of polycrystalline metals M, Pd (top), Pt (middle) and Au (bottom) in  $O_2$  saturated 0.1 M TBAClO<sub>4</sub>/DMSO electrolyte. Potentials vs. Li/Li<sup>+</sup>.<sup>26</sup> The peaks highlighted show the formation of the metal oxides (M-O vibrations around 450 - 500 cm<sup>-1</sup>) and the O-O vibration of  $O_2^-$  around 1110 cm<sup>-1</sup>. Increased intensity of both indicates both an increase in the coverage or concentration and a more upright or end-on adsorption site of  $O_2^-$ . The other peaks, present at the open circuit voltage (OCV), are all attributed to the DMSO solvent. b) the ORR with SHIN's on a GC electrode also in  $O_2$  saturated 0.1 M TBAClO<sub>4</sub>/DMSO. Potentials vs. Li/Li<sup>+</sup>.<sup>26</sup> In contrast to the spectra shown in a), no M-O vibration of adsorbed  $O_2^-$  is observed #, confirming correct operation of the SHIN particles, peaks are observed  $O_2^-$  at 1110 cm<sup>-1</sup> and at less positive potentials for C- $O_2^-$  showing that weakly interacting  $O_2^-$  moves to a less favourable adsorption site as the concentration/coverage increases. The bands marked \* are attributed to HO<sub>2</sub> at 1179 cm<sup>-1</sup> and the interaction of HO<sub>2</sub><sup>-</sup> with GC at 1450 cm<sup>-1</sup> due to trace water content. c) the ORR and OER on sputtered Au electrodes in  $O_2$  saturated 0.5 M LiClO<sub>4</sub> in DMSO showing the formation of Li<sub>2</sub>O<sub>2</sub> during the ORR and its consumption during OER.<sup>27</sup> Adapted and reproduced with permission of Galloway and Hardwick and Qiao and Ye.

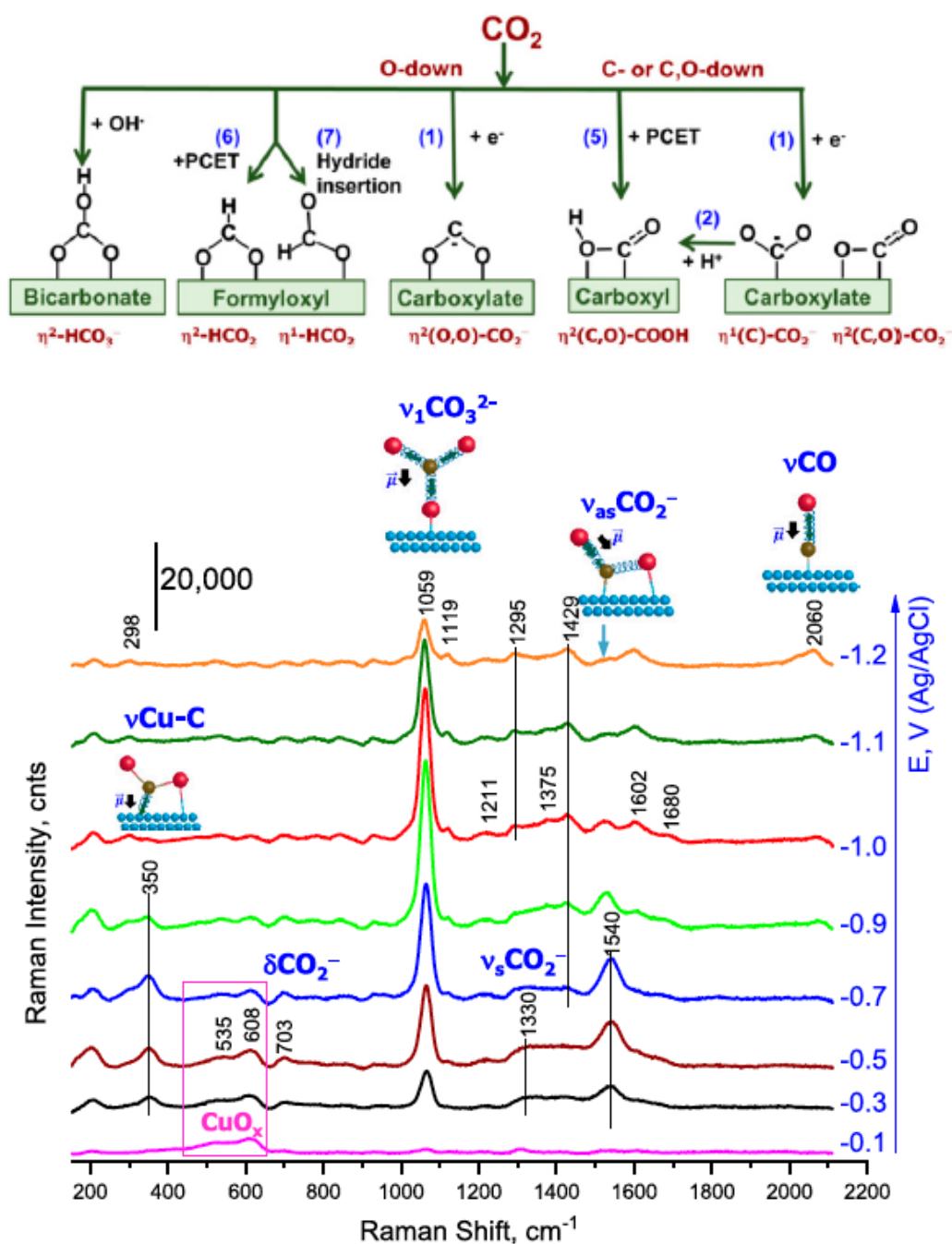
The borrowed SERS strategy, in which a SERS active substrate is coated with a thin layer of another material, thereby transferring the enhancement to the new surface, was utilised by Diaz-Morales *et al.*<sup>28</sup> to study OER on nickel oxyhydroxide (NiOOH) surfaces. Approximately 5 monolayers of Ni were plated on to an electrochemically roughened Au SERS substrate. The pH dependent Ni(OH)<sub>2</sub>/NiOOH redox couple is clearly visible in the cyclic voltammograms of this surface obtained in alkaline to neutral pH NaOH/NaClO<sub>4</sub> electrolytes. The SERS show peaks associated with the Ni hydroxide and oxyhydroxide species as well as an active oxygen species with a peak between 800-1150 cm<sup>-1</sup>, which was identified as the superoxo O-O vibration of NiOO<sup>•</sup>. They go on to suggest that this species acts as the O<sub>2</sub> precursor when the pH > 11.

### **Electrochemistry of carbon monoxide and carbon dioxide**

The concept of using the electrochemical reduction of CO<sub>2</sub> to produce a variety of fuels and commodity chemicals is an increasing research area in electrocatalysis.<sup>29</sup> CO is both a product (partial reduction) and proposed intermediate in this process as and in the electrocatalytic oxidation of organic compounds, such as methanol, as well as being a contaminant in reformat produced H<sub>2</sub> used as a fuel in low temperature fuel cells. SERS measurements are able to probe the metal-adsorbate vibrations providing information that is complementary to that obtained using IR and, where the catalyst is a roughened electrode surface or nanoparticles, directly study the working catalyst. Two studies of CO<sub>2</sub> reduction and one of CO oxidation are highlighted below.

High surface area Cu electrodes are one of the more promising electrocatalysts for CO<sub>2</sub> reduction. Chernyshova and coworkers<sup>30</sup> studied the reaction at roughened Cu electrodes, obtaining the electrochemical and SERS data using the same surfaces and combining these with density functional theory (DFT) and isotope exchange experiments to provide further information regarding the reaction mechanism. In particular they were able to show that the first intermediate of the CO<sub>2</sub> conversion to formate on Cu is a carboxylate anion \*CO<sub>2</sub><sup>-</sup> coordinated to the surface through one of its C–O bonds with the η<sup>2</sup>(C,O)-CO<sub>2</sub><sup>-</sup> structure (Figure 4). Consequently, the authors validated Hori's hypothesis<sup>31,32</sup> that CO<sub>2</sub> electroreduction starts with a common first intermediate. The η<sup>2</sup>(C,O)-CO<sub>2</sub><sup>-</sup> structure was also observed at potentials much more anodic than the onset of the CO<sub>2</sub> electroreduction. This suggests a critical role of additional cooperative effects such as surface defects, residual surface oxide, and co-adsorbed electron donors, which are yet to be understood. Finally, it was concluded that the electrocatalytic activity of the metal is related to the strengths of the metal–C and metal–O bonds of η<sup>2</sup>(C,O)-CO<sub>2</sub><sup>-</sup>.





**Figure 4:** Proposed first intermediates of CO<sub>2</sub> reduction and potential dependant SERS spectra of roughened Cu in CO<sub>2</sub> saturated 0.1 M NaHCO<sub>3</sub>. Reproduced with permission from Chernyshova et al.<sup>30</sup> Attribution of peaks in the spectra to the various intermediates in CO<sub>2</sub> reduction are shown. The intensities of the peaks increase with coverage of the adsorbed species, but are also dependent on the orientation, with those vibrational modes that have a dipole component  $\vec{\mu}$  perpendicular to the Cu surface exhibiting the largest peaks. Thus the relative intensities of the peaks are not straightforwardly related to the relative coverages of the species.

Whilst CO<sub>2</sub> reduction at Cu produces the most hydrocarbons, reduction at Ag and Au electrodes yields the greatest Faradaic efficiency for CO production<sup>33</sup>, which is attributed to the weaker binding of CO to these surfaces. Modification of Ag electrode surfaces by N-containing additives had been shown to enhance CO<sub>2</sub> conversion<sup>34</sup> and Oberst et al.<sup>35</sup> extended this work to Au surfaces, studying the adsorption of the modifiers (benzotriazole and ethanolamine) and CO adsorption using SERS at roughened Au electrodes in alkaline electrolyte. They compared their results to cyclic voltammograms and extracted Tafel slopes obtained at smooth Au electrodes. In contrast to their earlier findings on Ag, addition of benzotriazole was found to have little effect on both the CO<sub>2</sub> activity and product distribution, which they attribute to the fact that CO adsorption on Au is much weaker than that on Ag (ca. 0.28 eV *versus* ca. 0.40 eV, respectively).<sup>36</sup> Modification of the surface by ethanolamine, which is a CO<sub>2</sub> scavenger did enhance the activity on Au, which they attributed to a local increase in the local CO<sub>2</sub> availability at the Au electrode surface.

Fuel cell electrocatalysts are typically nanoparticle in nature, which poses difficulties for SERS characterisation, especially for non-SERS active Pt-based alloy nanoparticles, which are the more common electrocatalysts for the H<sub>2</sub> anode reaction in reformate fuelled cells. Liang and coworkers<sup>37</sup> have taken an innovated approach to the study of such alloy nanoparticles by anchoring the Pt-based nanocrystals onto the SiO<sub>2</sub> shell of SHIN particles. The modified SHIN particles were then used to study catalytic CO electrooxidation on Pt and PtFe bimetallic nanoparticles. The modified SHIN particles were deposited on to a GC electrode for both the voltammetric and SERS measurements and the Pt<sub>1</sub>Fe<sub>x</sub> (x = 0, 0.5, 1, 1.5) particles were activated by cycling from -0.25 V to 1.0 V vs. SCE in 0.1 mol dm<sup>-3</sup> HClO<sub>4</sub>, which resulted in dissolution of some of the Fe to produce a Pt rich surface. Spectra were collected in CO saturated solution, with peaks corresponding to the Pt–CO and C–O stretching modes being observed, with greater intensities observed for those catalysts which contained Fe. The frequency of the Pt-CO stretching peak was found to decrease with increasing Fe content, indicating a change to the electronic state of the Pt (d-band centre), which weakens the Pt-CO bond and enhances the electrocatalytic activity beyond that accounted for by the increased surface area of the particles upon leaching of Fe from the surface.

### Formic acid oxidation

The electrooxidation of formic acid continues to be of interest both as an intermediate in the oxidation of other small organic molecules and as fuel itself for direct formic acid fuel cells<sup>38</sup>. Pt monolayers coated Au nanoparticles (Au@Pt) have been shown to be active electrocatalysts for formic acid oxidation at room temperature<sup>39</sup>. Two recent mechanistic SERS studies have been reported. The first by Jeong and Kim<sup>40</sup> used Au@Pt substrates



that were prepared by self-terminating electrodeposition of Pt onto dendritic Au rod (DAR) structures and both the electrochemical and SERS data were obtained using the same electrodes. The electrocatalytic activity of formic acid was found to be dependent on the Pt coverage and thickness. CO was used as a probe to determine the number of potential step cycles required to fully cover the Au surface with Pt through observation of the characteristic Pt-CO modes between 380-490  $\text{cm}^{-1}$  and the C-O stretching mode on Au at 2094  $\text{cm}^{-1}$ . Surfaces with island-type Pt layers on Au (low Pt coverage) exhibited electrochemical behaviour attributed to the direct oxidation of formic acid, whilst the indirect pathway, wherein  $\text{CO}_{\text{ads}}$  is as an intermediate, was observed as the Pt coverage increased. In contrast,  $\text{CO}_{\text{ads}}$  was observed in the SERS of the low Pt coverage surfaces, indicating that the indirect electrooxidation of formic acid occurs.

In a more recent paper, Xie et al.<sup>41</sup> combined EC-SERS and high-frequency heating technology using a thermocouple microelectrode loading with round Au@Pt nanoparticles which also served as the SERS substrate to investigate the formic acid electrooxidation at different temperatures. The cyclic voltammetry data (from 25 °C to 100 °C) indicated that formic acid oxidation was enhanced significantly as the temperature increased. The SERS data showed that CO oxidative desorption from the Pt shell was promoted at higher temperatures, accounting for the improved the catalytic activity, but did not support any change in the mechanism of the formic acid oxidation reaction.

## Summary

45 years after its discovery SERS remains a valuable tool for the study of electrode processes and the SERS studies presented herein highlight the mechanistic insights that can be achieved, particularly for electrocatalytic reactions in which the reactants or intermediates are bound to the electrode surface. However, given the need to nanostructure the surface or use invasive probes to achieve enhancement, it is view of the authors that continued care needs to be taken when comparing electrochemical data obtained on other electrode surfaces to the SERS data. This is not meant as a direct criticism of those papers reviewed, but more as a request to those who continue to employ SERS to study electrode reactions, especially those that may prove to be structure sensitive or for which perturbation of mass transport may be important. As illustrated by several of the studies presented above, the nanostructures required for SERS or to achieve the electrocatalytic activity can in fact prove to be the same, making SERS an excellent method for the mechanistic study of electrocatalytic reactions.

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## Author contributions

AJK, GRSB, and AER contributed equally to the preparation of this manuscript.

## Conflict of interest

The authors declare no competing financial interests.

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Papers of particular interest, published within the period of review, have been highlighted as

\* Paper of special interest

\*\* Paper of outstanding interest.

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