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Local monitoring of surface chemistry with Raman spectroscopy

Andrzej Kudelski

Abstract The efficiency of Raman scattering from molecules in some nano-resonators can increase by many orders of magnitude. Sometimes, in Raman measurements carried out with such resonators, it is possible to record a spectrum from only a few (or even a single) molecules. In this contribution, we show that resonator-enhanced Raman scattering is very useful for analysis of the electrochemically formed carbon. Carbon material has been formed on the surface of the copper-modified silver electrode during the electrochemical reduction of CO_2. The Raman spectra measured were often from only a few carbon clusters. By the analysis of a large series of such spectra, we managed to identify large graphite-like rings and polyenes with various lengths. Some other applications of resonator-enhanced Raman scattering to local characterisation of electrode surfaces (e.g. studies of CO adsorption on gold) are also presented.

Keywords SERS · Surface-enhanced Raman scattering · Amorphous carbon · Carbon monoxide

Introduction

The pioneering work concerning measurements of Raman spectra from small specific regions in a sample was realized

A. Kudelski (✉)
Department of Chemistry, Warsaw University,
Pasteur 1,
02-093 Warsaw, Poland
e-mail: akudel@chem.uw.edu.pl

in the 1970s by the groups of Etz [1] and Delhaye [2]. These groups managed to successfully couple Raman spectroscope with the optical microscope. The spatial resolution of such Raman measurements, as in other purely optical techniques, is restricted, however, by the Abbe's diffraction limit to $\lambda/2$, where λ is the wavelength of the incident radiation [3]. Actually, in standard confocal Raman microscopic measurements, one measures signal from the area on the order of 1 μm^2, and one can only distinguish local differences between various parts of the studied surface when the sample reveals inhomogeneity at least on the micrometer scale (for examples of microscopic Raman measurements for electrocatalysts, see [4–7]).

On the other hand, for many materials, only very small parts of their surface, often with the dimension below 1 nm, determine their useful properties. For example, for catalysts composed of metal clusters on the support, the active areas of the catalysts are only surfaces of these metal clusters [8, 9]. Sometimes, even for single crystals of pure elements, only a small part of the crystal surface is catalytically active (e.g. on the Ru (0001), only step edges of the surface are catalytically active during NO dissociation [10]). In standard surface measurements, when the vibrational spectrum is accumulated from at least 1 μm^2, the contribution from "special" areas of the sample can be very difficult to detect and analyse because it can be masked by the contributions from other areas. Fortunately, it is possible to record vibrational spectrum from areas significantly smaller than allowed by the Abbe's diffraction limit. The simplest solution is the creation of a nano-resonator or of a system of nano-resonators on the analysed surface. As has been shown by many groups, some nano-resonators created from metal clusters provide local enhancement of the electric field by a factor higher than 10^2 [3, 11–13]. For

Raman bands with a small Raman shift, the increase in the efficiency of Raman scattering is roughly proportional to the fourth power of the field enhancement [3]. Therefore, the field enhancement of 10^2 may lead to the increase in the efficiency of Raman scattering by a factor of 10^8 (since for some resonators, the field enhancement can be higher than 10^3, local electromagnetic Raman enhancement can sometimes exceed 10^{12} [3]). In addition to this electromagnetic enhancement, the efficiency of Raman scattering for some adsorbed molecules can be also increased by the resonance process similar to the ordinary resonance Raman process occurring in the metal–ligand complexes [14]. The efficiency of the generation of Raman signal is sometimes so high (because of historic reasons, this enhancement effect is called surface-enhanced Raman scattering (SERS)) that it is possible to observe a good quality Raman spectrum even from a single molecule [15–17].

Large enhancement factors of the electromagnetic field are only achieved at very small parts of the surface of the resonator (so-called hot spots). Therefore, only a very small part of molecules adsorbed on highly SERS-active surfaces (in other words, surfaces at which very large SERS enhancement factors are achieved) actually contributes to the measured SERS spectrum. For example, Kneipp et al. have shown that for some dyes adsorbed on silver nanoparticles, only 0.01% of the adsorbates give almost all measured SERS signal [18]. As one can easily calculate, the surface density of silver atoms is about 10^7 atoms per 1 μm^2. The density of adsorbed molecules is usually considerably smaller than this value. It means that when only about 10^{-4} of the adsorbates gives almost all measured SERS signal and when the average lifetime of molecules in the "hot spots" is not significantly shorter than the accumulation time of the spectrum, by using confocal Raman microscope, we can measure Raman spectrum dominated by the contribution from a relatively small number of molecules adsorbed on the highly SERS-active substrate [19–23].

In this paper, we show that measurements of Raman spectra of "a few molecules" can be used for the spectroscopic identification of species even when their contribution to the averaged spectrum of the sample cannot be reliably identified. First, by the measurements of Raman spectra of a few molecules, we deliver the unquestionable evidence for the presence of the bridge-bonded CO on the gold surface, whereas in these experimental conditions, the contribution from the bridge-bonded CO to the average spectrum can hardly be seen. Then, we describe our recent studies on the formation of carbon clusters during the catalytic electrochemical reduction of CO_2. On the basis of characteristic bands that appeared in a long series of SERS spectra of a few molecules, we were able to identify various carbon clusters. Some other applications of resonator-enhanced Raman scattering to the local characterisation of electrode surfaces are also discussed.

Experimental details

Surface system of very efficient nano-resonators can be formed using many various methods. In this work, we use the electrochemical roughening of the metal surface. This method consists of dissolution and subsequent deposition of the electrode material. Electrochemical roughening and other electrochemical experiments were carried out in a conventional three-electrode cell with a large platinum sheet as the counter-electrode and an Ag/AgCl (0.1 M KCl) electrode as the reference one (all potentials are quoted versus this electrode). The silver substrates were roughened by three successive negative–positive–negative cycles in a 0.1-M KCl aqueous solution from −0.3 to 0.3 V at a sweep rate of 5 mV s^{-1} [24]. The cycling was finished at −0.3 V, and then the silver electrode was kept for 5 min at −0.4 V. After that, the working electrode was removed at an open circuit potential and very carefully rinsed with water.

Figure 1 shows the scanning electron microscope picture of the silver substrate after the roughening procedure described above. By comparing the intensities of Raman signals for the adsorbed and non-adsorbed pyridine molecules (a model system for SERS measurements), we estimated that the average SERS enhancement factor for this substrate was about 10^6–10^7. The actual enhancement factor at hot spots should be significantly higher than the average one.

The electrochemical reduction of CO_2 was carried out on the copper-modified SERS-active silver electrode. Copper was electrochemically deposited on the roughened Ag substrate from a 0.01-M $CuCl_2$ solution. The reduction charge density was set to about 3 mC cm^{-2} corresponding to the average thickness of Cu layer of about 5 atoms.

Gold electrodes were roughened in a 0.1-M KCl solution by one hundred cycles of potential scans between −0.6 and 1.25 V at a sweep rate of 50 mV s^{-1}. The cycling was finished at −0.6 V, and the gold electrode was kept for 5 min at this potential. Afterwards, the Au electrode was removed at open circuit potential and very carefully rinsed with water.

Raman spectra of carbon deposits have been recorded with an ISA T64000 (Jobin Yvon) Raman spectrometer equipped with an Olympus BX40 microscope with a 50× long-distance objective. A Laser-Tech model LJ-800 mixed argon/krypton laser provided excitation radiation of 514.5 nm. The temporal instability of intensity of the laser radiation was less than 5%.
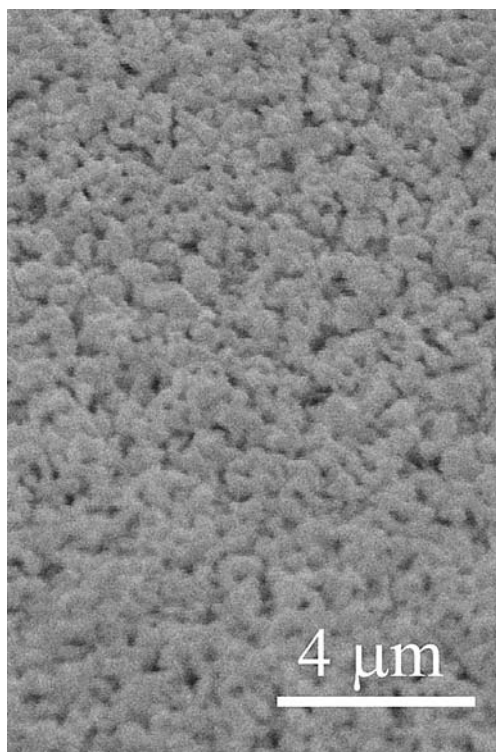
Fig. 1 Scanning electron micrograph of the electrochemically roughened SERS-active silver electrode. The electrode was roughened by three successive negative–positive–negative cycles in a 0.1-M KCl aqueous solution from −0.3 to 0.3 V at a sweep rate of 5 mV s^{-1}

CO spectra were recorded with a LabRAM 1000 (Dilor) Raman system. Excitation radiation of 632.8 nm was provided by a He–Ne laser. The parameters of the optical microscope were the same as those of the T64000 device.

Results and discussion

Adsorption of CO on the gold surface

Adsorption of CO molecules on various surfaces is extensively studied by many groups, since carbon monoxide is an important poison of the catalyst in many processes [25, 26]. CO molecules can be bonded to the metal surface via various number of metal atoms, and hence, different types of CO adsorption sites are observed, in general, namely a-top, bridge-bound and 3-fold hollow [27]. Determination of the actual bonding of CO molecules to the metal surface is often very useful in studies of mechanisms of some catalytic processes.

Figure 2 shows SERS spectrum accumulated during 200 s (2×100 s) of CO adsorbed at an electrochemically roughened gold electrode. This measurement was carried out for the Au electrode soaked in a 0.1-M KCl aqueous solution saturated with CO at p_{CO}=1 bar. The electrode

potential was set to +40 mV. As can be seen in Fig. 2, measured spectrum is dominated by the strong band at 2117 cm^{-1}, which is characteristic for CO adsorbed namely on-top sites [27, 28]. In this spectrum, no other reliable band can be identified in the wavenumber range between 1850 and 2000 cm^{-1} (the contribution from CO molecules interacting with two and more gold atoms should appear in the region between 1850 and 2000 cm^{-1} [27]). To partially eliminate the averaging effects caused by (a) the rearrangement of the atomic structure of the hot spot, (b) the change of the orientation of adsorbed CO molecules versus the gold surface and (c) the diffusion of CO molecules in and out of hot spots, we measured few hundred SERS spectra with significantly shorter accumulation time (25 s). We found that in some spectra, there is a clearly visible Raman band at about 1956 cm^{-1}. An example series of four subsequently measured SERS spectra, in which this band appears, is shown in the inset in Fig. 2. The band at 1956 cm^{-1} is characteristic for the bridge-bonded CO (CO molecules simultaneously interacting with two gold atoms) [28]. It means that measurements of SERS spectra of a few molecules allowed the identification of stronger-bonded CO despite that the contribution from the bridge-bonded CO to the average spectrum cannot be noticed in these experimental conditions.
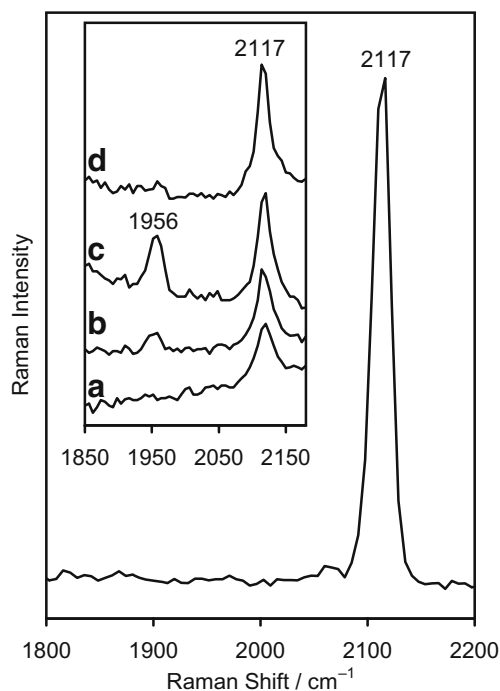

Fig. 2 SERS spectrum of CO adsorbed at the roughened gold electrode. Accumulation time 2×100 s. The measurement was carried out for the electrode soaked in a 0.1-M KCl aqueous solution saturated with CO at p_{CO}=1 bar. The electrode potential: +40 mV. *Inset* four subsequently measured spectra recorded using the accumulation time 25 s
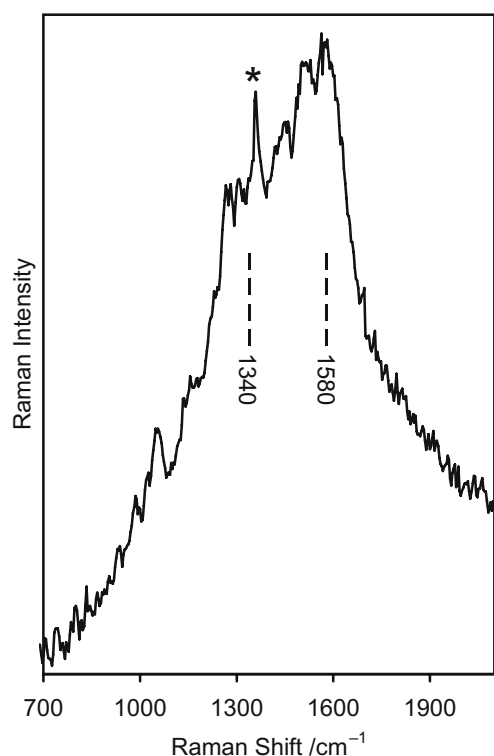
Fig. 3 SERS spectrum of carbon material formed on the surface of the copper-modified silver electrode during electrochemical reduction of CO_2. Accumulation time is 15 s. The electrochemical reduction of CO_2 was carried out for 10 min at the potential of −2.1 V in a 0.1-M $KHCO_3$ aqueous solution saturated with CO_2 at pCO_2=1 bar. The *asterisk* marks the band at 1,360 cm^{-1}

Analysis of carbon materials

Chemical (or electrochemical) reduction of carbon dioxide is considered an excellent candidate for the key process in the efficient long-term energy storage [29–32]. When CO_2 is electrochemically reduced on copper, energy carriers (methane, ethylene) and many compounds valuable in the chemical industry (acetaldehyde, ethanol, propionaldehyde, acetone, allyl alcohol, propanol, formic and acetic acids) are produced [32–34]. Moreover, potentially useful carbon material is also formed during electrochemical reduction of CO_2 [34–37].

In this study, we analysed the composition of carbon material produced on the copper-modified silver electrode during electrochemical reduction of CO_2 for 10 min at 295 K. The electrochemical reduction of CO_2 was carried out at the potential of −2.1 V in a 0.1-M $KHCO_3$ solution saturated with CO_2 at pCO_2=1 bar. Figure 3 shows SERS spectrum of products formed on the electrode surface. Accumulation time of this spectrum was 15 s. As can be seen in Fig. 3, the measured spectrum is dominated by two broad overlapping bands centred at about 1340 and

1580 cm^{-1}. The spectrum composed of such two bands is typical of amorphous carbon and has been reported in many previous contributions [19, 20, 22, 23]. In addition to two broad "background" bands, one can also see some narrow features. The strongest of these narrow bands, located at 1360 cm^{-1} (this band is marked with the asterisk in Fig. 3), probably originates from the diamond-like carbon cluster(s) [22]. However, intensities of all narrow features in spectrum presented in Fig. 3 is comparative to the "noise" level, and therefore, any identification of various carbon clusters cannot be reliable.

As mentioned in the "Introduction", when the accumulation time is relatively short, the measured SERS spectra are often dominated by the contribution from a very small part of species present in the focal area of the Raman spectroscope (in experiments carried out with the Raman microscope, it is actually a small number of molecules). Because of the diffusion of clusters (molecules) in and out of the hot spots, which changes the number of effectively scattering species, subsequently measured SERS spectra, which are dominated by the contribution from only a small number of carbon clusters, should reveal significantly different intensities. In the
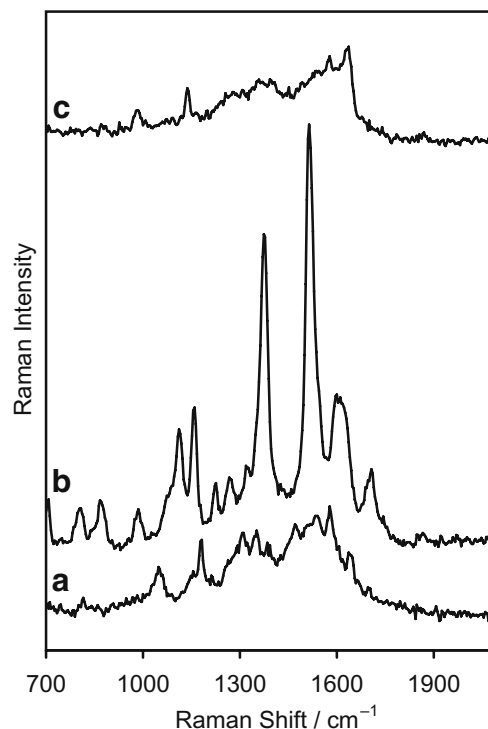

Fig. 4 Three successively measured SERS spectra of the carbon material formed on the surface of the copper-modified silver electrode during the electrochemical reduction of CO_2 (for details see Fig. 3). Each spectrum was accumulated for 1 s. Spectra are presented at the same scale, vertically shifted for the sake of clarity

spectra dominated by the contribution from a single carbon cluster (or a small number of clusters), some pronounced narrow Raman bands should also be seen. We clearly observed both effects characteristic for SERS spectra of a "few clusters" in a series of spectra recorded with the accumulation time of 1 s (of course, shorter accumulation time may also be used). Three subsequently measured SERS spectra, which very well illustrate both effects mentioned above, are shown in Fig. 4. As can be seen in Fig. 4, one can obtain a Raman spectrum dominated by the contribution from an individual (or only a few) carbon cluster with very large signal-to-noise ratio. It is worth to note that because of a large energy density in the hot spot, further thermally activated diffusion of the carbon cluster from the hot spot is very likely, and therefore, the signal-to-noise ratio cannot be improved by using a longer accumulation time. Figure 5 presents some example spectra of carbon materials formed during the electrochemical reduction of CO_2, in which narrow Raman bands can be clearly identified. A strong band at about 1590 cm^{-1} (see spectrum b) is characteristic for the in-plane stretching mode of the monolayer of hexagonally ordered carbon atoms [23]. The bands at slightly lower

frequencies (e.g. the band at 1570 cm^{-1} in spectrum d and the band at 1552 cm^{-1} in spectrum e) are because of the smaller graphite-like ring structures [22]. The bands in the regions 1460−1530 cm^{-1} and 1100−1170 cm^{-1} (e.g. the bands at 1515, 1160, 1115 cm^{-1} in spectrum a) are mainly associated with C=C and C-C stretching vibrations, respectively, in various carbon chain clusters [23]. The band at about 1370 cm^{-1} (see spectra a, c and d) may be ascribable to the D mode in the microcrystalline graphite [22].

Five spectra in Fig. 5 are presented only as examples of the spectra that we have measured for this system. Actually, about 1,000 spectra were recorded, and about 50 spectra revealing strong narrow Raman bands were carefully analysed. It is worth to note that in no spectrum analysed, a set of bands characteristic for C_{60} and C_{70} fullerenes were found (for SERS spectra of fullerenes see [23]). Previous studies show that there is no preferential contribution of any kind of carbon cluster to the SERS spectra revealing strong fluctuating narrow Raman bands [38]. Therefore, one can conclude that fullerenes are not produced in the significant percentage during the electrochemical reduction of CO_2 on copper electrode.
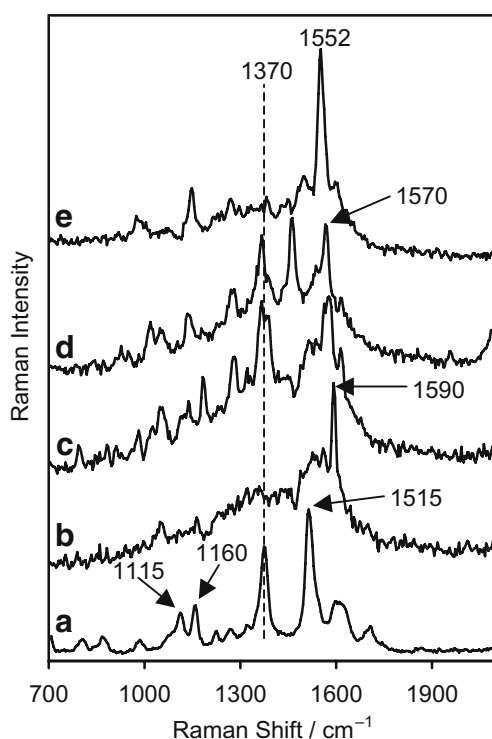
Summary and further outlook

In this contribution, we show that measurements of Raman spectra of a few molecules can be used for the spectroscopic identification of species even when their contribution to the averaged spectrum of the analysed sample cannot be reliably identified. For example, using a few molecules Raman technique, we identified various carbon clusters in the carbon material formed during the electrochemical reduction of CO_2.

A few molecules Raman measurements can be also carried out in such a way that we are able to control the position of the hot spot (induced by a fine tip made of a metal that supports surface plasmon resonance) on the studied surface. In other words, it is possible to couple Raman spectroscopy and scanning probe microscopy (STM or AFM), forming a new spectroscopic–microscopic tool, the so-called tip-enhanced Raman scattering (TERS) spectroscopy. Tip-enhanced Raman scattering measurements are complex, and therefore, as far as we know, only one example of a practical problem aimed at local TERS measurements has been published [39]. However, in the near future, many important practical applications of this technique are expected to appear.

Fig. 5 Five spectra of the carbon materials formed on the surface of the copper-modified silver electrode during the electrochemical reduction of CO_2 (for details see Fig. 3) that reveal relatively intensive narrow Raman bands. Accumulation time is 1 s

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