SERS based detection of herbicide MCPA using electrochemically synthesized 2D-silver nanodendrites functionalized with cyclodextrin

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Abstract: Surface Enhanced Raman Spectroscopy (SERS) is a powerful analytical technique that has found application in trace detection of a wide range of contaminants. In this paper we report on the fabrication of 2-D silver nanodendrites, on silicon chips, synthesized by electrochemical reduction of AgNO₃ at microelectrodes. The formation of nanodendrites is tentatively explained in terms of electromigration and diffusion of silver ions. Electrochemical characterization suggests that the nanodendrites do not stay electrically connected to the microelectrode. The substrates show SERS activity with an enhancement factor on the order of 10⁶. Density functional theory (DFT) simulations were carried out to investigate the suitability of the fabricated substrate for pesticide monitoring. These substrates can be functionalized with cyclodextrin macro molecules to help with detection of molecules with low affinity with silver surfaces. A proof of concept is demonstrated with the detection of herbicide 2-methyl-4-chlorophenoxyacetic acid (MCPA).

Keywords: Surface Enhanced Raman Scattering; Electrochemistry; Nanodendrites; MCPA;

• Introduction

Photonic sensors are being applied to a wide variety of sensing application. [1] Such sensors can be based on fluorescence spectroscopy[2], infrared spectroscopy [3], plasmonic based sensors [4], or Raman spectroscopy[5] based. Of these, Surface Enhanced Raman Scattering (SERS) is an emerging optical based technique that has shown tremendous potential for trace analysis of contaminants [6] relevant to the food or environmental sectors [7, 8]. In SERS, the Raman signal is significantly enhanced at the surface of metallic nanostructures. Enhancement is generally divided into chemical and electromagnetic enhancements [9]. Chemical enhancement relates to the increased hyperpolarizability of the target molecule upon adsorption onto the SERS surface while electromagnetic enhancement occurs due to the plasmonic nanogaps or “hotspots” located in between the metallic nanostructures. In the last couple of decades, a number of approaches have been investigated for fabrication of SERS substrates [10]. Typically, fabrication techniques employed include UV photolithography [11], electron beam lithography [12], nanoimprint lithography [13], and templating [14]. The morphology of the nanostructures includes particles [15], triangles [16] or sphere [17].
Recently, SERS based on nano dendritic structures have also been reported. Techniques used to obtain the dendrites include galvanic displacement [18, 19] and chemical methods [20-22]. Direct electrochemical methods are also used and generally require the addition of surfactants or additional chemicals to stabilize the growth [23]. In those reports, the SERS nanodendrites were grown in 3D [24]. While this provides a higher density of hot spots and therefore higher Raman enhancement, these structures are more prone to be washed away during cleaning steps and when carrying out the analysis in aqueous conditions.

In the present paper, we report on the rapid and cost-effective synthesis of 2D silver nanodendrites on Si substrates. The synthesis is based on electrochemical reduction of silver salts at microelectrodes. This approach requires only low volumes of chemicals of relatively low toxicity and is straightforward to be scaled up. The fabrication method presented here occurs on the order of seconds whereas other electrochemical methods can take up to an hour [23]. The SERS substrate fabrication was visualized under a microscope, and it was observed that the nanodendrites grew horizontally along the substrates. The formation can be explained by the interplay between electromigration and mass transport of silver ions. Electrochemical characterization of the fabricated substrates suggests that the nanodendrites are not fully electrically connected to the microelectrode after deposition. These samples show SERS activity with an enhancement factor (EF) of ~10^6 obtained. To demonstrate the efficacy of the sensors, 2-methyl-4-chlorophenoxyacetic acid (MCPA) was selected as it is a widely used phenoxy herbicide used to control broad leaf weeds in pasture and cereal crops. Atomistic simulations were undertaken and revealed that the interaction between MCPA and the Ag surface was unfavorable. To overcome this limitation, substrates were functionalized with γ-cyclodextrin. Cyclodextrins are cyclic oligosaccharides made up of repeating glucopyranose units [25] and have been shown to form inclusion complexes with organic contaminants owing to the hydrophobic moieties in their core [26]. Using this approach, a limit of detection of 1mM MCPA in water was obtained.

- Materials and methods
  1. Materials

Silver nitrate (AgNO₃), 4-Aminobenzothiol, Ruthenium hexafluoride, Di-methyl sulfoxide (DMSO) and 2-methyl-4-chlorophenoxyacetic acid, phosphate buffer saline (PBS, 50 mM, pH 7.4) containing Fe(CN)₆³⁻/⁴⁻ were obtained from Sigma-Aldrich. Heptakis-(6-deoxy-6-mercaptop)-gamma-Cyclodextrin (γ-CD) was purchased from Cyclodextrin-shop. All aqueous solution were prepared using ultra-pure Milli-Q water (18.2MΩ.cm⁻¹, Milli-Q). All chemicals were used as received without further purification.

  2. Fabrication of microelectrode on chip

Silicon chip bearing Pt microelectrode was fabricated as described in [27, 28], see Figure S1 (supplementary information). Briefly, the sensors were fabricated on four-inch silicon wafer substrates with a 300 nm layer of thermally grown silicon dioxide. Firstly, the working electrodes were patterned using photolithography and thermal evaporation (50 nm of Pt, with 10 nm of Ti adhesion layer) followed by lift off. A second optical lithographic and metal
deposition process (Ti 10 nm/Au 100 nm) was undertaken to define HDMI pin-out, interconnection tracks, as well as the on-chip counter electrode (500 μm wide × 6 mm long). A third similar step was used to define the Pt (Ti 10 nm/Pt 100 nm) on-chip reference electrode (500 μm wide × 6 mm long. Finally, 500 nm of PECVD SiN was blanket deposited on the whole wafer, and openings over the working/counter/reference electrodes and electrical contacts defined by lithography and dry etching.

3. Electrochemical Characterisation

Cyclic voltammetry procedures were undertaken using a portable CH Instrument 1220C bipotentiostat (CH Instruments, Inc Austin, Tx). A three-electrode configuration was used for electrochemical deposition of Ag nanodendrites with Pt microband arrays as working electrodes, gold on-chip counter electrode and platinum on-chip pseudo reference electrode. Electrochemical impedance spectroscopy (EIS) measurements were carried out using Autolab Bipotentiostat/Galvanostat (Metrohm, Netherlands) undertaken using a three-electrode silicon sensor chip with Pt microelectrode arrays as working electrodes, gold on-chip counter electrode and platinum on-chip pseudo reference electrode. (Frequency range: 0.01 Hz–10 kHz; amplitude: 5 mV).

4. Fabrication of Ag nanodendrites

SERS substrates were prepared using 10 mM AgNO₃ aqueous solutions. For electrochemical deposition, a small aliquot (2μL) of the silver solution was deposited on a chip surface covering all three electrodes (working, on chip pseudo reference and counter electrodes). Chronoamperometry was applied to fabricate the SERS substrates by electrodeposition followed by rinsing in DI water and drying under a nitrogen flow for several seconds.

5. Optical, AFM and SEM characterization

An electrochemical setup could be placed under the microscope in order to visualize and record the deposition process. A Leica DMRB microscope equipped with a 20x objective (Olympus LMLPLFN, 0.40 NA) and a Thorlabs C1284R13C camera was used. SEM characterization was undertaken with a FEI QUANTA 650 HRSEM with energy dispersive X-ray spectroscopy (EDX Oxford Instruments INCA energy system). AFM images were undertaken in tapping mode with a Bruker Nanoscope dimension icon atomic force microscope. Electrochemical characterization of the substrates was undertaken using cyclic voltammetry as described above.

6. Raman measurements

Raman spectra were acquired with a Horiba XploRA Plus confocal Raman microscope equipped with a 532 nm laser. For measurements in liquid, the SERS substrate were placed in a dedicated holder. A 2μL aliquot of the solution was deposited over the substrate and
covered with a glass slide coverslip. All measurements were acquired using a 10x microscope (Olympus, 0.25 NA). All spectra presented herein are an average of 10 individual scans. A laser power of 0.35 mW and an integration time of 10s were used. Smoothing and baseline correction were undertaken with Labspec 6 software.

### 7. Computational details

Density Functional Theory (DFT) calculations were carried out using the VASP5 code [29, 30]. The core electrons were described by pseudopotentials constructed with the projector augmented-wave (PAW) method [31], where Ag 5s\(^1\) and 4d\(^{10}\), O 2s\(^2\) and 2p\(^4\), Cl 3s\(^2\) and 3p\(^5\), C 2s\(^2\) and 2p\(^2\), and H 1s\(^1\) are considered valence states. The exchange-correlation functional was approximated with the Perdew–Burke–Ernzerhof (PBE) functional [32]. The cut-off energy for the plane waves is set to 400 eV, and the convergence criteria used for energy and atomic forces are 10\(^{-4}\) eV and 0.02 eV Å\(^{-1}\), respectively. Spin polarization was considered for all calculations, with a Γ-point sampling grid. The Ag surface was cleaved from a bulk fcc structure with an equilibrium DFT lattice parameter 4.17 Å. Our surface model uses a Ag (111)-oriented slab with four layers, a side length of 17.67 Å and hexagonal symmetry. The supercell size was selected to minimize the adsorbed molecule’s periodic interactions across the periodic boundary conditions. The adsorption was simulated by DFT relaxation of a single MCPA molecule at different orientations with respect to the surface in order to assess the most favorable configuration. The adsorption energies (E\(_{\text{ads}}\)) were computed with the following expression, including vdW interactions with the Grimme’s D3 method [33]:

\[
E_{\text{ads}} = E_{\text{total}} - E_{\text{surface}} - E_{\text{adsorbate}}
\]

*Equation 1*

Where \(E_{\text{surface}}\) and \(E_{\text{total}}\) are the energy of the system before and after the adsorption of the respective adsorbate. The energy of the adsorbed molecule (\(E_{\text{adsorbate}}\)) was calculated for an isolated molecule, using the same computational setup as the SERS surface.

- **Results and Discussion**
  - **1. Fabrication of the SERS substrates**

*Figure 1*(a) Photograph of a silicon chip used for the electrochemical based fabrication of the SERS substrate; (b) Electrochemical setup on the microscope stage
Silicon chips used for the fabrication of the SERS sensors can be seen in Figure 1 (a). These sensors chips were originally developed for electrochemical based sensing applications [34]. The chips have a HDMI-C edge connector format for easy connectivity to a potentiostat and bear eight individually addressable electrodes. Interdigitated Pt microbands arrays (1 \( \mu \)m wide, 40 \( \mu \)m long, 50 nm height and 2 \( \mu \)m gap) were used for SERS substrate fabrication. Figure 2 (b) shows the experimental setup used to record videos of nanodendrites formation. The sensors chips were placed in a dedicated holder and a small aliquot of a AgNO\(_3\) solution dropped on top of the electrodes. Chips were then covered with a coverslip and imaged under the microscope, allowing real time monitoring of the SERS sensors fabrication.

Considering that electrodeposition takes only 10 s (vide infra), the present approach is rapid, low cost, scalable (multiple electrodes can be coated at the same time) and environmentally friendly approach. Also, unlike silver nanoparticle synthesis using wet chemistry, the nanostructures do not require stabilizing agents and are pure silver, allowing easy post-synthesis functionalization via, e.g., thiol chemistry. This method also ensures that no residues, such as citric acid, would be incorporated into the metallic nanostructured surface which could potentially interfere with the recorded spectra.

2. Electrodeposition process

Figure 2 (a) shows a cyclic voltammogram acquired at a scan rate of 100 mV/sec at a single Pt microband. When the CV is swept cathodically it is observed that an under deposition of silver is initially observed at -0.2 V. By increasing the applied potential further, below -0.6 V, a rapid dendritic silver growth is observed. Dendrites continue to grow during the reverse (anodic) sweep until the applied potential is more positive than -0.6V. As the anodic sweep is swept more positive a sharp peak can be seen at a potential of ~0.1V. This sharp peak corresponds to the stripping of electrodeposited silver. Following CV characterization, SERS substrates were subsequently fabricated using an amperometric approach where a potential of -0.65 V applied to the working electrode for 10 s. A typical current vs time plot is presented in Figure 2 (b). It can be seen that in this deposition process, the current does not plateau but instead keeps increasing exponentially as the potential is applied with time. This suggests that the
overall deposition process is not diffusion limited since the growth continues laterally across the electrode surface.

Figure 2 (c) and (d) are optical micrographs of an interdigitated electrode recorded after 2 and 7 s, respectively (a video is available in the SI). As expected, the silver deposition starts initially on the working electrode. Interestingly, under the experimental conditions chosen here, the silver deposition is observed to grow laterally away from the working electrode. The lateral growth rate was measured to be about 10 μm/sec.

3. Electrodeposited electrode topology

When inspected under a 100X magnification, the electrodeposited material adopts a dendritic like formation, with a number of stalks originating from the working electrode. As the deposition process continues, these stalks are decorated with lateral branches, see Figure 3 (a), and the dendrites grow along the substrate, away from their original locations. No overlap between the branches, or growth in a vertical direction was observed. Figure 3 (b) shows a typical SEM of the electrodeposited material, where the dendritic structure can be observed in more details. The dendrites were composed of nanoparticle clusters in close proximity to each other. The top surface of these nanostructures appeared flat, and the lateral dimensions is typically 200 nm and ranges from 20 to 500 nm. A high number of nanosized gaps (that can support electromagnetic hot spots) can be observed between adjacent nanostructures. Figure 3 (c) shows a typical AFM image of the electrodeposited electrode. The dendritic structure is clearly observed. Higher resolution AFM suggest that the branches of the nanodendrites are actually composed of an aggregation of smaller nanostructures that are about 60 nm in size, see Figure 3 (d)

4. Electrochemical characterization

The nanocluster dendrite formation observed under the microscope (video in SI Figure 2) as well as the SEM and AFM images in Figure 4, suggest there is always a continuous path from any point on the nanodendrites back to the working microelectrode. To test whether the nanodendrites were electrically connected to a microband, CV characterization of a modified electrode using a 10 mM ruthenium in 10 mM PBS solution was undertaken. Ruthenium was chosen as its redox reaction occurs at negative potential – and therefore away from the silver
stripping potential observed at 0.1 V. Figure 4 ((a)-(c)) shows silver nanodendrites formed following electrodeposition for 1, 5 and 12 sec, respectively, with the corresponding CVs presented in Figure 4 (d). As can be seen, the current measured at -0.23 V (corresponding to the reduction of Ru) is 12.5 nA for a bare electrode and 12.5 nA, 13.9 nA and 13.3 nA for samples with 1, 5 and 12 s silver depositions, respectively. As the nanodendrites grow, it is expected that the measured faradaic current should grow accordingly. However, the measured signals are very similar from the ones measured at the bare microelectrode. In addition, the signal measured at 12 s electrode is smaller than the one measured at 5 sec despite the spread of the silver increasing the footprint of the electrode from 60 to 150 microns. The lack of correlation between signal intensity and electrode surface area suggests that the silver nanodendrites do not participate in the electrochemical reaction and that they are thus not fully electrically connected to the original microelectrode. However, this is good for SERS substrates as it indicates the presence of significant number of nano gaps or hotspots. The small increase observed may be attributed to an increase in surface area at the microelectrode itself. One possible explanation for the observed behavior is that after application of the deposition potential, the open potential of the electrode is close to the silver stripping potential and, as a result, silver dissolves slightly back into solution, see video S1, but does not dissolve completely.

To further study this hypothesis, electrochemical deposition using cyclic voltammetry (three full scans) was undertaken using different voltage windows. In the first set of experiments, the potential range was set to be -1.0 V to 0.0 V, i.e., with the most positive potential maintained below the potential for Ag stripping. Figure 5 (a) shows an optical micrograph of the corresponding electrode. It can be seen that the nanodendrites grew in three waves as evidenced by the concentric rings. This suggests that under these conditions, the nanodendrites are still electrically connected to the original microelectrode. A second CV-based deposition was undertaken using a wider potential window of -1.0 V to 0.2 V, i.e., above the Ag stripping voltage. In this case, the first cycle showed the typical slow controlled 2D growth of nanodendrites as observed previously. However, during the second deposition, the silver growth was observed to switch to a more vertical direction from the surface of microelectrode occurred more rapidly. The resulting silver deposition appeared to larger agglomerates which were not dendritic in nature see Figure 5 (b). We hypothesize that the
increased concentration of silver in the vicinity of the working electrode, following the stripping process, resulted in a rapid silver deposition with a different morphology.

![](image)

*Figure 5 Consecutive depositions undertaken using cyclic voltammetry when the highest potential is (a) lower and (b) higher than the stripping potential of the silver*

.5. Electrochemical formation process

Concerning 2D growth, the 2D morphology of the nanostructure can be explained in terms of mass transport and interplay between diffusion and electromigration. During the initial electrochemical deposition, silver ions located in the diffusion layer adsorb on the surface of the microelectrode where they are reduced, forming seed nanoparticles that effectively increase the surface roughness of the electrode. During this initial process, the volume just above the electrode becomes depleted in Ag ions limiting the electrode formation in the vertical direction. However, there are still Ag ions in the horizontal plane, i.e., along the chip surface, allowing the electrode to grow laterally. As the process continues, the electrode spreads along the substrate, effectively ‘chasing’ available Ag ions. The dendritic pattern of the electrode can be explained in term of electric fields. As the electrode spreads, the newly deposited silver supports the electric field underpinning the electrodeposition process. The electric fields at adjacent branches are equal thereby preventing the bridges shorting and instead favoring the electrode extension away from the original electrode.

.6. Silver nanodendrites as Surface Enhanced Raman Scattering substrates

The electrodeposited silver nanodendrites consisted of a high density of metallic nanostructures with associated nanogaps. It was found that the 2D nanodendrites were strongly attached to the silicon surface of the sensor chip and did not lift off when washed or used in aqueous test solutions. By contrast, the 3D structures were found to detach easily from the surface of the chip and were not studied further.). Initial Raman experiments showed that the as fabricated silver nanodendrites could support plasmonic hot spots and therefore could be attractive for SERS applications. In order to test their SERS capabilities, a monolayer of Raman reporter 4-Aminobenzothiol (4ABT) was deposited on the nanodendrites surface, and its Raman response recorded and compared to the that obtained from bulk 4-ABT; under the same experimental conditions, see Figure 6. The peak assignment can be found in SI. As can be seen, the Raman signal is significantly higher for the monolayer than it is for the solid
confirming a SERS response. The enhancement factor (EF) was then calculated using the following equation [37]:

\[
EF = \frac{I_{\text{Surface}}/N_{\text{Surface}}}{I_{\text{Bulk}}/N_{\text{Bulk}}}
\]

where \(I_{\text{Surface}}\) and \(I_{\text{Bulk}}\) are the intensities of the SERS peak and normal Raman peak respectively, and \(N_{\text{Surface}}\) and \(N_{\text{Bulk}}\) are the number of molecules illuminated by the laser spot on the SERS substrates (surface) and in the 4-ABT powder (volume), respectively. \(N_{\text{Surface}}\) and \(N_{\text{Bulk}}\) were evaluated using data from [38], see SI for a detailed description on approach used and SEM data to calculate the roughness factor. The enhancement factor of 4-ABT on the silver nanodendrites is calculated to be \(3.19 \times 10^6\). This is consistent with the EF observed for 3D nanodendrites. [35]

![Figure 6 Raman spectra of (a) 4-ABT powder and (b) a monolayer of 4-ABT deposited on the silver nanodendrites](image)

7. Interaction between target pesticides and SERS substrates

MCPA is a widely used herbicide used to control weed growth in agricultural fields that has been found at exceeded level (limit of 0.1 ppb or 0.1 µg/L in EU’ WFD) in water bodies in Ireland and Europe. The measured bulk Raman spectrum of MCPA with the associated peak assignment are presented in SI (Figure S3). However, initial SERS experiments failed to detect MCPA even at elevated concentrations ~100 mM. To understand why this was the case, a DFT simulation study was undertaken to explore the adsorption of MCPA at the silver surfaces. Figure 7 (a) to (d) represent the geometries from the most to the least favorable adsorption orientations. The computed adsorption energies in a range between -0.15 eV (Fig. 7 (a)) to -0.01 eV (Fig. 7 (d)) showing that the MCPA molecule is very weakly adsorbed in all potential configurations.
In the most energetically favored configuration Figure 7 (a), with an adsorption energy of -0.15 eV, the molecule-surface interactions seem to be mediated by the acid and methyl groups in MCPA. We simulated an O-Ag distance (between the terminating O and the closest Ag atom at the surface) of 2.55 Å, and H-Ag distances (between H in methyl and their closest surface Ag) in a range between 2.73-3.44 Å. In Figure 7 (b) the methyl group stays far from the surface, and the acid group mainly mediates the adsorption. In this case, the computed adsorption energy is weaker than in (a), with a computed adsorption energy of -0.07 eV and bond distances between MCPA and the surface of 3.14 Å for O and 2.61 Å for the terminating H.

In the remaining possible interaction modes, the carbonyl group is directed away from the surface and the weak interaction is mediated by the methyl, H and Cl terminations in the aromatic ring. The distances between the molecule and their closest Ag atoms on the surface are 3.08 Å for Cl, 2.67 Å for H in the ring and 3.16 Å for H in the methyl group. Rotating the MCPA molecule so that the terminating H interacts with the surface at distances between 2.76-3.30 Å, and the O from the –OH of the acid sits 2.89 Å from the surface gives the weakest interaction mode.

These results suggest that the interaction of the target pesticide with the SERS substrate is very weak, making detection of MCPA very challenging in agreement with experiments carried out on pristine dendrite substrates where SERS spectra of MCPA were not obtained.

.8. Functionalization of SERS substrate with γ-cyclodextrin

To address this limitation, functionalization of the SERS substrate was undertaken using cyclodextrin. Cyclodextrins are cup shaped macromolecules with a hydrophobic core and a hydrophilic outer rim. For this reason, they have been used extensively to increase dissolution of drugs or other compounds having hydrophobic properties [36]. They were also shown to form host-guest complexes with pesticides such as MCPA [37]. In the present work, γ-cyclodextrin with internal dimensions of 0.78nm (diameter) by 0.79nm (height) was used to modify the electrodes. By coating the sensors with this molecule, it should be possible to bring
the target analyte to the surface and allow its detection using Raman based techniques. Functionalization of the developed SERS substrates was undertaken by incubation for 10 minutes in thiol γ-cyclodextrin solution in DMSO followed by thorough rinsing with pure DMSO.

![image]

**Figure 8** (a) EIS Nyquist plot for each stage of deposition and functionalization; (b) table for EDX of elemental analysis of the dendrites after functionalization; (c) SEM of deposited Ag nanodendrites; (d) EDX/SEM showing presence of S on surface confirming γ-CD functionalization

Electrochemical Impedance Spectroscopy (EIS) can effectively determine the electron charge transfer resistance (Rct) and was used to study the different modifications of the Pt working microelectrods. The electrochemical behaviour of bare Pt electrode, Ag nanodendrite/Pt, and γ-cyclodextrin /Ag nanodendrite/Pt are presented in Figure 8 (a). The Nyquist plot obtained from EIS studies was fitted with an equivalent circuit (NOVA software). The electron transfer resistance (Rct) values for bare Pt microelectrodes, Ag nanodendrite/Pt, and γ-cyclodextrin /Ag nanodendrite/Pt were found to be 10.8MΩ, 9.16 MΩ and 15.1 MΩ respectively. The decrease in the electron transfer resistance of the Ag nanodendrite/Pt is due to higher surface area. However, the Rct value increases significantly as γ-cyclodextrin is attached on the surface, showing its electrical isolating properties. Similar insulating properties were reported for cyclodextrins. [38] This further suggested that the microelectrode modification for MCPA detection was successful. Figure 8 (c) shows a SEM image of a typical silver deposition, while figure 8 (d) shows the same SEM with elemental analysis with the purple colour representing the presence of sulphur. This confirms the deposited thiolated cyclodextrin layer on the surface of the silver. The table shown figure 8 (b) shows the full elemental analysis for the sample.
9. Detection of MCPA using modified SERS substrate

To confirm this, SERS spectra were recorded in DI water in both the presence and absence of MCPA. A typical spectrum of the functionalized substrates in DI water is shown in figure 9 bottom panel. The spectrum shows peaks at 446, 487/498, 673, 720, 933, 1026 and 1264 cm\(^{-1}\) onwards. The two peaks at 636 cm\(^{-1}\) and 680 cm\(^{-1}\) can be attributed to CS bond of the thiolated cyclodextrin. The rest of the spectrum shows a series of broad peaks between 1100 and 1700 cm\(^{-1}\) that correspond to the various CC and CH vibration of γ-cyclodextrin scaffold.

Figure 9 top panel shows the Raman spectrum of the γ-cyclodextrin functionalized substrate incubated in a 1 mM solution of MCPA. Some features like the peaks at 487/498, 932 and 1026 cm\(^{-1}\) seen in DI water only are still present. However, new peaks emerge at 357, 804, 881, 1081/1095 and 1237 cm\(^{-1}\) and are attributed to the MCPA/γ-CD complex. Also, some peaks present in the original sample are shifted or split (640/657 or 743 cm\(^{-1}\)). The change observed in the Raman spectrum suggest that the MCPA molecule interacts strongly with γ-cyclodextrin core. The strong coupling leads to a restriction of the number of vibrations from both the host and the guest and results in new vibrations for the host/guest system. Similar
observations have been reported for FTIR analysis [39]. These results confirm the DFT simulations, and that modification of the surface with γ–CD is sufficient to capture MCPA allowing subsequent SERS detection. This approach may be extended to other molecules where SERS detection is difficult.

- Conclusions

In this paper, we report on the fabrication of 2D silver nanodendrites on silicon chips by electrochemical deposition at platinum microelectrodes. The dendritic structuring can be explained by the interplay of electromigration and diffusion of silver ions. Characterisation of the modified electrode by cyclic voltammetry revealed the deposited silver nanostructures were not electrically connected to the original microelectrode. High resolution imaging revealed the sample had a high density of nanostructures and nanogaps, necessary for SERS effect to occur. Raman reporter 4-ABT was used to calculate an enhancement factor of c.a. $10^6$. Density functional theory (DFT) simulations were revealed the interaction between herbicide MCPA and silver surface was weak. To increase this interaction, the silver nanodendrites were functionalised with thiolated cyclodextrin, and SERS based detection of the pesticide reported. This concept can be extended to other contaminants with low affinity to silver.


