

Motivation

Electrochemical reactions can be probed by surface enhanced *operando* Raman Spectroscopy (SERS). Plasmonic metallic nanostructured substrates enhance the Raman signal intensity of analyte molecules by several orders of magnitude^[1].

Using that methodology, we report:

- ❖ Fabrication of Ag nanovoid SERS substrates by a Langmuir-Blodgett approach and subsequent bipolar electrodeposition
- ❖ Optimization of Ag-nanovoid substrates towards their highest Raman enhancement
- ❖ *Operando* Raman spectra suggest CO and C₂ product formation

Raman Scans for the Highest Surface Enhancement

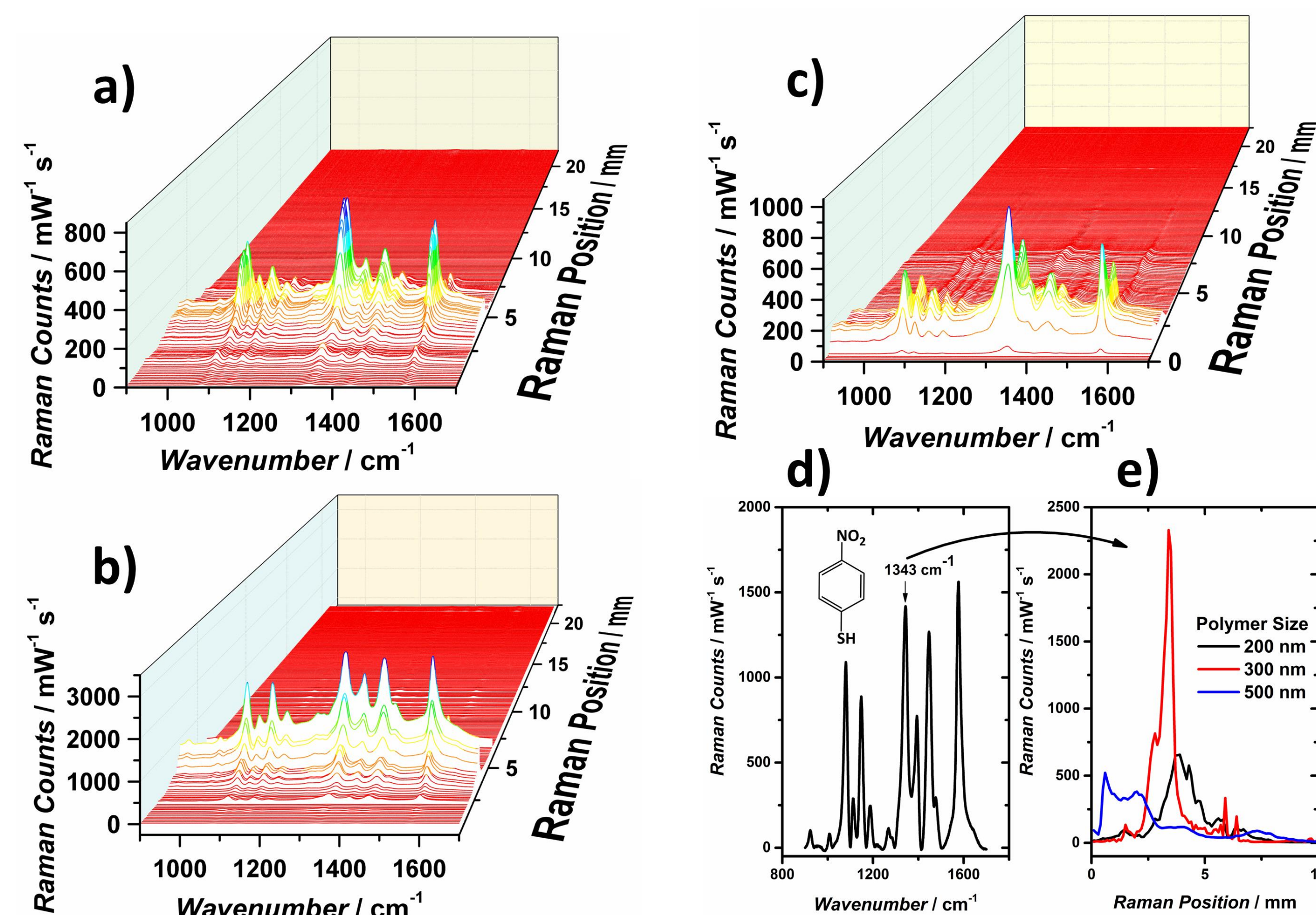


Figure 3. Raman scanning across the nanostructured samples with 100 μm increment using various nanosphere sizes: a) 200 nm, b) 300 nm, c) 500 nm. The samples were incubated in 4-NTP for 3 h. d) Raman spectrum of 4-NTP at 3.5 mm distance from the cathodic edge of the sample coated with 300 nm nanospheres. e) Change of intensity of the N-O band at 1343 cm^{-1} along the respective substrate.

Polymer templating: Langmuir-Blodgett Approach

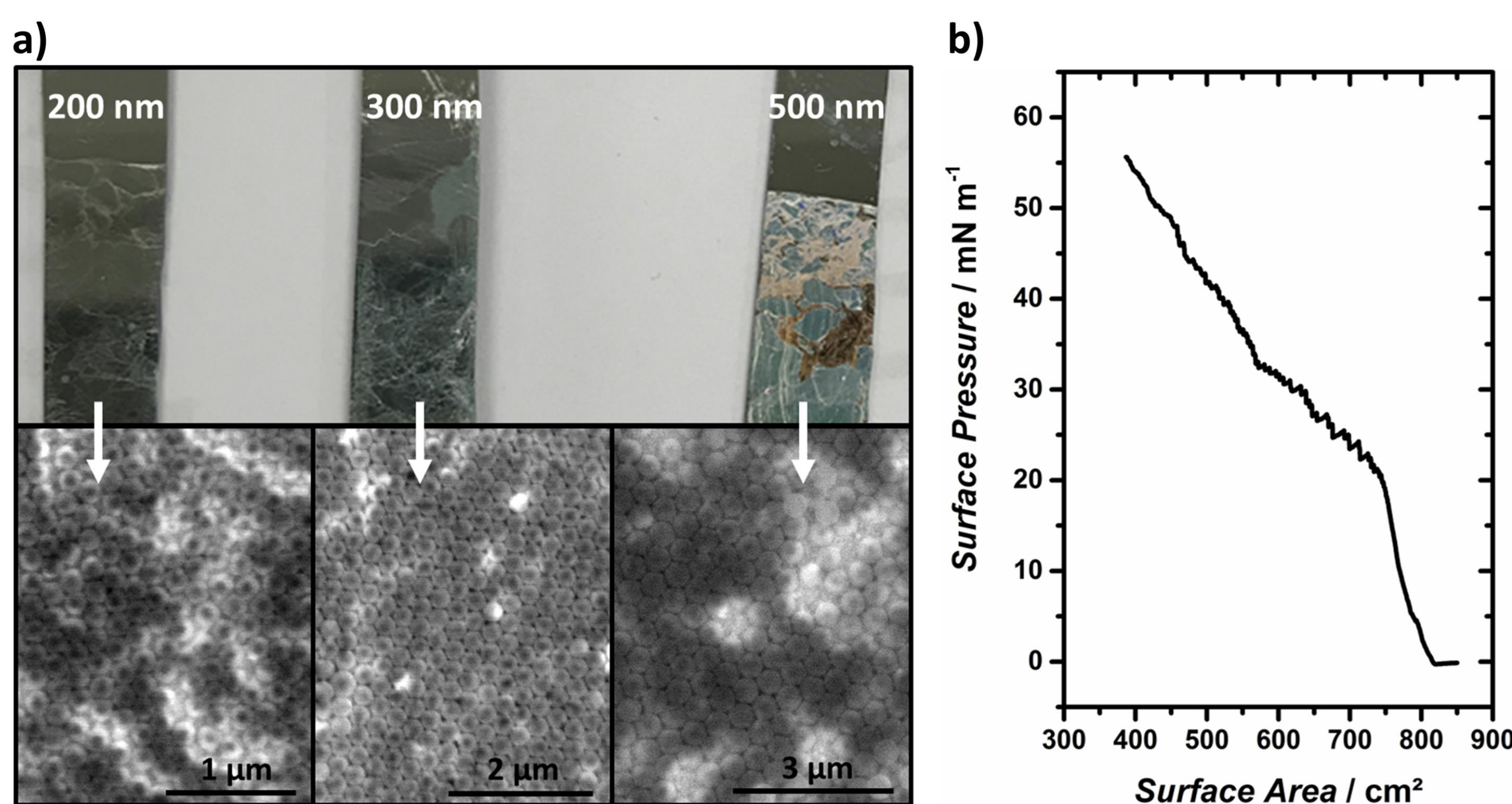


Figure 1. a) SEM characterization of the differently templated substrates produced by Langmuir-Blodgett deposition employed for bipolar electrodeposition. From left to right 200, 300 and 500 nm nanospheres. b) Surface pressure vs. surface area isotherm for the deposition of 300 nm nanospheres onto a Ag-coated Si wafer. The surface pressure is further increased after the first plateau at 25 mN m⁻¹ to ensure a densely packed nanobeads monolayer film at the water-air interface.

Bipolar Electrodeposition: Layer Thickness Gradients

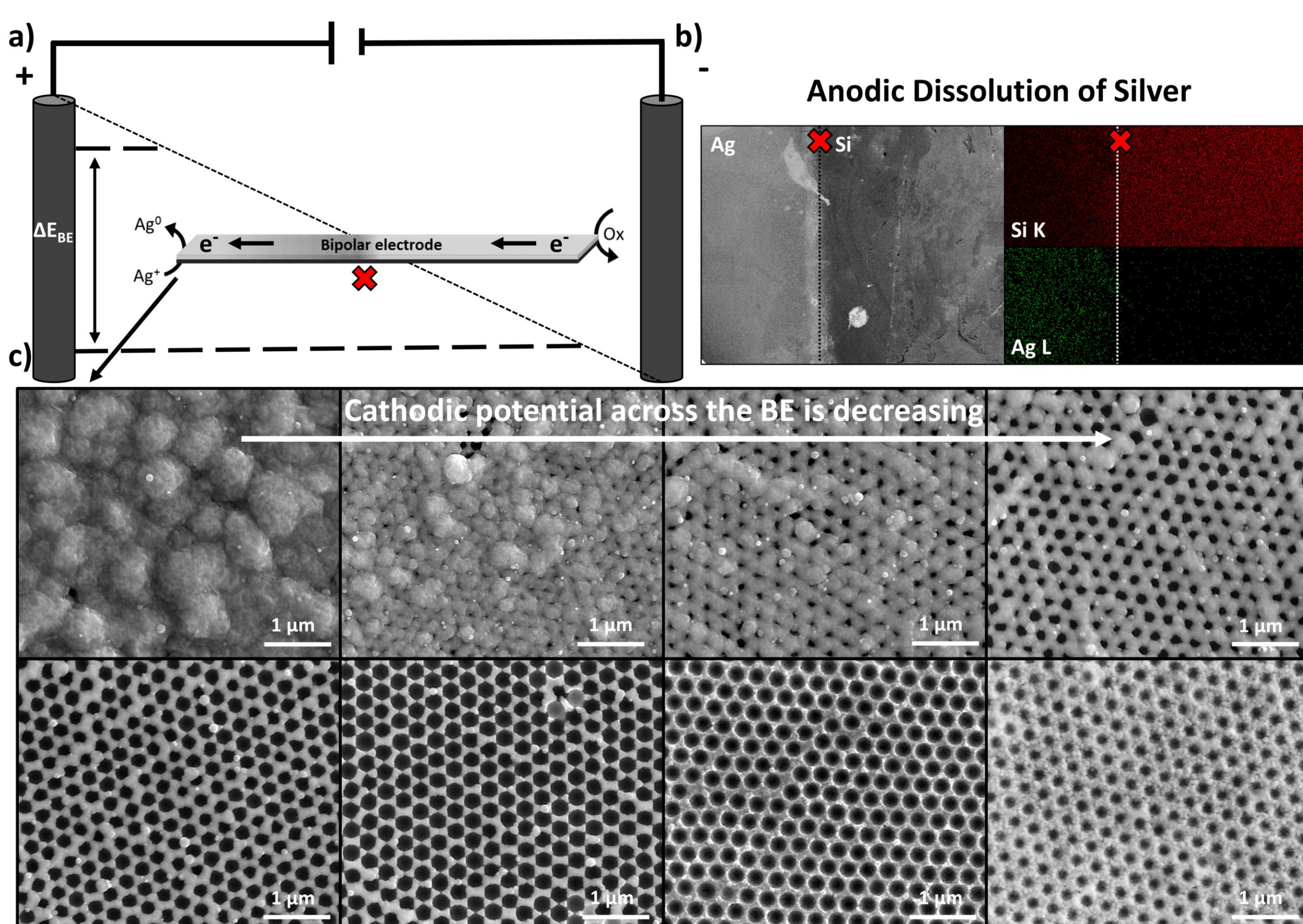


Figure 2. a) Schematic representation of a BPE setup. b) Red cross marks the position on the BE sketched in Fig. 1 a. Anodic dissolution of Ag proved with EDX mapping of Ag and Si. c) SEM characterization of the void gradient across the BE from the cathodic pole (upper left) towards the middle of the BE (lower right).

Electrochemical CO₂RR SERS Experiments

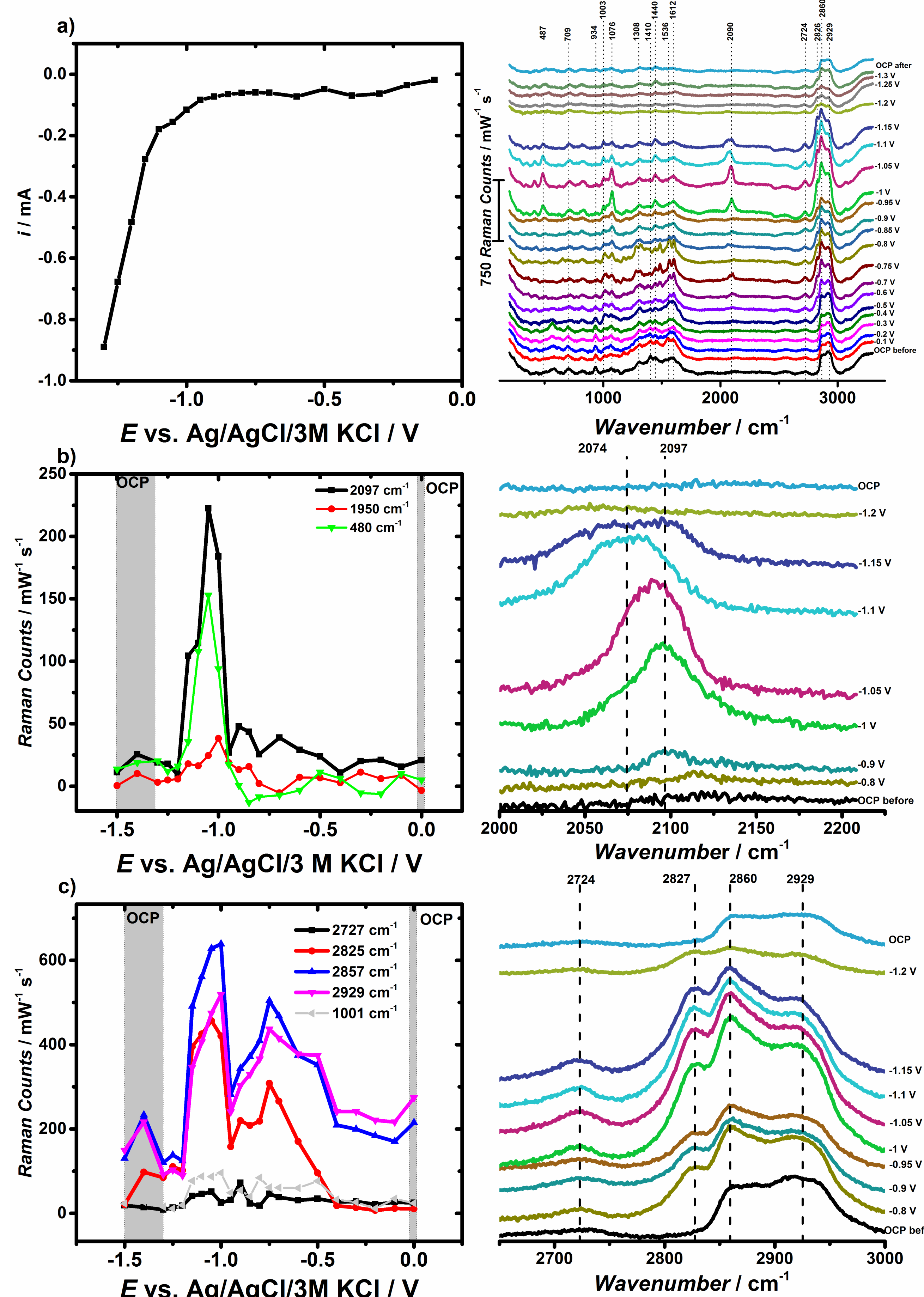


Figure 4. a) left: *i*-V curve of the potential step experiment in 0.1 M KHCO₃ on circular (d = 2 cm) Ag nanovoid substrate during Raman investigation. Each potential was held for 120 s. right: Raman spectra (counts per mW and s) recorded after 60 s during each individual potential application. b) left: Potential-dependent peak intensities of CO associated peaks^[2,3] during the electrochemical reduction of CO₂. right: Stark tuning of the CO peak during cathodic potential sweep from -1 V vs. Ag/AgCl/3 M KCl until -1.1 V vs. Ag/AgCl/3 M KCl. c) left: Peak intensities in the CH stretch region^[4] at around 2800 cm⁻¹. Peaks corresponding to CH formation increase sharply beyond cathodic potentials of -0.95 V vs. Ag/AgCl/3M KCl. right: Magnification of the peaks occurring in the Raman spectra.

References

- [1] Cardinal, M. F., Van der Ende, E., Hackler, R. A., McAnally, M. O., Stair, P. C., Schatz, G. C., van Duyne, R. P. *Chem. Soc. Rev.* 2017, 46, 3886–3903.
- [2] Beltramo, G. L., Shubina, T. E., Koper, M. T. M. *ChemPhysChem* 2005, 6, 2597–2606.
- [3] Cooney, R. P., Fleischmann, M., Hendra, P. J. J. *Chem. Soc., Chem. Commun.* 1977, 235.
- [4] McQuillan, A., Hendra, P. J., Fleischmann, M. J. *Electroanal. Chem.* 1975, 65, 933–944.

Conclusions

- ❖ Layer thickness void gradient electrodeposited by bipolar electrochemistry
- ❖ Ag nanovoids were optimized towards their highest signal enhancement
- ❖ Highest enhancement achieved with 300 nm nanosphere templates and a void opening of 190 nm
- ❖ Signal enhancement sufficient to study the CO₂RR by *operando* Raman spectroscopy
- ❖ Results suggest the formation of CO and C₂ products in contrast to the widely accepted EtOH, MeOH and HCOOH product preference