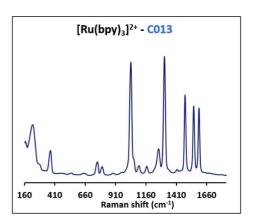
In situ, fast and sensitive: Electrochemical SERS with screenprinted electrodes

Substrates for surface-enhanced Raman spectroscopy (SERS) are typically fabricated with complex (micro/nano)structures of noble metals, enabling trace level detection of analytes. Due to the high costs and reactivity of these SERS substrates, they often have a limited shelf life. Development of new substrate materials which minimize these issues yet maintain the same performance standards is a constant concern. Screen-printed electrodes can be

easily fabricated using different metallic materials with the well-established screen-printing method, leading to mass production of versatile, cost-effective, and disposable devices. In this Application Note, the feasibility of using readily-available screen-printed metal electrodes as suitable substrates for the fast and sensitive detection of different chemical species by in situ electrochemical SERS (EC-SERS) is shown.

INTRODUCTION

Substrates for surface-enhanced Raman spectroscopy (SERS) are typically fabricated with complex (micro/nano)structures of noble metals to obtain high surface-area plasmonic surfaces, which are capable to enhance this effect and, therefore, the detection of chemical species at very low concentrations. These substrates are frequently highpriced and because their high reactivity, they often have a limited shelf life. Development of new SERS substrates that minimize these issues but preserving a good analytical performance is a constant concern. Screen-printed electrodes can be easily fabricated with different metallic materials and the wellestablished screen-printing method leading to mass production of versatile, cost-effective and disposable devices. They could be promising SERS substrates. In this Application Note, the feasibility of using readily- available screen-printed metal electrodes as cost-effective and disposable substrates for the fast and sensitive detection of different chemical species by in situ electrochemical SERS (EC-SERS) is shown.



EQUIPMENT

The fabulous, compact and integrated instrument for Raman Spectroelectrochemistry, SPELEC-RAMAN, was used. This instrument integrates in only one box: a spectrometer, a laser source (785 nm) and a bipotentiostat/galvanostat.

Screen-printed metal electrodes (refs. C013 (Silver), 220BT (Gold), CU10 (Copper), SPCU10 (Silver/Copper)) were placed in the Raman cell (RAMANCELL) coupled with the RAMANPROBE, which allows to perform Raman measurements of the electrode surface at the optimal focal distance.

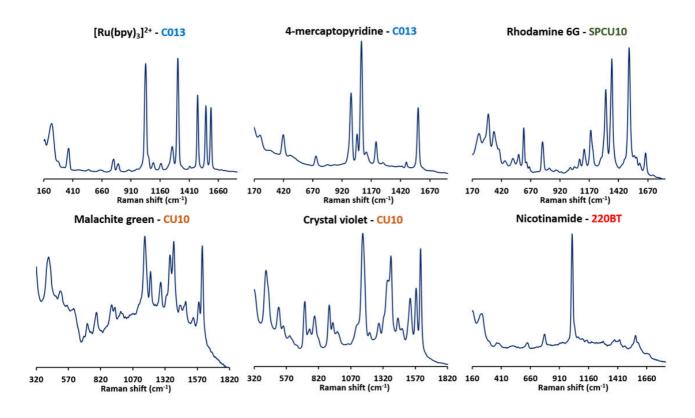


METHODS

Screen-printed electrodes were electrochemically activated by cyclic voltammetry: C013 (from +0.3 V to -0.4 V), 220BT (from +0.6 to +1.2 V to -0.2 V), CU10 (from +0.15 V to -0.6 V) and SPCU10 (from +0.10 V to -0.4 V). A 60 μL solution of 0.1 M KCl containing the specific analyte was used for the in situ and

simultaneous activation and detection. Concentrations were: 250 nM for $[Ru(bpy)_3]^{2+}$, 2 μ M for 4-mercaptopyridine, 20 μ M for Rhodamine 6G, 15 nM for Malachite green, 2.5 μ M for Crystal violet and 80 μ M for Nicotinamide.

RESULTS



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Spectroelectrochemical Raman instrument (785 nm laser)

SPELECRAMAN is an instrument for performing spectroelectrochemical Raman measurements. It combines in only one box a laser class 3B (785 nm \pm 0.5), a bipotentiostat/galvanostat and a spectrometer (wavelength range 787 – 1027 nm and Raman shift 35 - 3000 cm $^{-1}$) and includes a dedicated spectroelectrochemical software that allows optical and electrochemical experiments synchronization.



Raman Probe

Reflection probe designed to be used with a single excitation 785 nm wavelength (up to 500 mW). Suitable to work with DropSens Raman Cell for Screen-Printed Electrodes or with any conventional Raman set-up.



Raman Cell for Screen-Printed Electrodes

Black teflon reflection cell for performing Raman Spectroelectrochemistry with screen-printed electrodes in combination with ref. RAMANPROBE.

