In situ, fast and sensitive: Electrochemical SERS with screen-printed 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 high-priced 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 well-established 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.

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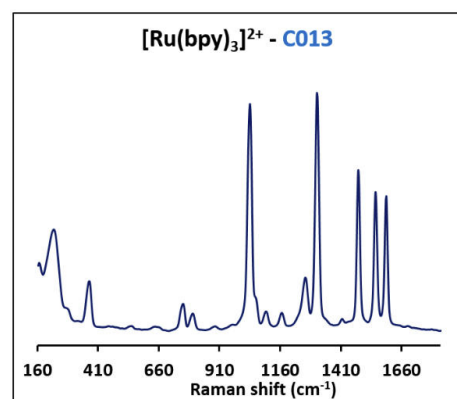
EQUIPMENT

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 µM for 4-mercaptopyridine, 20 µM for Rhodamine 6G, 15 nM for Malachite green, 2.5 µM for Crystal violet and 80 µM for Nicotinamide.
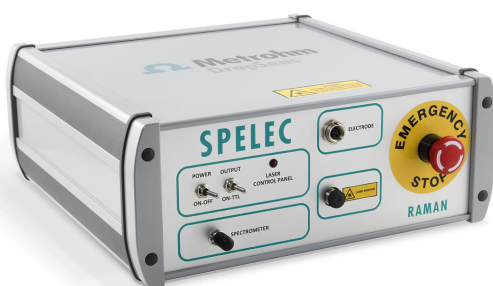
RESULTS

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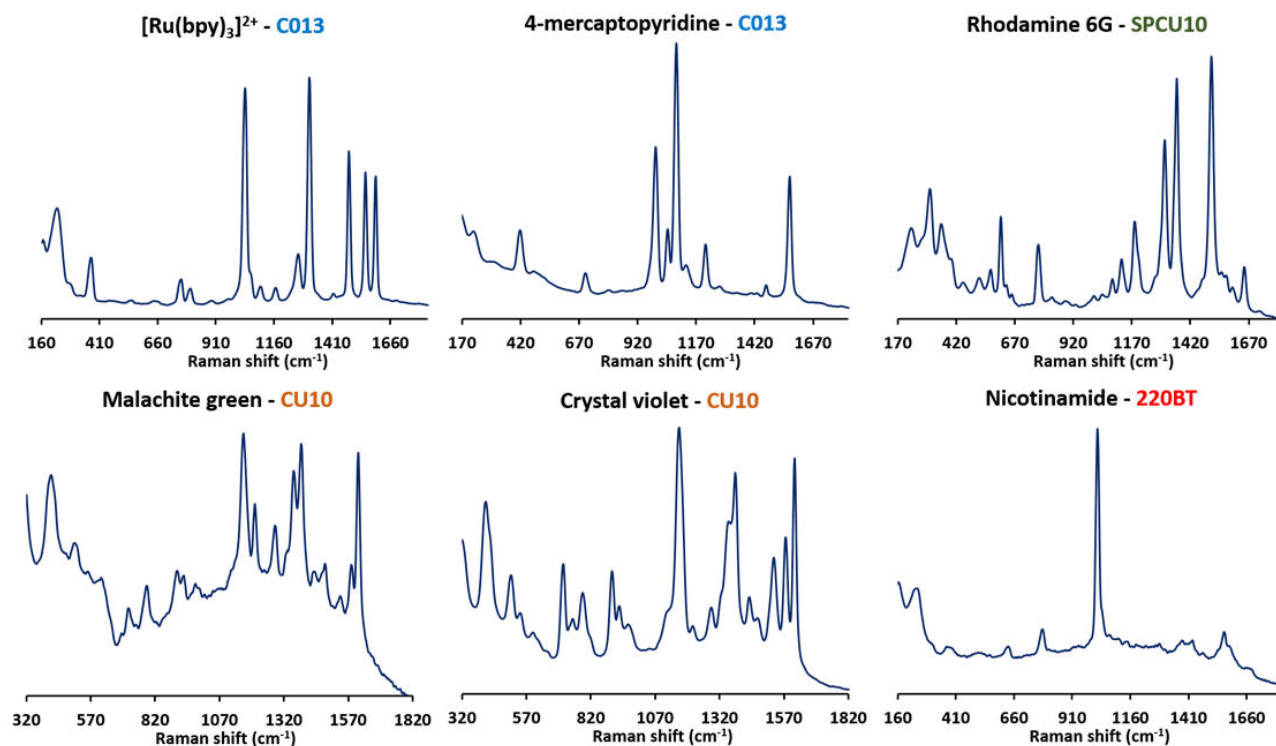
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Spectroelectrochemical Raman instrument (785 nm laser)

SPELECRAMAN is an instrument for performing spectroelectrochemical Raman measurements. It combines in only one box a laser class 3B (785 nm ± 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.

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