

## The carbon battle: characterization of screen-printed carbon electrodes with SPELEC RAMAN

### Introduction

Carbon materials have a fantastic behavior as electrode surfaces because they are cost-effective, chemically inert, have a low background current and a wide potential window. Although the carbon era seemed to come to an end, the development of new carbon nanomaterials has provided novel applications for carbon in the 21<sup>st</sup> century. Physical and chemical properties of these materials depend mainly on their structure, so their characterization is essential to choose the right material for the appropriate applications.

Raman spectroscopy is a very attractive technique for material characterization and allows to know in an effortless way some information about the structure of carbon materials in terms of the  $sp^2$  and  $sp^3$  bonds, and, therefore, about their possible properties. In general, the G band of the Raman spectra (around  $1580\text{ cm}^{-1}$ ) could provide information on the fraction of  $sp^2$  bonds and the D band (around  $1300\text{ cm}^{-1}$ ) could provide information on the fraction of  $sp^3$  bonds (and some disorder in the structure). In some cases, a  $G'$  band also appears around  $2600\text{ cm}^{-1}$  that could provide some knowledge on the layered structure of some of these materials.

DropSens screen-printed electrodes (SPEs) are low-cost, disposable devices, which are available with working electrodes fabricated in several carbon materials. Their properties can be studied by Raman spectroscopy as described in this Application Note.

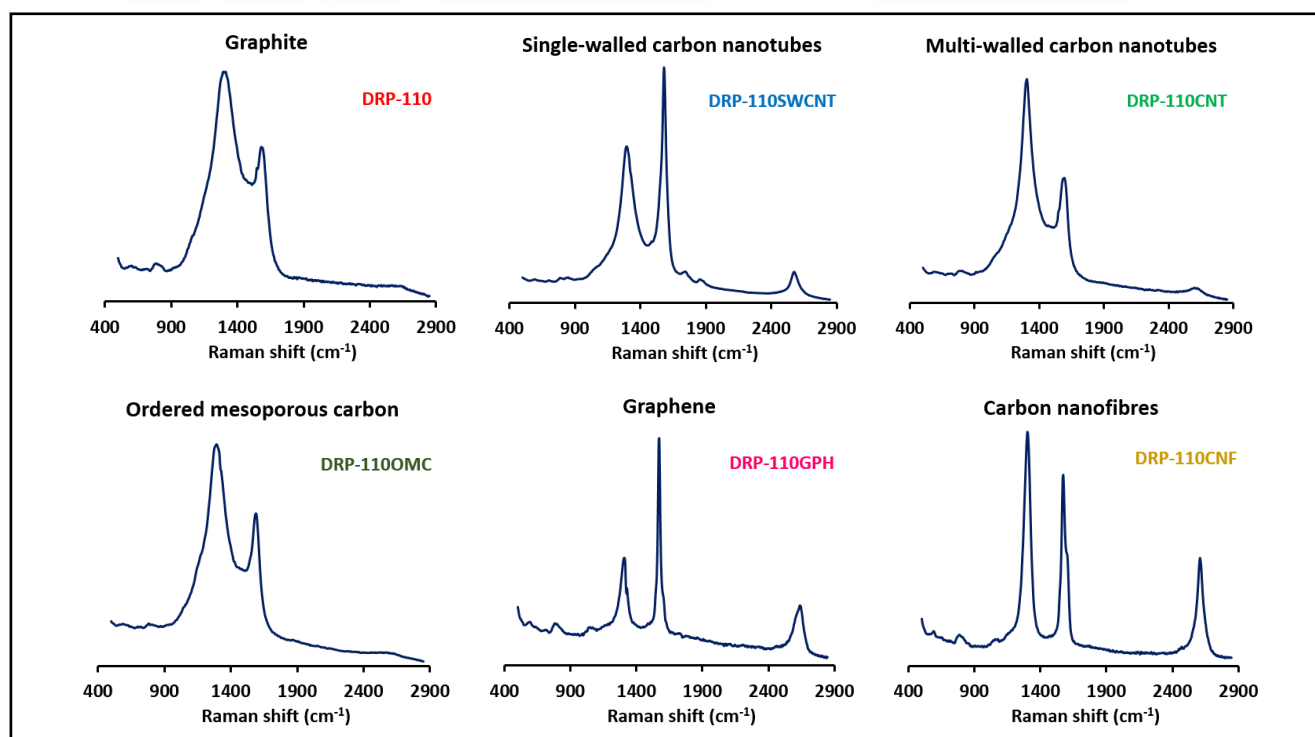
### Equipment

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



Screen-printed electrodes (refs. **DRP-110**, **DRP-110SWCNT**, **DRP-110CNT**, **DRP-110OMC**, **DRP-110GPH**, **DRP-110CNF**) were placed in a specific cell for this type of devices (**DRP-RAMANCELL**) coupled with the **DRP-RAMANPROBE**, which allows to perform the Raman measurements of the electrode surface at optimal focal distance. Integration time was 20 s.

### Results



## In situ, fast and sensitive: Electrochemical SERS with screen-printed electrodes

### 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.

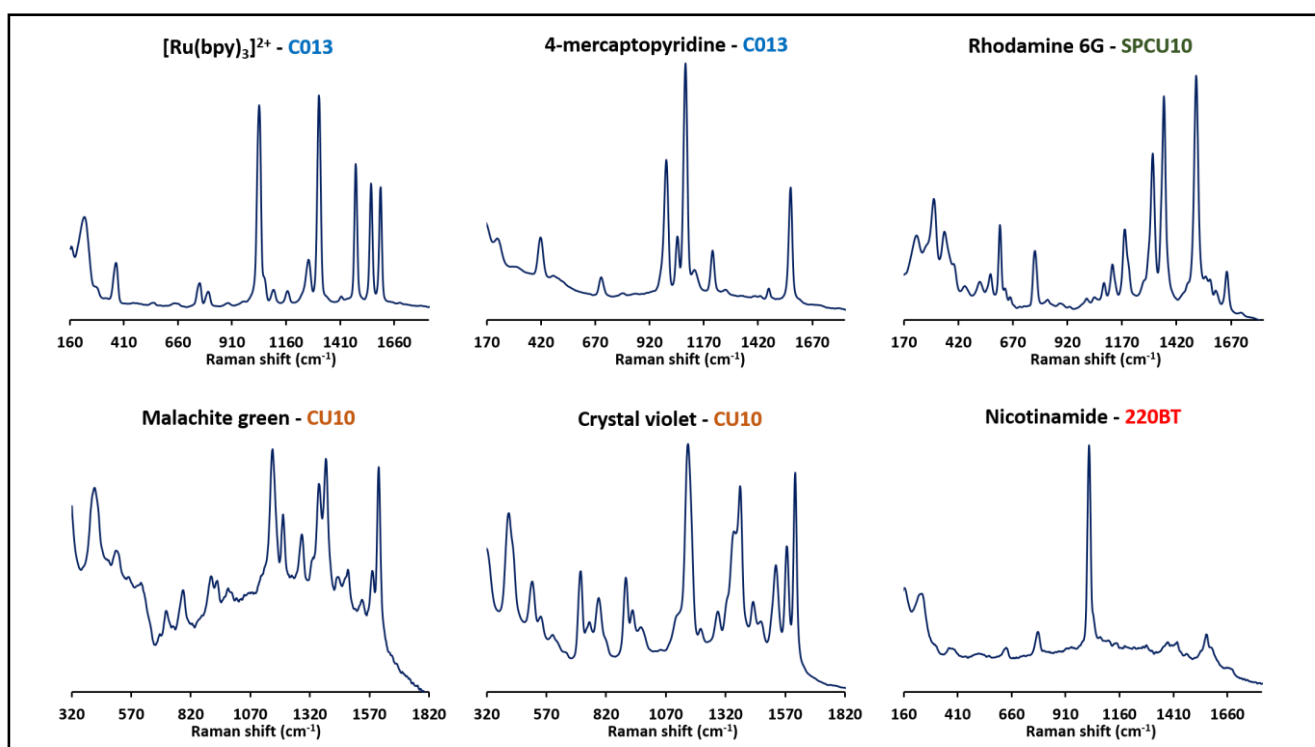
Screen-printed electrodes can be easily fabricated with different metallic materials and the well-established screen-printing method leading to mass production of versatile, cost-effective and disposable devices. They could be promising SERS substrates.

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.

### 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  $\mu$ L 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  $[\text{Ru}(\text{bpy})_3]^{2+}$ , 2  $\mu$ M for 4-mercaptopyridine, 20  $\mu$ M for Rhodamine 6G, 15 nM for Malachite green, 2.5  $\mu$ M for Crystal violet and 80  $\mu$ M for Nicotinamide.

### Results



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

## Fancy a functional group? Usual Raman vibrational frequencies

### Introduction

**SPELEC RAMAN** is a compact instrument that allows to perform Raman spectroelectrochemical experiments in a simple and elegant way. This instrument integrates in only one box: a high-resolution spectrometer, a laser source (785 nm) and a bipotentiostat/galvanostat, and it can be controlled by an excellent spectroelectrochemical software.



Although the SPELEC RAMAN will facilitate the Raman spectroelectrochemical measurements, the interpretation of data should be performed by you. In this Application Note, we describe the main vibrational frequencies for different functional groups and a probable intensity of the signal. It must be considered that these properties could vary significantly according to the structural atomic environment of the functional groups of the complete molecules or by strong interaction with surfaces as it happens with the SERS effect.

### Vibrational frequencies

Functional group	Region (cm <sup>-1</sup> )	Signal
Lattice vibrations	100 - 210	strong
Metal-O	150 - 450	strong
C-C aliphatic chain	250 - 400	strong
Se-Se	290 - 330	strong
S-S	430 - 550	strong
S <sub>2</sub> O <sub>3</sub> <sup>2-</sup>	430 - 470	strong
Si-O-Si	450 - 550	strong
C-I	480 - 660	strong
C-Br	500 - 700	strong
C-Cl	550 - 800	strong
C=S	580 - 680	strong
C-C aliphatic chain	600 - 1300	medium
C-S aliphatic	630 - 790	strong
C-F	720 - 800	strong
IO <sub>3</sub> <sup>-</sup>	740 - 760	very strong
BrO <sub>3</sub> <sup>-</sup>	780 - 805	strong
C-O-C	800 - 970	medium
O-O	845 - 900	strong
ClO <sub>4</sub> <sup>-</sup>	920 - 935	strong
ClO <sub>3</sub> <sup>-</sup>	930 - 940	strong
PO <sub>4</sub> <sup>3-</sup>	940 - 960	medium
SO <sub>4</sub> <sup>2-</sup>	965 - 1035	strong
SO <sub>3</sub> <sup>2-</sup>	970 - 990	strong
S <sub>2</sub> O <sub>3</sub> <sup>2-</sup>	985 - 1015	medium
C-C aromatic ring	990 - 1100	medium/strong
C-C aliphatic chain	1000 - 1250	strong
NO <sub>3</sub> <sup>-</sup>	1020 - 1070	strong
C=S	1020 - 1225	strong
HCO <sub>3</sub> <sup>-</sup>	1025 - 1045	strong
C-O-C asym.	1060 - 1150	weak
CO <sub>3</sub> <sup>2-</sup>	1075 - 1095	strong
C-S aromatic	1080 - 1100	strong

Functional group	Region (cm <sup>-1</sup> )	Signal
R-SO <sub>3</sub> H	1145 - 1240	weak
R-CO <sub>2</sub> <sup>-</sup>	1315 - 1435	medium
NO <sub>2</sub> <sup>-</sup>	1320 - 1330	strong
C-NO <sub>2</sub> asym.	1340 - 1380	strong
N=N aromatic	1365 - 1450	very strong
C-C aromatic ring	1370 - 1400	medium
CH <sub>2</sub> , CH <sub>3</sub> bending	1380 - 1470	medium
C-C aromatic ring	1450 - 1500	medium
C=C	1500 - 1900	strong
C-NO <sub>2</sub> asym.	1530 - 1590	medium
N=N aliphatic	1550 - 1580	medium
HN-C=O (amide)	1550 - 1700	strong
C-C aromatic ring	1580 - 1600	strong
R-CO-R (ketone)	1600 - 1710	medium
R-COOH (acid)	1610 - 1740	medium
C=N	1610 - 1680	strong
H <sub>2</sub> O bending	1640	weak
R-(CO)-H (aldehyde)	1710 - 1725	medium
R-(CO)O-R (ester)	1710 - 1745	medium
R-(CO)-O-(CO)-R	1740 - 1830	medium
R-N=C=S	2020 - 2100	medium
C≡C	2070 - 2250	strong
R-N≡C	2090 - 2170	medium
R-S-C≡N	2100 - 2170	medium
N <sub>3</sub> <sup>-</sup>	2110 - 2160	medium
R-N≡N	2200 - 2280	medium
C≡N	2200 - 2260	medium
R-N=C=O	2230 - 2270	weak
R-S-H	2530 - 2610	strong
OC-H (aldehyde)	2680 - 2740	weak
N-CH <sub>3</sub>	2750 - 2800	weak
CH <sub>2</sub>	2700 - 2800	strong

### References

Degen, I. A.; Newman, G. A. Spectrochim. Acta Part A Mol. Spectrosc. 1993, 49 (5-6), 859-887.

Lin-Vien, D.; Colthup, N. B.; Fateley, William G. Grasselli, J. G. The Handbook of Infrared and Raman Characteristic Frequencies of Organic Molecules; Academic Press, 1991.