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 21st 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 sp² and sp³ bonds, and, therefore, about their possible properties. In general, the G band of the Raman spectra (around 1580 cm⁻¹) could provide information on the fraction of sp² bonds and the D band (around 1300 cm⁻¹) could provide information on the fraction of sp³ bonds (and some disorder in the structure). In some cases, a G' band also appears around 2600 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 Spectroelecrochemistry, 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.

Results

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.
**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 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 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.

**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.

**Results**

![Graphs showing Raman shift vs. concentration for different analytes.](image-url)
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**

<table>
<thead>
<tr>
<th>Functional group</th>
<th>Region (cm⁻¹)</th>
<th>Signal</th>
</tr>
</thead>
<tbody>
<tr>
<td>Lattice vibrations</td>
<td>100 - 210</td>
<td>strong</td>
</tr>
<tr>
<td>Metal-O</td>
<td>150 - 450</td>
<td>strong</td>
</tr>
<tr>
<td>C-C aliphatic chain</td>
<td>250 - 400</td>
<td>strong</td>
</tr>
<tr>
<td>Se-Se</td>
<td>290 - 330</td>
<td>strong</td>
</tr>
<tr>
<td>S-S</td>
<td>430 - 550</td>
<td>strong</td>
</tr>
<tr>
<td>SiO₂⁺</td>
<td>430 - 470</td>
<td>strong</td>
</tr>
<tr>
<td>Si-O-Si</td>
<td>450 - 550</td>
<td>strong</td>
</tr>
<tr>
<td>C-I</td>
<td>480 - 660</td>
<td>strong</td>
</tr>
<tr>
<td>C-Br</td>
<td>500 - 700</td>
<td>strong</td>
</tr>
<tr>
<td>C-Cl</td>
<td>550 - 800</td>
<td>strong</td>
</tr>
<tr>
<td>C=S</td>
<td>580 - 860</td>
<td>strong</td>
</tr>
<tr>
<td>C-C aliphatic chain</td>
<td>600 - 1300</td>
<td>medium</td>
</tr>
<tr>
<td>C-S aliphatic</td>
<td>630 - 790</td>
<td>strong</td>
</tr>
<tr>
<td>C-F</td>
<td>720 - 800</td>
<td>strong</td>
</tr>
<tr>
<td>IO₃⁻</td>
<td>740 - 760</td>
<td>very strong</td>
</tr>
<tr>
<td>BrO₃⁻</td>
<td>780 - 805</td>
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</tr>
<tr>
<td>O-O</td>
<td>800 - 970</td>
<td>medium</td>
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<tr>
<td>Cl₂O₃</td>
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<tr>
<td>ClO₂⁺</td>
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<tr>
<td>Cl₂O₃</td>
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<tr>
<td>PO₂⁺</td>
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<tr>
<td>SO₃⁺</td>
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<td>SO₂⁻</td>
<td>970 - 990</td>
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<tr>
<td>C-C aromatic ring</td>
<td>990 - 1100</td>
<td>medium/strong</td>
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<td>C-C aliphatic chain</td>
<td>1000 - 1250</td>
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</tr>
<tr>
<td>NO₂</td>
<td>1020 - 1070</td>
<td>strong</td>
</tr>
<tr>
<td>S</td>
<td>1020 - 1225</td>
<td>strong</td>
</tr>
<tr>
<td>HCO₂⁻</td>
<td>1025 - 1045</td>
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</tr>
<tr>
<td>C-O-C asymmetric</td>
<td>1060 - 1150</td>
<td>weak</td>
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<tr>
<td>CO₂⁻</td>
<td>1075 - 1105</td>
<td>strong</td>
</tr>
<tr>
<td>C-S aromatic</td>
<td>1080 - 1100</td>
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<table>
<thead>
<tr>
<th>Functional group</th>
<th>Region (cm⁻¹)</th>
<th>Signal</th>
</tr>
</thead>
<tbody>
<tr>
<td>R-SO₂-H</td>
<td>1145 - 1240</td>
<td>weak</td>
</tr>
<tr>
<td>R-CO₂⁺</td>
<td>1315 - 1435</td>
<td>medium</td>
</tr>
<tr>
<td>NO₂⁻</td>
<td>1320 - 1330</td>
<td>strong</td>
</tr>
<tr>
<td>C-NO₂⁺ asymmetric</td>
<td>1340 - 1380</td>
<td>strong</td>
</tr>
<tr>
<td>N≡N aromatic</td>
<td>1365 - 1450</td>
<td>very strong</td>
</tr>
<tr>
<td>C-C aromatic ring</td>
<td>1370 - 1400</td>
<td>medium</td>
</tr>
<tr>
<td>CH₃ bending</td>
<td>1380 - 1470</td>
<td>medium</td>
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<tr>
<td>C-C aromatic ring</td>
<td>1400 - 1500</td>
<td>medium</td>
</tr>
<tr>
<td>C=O</td>
<td>1450 - 1500</td>
<td>medium</td>
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<tr>
<td>C-NO₂⁺ asymmetric</td>
<td>1530 - 1590</td>
<td>medium</td>
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<tr>
<td>N≡N aliphatic</td>
<td>1550 - 1580</td>
<td>medium</td>
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<tr>
<td>HN-C≡O (amide)</td>
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<tr>
<td>C-C aromatic ring</td>
<td>1580 - 1600</td>
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<tr>
<td>R-CO-R (ketone)</td>
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<tr>
<td>R-COOH (acid)</td>
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<tr>
<td>C=N</td>
<td>1610 - 1680</td>
<td>strong</td>
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<tr>
<td>H₂O bending</td>
<td>1620 - 1640</td>
<td>weak</td>
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<tr>
<td>R-(CO)₃-H (aldehyde)</td>
<td>1710 - 1729</td>
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<tr>
<td>R-(CO)₃O-R (ester)</td>
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<td>medium</td>
</tr>
<tr>
<td>R-(CO)₃O-(CO)₃R</td>
<td>1740 - 1830</td>
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<tr>
<td>R-N=C=S</td>
<td>2020 - 2100</td>
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<tr>
<td>CsC</td>
<td>2070 - 2250</td>
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<tr>
<td>R-N=CsN</td>
<td>2090 - 2170</td>
<td>medium</td>
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<tr>
<td>R-S=C₄N</td>
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</tr>
<tr>
<td>N₃</td>
<td>2110 - 2160</td>
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<tr>
<td>R-N=SiN</td>
<td>2200 - 2280</td>
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<tr>
<td>CsN</td>
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<tr>
<td>R-N=Si=O</td>
<td>2230 - 2270</td>
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<tr>
<td>R-S=H</td>
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<td>OC-H (aldehyde)</td>
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<tr>
<td>CH₄</td>
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</tbody>
</table>

**References**
