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Electrochemical Evaluation of Dopamine Detection on Pyrolysed Carbon and Gold Electrodes

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Introduction

Carbon electrodes have been widely used as electrode material in dopamine detection [1]. To obtain arrays of microelectrode structures, gold has been a preferable material due to easy lithographic fabrication techniques [2].

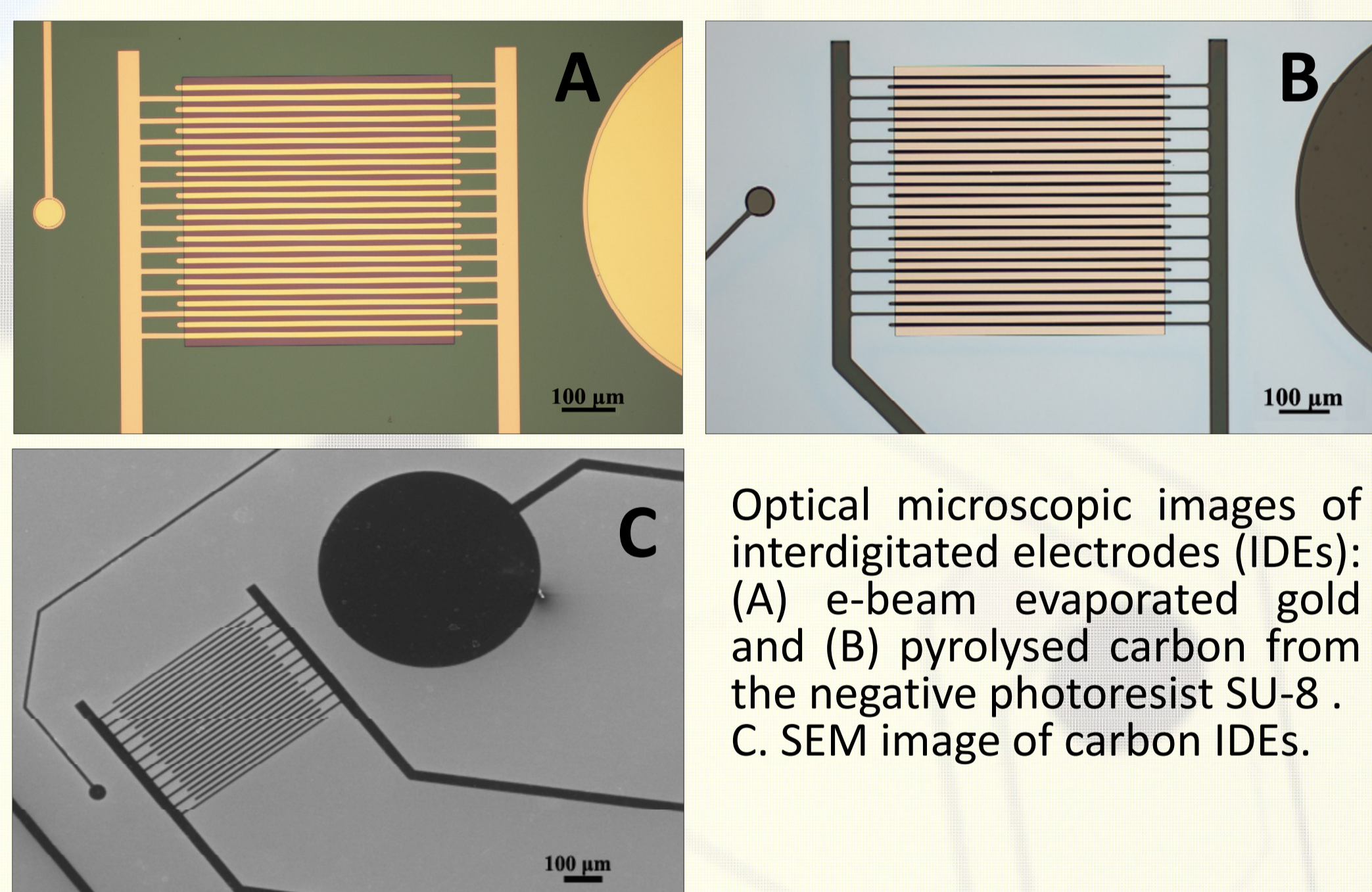
Gold electrodes need, however, a modification, e.g. thiol SAM [3], to eliminate the effect of fouling in longer measurements of dopamine.

Aim

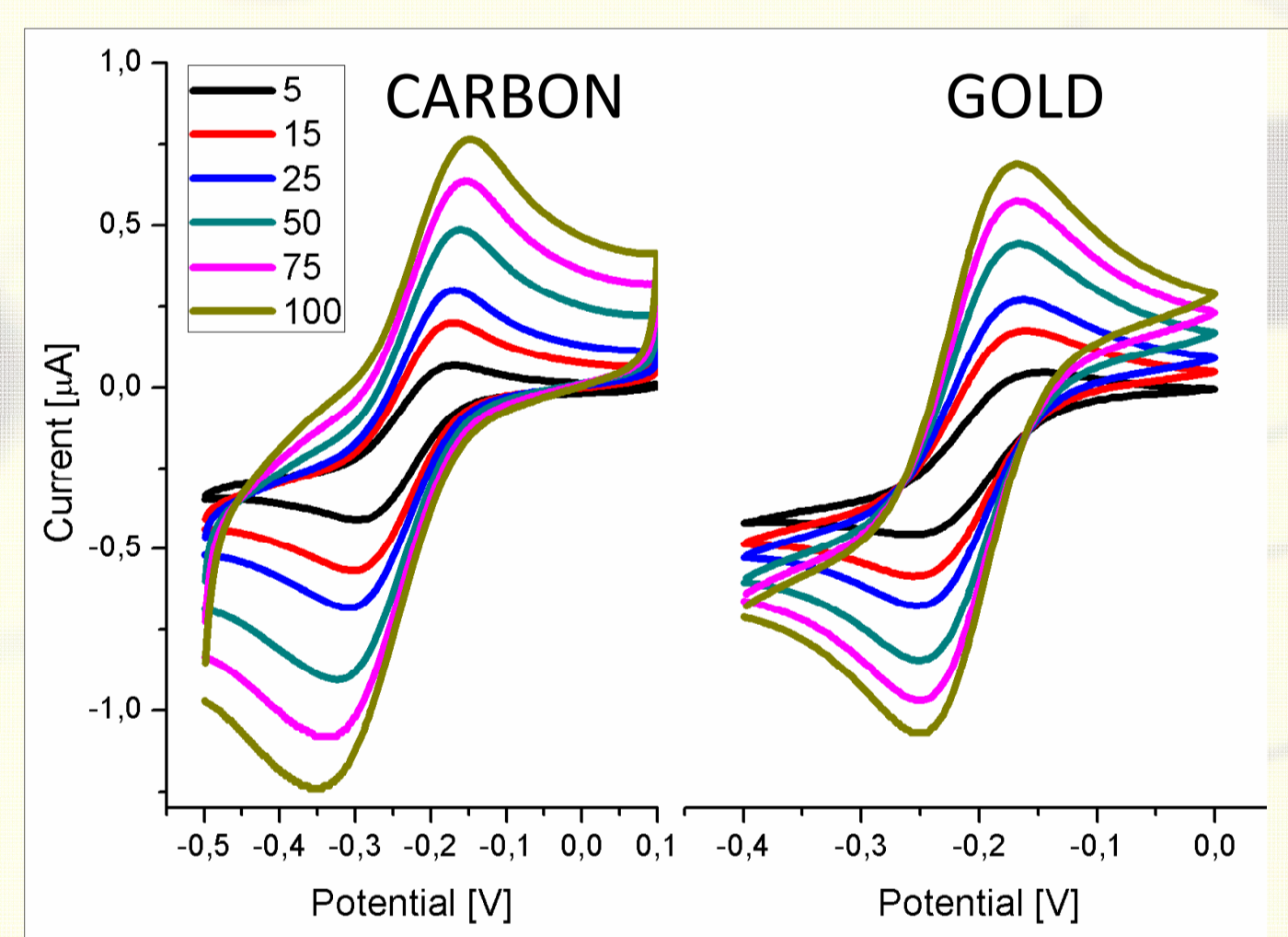
- We characterized the electrochemical behaviour of interdigitated electrodes (IDE) of pyrolysed carbon (SU-8 patterned structures) and gold
- We tested the materials based on the characteristics of dopamine detection.

Electrochemical Characterization

The electrochemical and materials properties of gold (fig. A) and pyrolysed carbon IDEs (fig. B and C) were characterized using cyclic voltammetry and electrochemical impedance spectroscopy (EIS).



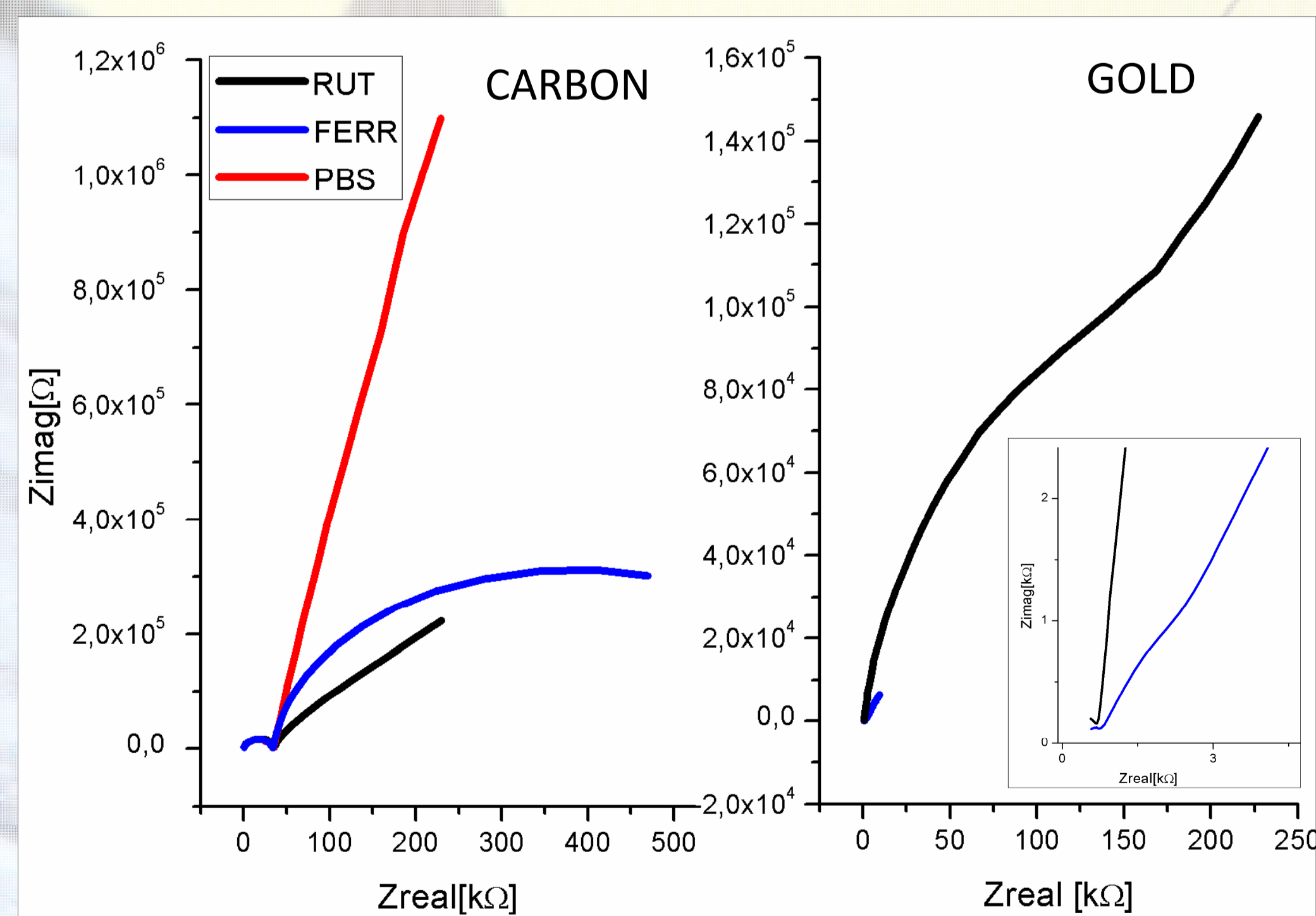
Optical microscopic images of interdigitated electrodes (IDEs): (A) e-beam evaporated gold and (B) pyrolysed carbon from the negative photoresist SU-8. C. SEM image of carbon IDEs.



Cyclic Voltammetry

Cyclic voltammograms at different scan rates of 1 mM ruthenium hexamine chloride (II/III) in PBS (pH 7) on IDE of pyrolysed carbon (left) and gold (potentials vs. Ag/AgCl reference electrode and sweep rate: 50 mV s⁻¹).

The CVs showed good behaviour for IDE of pyrolysed carbon ($\Delta E_p=150\text{mV}$) and gold ($\Delta E_p=90\text{mV}$). However, for the carbon IDE the thin and long leads of the electrode design caused increased resistance resulting in higher ΔE_p .



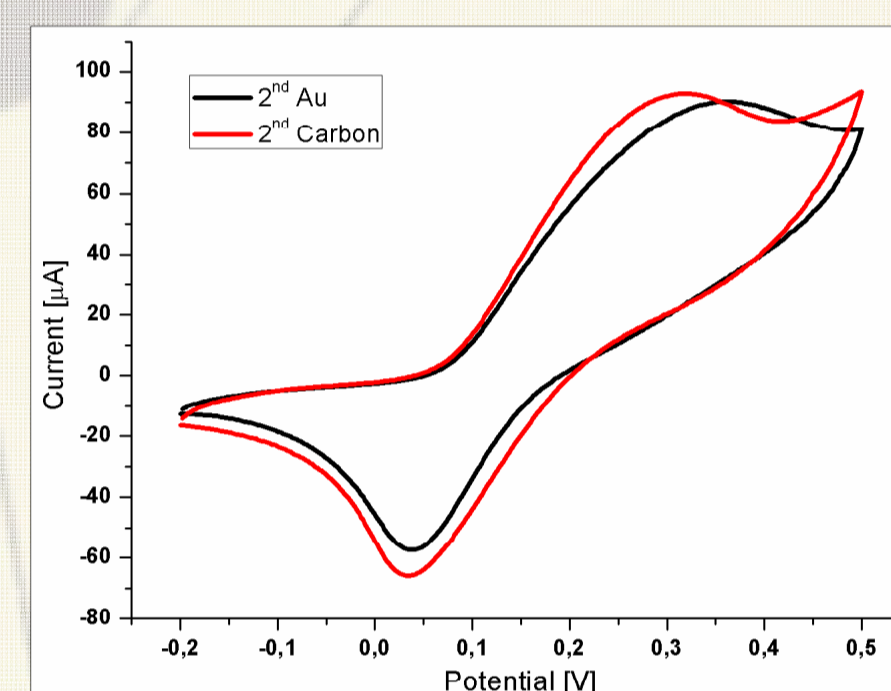
EIS

Nyquist plots for carbon and gold IDEs in 1mM ruthenium (II/III) hexaammine (RUT), 10mM potassium hexacyanoferrate (II/III) (FERR), PBS pH7. Inset: zoom-in of the impedance spectra for gold IDE.

Interestingly, the semi-circle in the impedance spectrograms seems to depend on the bulk property of pyrolysed carbon only, not on the solution composition, suggesting an intrinsic electroactive behaviour of the material.

Dopamine Detection

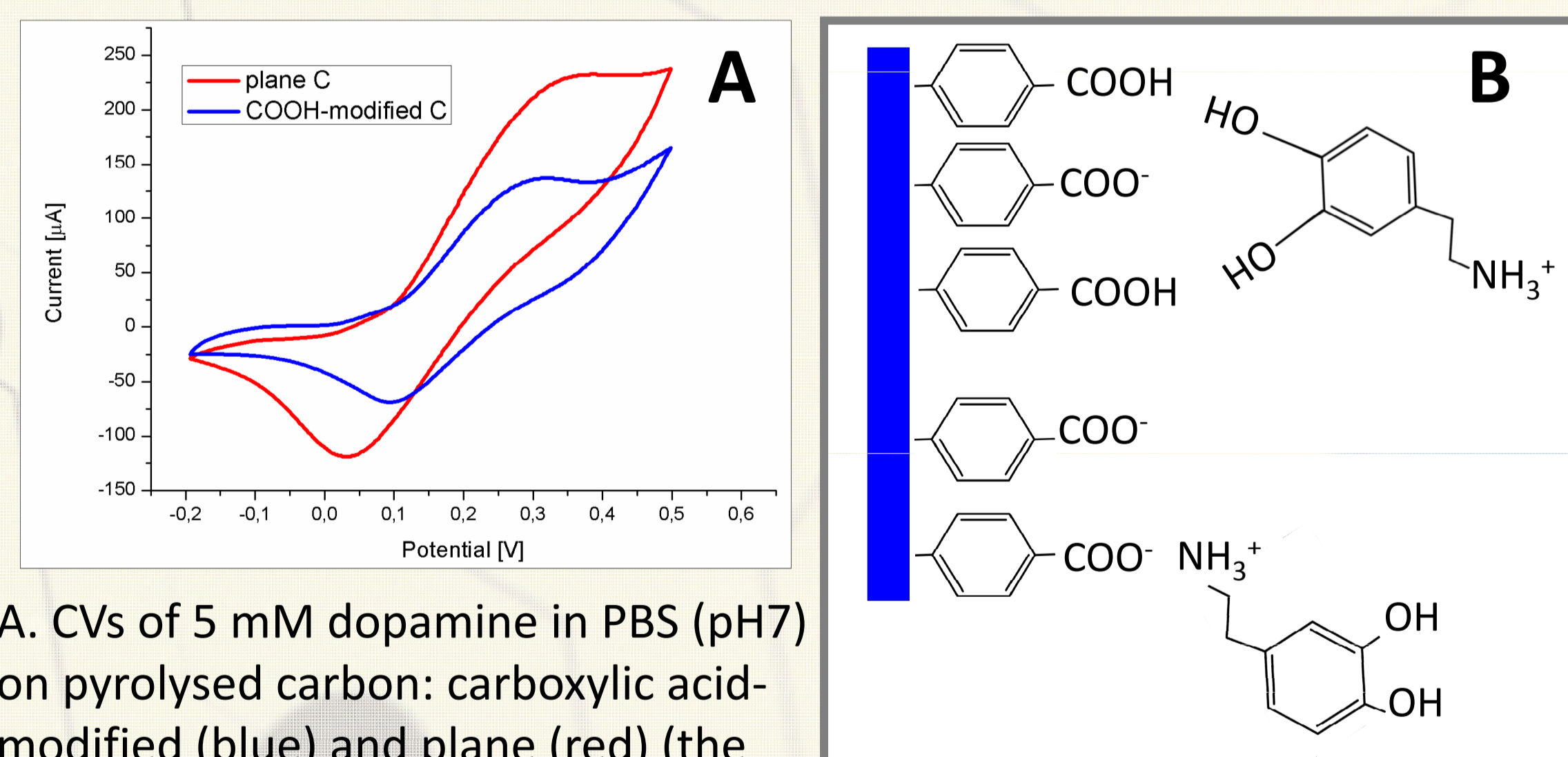
The CVs (2nd cycle) in the figure below show that for carbon the peaks are well-defined and the peak currents are slightly higher. Additionally, the characteristic electrode fouling caused by dopamine deposition during continued detection [3] is less pronounced on carbon.



Cyclic voltammograms of 5 mM dopamine in PBS (pH 7) on gold (black) and pyrolysed carbon (red) (the 2nd CV is shown for each material; potentials vs. Ag/AgCl RE and sweep rate: 50 mV/s).

Electrode conditioning: diazonium salt modification

The carbon electrode surface was electrochemically modified with carboxylic groups by diazonium salt chemistry. The modification resulted in lower response (fig. A), but interestingly the peak current ratio increased toward unity and facilitated the electrode stabilization after 5 cycles. This phenomenon can be due to the close vicinity of the electroactive group in dopamine (OH group) with the carboxylic acid, leading to faster kinetics of dopamine oxidation (lower ΔE_p) at the carboxylic acid-modified electrodes [4].



A. CVs of 5 mM dopamine in PBS (pH7) on pyrolysed carbon: carboxylic acid-modified (blue) and plane (red) (the 2nd CV is shown: potentials vs. Ag/AgCl RE and sweep rate: 50 mV/s).

B. The proposed orientation of dopamine at carboxylic modified carbon electrode.

Conclusions

- Carbon electrodes have better performance in dopamine detection compared to gold and since it is technologically possible to fabricate carbon microelectrode arrays, these are preferable for dopamine exocytosis detection.
- Carboxylic acid-modified carbon electrodes improve the dopamine orientation leading to stabilization of the electrode, which can be useful for long-term amperometric monitoring of dopamine release from differentiating neuronal stem cells.

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