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Two-Step Nanostructuring of Carbon Electrodes for Multiplexed Electrochemical Sensing Using Off-Axis MPECVD and Laser Micropatterning

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Summary:

Graded carbon nanomaterials were synthesized using off-axis microwave plasma-enhanced chemical vapor deposition and patterned via laser direct writing to easily create multiplexed electrochemical sensors. These electrodes exhibit high sensitivity and selectivity for multiple analytes due to the gradient in structural and electronic properties across the active surface. The approach provides a scalable platform for integrated sensing systems with minimal cross-talk and enhanced electrochemical performance.

Keywords: carbon nanomaterials, electrochemical sensing, plasma deposition, laser patterning, multiplexed sensors

Background, Motivation and Objective

Electrochemical sensing platforms are increasingly demanded for rapid, low-cost, and multiplexed chemical detection in environmental and biomedical applications. Traditional fabrication approaches often struggle to provide both high spatial resolution and material diversity across sensor arrays. Carbon nanomaterials (CNMs) offer tunable electronic and surface properties beneficial for sensing, but uniform films limit functional diversity [1]. This work introduces a new strategy for creating graded carbon nanomaterials (GCNs) using off-axis microwave plasma-enhanced chemical vapor deposition (MPECVD), enabling spatially varying properties on a single substrate. Laser direct writing defines electrode geometries, creating a versatile, miniaturized sensor platform.

Description of the New Method or System

We report the synthesis of GCNs with a controlled gradient in nanostructure and composition across the substrate, achieved via off-axis MPECVD (SEKI Technotron AX5400S, 2.45 GHz, 1300 W) by modulating plasma-substrate interaction. These films are patterned into independent microelectrodes using laser direct writing (5W JPT Air-Cooled UV-Laser), enabling a multiplexed sensor array. This integrated method provides a scalable route for engineering spatially resolved electrochemical functionalities on a single chip.

Results

Carbon nanostructures synthesised by off-axis MPECVD exhibit pronounced morphological gradients that intensify with increasing angular displacement from the plasma centre (Fig. 1). Morphological analysis via scanning electron microscopy (SEM) revealed a distinct variation in nanostructure across the substrate.

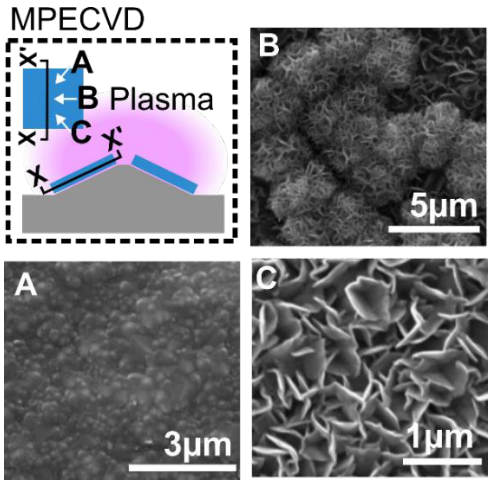

Fig. 1. Schematic representation of the off-axis synthesis process by MPECVD and corresponding SEM pictures of the different spots considered

The upper region (A) exhibited a uniform, flat, and regular surface morphology. In contrast, the middle region (B) displayed a heterogeneous distribution, characterized by both medium and small-sized overlapping nanowall-like structures. The lower region (C) consisted of homogenous nanowall-covered electrodes [2].

Electrochemical impedance spectroscopy (EIS) provided further insights into the structural diversity. While regions (A) and (C) showed spectra consistent with a single circuit element, the intermediate region (B) required a dual-element fit when using the ferri/ferrocyanide ($Fe(CN)_6^{3-/4-}$) redox couple, indicating structural and electrochemical heterogeneity (Fig. 2a).

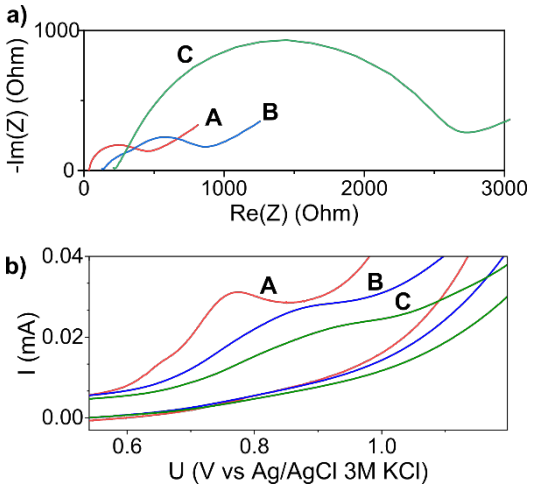

Fig. 2. (a) Nyquist plot of $Fe(CN)_6^{3-/4-}$ in 100mM PBS and (b) voltammograms of 100mg/l metoprolol in PBS for the three discretized single electrodes from the single synthesized off-axis sample

Interestingly, metoprolol detection by cyclic voltammetry (CV) shows that oxidation was most favorable on structure (A), as evidenced by a higher peak current and a lower oxidation potential (Fig. 2b). This trend was followed by structure (B), with structure (C) exhibiting the least favorable behavior despite its higher surface area. EIS measurements supported this observation, showing that structure (C), while presenting a dense structure of carbon nanowall, had a significantly higher charge transfer resistance (R_{ct}) compared to (A).

This spatial electrochemical fingerprinting technique enables high-throughput screening of nanocarbon libraries directly on-chip, facilitating the identification of the most electrochemically responsive nanostructures without requiring individual fabrication. The integration of SEM, EIS, and CV validates the graded nanocarbon platform as a versatile and efficient tool for the rapid evaluation of electrochemical materials, thereby accelerating the assessment of sensor batches.

References

List and number all bibliographical references at the end of the paper. When referenced within the text, enclose the citation number in square brackets, i.e. [1]

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