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In-situ raman analysis of carbon nanowalls during electrochqmical measurement

This study focuses on the synthesis of carbon nanowalls (CNWs) and nitrogen-doped CNWs using the RI-PECVD method and their investigation through in situ Raman spectroscopy during voltammetric cycling and potentiostatic charging under both reduction and oxidation potentials. CNWs were synthesized on Ti/ SiO₂/Si substrates. Electrochemical experiments were conducted in a three-electrode cell with CNWs as the working electrode, and analytes such as urea, citric acid, and hydrogen peroxide (H_2O_2) were used to study their effects during in situ Raman measurements. The Raman spectra of CNWs and N-doped CNWs were recorded in a voltage range of -1 V to 1 V (vs. Ag/AgCl), revealing no significant shifts in peak positions but showing an increase in the G to 2D peak ratio at higher voltages, indicating strong electron doping. The cyclic voltammetry results demonstrated that nitrogen doping enhances the reductive current of CNWs, with a clear reduction peak observed at -0.7 V across all analytes. The ID/IG peak ratio of N-doped CNWs increased upon analyte addition, suggesting the introduction of defects and restoration of sp2 domains. Furthermore, the position of the G and 2D peaks shifted significantly in response to different analytes. Sharper fluctuations were observed in N-doped CNWs. These results not only provide valuable insights into the electrochemical properties of CNWs but also highlight their potential for electrochemical sensing applications, offering a promising avenue for future research and development in this field.

Key words: carbon nanowalls, in situ raman, nitrogen doping, electrochemical reduction. **PACS number(s):** 61.46.–w.

1 Introduction

Raman spectroscopy, particularly in its in situ form, plays a crucial role in the study of electrochemical reactions. This technique, which is the preferred method for characterizing graphene and other carbon-based materials due to its non-destructive nature, provides real-time insights into several important areas, including interfacial phenomena, doping, interlayer coupling, structural defects, and chemical functionalization [1]. In-situ Raman spectroscopy is particularly valuable as it enables the real-time visualization and monitoring of electrochemical reactions [2–8]. The emergence of vibrational bands, which correspond to the presence of specific bonds or compounds, under applied potentials can reveal the reasons behind improved electrocatalytic performance [9]. Additionally, peak position shifts often indicate chemical composition changes resulting from chemical interactions, providing critical information about reaction mechanisms. This feature is fundamentally significant because certain chemical changes related to the reaction mechanism occur exclusively during the reaction itself and are reversed afterward. Changes detected through ex-situ techniques may not appear in in-situ characterization measurements and could, therefore, be entirely unrelated to the actual reaction [10]. Such spectroscopic data can be used

to gather diverse information about electrochemical reactions, including the structural transitions of electrocatalysts, interfacial species on surfaces, and localized species in the electrolyte within the electrical double layer (EDL) region [1]. During the electrochemical process, electrodes coated with active materials are exposed to harsh chemical and electrochemical conditions. Consequently, many materials are unable to preserve their structure under these operating conditions. Structural changes frequently take place either just before or at the early stages of electrocatalysis. Structural changes are commonly caused by redox reactions, where electrochemical reduction or oxidation leads to the transformation of electrocatalysts into species with varying oxidation states. Additionally, phase transitions occur when a chemically unstable phase converts to a stable one, and decomposition happens when electrochemically unstable materials with weak internal bonds break down [2, 11–13].

The integration of Raman spectroscopy with electrochemistry, known as Raman spectroelectrochemistry, has already demonstrated its effectiveness in investigating graphene, fullerenes, and carbon nanotubes [14]. In graphene's Raman spectra, the G and 2D modes, symmetry allowed features, are of particular interest [15, 16]. While these modes are also observed in Raman spectra of graphene-derived materials, their specific Raman shifts, line widths, and intensities are influenced by factors such as laser excitation energy, the number of graphene layers, doping levels, and strain [17, 18]. Additionally, the D peak may appear in the Raman spectra of certain graphene samples, indicating the presence of symmetry disrupting perturbations. Recent research has explored the spectroelectrochemical behavior of the D band, highlighting its tunability in response to applied potential, both reversibly and irreversibly [12, 19]. In recent years, the electrochemical properties of graphene-based nanomaterials have been studied in detail using in-situ Raman spectroscopy. For example, Milan Bouša et al. investigated graphene oxide and graphene nanoplatelets with in-situ spectroelectrochemistry during voltammetric cycling and potentiostatic charging at both reductive and mildly oxidative potentials [12]. Minkyung Choi et al. conducted in-situ Raman measurements of a graphene microbridge on SiO₂/Si substrates in air at a current density of up to $2.5\bar{8} \times 10^8 \text{ A/cm}^2$ [20]. Additionally, in a study by Binder et al., the authors induced hydrogen chemisorption on a bilayer graphene sample by intentionally applying a high gate voltage. The chemisorption process was investigated using in-situ Raman spectroscopy, observing the emergence of Si-H

and C-H modes and an increase in the intensity of the D-band. This process was partially reversible when negative gate voltages were applied. Thus, by varying the gate voltage, the authors achieved an electrical switch for hydrogen chemisorption on graphene [21]. However, despite these advancements, there is no information in the literature on the study of the electrochemical properties of CNWs using in-situ Raman spectroscopy. In addition, due to high specific area and peculiar morphology, CNWs are expected to react on external changes (electrolyte media and potential) noticeably strongly.

Carbon nanowalls (CNWs) are a form of carbon allotrope composed of three-dimensional networks of vertically aligned graphene sheets [22]. They are attracting increasing interest as a novel material for electrochemical sensing devices due to their high electrical and thermal conductivity, excellent electrocatalytic activity, large surface area, and high sensitivity to various analytes. The free bonds at the edges of the vertically aligned graphene sheets make CNWs a promising electrode material for electrochemical probing [23–29]. Despite their unique behavior as electrode materials, the mechanisms behind many of their specific properties are still not fully understood. The impact of different analytes such as urea, hydrogen peroxide (H_2O_2) , and citric acid on the electrochemical properties of CNWs can be thoroughly examined using in-situ Raman spectroscopy. Urea is a key biomarker in medical diagnostics, particularly for kidney function monitoring, while hydrogen peroxide is widely used as an indicator of oxidative stress and plays a critical role in biochemical and environmental processes. Citric acid, on the other hand, is an important organic acid involved in metabolic pathways and is commonly found in food and pharmaceutical industries.

Thus, the work focuses on the synthesis of CNWs and nitrogen-doped CNWs, which are synthesized using the RI-PECVD method. The CNWs were investigated using in situ Raman spectroscopy during voltammetric cycling, a process involving the measurement of Raman spectra of the CNWs at different electrochemical potentials, as well as potentiostatic charging at both reducing and oxidizing potentials. This investigation provides insights into the changes in the structure and properties of CNWs under different electrochemical conditions.

2 Materials and methods

2.1 Methods

The synthesis of CNWs films is carried out using the RI-PECVD method. The experimental setup, synthesis processes are described in detail in previous work [26, 30]. CNWs were synthesized on Ti SiO₂\Si substrates (4×4 cm² in size), with both Ti and SiO₂ layers having a thickness of 200 nm. A gas mixture of CH_4 (100 sccm) and H_2 (50 sccm) was introduced into the chamber for growth without nitrogen addition, while for nitrogen-assisted growth, 20 sccm of N₂ was also introduced. The total gas pressure was maintained at 3 Pa. Both the surface-wave plasma (SWP) microwave source and the capacitively coupled plasma (CCP) very high frequency (VHF) source operated at 400 W. During the CNW growth, the substrate heater temperature was consistently maintained at 800 °C. All in-situ electrochemical experiments were conducted using a three-electrode electrochemical cell with a 30 mL volume (Dek Research) [31–33], where the CNWs film served as the working electrode, as illustrated in Figure 1. A Pt wire was used as counter electrode, while a Ag/AgCl (3 M KCl, $E^\circ = 0.197$ V) electrode was used as reference electrode. The 0.1 M phosphate buffer solution (PBS (pH 7.2, Sigma Aldrich)) was used as supporting electrolyte. The Metrohm potentiostat (µStat-i 400) was used to perform the electrochemical measurements. Urea (98%), citric acid (99%) and hydrogen peroxide (30%), purchased from Sigma-Aldrich, were used as analytes to investigate the electrochemical reaction during in-situ Raman measurements.

The Raman spectra were recorded by Raman spectrometer (NT-MDT Solver Spectrum). A 473 nm diode laser was focused on the surface of the CNWs films utilizing a $50 \times$ long working distance microscope objective. The laser power was maintained at 0.7 mW and exposure time was set to 60 seconds.



Figure 1 – Schematic illustration of in-situ Raman spectroscopy system.

3 Results and discussion

Figure 2 shows the Raman spectra of CNWs films synthesized at 0 and 20 sccm nitrogen flow rates. Typical D, G, D', G' (2D), and G + D peaks are observed in the CNWs Raman spectra [34]. The D peak is characteristic of samples with defects in sp²-structures. The presence of the G peak indicates the synthesis of graphitized carbon. The D' shoulder peak arises from edges as well as lattice defects in the graphene structure and indicates disorder in the final dimensions of the sp² crystal. The appearance of the

G' peak indicates long-range order in the structure [35, 36].

Figure 3 presents the Raman spectra for (a) CNWs and (b) N-doped CNWs, recorded over a potential range of -1 V to 1 V (vs. Ag/AgCl) in 0.2 V increments during electrochemical measurements in PBS. The voltage range of -1 to 1 V was selected, as further increases in both negative and positive voltages result in material degradation and detachment from the substrate. Analysis indicates no significant effect on the peak positions with increased voltage. Moreover, the analysis of the D to G peak intensity ratio demonstrated minimal variation, whereas the G to 2D peak ratio exhibited an increase at higher voltages of +1 V (see Figure S1). This behaviour is indicative of strong electron doping [37–39]. Doping

will increase the number of charge carriers, thereby increasing the probability of a scattering event. Consequently, the 2D peak intensity should decrease [2, 3, 40].



Figure 2 – Raman spectroscopy analysis of the CNWs films synthesized at 0 and 20sccm nitrogen flow rate.



Figure 3 – Raman spectra of (a) CNWs and (b) N-doped CNWs, recorded in the potential range from -1 V to 1 V (vs. Ag/AgCl) with a step of 0.2 V in the PBS electrolyte.

The electrochemical characteristics of CNW films were assessed using a three-electrode setup with 0.1 M PBS solution serving as the electrolyte. Figure 4 shows the cyclic voltammetry (CV) of CNWs, and N-doped CNWs between -1 V and 1 V (vs. Ag/AgCl) at a scan rate of 20 mV/s in the (a) bare PBS solution, and in the presence of 5 mM (b) urea, (c) H_2O_2 , (d) citric acid. As the potential is swept in a cyclic voltammogram,

a peak current is produced within a certain potential range where the working electrode interacts with the substance, indicating the occurrence of the reaction. It is notable from Figure 4 that reductive current significantly increases in the case of N-doped CNWs (after nitrogen doping of CNWs). A clear reduction peak can be observed for CNWs and N-doped CNWs in all studied analytes at -0.7 V versus Ag/AgCl.



Figure 4 – Cyclic voltammograms obtained using undoped CNWs (a), and N-doped CNWs (b) in the PBS solution, and in the presence of 5 mM urea, H₂O₂, citric acid.

Figure 5a shows the ratio of ID/IG peak when 5mM of different analytes were added to the surface of the CNWs and N-doped CNWs films. The ID/IG peak ratio of the CNWs remains unchanged upon the addition of analytes. In contrast, for N-doped CNWs, the initial ID/IG ratio is 1.4 and increases to 1.6 upon the addition of analytes such as H_2O_2 , citric acid, and urea. An increase in the ID/IG ratio suggests the restoration of sp² domains caused by the introduction of defects of various types (e.g., vacancies, functionalization) [41– 43]. The observed changes might be attributed to the intercalation of H+ ions from acidic electrolytes or the incorporation of water molecules into the CNWs film. These processes can cause distortions in the periodic lattice structure of CNWs [41].

Figure 5b shows the ratio of the ID/IG peaks of CNWs in PBS solution and in different analytes at applied -0.7 V negative potential to the CNWs film. The analysis indicates that applying a negative potential has

no significant effect on the ID/IG peak ratio, demonstrating the structural stability of the CNWs. The specifics of the Raman spectra analysis of the CNWs films can be found in the Supporting Information (see Figure S2).

Summarizing, the addition of analytes such as urea, H_2O_2 , and citric acid to the surface of CNWs results in the formation of a defective material (without applying an external potential). To gain deeper insights into the mechanism of electrochemical reduction of CNWs, a constant potential of -0.7 V was applied to the electrodes in a PBS solution with the addition of various analytes, and the resulting electrodes were characterized using Raman spectroscopy (Fig. 5). As shown, regardless of the type of analyte, the electrochemically reduced CNWs exhibited minimal modification of structural parameters (with the ID/IG ratio remaining nearly unchanged). This may be attributed to the lower efficiency of O-group removal, leading to a reduced number of defects [44, 45].



Figure 5 – (a) Ratio of the ID/IG peaks of CNWs when 0.5 mM of different analytes were added to the surface of the CNWs film. (b) Ratio of the ID/IG peaks of CNWs in PBS solution and in different analytes at applied -0.7 V negative potential to the CNWs film.

Figure 6(a) and (b) clearly demonstrates the effect of different analytes on the position of the G and 2D peaks, respectively. The positions of the G and 2D peaks are changed by +2 and +3 cm⁻¹, respectively, upon addition of analytes. The fluctuations in the Raman spectra of N-doped CNWs are much sharper, with the position of the G and 2D peaks changing by +4 and +9 cm⁻¹, respectively, upon addition of analytes. The G and 2D band shifts are governed by mild oxidation/reduction and/or

by charging-induced lattice expansion and lattice contraction upon addition of different analytes. The blue shift observed in the Raman bands, moving to higher wavenumbers, is attributed to the growing structural disorder resulting from the presence of oxygen-containing functional groups attached to the graphene sheets. These imperfections stem from intrinsic defects introduced by the attachment of oxygen functional groups to the plane and edges of graphene sheets [46–49].



Figure 6 – The G-peak (a), and 2D-peak (b) position extracted from the in-situ Raman spectrum vs different analytes.

4 Conclusions

In conclusion, this study comprehensively investigated the structural and electrochemical properties of CNWs and N-doped CNWs through Raman spectroscopy and cyclic voltammetry under varying conditions. The introduction of analytes such as urea, H_2O_2 , and citric acid led to noticeable changes in the structural parameters of the CNWs, with the ID/IG ratio increasing in N-doped CNWs, indicating defect formation and restoration of sp² domains. Electrochemical measurements demonstrated that applying a constant potential of -0.7 V in the presence of analytes minimally affected the structural integrity of the CNWs, as evidenced by the stable ID/IG ratio. However, N-doped CNWs exhibited sharper fluctuations in the positions of the G and 2D peaks, reflecting their enhanced sensitivity to analytes and structural

changes due to oxidation/reduction processes. The observed blue shifts in Raman bands were attributed to structural disorder induced by oxygen functional groups.

Overall, the results highlight the structural stability and tunable properties of CNWs and N-doped CNWs, making them promising materials for applications requiring robust electrochemical performance and analyte sensitivity. Further studies focusing on the mechanisms of defect formation and reduction processes could provide deeper insights into optimizing their functionality for specific applications.

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Figure S1 – (a) Dependences of the intensity ratio of the D and G peaks, and (b) dependence of the intensity ratio of the G and 2D peaks on the applied potential vs. Ag/AgCl.



Figure S2 – (a) Dependences of the intensity ratio of the G and 2D peaks, (b) dependence of the intensity ratio of the G and D' peaks, and (c) dependence of the intensity ratio of the G and 2D peaks at -0.7V on the different analytes.