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Impact of plasma-induced surface chemistry on electrochemical properties of microfabricated pyrolytic carbon electrodes

Galina Pankratova*, Jesper Yue Pan, Stephan Sylvest Keller

National Centre for Nano Fabrication and Characterization, DTU Nanolab, Technical University of Denmark, 2800 Kongens Lyngby, Denmark

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ABSTRACT

Plasma technology is a widely used approach for carbon activation and enhancing the surface energy by generating various functional groups. Gas selection is an important factor determining the type of functional groups to be formed on carbon surfaces. In this study, we investigate the impact of plasma-induced chemical surface alterations on performance of pyrolytic carbon as electrode material. Pyrolytic carbon electrodes were microfabricated by pyrolysis of SU-8 structures defined using UV lithography and treated using Ar, O₂, N₂ and air plasma gases. The resulting surface chemistry and geometry were characterized by X-ray photoelectron spectroscopy and atomic force microscopy. Close inspection of electrochemical properties was done by using both outer (Ru(NH₃)₆³⁺/²⁻) and inner (Fe(CN)₆³⁻/⁴⁻ and dopamine) redox systems. The electrochemical performances of the carbon electrodes treated with various plasma gases were compared based on information on heterogeneous electron transfer rates determined by cyclic voltammetry and electrochemical impedance spectroscopy. This work provides a fundamental insight into electrochemistry of plasma-modified pyrolytic carbon surfaces and strategies on how to enhance surface properties overcoming possible electron transfer limitations for future enhancement in carbon-based electrochemical applications.

1. Introduction

During the past decades, carbon has become one of the most commonly used electrode materials in fundamental and industrial electrochemistry. Due to its chemical stability and inertness, reasonable electrical conductivity and low cost together with diversity in chemical and physical properties, this material finds a wide range of practical applications from energy conversion and storage to electroanalysis [1]. Among other advanced carbonaceous materials, pyrolytic carbon obtained through pyrolysis of thermosetting resins is a relatively new [2] and attractive substrate possessing a variety of advantages, such as a good biocompatibility, relatively inert electrochemistry and a wide potential window. It has proven an important role in applications such as chemical sensing [3,4], biosensing [5,6], cell monitoring [7], cell growth and differentiation [8–10] and microbatteries [11,12]. Structurally and electrochemically this type of pyrolytic carbon is similar to glassy carbon [13,14] and can amongst others be obtained by pyrolysis of nano- and micropatterned templates of a photoresist-based precursor under inert atmosphere. This simple and highly reproducible process allows fabrication of both two and three-dimensional structures with well-defined architecture at nano- and microscales. Furthermore, the chemical and electrochemical characteristics, e.g., conductivity and surface properties, of the final pyrolysed product can be widely varied by changing polymeric precursor, fabrication parameters and process conditions [15,16]. Such an approach enables a flexible and cost-effective production of conductive carbon structures with customized designs and tailored properties for particular applications.

Generally, all carbon materials possess a complex surface chemistry because of diversity in underlying microstructure, but also due to the presence of numerous surface bonds, which result in formation of various functional groups. This opens up for a wide range of possibilities for surface functionalization and specific chemical modification. From a technological point of view, surface modification is of great importance and one of the main advantages of using carbon in applications, where surface-specific interactions or reactions determine the overall performance. Various methods such as electrochemical covalent modification [17–19], polymer coatings [20,21], UV treatment [22,23] or oxidation using strong acids [24] can be applied to tailor the surface chemistry of carbon. Plasma processing is a fast and highly efficient way for surface modification of carbon-based materials [9,25,26]. In this technique,
discharge of exited species primarily breaks bonds between sp² hybridized carbon atoms on the surface. The resulting unsaturated bonds react with the free radicals generated by the plasma, which results in the formation of various polar functional surface groups [27,28]. In such a way, gas plasma treatment leads to modification of the top nanometre layer providing significant surface activation, increase of the overall surface energy, hydrophilicity, chemical diversity and in some cases roughness [29–33].

A number of gases, such as O₂, N₂, Ar, air, H₂, CO₂ or water vapors, have been reported suitable for plasma activation on different carbon-based materials and the resulting surface chemical composition varied from gas to gas [31–36]. However, this phenomena has been considered mainly in terms of stability of surface functional groups introduced by plasma [32,34] or as a function of plasma treatment duration [30,33,34] and much less from an electrochemical performance point of view [37,38]. The character and impact of the introduced functional groups on the fundamental electrochemical properties of the plasma-treated carbon material has not yet been investigated systematically. This despite the fact that surface chemistry is an essential aspect when it comes to electrochemical applications [39–42], since electrochemical processes are of interfacial nature.

Here, we explore the influence of the surface chemistry induced by plasma processes on the electrochemical properties of pyrolytic carbon obtained from thermosetting polymeric precursors. More specifically, we direct our focus on carbon electrodes prepared by microfabrication methods highly relevant for applications facilitated by an electrode chip format. We report effects of surface functionalization using a number of plasma gases, such as Ar, N₂, O₂ and air, on the resulting surface chemistry and the electrochemical performance of the carbon electrodes. The fundamental understanding of the correlation between plasma-induced surface chemical alterations and electrochemical properties of pyrolytic carbon materials may allow progress for fast electrode preparation and modification and future enhancement of the performance of carbon-based electrodes for specific applications.

2. Materials and methods

2.1. Chemicals and materials

Pyrolytic carbon electrodes were fabricated on 4-inch N-type single side polished silicon wafers (Siegert Wafer) using SU-8 2000 series resist (Kayaku Advanced Materials), Propylene Glycol Methyl Ether Acetate (PGMEA) (mr-Dev 600, micro resist technology GmbH), Au (99.99%, Kurt J. Lesker) and Ti (99.995%, Kurt J. Lesker). The reagents, hexaammineruthenium (III) chloride Ru(NH₃)₆Cl₃, potassium hexacyanoferrate (III) K₃Fe(CN)₆, dopamine (3,4-dihydroxyphenethylamine, DA) hydrochloride, potassium chloride KCl, potassium dihydrogen phosphate KH₂PO₄, dipotassium hydrogen phosphate K₂HPO₄, were purchased from MERCK. The chemicals were at least of analytical grade and used as received. All solutions were prepared using Milli-Q grade water from a water purification system (Millipore, resistivity no less than 18.2 MΩ cm).

2.2. Fabrication of pyrolytic carbon electrodes

Electrode chips with a circular pyrolytic carbon working area of 4 mm diameter were fabricated with a process similar to the one optimized by Hassan et al. [43]. The electrode chip design and fabrication process are illustrated in Fig. 1. Briefly, a 600 nm thick insulating layer SiO₂ was thermally grown on the silicon wafers. A film of SU-8 2035 photosensitive with a thickness of 15 µm was spin coated on the substrate and patterned by UV photolithography (Fig. 1A-C). After development, the SU-8 structures were pyrolyzed at 1100 °C (PEO-604 Multipurpose Furnace, ATV Technologie, Germany) for 5 h with temperature ramping rates of 10 °C min⁻¹ to 1100 °C while purging with 20 slm of dry purified N₂ in order to maintain an inert atmosphere (Fig. 1D). The resulting pyrolytic carbon had a thickness of approximately 2 µm. The samples were cleaned in O₂ plasma (300 Plasma Processor, TePla) using 500 W for 2 min and 120 sccm O₂ flow. 10 nm Ti and 100 nm Au were deposited via e-beam deposition (FC-2000, Temescal) through a steel shadow mask to define the metal contacts (Fig. 1E). After a second plasma treatment, a 5 µm thick layer of SU-8 2005 was deposited and patterned by UV photolithography (Fig. 1F). This passivation layer left only the circular working electrode and the metal contact exposed. Finally, the wafers were diced in 10 × 16 mm chips using a diamond saw (DAD 321, DISCO), each 4-inch wafer containing 32 pyrolytic carbon electrode chips.

2.3. Plasma treatment of carbon

The microfabricated carbon electrodes were treated in low-pressure plasma system (Dienetic electronic, Zepto) under Ar, O₂, N₂ or clean dry air atmosphere. The chamber was pumped down to 0.20 mbar before opening the gas supply. When the chamber was stabilized at 0.60 mbar upon introduction of the processing gas, a discharge plasma with a radiation frequency of 80 kHz and a power of 120 W was initiated. The plasma process was carried out for 75 s at 0.60 mbar. The carbon chips were used in the follow-up measurements immediately after the plasma treatment.

Note, that plasma untreated or pristine carbon chips represent the electrode which were not exposed to the currently described low-pressure plasma treatment.

2.4. X-ray photoelectron spectroscopic (XPS) analysis

Surface chemical analysis was done on pristine and plasma activated carbon chips using a K-Alpha spectrometer (Thermo Fisher Scientific, UK) supported by Avantage software (version 5.943). The

![Fig. 1. Schematic illustration of the design and fabrication of the pyrolytic carbon electrodes in cross-sectional and top views: (A) spin-coating of SU-8 photosensitive on Si wafer with SiO₂ layer, (B) definition of electrode pattern by UV exposure, (C) development of uncrosslinked photosensitive, (D) pyrolysis process to obtain the carbon electrode, (E) deposition of metal contacts, (F) patterning of passivation layer by SU-8 UV photolithography.](image-url)
measurements were done using a monochromatic 400 μm AlKα X-ray spot. A pass energy of 200 eV was used for survey spectra and 50 eV for high-resolution spectra. The quantification and peak fitting was performed using OriginPro software. The background correction was subtracted using a Shirley function. The convolution was carried out by using Chi-square fitting of all analysed patterns at the same time.

2.5. Atomic force microscopy (AFM) characterization

AFM analysis was performed using a Dimension Icon AFM system from Bruker AXS GmbH (Karlsruhe, Germany) on untreated and plasma-treated carbon chips. The height images were captured in tapping mode with a silicon tip by scanning 1 μm × 1 μm areas with 512 scan lines per image. The surface topography images were analysed using NanoScope Analysis 1.7 software. The surface roughness was quantitatively evaluated by estimation of the arithmetic average of surface heights, Rₐ, measured across a 1 × 1 μm² surface area.

2.6. Electrochemical characterization of pyrolytic carbon

All electrochemical measurements were performed in 50 mM phosphate buffer (K₂HPO₄/K₃HPO₄) containing 100 mM KCl as a supporting electrolyte, pH 7.40 using an AUTOLAB potentiostat (AUTOLAB PGSTAT128N, Eco Chemie, Utrecht, The Netherlands) equipped with Nova 2.1 software. A three-electrode electrochemical set-up was used with Ag/AgCl|3M KCl as reference electrode, a platinum wire as a counter electrode and pyrolytic carbon as working electrode. Note that all potentials in this work are reported versus standard hydrogen electrode (SHE).

In this study, planar electrodes were used in order to minimize non-Faradaic effects and ensure a simplified regime of linear diffusion of electroactive species to the electrode surface. The electrodes were characterized by cyclic voltammetry and electrochemical impedence spectroscopy (EIS) using 0.5 mM K₃[Fe(CN)₆]₃, [Ru(NH₃)₆]Cl₃ or DA as a redox probe.

Cyclic voltammograms (CVs) were obtained over a wide range of scan rates (three orders of magnitude: 0.005, 0.01, 0.02, 0.05, 0.07, 0.1, 0.15, 0.2, 0.25, 0.3, 0.35, 0.4, 0.45 and 0.5 V s⁻¹) within different potential windows depending on the electroactive species tested: −0.3 to 0.35 V for Ru(NH₃)₆³⁺/²⁻, −0.1 to 0.9 V for Fe(CN)₆⁴⁻/³⁻, 0.05 to 0.7 V for dopamine/dopaminequinone (DA/DAQ). Uncompensated resistance was corrected using the IR drop compensation circuit in the Nova 2.1 control interface.

EIS was recorded in the frequency range 20,000 – 0.01 Hz for Ru(NH₃)₆³⁺/²⁻ and Fe(CN)₆⁴⁻/³⁻ or 20,000 – 0.2 Hz for DA/DAQ at 5 mV of AC amplitude, 10 frequencies per decade and a DC potential corresponding to the half wave potential of redox reaction for each electroactive species estimated from corresponding CVs at 0.1 V s⁻¹ to ensure equimolar concentrations of the oxidized and reduced forms. The EIS spectra were modelled using ZSimWin 3.60 (Princeton Applied Research, USA).

To estimate diffusion coefficients of Ru(NH₃)₆³⁺, Fe(CN)₆³⁻ and DA in the stated electrolyte solution, step potential chronoamperometry was applied by stepping potential from a value (0.20, 0.40 and 0.15 V), at which there is no redox process, to one, which drives an electrochemical reaction (−0.20, 0.0 and 0.51 V for Ru(NH₃)₆³⁻, Fe(CN)₆³⁻ and DA, respectively) and measuring the resulting current at a time interval of 5 msec. Diffusion coefficients of the electroactive species were calculated from I vs. t⁻¹/² plots (Fig. S1 in Supporting Information (SI)) applying the Cottrell equation (for complete details, see SI).

All solutions were degassed by purging N₂ for at least 15 min prior to any measurements. All reported data were obtained at room temperature (23 ± 1 °C) and with at least three independent measurements.

3. Results and discussion

3.1. XPS analysis of surface elemental composition

In order to evaluate the impact of the selected plasma gases on the elemental surface composition of pyrolytic carbon electrodes, the samples were analysed by XPS before and after plasma activation using Ar, O₂, N₂ or compressed air. The analysis revealed the distinctive availability of C and O on all samples (Fig. 2A-E). As expected, the highest C content of 79.5 ± 1.0% was observed for the untreated carbon electrodes which was consistently reduced after plasma processing and reached a minimum of 66.6 ± 0.7% in case of Ar plasma (Fig. 2F). Furthermore, plasma treatment resulted in a dramatic increase of the O content regardless the gas selection. The highest O concentration of 31.5 ± 0.5% was observed for the samples treated with Ar and the lowest of 22.6 ± 0.7% and 21.2 ± 0.6% with N₂ and air plasmas, respectively. These detected shifts in atomic percentage of C and O lead to an increased O/C content ratio compared to the untreated carbon (Table S1). Pristine carbon samples had the lowest O content of 20.4 ± 0.4% (Fig. 2F), which is quite high in comparison with similar pyrolytic carbon materials reported earlier [4,9,3,44]. It should be noted that the tested samples are not simply pyrolytic carbon as a bulk material, but electrode chips with metal contacts and a passivation layer (Fig. 1). Fabrication of such electrodes requires several additional processing steps after pyrolysis. These processes might facilitate the formation of oxygen-containing species on the pyrolytic carbon surface. Furthermore, the fabricated electrodes were exposed to ambient atmosphere conditions in the laboratory while stored for several months, which normally allows for air-induced oxidation of the surface [36,45]. XPS analysis on the electrode chips confirmed an O content as high as 16.7 ± 0.3% already immediately after fabrication (Fig. S2) indicating that oxidation during storage is negligible compared to initial process-induced oxidation. A large amount of these induced surface oxygen-containing functional groups remains accessible on the carbon surface for several weeks [32,34]. The amount of O detected on untreated carbon was relatively high in comparison with 1.5 to 6% of O content reported for similar pyrolytic carbon [4,9,32,44]. However, the level of O after O₂ plasma treatment on these pyrolytic carbon electrodes as reported by E. Peitola et al. [4] and J. I. Mendez-Linan et al. [32] was 27%. This is consistent with O content of 25.3 ± 1.1% measured on O₂ plasma-treated carbon in the current work. The fact that the O amount induced by O₂ plasma on pyrolytic carbon samples fabricated in different groups is similar, could probably be attributed to a certain level of “saturation” of the carbon surface with oxygen-containing functionalities.

Additionally on all plasma-treated patterns, Si2p (103 eV) peaks were identified. The content of Si is relatively low, not exceeding 1.9% and could be attributed to contamination from the underlying substrate.

3.2. XPS analysis of functional surface groups

3.2.1. C1s spectra

In order to further investigate the surface chemistry and the character of functional groups generated due to the plasma process on carbon, high resolution peaks were deconvoluted. In general, the identification of C bonding states in C1s spectra can be very complicated due to the complex composition and possible chemical shifts in binding energy caused by a number of potential structural defects [36,47]. The high-resolution spectra corresponding to the C1s regions were fitted as suggested by Gallo [48] and Vautard [49]. The deconvolution of the C1s spectra revealed a complex surface chemistry and identified the following individual components at specific binding energies: C = C and C–C (284.24 and 284.92 eV, respectively), C–N (285.43 eV), C = N / C–O (285.95 eV), C = O (287.19 eV), O=C–O (288.54 eV) and π* transition (292.92 eV) (Fig. S3).

The relative distribution of the listed components is summarized in Table 1. For untreated carbon chips, the main peaks are attributed to sp²
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(C = C) and sp\(^3\)-hybridized (C–C) C atoms. The area of these peaks was about 77% of the total peak area. The remaining fraction is mostly accounted for various oxygen-containing groups.

The quantitative analysis determined that all plasma processes lead to a significant decrease of the graphitic fraction correlated with C = C bonds (Table 1). The largest decrease of about 21% was observed for Ar plasma, an intermediary of about 17% for O\(_2\), and the lowest of around 12 and 14% for N\(_2\) and air plasma modifications, respectively. The fraction of sp\(^3\)-hybridized C–C bonds decreased for almost 4% in case of exposure to Ar and was not affected in case of the other gases used. Due to the unsaturated nature, sp\(^2\)-hybridized atoms are less chemically stable, and thus more accessible for plasma radicals. As a result, the double bonds were opened and reacted with active O or/and N atoms in the plasma atmosphere giving rise to various oxygen and nitrogen-

Table 1

| Plasma gas | C = C (%) | C-C (%) | C–N (%) | COH/C – N (%) | C = O (%) | O=C – O (%) | π-π* (%) |
|------------|-----------|---------|---------|---------------|-----------|-------------|----------|
| Ar         | 31.54±2.43| 21.79±1.39| N/A     | 9.53±0.57     | 22.64±1.36| 12.99±1.15  | 1.50±0.23 |
| O\(_2\)    | 35.53±2.67| 26.08±2.16| 6.01±0.52| 7.41±0.69     | 14.14±0.86| 9.09±1.12   | 1.72±0.35 |
| N\(_2\)    | 40.32±2.52| 26.52±2.11| 7.62±0.65| 6.33±0.33     | 9.45±0.65 | 7.38±0.65   | 2.36±0.41 |
| Air        | 38.52±2.31| 25.85±2.08| 9.58±0.62| 7.36±0.46     | 9.50±0.77 | 6.94±0.67   | 2.23±0.23 |
| No plasma  | 52.15±4.48| 25.48±1.79| N/A     | 3.29±0.15     | 9.03±0.33 | 6.21±0.53   | 3.83±0.49 |

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Fig. 2. Representative XPS survey spectra of pyrolytic carbon (A) before and (B-E) after plasma treatment using (B) Ar, (C) O\(_2\), (D) N\(_2\) gases and (E) air. The observed peaks correspond to O1s (531 eV), N1s (400 eV), C1s (284 eV). (F) Normalized atomic surface composition (obtained based on the corresponding XPS survey spectra) of pristine pyrolytic carbon and carbon treated with plasma generated from Ar, O\(_2\), N\(_2\) gases and air.

Fig. 3. Quantitative assignment of the deconvoluted (A) C1s, (B) O1s and (C) N1s high-resolution XPS spectra of pristine carbon and carbon treated with Ar, O\(_2\), N\(_2\), and air plasma.
containing functionalities (Fig. 3A). These alterations in surface chemistry were observed regardless of plasma gas choice.

However, a distinct impact and resulting surface chemistry of the investigated plasmas appears for some of the other chemical bonds due to specific gas properties. For instance, Ar-treated carbon demonstrated the highest O content on the surface, which could be explained by the larger radius of Ar ions impacting on the surface with a higher energy [50–52] and resulting in a higher enrichment with oxygen-containing groups upon re-exposure to ambient conditions [32]. For the same reason, Ar plasma lead to a reduction of the C–C fraction (Table 1), which was not observed for the other gases. O₂ possesses a strong oxidative nature and efficiency in breakage of primarily C = C but also C–C bonds and further formation of groups with more oxidized states of carbon. Specifically, this was confirmed by the significant changes in the high energy tail of C1s spectra and the abundance of formed oxygen-containing groups (Fig. S3). Air, as a mixture of mainly N₂ and O₂, and N₂ gas itself demonstrated a mild action in contrast to O₂ or Ar plasmas in terms of carbon bond breakage and functional derivative formation (Fig. 3A).

3.2.2. O1s spectra

Deconvolution of the high-resolution O1s peaks (Fig. S4) confirmed the presence of the oxygen-containing groups identified in the C1s spectra O–C = O (carboxyl or ester) at 531.55 eV, C = O (carbonyl) at 532.40 eV and C–OH (hydroxyl) at 533.85 eV [53] with obvious dominance of C = O groups on all samples. Quantitative analysis of the high-resolution spectra (Fig. 3B) proved the highest degree of oxygenation for Ar and O₂ plasma-treated carbon. In contrast, a lower concentration of oxygen-containing species was generated by N₂ and air plasmas. The presence of oxygen-containing functionalities was well inversely correlated with the sp² and sp³ fractions for all plasma conditions in reference to the pristine samples.

3.2.3. N1s spectra

Nitrogen-containing functionalities were a property of plasma processed surfaces using O₂, N₂ and air while these were absent on pristine and Ar treated samples (Fig. 2). The existence of nitrogen-containing groups on samples processed using O₂ can be explained by the fact that the treated surface presented highly reactive sites, which were still a subject of reaction with N₂ in the air, when they are exposed to atmospheric environment after the plasma treatment [32,36]. However, as expected, the highest content of nitrogen was detected on the N₂ and air processed carbon surfaces (Fig. 3C).

The detected nitrogen was identified in form of the four components (Fig. S5): pyrindinic (398.88 eV), amine and amide (400.01 eV), pyrrole/pyridine (401.29 eV) and quaternary nitrogen groups (402.72 eV) [53]. In all samples, the amine and amide fractions were remarkably dominant as depicted in Fig. 3C. However, the overall amount of introduced nitrogen varied from gas to gas (Fig. 3C). Pure O₂ plasma resulted in the least complement of C bound to N, since it arises due to the air contamination after the plasma treatment. In comparison, N₂ plasma as mono gas reasonably demonstrated a slightly higher level of nitrogenation of the carbon surface. Air, being a gas mixture of O₂ and N₂ readily available in the plasma chamber, introduced the largest amount of nitrogen-containing functionalities on the treated surfaces.

Based on the presented findings, it was concluded that the choice of gas indeed had an effect on the resulting chemical modification of the surface layer of pyrolytic carbon. As mentioned above, Ar and O₂ plasmas were concluded to be more efficient in terms of the amount of oxygen bound to surface. Significant smaller content of O was generated by N₂ or air plasma radiation, while these gases appeared to introduce remarkably higher quantities of nitrogen-containing functionalities.

3.3. AFM analysis

Besides chemical modification, it is well known that plasma treatment also can change the surface morphology by etching effects [29,54]. To understand the plasma effect on the surface roughness of the pyrolytic carbon electrodes, AFM characterization was employed. The measured topographies of untreated and plasma-treated carbon electrodes are visualized in Fig. 4A-E. The mean Rq values of the entire data sets were calculated to provide an overall description of height variations of the surfaces. The untreated carbon samples demonstrated a relatively smooth and uniform structure with an Rq value of 0.65 ± 0.06 nm, which is a typical average for carbon films obtained by pyrolysis of photoresist at 850 - 1100 °C [4,55]. The plasma-treated carbon chips showed about two-fold higher roughness, which is in good agreement with data reported for other pyrolytic carbons fabricated and processed under similar conditions [4,56,59]. The increased roughness (Fig. 4F) of the analysed surfaces after plasma process can be explained by the etching effects. It should be noted that due to the similar atom sizes (i.e., 0.66 Å atomic radius of O and 0.70 Å of N), O₂, N₂ or air plasmas resulted in similar and smoother carbon surfaces compared to Ar radiation: 1.05 ± 0.02 nm for O₂, 1.09 ± 0.14 nm for N₂, 1.03 ± 0.04 nm for air plasmas. It is well known from the literature [29,32,56], that Ar plasma generally leads to a higher surface roughness due to its relatively high atomic radius of 0.94 Å, resulting in higher energy transfer capacity and deeply etched surfaces. The Rq value for the Ar treated carbon electrodes was 1.30 ± 0.02 nm and represented the highest surface roughness amongst the tested samples.

3.4. Electrochemical characterization by cyclic voltammetry

3.4.1. Three redox systems – three distinct responses

Next, the impact of plasma-induced surface functionalization on electrochemical properties of pyrolytic carbon electrodes was investigated. Based on the principle of their different sensitivity to carbon surface chemistry, the following types of electroactive species were used in this study: Ru(NH₃)₆³⁺/²⁻, representing the simplest case of an outer-sphere electron transfer reaction, Fe(CN)₆³⁻/⁴⁻ and DA/DAQ, two redox systems classified as inner-sphere electrode reactions and undergoing distinct electron transfer mechanisms [57,58]. Indeed, by comparison of electrochemical behaviour of the three selected species on pristine and O₂ plasma-treated carbon chips, it was apparent that they responded differently to plasma treatment (Fig. 5). As an outer-sphere redox system lacking any adsorption or electrocatalytic steps, Ru(NH₃)₆³⁺/²⁻ redox probe demonstrated its insensitivity to the surface preparation confirmed by a well-recognizable couple of redox peaks with no significant differences between untreated or treated carbon with peak-to-peak separation, ΔEp, of ~86 mV in both cases (Fig. 5A).

In contrast, the electron transfer of Fe(CN)₆³⁻/⁴⁻ was completely inhibited on pristine carbon (Fig. 5B) and fully restored (ΔEp = 257 ± 15 mV) on plasma processed electrodes. Although it is a simple one-electron reaction system alike Ru(NH₃)₆³⁺/²⁻, it undergoes complex electrocatalytic interactions with the electrode surfaces [42,59,63], the mechanisms of which are still not fully understood [42,57,60].

The electrochemical oxidation of DA is a 2e⁻ /2H⁺ reaction strongly dependant on the electrode surface chemistry [57,61]. In the current study, DA demonstrated electron transfer activity on both untreated and O₂ plasma-treated surfaces. However, the kinetics were significantly slower on untreated surfaces (ΔEp = 375 ± 20 mV) compared to plasma-treated carbon (ΔEp = 173 ± 23 mV) (Fig. 5C). The kinetic improvements can be explained by a more anionic carbon surface after the plasma process resulting in an attractive electrostatic interaction with cationic DA at neutral pH.

It should be noted that according to the performed XPS analysis, there were no dramatic differences in atomic surface composition (i.e., O and C percentage) between pristine and plasma-treated carbon (Fig. 2F). Despite this, a short-time plasma treatment had a great impact on the electrochemical behaviour of Fe(CN)₆³⁻/⁴⁻ and DA/DAQ, and allowed a well-defined electron transfer reaction on the activated pyrolytic carbon electrodes (Fig. 5B, 5C). This was attributed to cleaning of the surface,
but also modification through introduction of polar functional groups and demonstrates the benefit of plasma treatment for specific electrochemical applications. It should be mentioned, that improved electrochemical performance of pyrolytic carbon in respect to a number of redox probes has been demonstrated through the application of O$_2$ plasma earlier [4, 9, 56]. Furthermore, the gas choice may additionally have significant influence on the redox reactions, e.g., in the current case study, dramatic impact on Fe(CN)$_6^{3-/4-}$ and DA/DAQ or minor effects on Ru(NH$_3$)$_6^{3+/2+}$ (Fig. 6).

3.4.2. Outer-sphere Ru(NH$_3$)$_6^{3+/2+}$ electrode reaction

As a subject of outer-sphere electron transfer reaction, Ru(NH$_3$)$_6^{3+/2+}$ does not chemically interact with specific sites or functional groups at the electrode surface. It lacks strong interactions with the surface and is expected to interact at the distance of a solvent layer from the electrode. As a consequence, reduction and oxidation of Ru(NH$_3$)$_6^{3+/2+}$ at the electrode surface is nearly the same as if it would happen in the bulk solution [62]. This well characterized electrochemical redox probe is mainly dependant on the electronic structure of a particular carbon electrode material and is considered insensitive to surface preparation. For this reason, Ru(NH$_3$)$_6^{3+/2+}$ is widely used as the null case for electrocatalysis [57] and as a control probe in the current study. CVs recorded over a wide range of scan rate confirmed the lack of surface sensitivity of the redox reaction on the carbon electrodes treated utilizing the different plasma gases. Independently of the gas used for activation of the carbon, symmetric voltammograms with a pair of

Fig. 4. Representative AFM images of pyrolytic carbon electrodes (A) before and after plasma treatment using (B) Ar, (C) O$_2$, (D) N$_2$, (E) air and (F) estimated arithmetic average of surface heights, $R_a$, on the corresponding carbon samples.

Fig. 5. Representative CVs recorded in 50 mM phosphate buffer and 0.1 M KCl supporting electrolyte at 0.1 V s$^{-1}$ scan rate towards 0.5 mM (A) Ru(NH$_3$)$_6^{3+}$, (B) Fe(CN)$_6^{3-/4-}$, and (C) DA on pyrolytic carbon electrodes before (black) and after (red) O$_2$ plasma activation.
well-defined redox peaks were observed (Fig. 6A, Fig. 7). The values of anodic and cathodic peak potentials, $E_{pa}$ and $E_{pc}$, respectively, remained constant with increasing scan rate and the potential separation between the peak, $\Delta E_p$, was independent of the scan rate for all plasma conditions tested (Fig. 7). Furthermore, the $\Delta E_p$ values were independent of the plasma gas used for electrode modification (Fig. 6A) and in all cases...
equal to approximately 85 mV (Table 2). This confirmed that Ru (NH₃)₆⁺/²⁺ was not influenced by the difference in surface chemistry and displayed equally efficient electron transfer with pyrolytic carbon electrodes after plasma processing with Ar, O₂, N₂ or air radiation. These observations are in good agreement with earlier studies [59,63] reporting no effect on the ΔEᵢ of Ru(NH₃)₆⁺/²⁺ on glassy carbon before and after covariant modification of electrodes with a monolayer of organic molecules. The experimentally observed value of peak-to-peak separation is close to the theoretical value of ~60 mV for fast one-electron transfer reactions at room temperature [62], confirming that the investigated electrochemical system was nearly reversible on the experimental time scale used in cyclic voltammetry. Furthermore, the current, i, was proportional to the square root of the scan rate, v¹/². The plots of i vs. v¹/² (Fig. S6) were linear over three orders of scan rate (0.005 – 0.5 V s⁻¹) (R² < 0.99), which indicated that the current was controlled by linear diffusion. Electrochemical reversibility of a system refers to the rapid electron transfer reaction at the electrode surface, which immediately appears in the Nernstian equilibrium established upon any change in applied potential. This also implies that no kinetic parameters could be found from the experimental cyclic voltammetry data.

Considering reversibility of the system and its insensitivity to plasma surface functionalization, the Ru(NH₃)₆⁺/²⁺ redox system was applied to determine the active surface area of the pyrolytic carbon electrodes. The estimation was based on the linear dependence Iₛ vs. v¹/² (Fig. S6) by applying the Randles-Sevcik equation (detailed description can be found in SI.3). The calculated active surface area (Table S2) of the electrodes did not vary significantly (1-6%) for the tested plasma conditions, which indicates that all gases of interest provided similar degree of activation of the carbon surfaces. However, it should be mentioned, that the highest surface area was estimated for carbon electrodes activated with Ar plasma. This minor (about 3 to 6% with respect to the other plasma conditions), but reproducible surface area gain can be explained by the higher surface roughness induced by physical etching in the Ar plasma as observed during AFM analysis (Fig. 4).

3.4.3. Inner-sphere Fe(CN)₆³⁻/⁴⁻ electrode reaction

As an inner-sphere electrochemical redox probe, Fe(CN)₆³⁻/⁴⁻ is classified as surface-sensitive redox system [57]. In comparison to the CVs obtained on the pristine electrodes (Fig. 5), it is evident that the CVs recorded on plasma-activated carbon exhibited a pair of well-defined redox peaks for all plasma gases (Fig. 6B). Therefore, all plasma can be used to significantly activate the Fe(CN)₆³⁻/⁴⁻ redox reaction on the carbon surface. The values of peak separation were essentially greater than the ones reported for Ru(NH₃)₆⁺/²⁺, which indicates that slower electron transfer kinetics on the time scale of the potential sweep. Furthermore, CVs recorded over a three order of magnitude range of scan rate demonstrated that the peak potential moved apart with increasing scan rate for all studied cases (Fig. 8). The ΔEᵢ values and the degree of the potential shift with scan rate were clearly different depending on the gas used in the plasma treatment of the carbon electrodes. Fe(CN)₆³⁻/⁴⁻ demonstrated the largest ΔEᵢ of 467 mV on Ar treated electrodes, a minimum of 159 mV on air activated carbon and intermediate ΔEᵢ on O₂ and N₂ plasma-processed electrodes (Table 2). The large variation of the ΔEᵢ values proved a strong dependence of Fe(CN)₆³⁻/⁴⁻ electron transfer on carbon surface pretreatment and chemistry. Furthermore, the observed anodic and cathodic peak current responses (Fig. 4B) were also largely affected by the plasma gas choice with the highest currents measured for air plasma-treated carbon surfaces (Fig. 4B, Fig. 6). It is important to note that, the latest effect cannot be attributed to differences in available working electrode surface area, since it was estimated to be approximately the same regardless of the gas used (Table S2). Moreover, the lowest currents were registered for Ar plasma-treated carbon surfaces (Fig. 4B), which were estimated to have slightly higher surface area compared to the other patterns (Table S2). Therefore, such alterations can be directly attributed to the interactions between Fe(CN)₆³⁻/⁴⁻ and specific functional groups introduced onto the carbon surface during plasma treatment.

With the voltammetric profiles in Fig. 8, the variations of peak-to-peak separation can be easily investigated to evaluate the heterogeneous electron transfer rate constant, kᵢ². This quantity is an important parameter to characterize performance of an electrode material in electroanalytical applications. It is commonly used to report the speed of electron transfer between the redox species and the electrode surface and whether the electrode material or its properties limit the overall electrochemical reaction rate. Electron transfer rates between Fe(CN)₆³⁻/⁴⁻ and plasma treated carbon electrodes were determined by applying the extended approach reported by Lavagnini et al. [64]. (Fig. S7), combining the Nicholson [65] and Klinger and Kochi [66] methods and suitable for both quasi-reversible and totally irreversible cases (see details in SI4). The estimated kᵢ² values for Ar, O₂, N₂ and air plasma-treated carbon electrodes and Fe(CN)₆³⁻/⁴⁻ redox probe are summarized in Table 2. The estimated values for N₂ and air plasma treated pyrolytic carbon are similar to the values reported for commercial glassy carbon electrodes [67], which is in excellent agreement with findings reported earlier [14].

### Table 2

| Plasma gas | Ru(NH₃)₆⁺/²⁺ | Fe(CN)₆³⁻/⁴⁻ | DA/DAQ |
|------------|-------------|--------------|--------|
| Ar         | 0.085±0.002 | 9.43±0.63    | 6.25±0.55 |
| O₂         | 0.086±0.001 | 7.86±0.20    | 7.63±0.20 |
| N₂         | 0.085±0.001 | 6.66±0.06    | 9.43±0.54 |
| Air        | 0.085±0.001 | 6.62±0.01    | 9.28±0.01 |

| \( \Delta E_p \) V | \( R_{CT} \) kΩ | \( CV \) kA cm⁻² | \( R_{CT} \) kΩ | \( CV \) kA cm⁻² | \( R_{CT} \) kΩ | \( CV \) kA cm⁻² |
|-------------------|-----------------|-------------------|-----------------|-------------------|-----------------|-------------------|
| Ar                | 0.046±0.002    | 2.95±0.05         | 1.17±0.11       | 0.203±0.022       | 3.72±0.19       | 3.29±0.69         | 4.17±0.90         |
| O₂                | 0.257±0.015    | 6.37±0.23         | 2.24±0.18       | 0.175±0.023       | 4.28±0.28       | 2.61±0.06         | 5.29±0.13         |
| N₂                | 0.196±0.001    | 12.50±0.29        | 3.74±0.28       | 0.259±0.018       | 1.53±0.58       | 3.78±0.24         | 3.67±0.31         |
| Air               | 0.159±0.010    | 14.10±0.38        | 6.75±0.74       | 0.166±0.020       | 5.18±0.28       | 2.23±0.21         | 6.38±0.60         |

* \( \Delta E_p \) values were taken from corresponding CVs at scan rate of 0.1 V s⁻¹.

* \( R_{CT} \) values were obtained from EIS spectra fitting.

* \( CV \) values were calculated based on EIS data.

* \( DV \) values were calculated using Nicholson and Klinger and Kochi methods (Fig. S7) based on CVs at various scan rates.
and Ar plasma-treated carbon, respectively (Table 2).

In order to evaluate the kinetics of the redox couple DA/DAQ on the pyrolytic carbon, the $\Delta E_p$ as a function of scan rate was investigated by applying the combination of Nicholson and Klinger and Kochi approaches (SI4, Fig. S8B) based on the CVs recorded over a broad range of scan rates (Fig. 9) on the electrodes treated with Ar, O$_2$, N$_2$ or air plasma. The $k^0$ values (estimated within the timescale where electron transfer suppression/electrode fouling is negligible, for more details see SI5) for Ar, O$_2$, N$_2$, air plasma-treated carbon chips and DA/DAQ are summarized in Table 2. The values estimated herein are within reasonable range of values reported for DA on various carbon material [73,74].

3.5. Electrochemical characterization by EIS

EIS is another useful method allowing a simple evaluation of $k^0$ for an electrochemical system, including reversible cases, where cyclic voltammetry is hardly applicable. Fig. 7 shows the impedance spectra for Ru(NH$_3$)$_6^{3+/2+}$, Fe(CN)$_6^{3-/4-}$ and DA/DAQ on the plasma-treated carbon electrode chips fitted using modified Randles circuits, which are widely used to describe simple electron transfers at the liquid electrolyte/electrode interfaces [67,74]. A Randles circuit (Fig. 7A, inset) with an uncompensated solution resistance, $R_S$, charge transfer resistance, $R_{CT}$, Gerischer element, $G$, and non-ideal double layer capacitance, introduced by the constant phase element, CPE, was used to fit the electron transfer of the Ru(NH$_3$)$_6^{3+/2+}$ redox probe. This outer-sphere electrochemical redox system carries out electron transfer through a layer of solvent in direct contact with the electrode surface and the redox process of Ru(NH$_3$)$_6^{3+/2+}$ at the electrode is essentially the same as in the bulk. Therefore, the Gerischer impedance, originally used to model a homogeneous reaction in solution, is a reasonable element to include in the circuit. The equivalent circuit model applied for the fitting of EIS spectra obtained for Fe(CN)$_6^{3-/4-}$ and DA/DAQ includes Warburg impedance, $W$, or mass transfer resistance instead and is depicted in Fig. 7B and 7C, inset. The chi-squared, $\chi^2$, test value, expressing the fitting accuracy with regard to the experimental data, was within the range of $10^{-4}$ for all obtained EIS spectra for Ru(NH$_3$)$_6^{3+/2+}$ and Fe(CN)$_6^{3-/4-}$ redox probes and confirmed satisfactory approximation with the chosen equivalent circuit. The $\chi^2$ for DA/DAQ redox reaction was within $10^{-3}$ for all spectra, which indicates that the chosen equivalent circuit model does not perfectly fit the whole EIS spectrum.

Fig. 8. Representative CVs recorded in 50 mM phosphate buffer and 0.1 M KCl supporting electrolyte at scan rates 0.5 - 0.005 V s$^{-1}$ for 0.5 mM Fe(CN)$_6^{3-/4-}$ on carbon electrodes treated with (A) Ar, (B) O$_2$, (C) N$_2$ and (D) air plasmas. The arrows indicate shifts in anodic and cathodic peak potentials, $E_{pa}$ and $E_{pc}$, respectively.
DA is well known to adsorb and polymerize on the electrode surfaces [61,68,75,76], which leads to surface fouling/passivation and electron transfer inhibition [76–79]. Obviously, such effects may limit the use of EIS for $k_0$ estimation, since the measurements are conducted over a long time under constantly applied potential conditions. In order to minimize these non-Faradaic contributions to the $R_{CT}$ component, the EIS profiles were measured from high to low frequency range. In this case, the electrode passivation effects became “visible” at lower frequencies (i.e., later period of the experiment) and mostly influenced the Warburg component, which results in an overall lower fitting accuracy (Fig. S9).

However, this approach allowed the shortest possible experimental time for estimation of reasonable $R_{CT}$ values (for more details see SI6, Fig. S9).

The estimated $R_{CT}$ values (Table 2) based on the EIS spectra fitting for the tested redox systems can be considered as indirect evaluation of the electron transfer reaction rate reflecting the electrochemical reaction kinetics. Therefore, $R_{CT}$ can be used to evaluate $k_0$ (for complete details, see SI7). The calculated rate constants displayed the lowest electron transfer rate of Fe(CN)$_6^{3-/4-}$ in case of the Ar treated carbon surface while it was highest for $N_2$ and air plasma-treated pyrolytic carbon electrodes. In case of DA/DAQ, the fastest electron transfer was achieved on the air plasma treated electrodes and the slowest on $N_2$ plasma activated carbon. It should be noted that in theory, the estimated $k_0$ values obtained with different methods should be identical. Although the values obtained from EIS and cyclic voltammetry follow the same overall trends and are of the same order of magnitude, the observed electron transfer rate constants for Fe(CN)$_6^{3-/4-}$ calculated based on EIS data were about two times lower than the ones obtained from cyclic voltammetry. At the same time in case of DA/DAQ, the EIS estimated $k_0$ values were slightly higher than the ones calculated based on cyclic voltammetry. Such differences of up to one order of magnitude between the electron transfer rate constants derived by the two methods have been reported for other redox reactions on carbon electrodes and have been attributed to the difference in the electrochemical mechanisms for the tested redox systems [74]. Another possible reason might be a different experimental timeframe of EIS and cyclic voltammetry differently affecting various electrochemical reactions.

Despite the fact that there were very small changes in peak currents and peak potentials in case of Ru(NH$_3$)$_6^{3+/2+}$ redox system, $k_0$ values derived from corresponding $R_{CT}$ (Table 2) still demonstrated that plasma
activation with various gases had a minor effect on the kinetics of the carbon, as expected for an outer-sphere redox system. Plasma processes as the ones used in this study are unable to change the electronic structure of the bulk material. They will only affect the top layer of the pyrolytic carbon, modifying the chemical composition and possibly the surface charge. Therefore, these very minor effects might be ascribed to the changes in surface chemistry. Following the EIS data obtained for Ru(NH$_3$)$_6^{3+/2+}$, N$_2$ and air plasmas appear only to be slightly better in terms of electron transfer in the range of working gases tested. In contrast, the electron transfer between the electrodes and Fe(CN)$_6^{3-/4-}$ or DA/DAQ was much more affected by the changes in surface chemistry of carbon implying some surface interactions associated with electron transfer processes. Although there was a difference in numbers between carbon implying some surface interactions associated with electron transfer processes. Nevertheless, different impact of this surface associated oxygen on the electron transfer of Fe(CN)$_6^{3-/4-}$ was observed ranging from Ar to air treated samples. This phenomenon can be attributed not only to the presence of oxygen on carbon as such, but also to the amount of oxygen, and the type and proportion of oxygen-induced groups on the surface. Within the gas range tested, the trend of increasing $k^2$ for Fe(CN)$_6^{3-/4-}$ was in direct correlation with a decreasing amount of surface oxygen groups introduced by a particular plasma gas. The Ar plasma, for example, resulted in the highest increase of carboxylic and hydroxyl groups, which might significantly contribute to a negative charge of the carbon surface. This caused a repulsion between the electrode and Fe(CN)$_6^{3+/4-}$ anions and interfered with the electro - redox species interactions. As a consequence, the electron transfer kinetics of the reaction were hindered, which was directly reflected in the cyclic voltammetry and EIS data. In contrast, N$_2$ or air plasma, demonstrating the most favourable conditions for the redox process of Fe(CN)$_6^{3-/4-}$ on the pyrolytic carbon, introduce a lower portion of the above-mentioned negatively charged groups. Furthermore, these plasma gases induced the formation of the highest fraction of nitrogen-containing group, mainly amines, which in turn might further contribute with positive surface charge at neutral pH. It should be noted here that Fe(CN)$_6^{3-/4-}$ undergoes complex electrochemical mechanisms, the nature of which are not completely clear yet [42,57,60]. This means that there could be more complicated processes not considered in the current work, which might have a significant influence on the electron transfer reaction occurring on the carbon surfaces.

3.6. Surface chemistry and electrochemical performance

It is evident that the oxygen-containing groups residing on the carbon surface have a strong impact on the electrochemical properties of an electrode material. For instance, surface oxygenation of pyrolytic graphite slows down the electron transfer of Fe(CN)$_6^{3-/4-}$ redox couple [80]. In contrast to that, it has been shown that oxygenated species at the ends of single-walled [81] carbon nanotube are able to speed up the heterogeneous electron transfer kinetics of the same redox reaction. Similarly, multi-walled [80] carbon nanotubes exposed to air have also been reported to exhibit a rapid electron transfer for Fe(CN)$_6^{3-/4-}$. The authors [80] explain this contrasting electrochemical behaviour of these carbon materials with the structural differences between pyrolytic graphite and carbon nanotubes affecting the nature of the formed oxygen-containing functional groups on the edge plane.

In the current study, all tested carbon surfaces carried oxygen-containing moieties as confirmed by XPS and discussed above.
Interestingly, in the current work, Ar plasma induced the highest content of carboxylic and hydroxyl groups, but the treatment did not lead to the highest electron transfer rates for DA. The greatest $k_0$ values were detected for air activated carbon, although this gas generated the lowest portion of the oxygen-containing groups amongst other plasma gases applied (Fig. 2F). Furthermore, $N_2$, resulting in very similar carbon surfaces in terms of both types and amounts of the induced surface functionalities, demonstrated the slowest kinetics of DA/DAQ redox process. This clearly revealed no absolute correlation between DA/DAQ electron transfer characteristics, represented by $k_0$, and the amount of surface oxygen-containing groups as reported in earlier works discussed above. The presented results suggest that the electrostatic effects can influence the overall electron transfer of DA oxidation, but not necessarily as an exclusive factor impacting the performance of the system. This conclusion is consistent with previous reports on the DA heterogeneous electron transfer at glassy carbon electrodes [69,83]. The impact of individual oxygen-containing groups or their combination on DA electrochemistry have not been studied. Overall, the current findings provide strong evidence that plasma gas is a crucial factor to manipulate surface chemistry of carbon electrodes and impact the electrochemical performance of DA. However, DA oxidation, as all quinone redox reactions, is complicated, sensitive to electrode surface pre-treatment and dependant on multiple factors and experimental conditions [61,68,77,82,90]. The overall process can further be impacted by adsorption and possible self-catalysis of DA oxidation on carbon surfaces [83,85].

Our results suggest that, the alterations in $k_0$ can be attributed to the amount and type of various surface groups introduced by a particular plasma gas, but importantly, also by underlying redox reaction mechanisms for each system tested.

4. Conclusions

In summary, modification of carbon surfaces is one of the most challenging tasks in modern electrochemistry, where the electrode materials have to meet specific requirements in electroanalysis, sensing, corrosion or biomaterial applications. Plasma treatment is a widely used technology offering a rapid and eco-friendly approach to activate and modify the surface of carbon materials by generating various functional groups on the surface. amongst other technical characteristics, such as chamber pressure, process temperature, treatment time and configuration of the plasma chamber, the gas is an important factor affecting the resulting chemistry, type and ratio of the various functional groups on the carbon surface. We explored chemical changes induced by Ar, O$_2$, N$_2$ and air plasmas on pyrolytic carbon surfaces and proved that electrode kinetics are primarily affected by the generated surface modification in reference to the three redox systems, Ru(NH$_3$)$_6^{3+/2+}$, Fe(CN)$_6^{3-/4-}$ and DA/DAQ. While the specific study was performed with SU-8 as a precursor material for the fabrication of the electrodes, we are convinced that the findings presented in this study may be relevant for pyrolytic carbon fabricated with other photoresist precursor materials and for pyrolytic carbon surfaces in general. It is important to note that this work does not provide a specific recipe on which plasma is the most optimal for general surface functionalization of carbon. Electron transfer kinetics of any electrochemical system should be considered individually by taking into account the electrode material, the involved redox system and the specific surface preparation. In the current study, we demonstrated that the gas selection may drastically influence the electrochemical performance of the electrode material exemplified by the case of pyrolytic carbon electrodes towards such redox systems as Ru(NH$_3$)$_6^{3+/2+}$, Fe(CN)$_6^{3-/4-}$ and DA/DAQ. Based on the findings presented herein, plasma process can be considered not only as simply carbon activation, but also functionalization, which might be especially useful and impactful for electrochemical processes undergoing specific interactions with carbon surfaces, such as DA and related neurotransmitters. This study gains insight into the relationship between the plasma-induced surface chemistry and final electrode reactivity and significantly contributes to a better fundamental understanding of the properties of carbon electrode materials. This can further be relevant for various applications and redox systems, where the surface preparation can be critical for the electrochemical performance and the minor adjustments in experimental procedure result in great effects.

CRediT authorship contribution statement

Galina Pankratova: Conceptualization, Methodology, Investigation, Formal analysis, Validation, Visualization, Writing – original draft, Writing – review & editing, Funding acquisition. Jesper Yue Pan: Resources, Writing – original draft. Stephan Sylvester Keller: Methodology, Writing – review & editing, Project administration, Funding acquisition.

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

The authors declare the following financial interests/personal relationships which may be considered as potential competing interests.

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Supplementary materials

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References

[1] W. Zhang, S. Zhu, R. Luque, S. Han, L. Hu, G. Xu, Recent development of carbon electrode materials and their bioanalytical and environmental applications, Chem. Soc. Rev. 45 (2016) 715–752.
[2] O.J.A. Schueller, S.T. Brittain, C. Marzolin, Fabrication and characterization of glassy carbon MEMS, Chem. Mater. 9 (1997) 1399–1406.
[3] M.K. Zachek, P. Takmakov, B. Moody, R.M. Wightman, G.S. McCarty, Simultaneous decoupled detection of dopamine and oxygen using pyrlyzed carbon microarrays and fast-scan cyclic voltammetry, Anal. Chem. 81 (2009) 6258–6265.
[4] E. Pelhola, J.J. Heikkinen, K. Sovanto, S. Sainio, A. Aarva, S. Franssila, et al., SU-8 based pyrolytic carbon for the electrochemical detection of dopamine, J. Mater. Chem. B 5 (2017) 9093–9044.
[5] J.A. Lee, J. Hwang, L. Kwak, S. Park II, S.S. Lee, K.-C. Lee, An electrochemical impedance biosensor with aptamer-modified pyrolyzed carbon electrode for label-free protein detection, Sens. Actuators B 129 (2008) 372–379.
[6] S. Hemanth, A. Halder, C. Caviglia, Q. Chi, S.S. Keller 3D Carbon microelectrodes with bio-functionalized graphene for electrochemical biosensing, Biosensors 8 (2018) 70.
[7] Y.M. Hassan, C. Caviglia, S. Hemanth, D.M.A. Mackenzie, D.H. Petersen, S. S. Keller, Pyrlytic carbon microelectrodes for impedance based cell sensing, ECS Trans. 72 (2016) 35–44.
[8] G.T. Teixidor, R. Gorkin, P.P. Tripathi, G.S. Bish, M. Kulkarni, T.K. Maiti, et al., Carbon microelectromechanical systems as a substratum for cell growth, BioMed. Mater. 3 (2008) 34116.
[9] L. Amato, A. Heiskanen, C. Caviglia, F. Shah, K. Zör, M. Skolimowski, et al., Pyrolysed 3D-carbon scaffolds induce spontaneous differentiation of human neural stem cells and facilitate real-time dopamine detection, Adv. Funct. Mater. 24 (2014) 7042–7052.
[10] J. Mitra, S. Jain, A. Sharma, B. Basu, Patterned growth and differentiation of neural cells on polymer derived carbon substrates with micro/nano structures in vitro, Carbon 65 (2013) 140–155.
[11] G.T. Teixidor, C. Wang, M. Madou, Fabrication of 3D carbon microelectrodes for Li-Ion battery applications, NSTI-Nanotech. 3 (2006) 221–224.
[12] C. Wang, L. Taherabadi, G. Jia, M. Madou, Y. Yeh, B. Dunn, C-MEMS for the manufacture of 3D microbatteries, Electrochem. Solid-State Lett. 7 (2004) A435,
cobalt phthalocyanine for selective analysis of dopamine in presence of ascorbic acid, Electroanalysis 20 (2008) 851–857.

[74] E.P. Randviir, A cross examination of electron transfer rate constants for carbon screen-printed electrodes using electrochemical impedance spectroscopy and cyclic voltammetry, Electrochim. Acta 286 (2018) 179–186.

[75] D.M. Anjo, M. Kahr, M.M. Khodabakhsh, S. Nowinski, M. Wanger, Electrochemical activation of carbon electrodes in base: minimization of dopamine adsorption and electrode capacitance, Anal. Chem. 61 (1989) 2603–2608.

[76] W. Harreither, R. Trouillon, P. Poulin, W. Neri, A.G. Ewing, G. Safina, Carbon nanotube fiber microelectrodes show a higher resistance to dopamine fouling, Anal. Chem. 85 (2013) 7447–7453.

[77] F. Bernsmann, V. Ball, F. Addiego, A. Ponche, M. Michel, J.J. de Almeida Gracio, V. Tonazzo, D. Ruch, Dopamine-melanin film deposition depends on the used oxidant and buffer solution, Langmuir 27 (2011) 2819–2825.

[78] S. Alwarappan, K.S.A. Butcher, D.K.Y. Wong, Evaluation of hydrogenated physically small carbon electrodes in resisting fouling during voltammetric detection of dopamine, Sens. Actuators B 128 (2007) 299–305.

[79] E. Peltola, A. Arava, S. Sainio, J.J. Heikkinen, N. Wester, V. Jokinen, J. Kokkinen, T. Laurila, Biofouling affects the redox kinetics of outer and inner sphere probes on carbon surfaces drastically differently - implications to biosensing, Phys. Chem. Chem. Phys. 22 (2020) 16630–16640.

[80] X. Ji, C.E. Banks, A. Crossley, R.G. Compton, Oxygenated edge plane sites slow the electron transfer of the ferro-/ferricyanide redox couple at graphite electrodes, ChemPhysChem 7 (2006) 1337–1344.

[81] A. Chou, T. Blockling, N.K. Singh, J.J. Gooding, Demonstration of the importance of oxygenated species at the end of carbon nanotubes for favourable electrochemical properties, ChemComm (2005) 842–844.

[82] R.L. McCreery, Carbon electrode surface chemistry: optimization of bioanalytical performance, in: A.A. Boulton, G.B. Baker, R.N. Adams (Eds.), Voltammetric Methods in Brain Systems, Humana Press, Totowa, NJ, 1995, pp. 1–26.

[83] S.H. DeVall, R.L. McCreery, Self-catalysis by catechols and quinones during heterogeneous electron transfer at carbon electrodes, J. Am. Chem. Soc. 122 (2000) 6759–6764.

[84] A.J. Downard, A.D. Roddick, A.M. Bond, Covalent modification of carbon electrodes for voltammetric differentiation of dopamine and ascorbic acid, Anal. Chim. Acta 317 (1995) 303–310.

[85] B.D. Bath, H.B. Martin, R.M. Wightman, M.R. Anderson, Dopamine adsorption at surface modified carbon-fiber electrodes, Langmuir 17 (2001) 7032–7039.

[86] J.G. Roberts, B.P. Moody, G.S. McCarty, L.A. Sombers, Specific oxygen-containing functional groups on the carbon surface underlie an enhanced sensitivity to dopamine at electrochemically pretreated carbon fiber microelectrodes, Langmuir 26 (2010) 9116–9122.

[87] M.L.A.V. Heien, P.E.M. Phillips, G.D. Stuber, A.T. Seipel, R.M. Wightman, Overoxidation of carbon-fiber microelectrodes enhances dopamine adsorption and increases sensitivity, Analyst 128 (2003) 1413–1419.

[88] B.D. Bath, D.J. Michael, B.J. Trafon, J.D. Joseph, P.L. Runnels, R.M. Wightman, Subsecond adsorption and desorption of dopamine at carbon-fiber microelectrodes, Anal. Chem. 72 (2000) 5994–6002.

[89] G.E. Cabaniss, A.A. Diamantis, W.R. Murphy, R.W. Linton, T.J. Meyer, Electrocatalysis of proton-coupled electron-transfer reactions at glassy carbon electrodes, J. Am. Chem. Soc. 107 (1985) 1845–1854.

[90] S. Schindler, T. Bechtold, Mechanistic insights into the electrochemical oxidation of dopamine by cyclic voltammetry, J. Electroanal. Chem. 836 (2019) 94–101.