Electrocatalytic Activity of Carbonized Nanostructured Polyanilines for Oxidation Reactions: Sensing of Nitrite Ions and Ascorbic Acid

Darko Micić [a], Biljana Šljukić [a,*], Zoran Zujovic [b], Jadranka Travas-Sejdic [b,c], Gordana Ćirić-Marjanović [a]

[a] University of Belgrade, Faculty of Physical Chemistry, Studentski trg 12–16, 11158 Belgrade, Serbia
[b] Polymer Electronics Research Centre, School of Chemical Sciences, University of Auckland, 23 Symonds Street, Auckland, New Zealand
[c] MacDiarmid Institute for Advanced Materials and Nanotechnology, Victoria University of Wellington, P.O. Box 600, Wellington 6140, New Zealand

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ABSTRACT

A comparative study of the electrocatalytic activity of nitrogen-containing carbon nanomaterials, prepared by the carbonization of nanostructured polyaniline (PANI) salts, for the electrooxidation reactions is presented. Nanostructured PANI salts were synthesized by the oxidative polymerization of aniline with ammonium peroxydisulfate in an aqueous solution in the presence of 5-sulfosalicylic acid (PANI-SSA), 3,5-dinitrosalicylic acid (PANI-DNSA) as well as without added acid (PANI), and subsequently carbonized to c-PANI-SSA, c-PANI-DNSA and c-PANI, respectively. Glassy carbon tip was modified with nanostructured c-PANIs and used for the investigation of sensing of nitrite and ascorbic acid in aqueous solutions as model analytes by linear sweep voltammetry. All three types of the investigated c-PANIs gave excellent response to the nitrite ions and ascorbic acid electrooxidation. The lowest peak potential for nitrite ion oxidation exhibited c-PANI (+0.87 V *vs.* SCE), and for ascorbic acid oxidation both c-PANI and c-PANI-SSA (*ca.* +0.13 V *vs.* SCE). Electrochemical data were correlated with structural and textural data obtained by Raman spectroscopy, X-ray diffraction, X-ray photoelectron spectroscopy, elemental and nitrogen sorption analysis.

1. Introduction

Development of highly sensitive, accurate, rapid and reliable analytical methods for determination of toxic nitrite (NO_2^-) ions, used as additives in food preservations and agriculture as well as corrosion inhibitors, and ascorbic acid (AA), well-known vitamin C, used as an antioxidant in the food and drink industry, is still of high importance in environmental, food and pharmaceutical analysis, and clinical diagnostics [1–4]. These two species were chosen as model analytes for comparative study of activity of different nanostructured carbonized polyanilines for electrochemical oxidation reactions as electroanalytical determination of NO_2^- and AA is frequently based on their electrochemical oxidation [5–8]. Electroanalytical methods are often used for determination of NO_2^- and

AA with only few reports on their simultaneous sensing that is of importance in biological samples. Both NO_2^- and AA are electroactive at standard carbon electrodes (glassy carbon (GC), carbon paste, etc.), but undesirably high overpotentials are required for their oxidation at these electrode substrates [9,10]. Consequently, the voltammetric determination of the two analytes, based on their oxidation reactions, suffers from the interference by other readily oxidizable species. An efficient way to improve the selectivity of the sensing of NO_2^- and AA is lowering the operating potentials of carbon electrodes by their modification. Various non-modified and modified carbon materials have been evaluated for the electrochemical sensing of NO_2^- [11–24] and AA [16–18,24–31].

Nanostructured carbon materials have also been investigated for the electroanalytical determination of NO_2^- and AA [32–43]. Fast electron transfer rate for AA oxidation has been observed at platelet graphite nanofibers due to a large number of active edge sites [41]. It was found that nanocrystalline graphite-like pyrolytic carbon film electrodes prepared under chemical vapour deposition temperatures higher than 1050 °C show a higher sensitivity for AA and lower overpotential in comparison with other carbon electrodes [37]. Carbon nanotubes (CNTs) have proved to have high sensitivity for both NO_2^- [33] and AA [40] detection due to the presence of edge plane sites and defects as well as due to high surface

area. However, CNTs have exhibited poor stability due to adsorption of the detected species on the electrode surface, and high limits of detection (LOD) due to the high background currents. Therefore, several modified CNT-based materials/composites were examined as electrodes for sensing of NO_2^- and AA [32,34–36,39,42]. Study of the electroanalytical performances of different graphene-based nanomaterials showed their high sensitivity and selectivity, and excellent reproducibility in determination of NO_2^- and AA [38,41,43].

The synthesis and application of nitrogen-containing carbon nanostructures (NCNS) has emerged in recent years as one of the fastest growing research topics in current carbon nanoscience and nanotechnology [44–50]. Numerous investigations were mainly focused on preparation and potential applicability of one-dimensional NCNS such as N-containing carbon nanotubes (NCNT) [44–46] and nanofibers [47]. Recently, N-containing graphenes also attracted considerable attention of scientific community and advanced technology sector [48,49]. All types of NCNS were examined mainly in catalysis/electrocatalysis [44–46,48], while scarcely were explored for sensor and biosensor applications [50,51]. Based on the fact that nanostructured N-containing conducting polymers, such as polyaniline (PANI), can easily be prepared with high level of morphology control [52], the carbonization of PANI nanostructures (nanotubes, nanofibers, nanorods, nanosheets) [53–56] appeared to be a new simple and efficient method for the preparation of different types of NCNS. Carbonized nanostructured PANIs were proved to be promising candidates for various applications, such as catalysts [57], electrocatalysts [58–60], field emitters [61], and supercapacitors [62,63]. Sensors and biosensors based on carbonized PANI have also been reported [64–66]. Recently we have investigated electroanalytical application of electrodes based on metal oxide composites with carbonized PANI support [67,68]. It was found that carbonized nanostructured PANI was itself electroactive for heavy metals detection [68].

In the present work the electrocatalytic activity of the carbonized nanostructured PANI salts for oxidations of NO_2^- and AA has been studied for the first time. The investigated carbonized PANI hydrogen sulfate (c-PANI) nanorods/nanotubes/nanosheets [54,63], carbonized PANI 5-sulfosalicylate (c-PANI-SSA) nanorods/nanotubes [60,63], and carbonized PANI 3,5-dinitrosalicylate (c-PANI-DNSA) nanorods [63,69] have similar molecular structure and morphology and at the same time offer substantial differences in surface N and C contents and textural properties [70,71]. These three carbonized PANI materials were previously investigated as the electrode materials for the electrochemical capacitors and as electrocatalysts for oxygen reduction reaction (ORR), and it was found that they exhibit very high charge storage capability [63] and high electrocatalytic activity for ORR [72]. However, the catalytic activity of these materials for the electrochemical oxidation reactions is not yet investigated. The question how diverse pore structures and N- and O-containing surface functionalities of structurally and morphologically similar N-containing carbon nanomaterials can influence their activity towards electrooxidation of NO_2^- and AA is addressed in detail.

2. Experimental

Materials – Aniline (p.a., Centrohem, Serbia) was distilled under reduced pressure and stored under argon prior to use. All other chemicals were of analytical grade and used as received from the manufacturers. All solutions were made with distilled water.

Syntheses of PANI precursors and their carbonization – Nanostructured PANI salt precursors were synthesized according to the procedures reported in the literature [54,60,63] by the gram-scale template-free oxidative polymerization of aniline with ammonium peroxydisulfate as an oxidant in three different media: a) in water, without added acid (PANI) [54,63], b) in the aqueous solution of 5-sulfosalicylic acid (PANI-SSA) [60,63], and c) in the aqueous solution of 3,5-dinitrosalicylic acid (PANI-DNSA) [63,69]. These were subsequently carbonized by means of gradual heating in a N_2-atmosphere up to 800 °C at a heating rate of 10 °C min^{-1} (Carbolite CTF 12/75/700 tube furnace with Eurotherm 815P Prog/Controller) to obtain c-PANI [54,63], c-PANI-SSA [60,63] and c-PANI-DNSA [63,69], respectively.

A scanning electron microscope (SEM, JEOL JSM 6610 LV, Japan) and a transmission electron microscope (TEM, JEOL TEM-2010, Japan) were used to characterise the morphology of the samples and X-ray diffraction (XRD) for analysis of their structural properties. The electrical conductivity of powders compressed between stainless pistons, within an insulating hard-plastic tube, was measured at room temperature by means of an ac bridge (Waynne Kerr Universal Bridge B 224), operating at a fixed frequency of 1.0 kHz. Elemental analysis (C, H, N and O) was carried out by the Elemental Analyzer Vario EL III (Elementar). X-ray photoelectron spectroscopy (XPS) spectra were recorded on a Kratos Axis Ultra DLD (Kratos Analytical, Manchester, UK), using monochromatic Al Ka X-rays (1486.69 eV) with X-ray power of 150 W. Survey spectra were collected with 160 eV pass energy, whilst core-level scans were collected with pass energy of 20 eV. Data analysis was performed using CasaXPS using Kratos' relative sensitivity factors.

Raman spectra were collected on a Thermo Scientific DXR Raman microscope, equipped with an Olympus optical microscope and a CCD detector. A diode-pumped solid-state laser with excitation wavelength of 532 nm was used. Fourier transform infrared spectroscopy (FTIR) spectra of the powdered samples were recorded in the range of 4000–400 cm^{-1} using a Nicolet 6700 FTIR Spectrometer (Thermo Scientific).

Adsorption-desorption isotherms for c-PANI samples were obtained by N_2 adsorption at 77 K using a Sorptomatic 1990 Thermo Finnigan device and analysed with software ADP version 5.17 CE Instruments. The mesopore volume, V_{meso}, and the mesopore surface area, S_{meso} were estimated according to the Dollimore and Heal method [63]. The specific surface area of micropores, S_{mic}, was determined by the Dubinin's method modified by Kaganer, and micropore volume, V_{mic}, was determined by Dubinin-Radushkevic equation [63].

Electrochemical measurements – Catalytic ink was prepared by adding c-PANI, c-PANI-SSA or c-PANI-DNSA (4 mg) into 1 ml of ethanol and water mixture (2:3), with homogenization by mixing in the ultrasonic bath for 30 min. As-prepared catalytic ink was used for fabrication of the working electrode by pipetting 10 μl of the catalytic ink onto polished glassy carbon tip (GCE, 5 mm diameter) and leaving it for the solvent to evaporate at the room temperature.

All electrochemical measurements were conducted at the Gamry PCI4/750 potentiostat/galvanostat using three–electrode cell of 15 cm^3 volume. Platinum electrode served as a counter one, with saturated calomel electrode (SCE) completing the circuit. Potentials within this work are given relative to SCE unless otherwise stated. The measurements were performed at the room temperature without removing oxygen from the solution.

AA and NO_2^- sensing was carried out using linear sweep voltammetry (LSV) with a scan rate of 50 mVs^{-1}. Supporting electrolyte used for AA sensing was pH 7 phosphate buffer as it simulates biological conditions, while supporting electrolyte for NO_2^- sensing was 1 mM perchloric acid ($HClO_4$) + 1 M sodium perchlorate ($NaClO_4$). The electrochemical determination of analytes concentrations was performed *via* the standard addition protocol with LOD evaluated using 3σ method.