Prussian Blue Modified Solid Carbon Nanorod Whisker Paste Composite Electrodes: Evaluation towards the Electroanalytical Sensing of H$_2$O$_2$

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Received 18 October 2011; Accepted 20 December 2011

Academic Editor: Boniface Kokoh

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Metallic impurity free solid carbon nanorod "Whiskers" (SCNR Whiskers), a derivative of carbon nanotubes, are explored in the fabrication of a Prussian Blue composite electrode and critically evaluated towards the mediated electroanalytical sensing of H$_2$O$_2$. The sensitivity and detection limits for H$_2$O$_2$ on the paste electrodes containing 20% (w/w) Prussian Blue, mineral oil, and carbon nanorod whiskers were explored and found to be 120 mA/(M cm$^2$) and 4.1 μM, respectively, over the concentration range 0.01 to 0.10 mM. Charge transfer constant for the 20% Prussian Blue containing SCNR Whiskers paste electrode was calculated, for the reduction of Prussian Blue to Prussian White, to reveal a value of 1.8 ± 0.2 1/s ($\alpha = 0.43$, $N = 3$). Surprisingly, our studies indicate that these metallic impurity-free SCNR Whiskers, in this configuration, behave electrochemically similar to that of an electrode constructed from graphite.

1. Introduction

The investigation of new carbon nanomaterials continues to be a hot topic. Such materials have received attention due to their reported optimal sensing properties [1, 2], for example, Gooding et al. have elegantly demonstrated that carbon nanotubes may “wire” biomolecules facilitating charge transfer between the electrode and the redox-active centre of the protein [3]. Despite the reported excellent properties of carbon nanomaterials, the question about the origin of the enhanced charge transfer speed and the reduction of the overpotentials is still questionable. This is due to the different crystallographic and chemical influences affecting the electrochemical properties of carbon nanotubes [4]. As Compton et al. [5, 6], Banks et al. [4, 7, 8], and later Pumera et al. [9, 10] have demonstrated, metallic impurities reside in carbon nanotubes which is inherent to their fabrication process can be responsible for the CNTs observed electroactivity towards selected analytes; for example, Banks et al. [11] concluded for the case of the electrochemical detection of D-glucose that the effect of metallic impurities dominates over edge plane crystallographic effects of the graphite edge plane like-sited/defects.

In a previous report [12] the electrochemical reduction of H$_2$O$_2$ on carbon nanorod paste electrode (SCNRPE) prepared without the use of d-metallic catalysts has been reported. In that study, hydrogen peroxide was selected as one of model compounds since its detection is often needed, for example, in studying oxidative stress in bio-systems [13, 14], low temperature fuel cell processes, [15, 16] and in the studies of corrosion processes [17, 18]. Paste electrodes, as selected in this study, as working electrodes are useful because they (1) are simple to prepare and handle, (2) demonstrate reasonable reproducibility, (3) have a low
background current, (4) can be easily re-cleaned, (5) have a low cost, (6) can be used in a wide potential range [19, 20], and (7) minimise diffusion within the nano material network neglecting the influence of thin layer diffusion allowing more readily to determine the charge transfer rate constants via cyclic voltammetry [21]. Also they can be easily modified with analyte-specific enzymes or redox mediators [19, 20].

In this paper we investigate the electrochemical behaviour of Prussian Blue (PB) as a charge transfer mediator due to its reported use as a H₂O₂ overpotential reducer [22–24], with metallic impurity-free solid carbon nanorod “Whiskers” (SCNR Whiskers), a derivative of carbon nanotubes behaving as the charge transfer catalysts. The SCNR “whiskers” were chosen due to their relative novelty and lack of metallic catalytic additives commonly found in carbon nanotubes where PB is selective to the reduction of O₂ and especially to H₂O₂, has high stability, and has no saturation effect for substrate [22]. PB has been previously used in a combination with carbon nanotubes, [23, 25] glassy carbon [26], and other materials [22] to prepare paste electrodes. To construct robust and fast prepared paste electrodes having direct electrical contact between the SCNR particles, we decided to blend the SCNR “whiskers” with PB. Note that the use of these nanomaterials allows one to deconvolute the true electrochemical parameters avoiding contributions from metallic impurities [4, 7–10]. The PB composite electrodes are evaluated towards the electroanalytical sensing of hydrogen peroxide and compared critically to that of simple graphite; surprisingly we find no advantage of using the SCNR “whiskers” in this context.

2. Experimental

The solid carbon nanorod (SCNR) “whiskers” are commercially available and were kindly provided by SCNTE and are in fact a subclass of multiwalled carbon nanotubes. Full characterisation has been reported previously of these materials in [27]. Such characterisation of the material with Raman spectroscopy reveals a large D-peak corresponding to high level of “kinks” on the tubes. In this case a large number of “kinks” and other features have been supposed to lead to the high edge plane character of the “tubes.” The relative density of the electroactive edge plane sites has been calculated from cyclic voltammetry measurements and was found to be ca. 13.3% being much higher than for the other forms of carbon materials [21]. Mineral oil (suitable for the preparation of Nujol mulls for IR, stabilizer free) to prepare carbon nanotube paste electrodes was obtained from Sigma-Aldrich. All other chemicals used were of analytical grade and were used as received without any further purification, obtained also from Sigma-Aldrich. All aqueous solutions were prepared using Milli-Q (Millipore) water with resistivity not less than 18.2 MΩ·cm.

To construct robust and fast prepared paste electrodes having direct electrical contact between SCNRs we decided to blend these with PB powder with mineral oil as a binder. The PB was decided not to be chemically attached to SCNR due to low electrical conductivity of dry PB, [28–30], experimentally shown in the work of Ricci et al. [26], where they needed to include unmodified glassy carbon particles into the paste to have useful electrochemical response that is, electrical connection between particles therein. The Prussian Blue modified carbon nanotube paste electrodes were prepared by weighting SCNR, PB powder, and the mineral oil in the needed proportions. All substances were carefully mixed with each other and the prepared paste was pressed into a cylinder constructed by BASi (type MF-2010, inner diameter of the tube 3.0 mm) previously cleaned with acetone and Milli-Q water. The surface of the electrode was re-cleaned by a soft clean filter paper and washed then with the Milli-Q water before each measurement cycle.

Electrochemical measurements were performed with an Autolab PGSTAT 30 potentiostat connected with a PC. A large area platinum mesh served as a counter electrode and an Ag/AgCl (3 M NaCl aq., BASi) was used as the reference electrode completing the circuit. All solutions in the electrochemical cell (5 mL) were purged for 15 minutes with Ar gas (99.9999%, AGA) prior to the start of the electrochemical experiments. All experiments were conducted at room temperature (25 ± 1°C).

Scanning electron microscopic (SEM) images were obtained using Helios Nanolab 600 FIB (FEI Company) instrument. Instrument settings: applied voltage: 10.00 kV, current: 43 pA, electron source to object distance (WD): 5.0 mm, and detector: TLD. For the electron photographing 10 μL of the ethanolic suspensions of carbon nanorods (1 mg/mL) were deposed onto precleaned Au(111) disks. This suspension was Sonicated 120 s in a sonobath (Elmasonic S 10, type 510, 60W, v = 37 kHz) prior to the deposition onto Au disks.

3. Results and Discussion

To understand the nature of the carbon nanorods (SCNR) used and to examine the material in light of its high proportionation of reported edge plane defects, predicted in [27], we performed SEM. As depicted in Figure 1 the SCNR are dispersed over a Au (111) surface lying horizontally tending to aggregate. Also, different sizes of the nanorods are obvious. Figure 2 presents a larger magnification of a group of nanorods and this image indicates that the surface structure of the nanorods is quite variable. Some of the rods seem to be quite smooth (large degree of graphite base planes visible), while some of them seem to have very rough surface (large degree of graphite edge planes and surface defects are visible). Figure 3 is an amplification of a SCNR having a high-surface roughness. It appears that the edge planes are oriented under 90° to the axle appearing on the side of the rod, so that the ends of nanorods are formed from the basal plane of graphite. On the other hand, some rods in Figure 2 expose base planes on the side(s) and the ends of the SCNR consist in edge planes. From the SEM images we concluded that the SCNRs have “dual” orientation and a very high ratio of exposed edge planes and defects. This phenomenon should make this material
quite electroactive, while the existence of exposed edge planes increases the charge transfer speed between the SCNR and a reacting substance [4, 31]. The SCNR “whiskers” have the lengths in the order of 1–5 microns, with a diameter from 20 nm to 1 μm which are made up of highly “kinked” bundles of nanorods and have no empty core just consisting in a single solid core with multiple walls making up the material. Raman spectroscopy of this material [27, 32] shows (using a 785 nm laser excitation wavelength) well-defined G peaks with a very large G* intensity and a smaller D:G ratio as compared with the commercial CNT material. The 785 nm excitation frequency allows observation of two key features in SCNR morphology as compared with MWCNTs which is due to the consistency of the material. The RBM vibrations present at 115 and 170 cm$^{-1}$ are also observed. The Raman data also show that SCNRs produced via CTCC are metallically conductive. Analysis of the purity (measured via ICP-MS) reveals a carbon mass % of 99.98 with a oxygen mass % of <0.05 and a silicon mass % of 0.01 indicating the absence of metallic impurities as it is often in the case of other commercially available carbon nanomaterials [5, 6].

3.1. Cyclic Voltammetric Studies of PB Modified Carbon Nanorod Paste Electrodes. To investigate the influence of the PB on charge transfer processes, using hydrogen peroxide as a model compound, two different pastes were prepared containing 10 and 20% (w/w) PB (see Table 1 for exact composition), total content of solid substances in the paste electrodes was always kept close to 70% (w/w) as it was found to be optimal as reported in a previous study [12]. Figure 4 shows three cyclic voltammetric curves resulting from the electrochemical reduction of hydrogen peroxide (10 mM) in 0.1 M phosphate buffer solution (pH = 7.0). Two of these curves are measured on the PB-modified SCNR paste electrode and one on the bare 0% (w/w) PB modified SCNR paste electrode. Clear reduction peaks corresponding to the electrochemical reduction of H$_2$O$_2$ are visible at the peak potential $-1.37$ V versus Ag/AgCl (3 M NaCl) at a potential sweep rate of 25 mV/s. When the electrode potential becomes more cathodic than $-1.6$ V, H$_3$O$^+$ ions start to reduce. When PB is added to the paste, the overpotential of the hydrogen peroxide reduction process significantly lowers. On the 10% PB-modified paste electrode no clear reduction peak of H$_2$O$_2$ appears ($v = 50$ mV/s). It seems that this reduction process starts from the potentials $-0.8$ V (being lower than that for 0% PB modified paste electrode), the reduction current of H$_2$O$_2$ reaches the maximum at $E \approx -1.4$ V and seems smoothly to continue to rise with the proton’s reduction process at more negative potentials than $-1.46$ V versus
H$_2$O$_2$ reduction process of SCNR paste electrodes containing 0% (w/w) PB (solid line), 10% (w/w) PB (dashed line), and 20% (w/w) PB (dotted line). A small reduction peak of H$_2$O$_2$ forms at peak potential $\Delta$Ep = 124 mV suggesting that the metallic impurity free SCNR Whiskers behave graphite-like.

A charge transfer rate constant for the reduction of Prussian Blue to Prussian White in 20% Prussian Blue containing SCNR Whiskers paste electrode was calculated applying Laviron equation [33]:

$$\log k_i = \alpha \log(1 - \alpha) + (1 - \alpha) \log \alpha - \log \frac{RT}{nFv} - \frac{\alpha(1 - \alpha)nF\Delta E_p}{2.3RT}$$

where $\alpha$ is charge transfer coefficient, $\Delta E_p$ is anodic and cathodic peak potential difference $[V]$, $F$ is Faraday number $[C/mol]$, $k_i$ is heterogeneous charge transfer rate constant, $n$ is number of electrons transferred in the reaction, $R$ is gas universal coefficient $[J/(K mol)]$, $v$ is CV potential sweep rate $[V/s]$, and $T$ is solution temperature $[K]$. $\alpha$ was found from the slope of the $E_p$ versus ln relationship (where $\Delta E_p > 200$ mV, at $n = 1$) of the same cathodic process: $KFe_{III}^{III}Fe^{II}(CN)_6 + K^+ + e^- \rightarrow K_2Fe^{II}Fe^{III}(CN)_6$. (2) (Prussian Blue) (Prussian White)

A charge transfer rate constant value of $1.8 \pm 0.2$ $1/s (\alpha = 0.43, N = 3)$ was consequently deduced.

3.2. Determination of the limit of Detection (LOD) and Sensitivity of 20% (w/w) PB-Modified SCNRPE. To investigate the electroanalytical properties of prepared PB-modified SCNR paste electrodes, the 20% (w/w) PB was selected due to lower H$_2$O$_2$ reduction overpotential and more obvious current maximum in the cyclic voltammogram of the H$_2$O$_2$ reduction process. First we investigated the rise of the reduction current of PB upon the concentration of added hydrogen peroxide. Despite the literature reports that the reduction current of PB should be dependent upon H$_2$O$_2$.
concentration in the solution, we observed no acceptable correlation there. Therefore we moved to investigate the electrochemical reduction process of H$_2$O$_2$ itself. As marked above, the hydrogen peroxide gave a small wave at potential −1.0 V versus Ag/AgCl (3 M NaCl), $v = 50$ mV/s. We repeated this experiment in the concentration range from 1.0 to 10.0 mM. Figure 6 shows the cyclic voltammograms of the reduction of H$_2$O$_2$ at different concentrations. The sensitivity of the PB-modified electrode in the concentration range studied was 37 mA/(M cm$^2$) at $v = 50$ mV/s. This is in the same range as found by us for unmodified SCNRPE (50 mA/(M cm$^2$)) [12] or by Ricci and Palleschi (45 mA/(M cm$^2$)) for PB-modified carbon paste electrode [22]. Calculated detection limit was 3.1 mM being better than found for unmodified SCNRPE [12] and the relative standard deviation of the H$_2$O$_2$ reduction peak current versus $C$ was higher: 20% (w/w) PB SCNR paste electrode (dashed line), $v = 50$ mV/s, 0.1 M phosphate buffer (pH = 6.9).

While no reoxidation of the water to H$_2$O$_2$ was observed (as it is obvious from the cyclic voltammograms also).

### 3.4. Investigation of the Redox Processes of K$_4$[Fe(CN)$_6$]: Determination of the Charge Transfer Coefficient $\alpha$ and the Charge Transfer Rate Constant $k_0$

To investigate charge transfer speed on the 20% PB modified SCNR PE, 10 mM solution of K$_4$[Fe(CN)$_6$] in 0.1 M phosphate buffer (pH = 7) was used as a probe. Cyclic voltammetric potential sweeps were performed in the potential range from −0.9 to +1.0 V versus Ag/AgCl and reverse. Data of the second cycle, measured in the potential sweep range from 0.5 to 6 V/s (where the relationship between $E_p$ versus ln $v$ was linear), were used for the calculation of $\alpha$ and $k_0$ values of the reduction process of K$_4$[Fe(CN)$_6$] applying the Laviron equation [33]. The $\alpha$, found from slope of the $E_p$ versus ln $v$ (where $\Delta E_p > 200$ mV, at $n = 1$) of the cathodic process (reduction of in situ presynthesized K$_4$[Fe(CN)$_6$]), has a value 0.6 and the average value for $k_0$ was 0.013 ± 0.005 s$^{-1}$. Value of $\alpha$ is the same as found by Huang in [37], but the charge transfer rate constant of the K$_4$[Fe(CN)$_6$] reduction reaction, found by them on CNT-modified Au electrode, was higher: $k_0 = 0.31$ s$^{-1}$ [37]. The lower reduction process rate constant observed in this investigation suggests that in this context, the structure of SCNRs is not significantly advantageous over other CNTs.
4. Conclusions

In this work SCNR whisker paste electrodes have been investigated. SEM images of these virtually metallic impurity free carbon nanorods were obtained showing the existence of edge plains of the graphite on the side of these rods and basal planes at the ends of these rods. Some of the rods seem to be quite smooth (large degree of graphite basal planes were visible), while most of them seem to have very rough side surface (large amount of graphite edge planes and surface defects were visible). It appears that the edge planes were oriented under $90^\circ$ to the axle exposing themselves on the side of the rod, so that the ends of this nanorod were formed from the basal plane of graphite. From the SEM images, we may conclude that the SCNRs have “dual” orientation and a very high ratio of exposed edge planes of the graphite. These images confirm the results of earlier Raman spectroscopy studies of these SCNR materials [12]. Observed properties should make this material more electroactive while the existence of exposed edge planes and large number of crystal lattice defects increases the charge transfer speed between the SCNR and a reacting substance.

Three different SCNR paste electrodes were prepared containing 0, 10, and 20% (w/w) PB. total content of solid substances in the paste electrodes was always kept close to 70% (w/w) as it was found to be optimal in a previous study [12]. The reduction and speedup of the $\text{H}_2\text{O}_2$ reduction process was the most intensive at 10% (w/w) PB-modified SCNR paste electrode when $\text{H}_2\text{O}_2$ and $\text{H}_2\text{O}_2^+$ reduction processes overlap. When the SCNR paste electrode containing 20% (w/w) PB-modified SCNR paste electrode was studied, a small reduction peak of $\text{H}_2\text{O}_2$ forms with a peak potential $-1.2 \text{~V versus Ag/AgCl (3 M NaCl)}$ ($v = 50 \text{ mV/s}$). Due to the presence of PB on the SCNR the overpotential of $\text{H}_2\text{O}_2$ reduction decreased by 60 mV compared to unmodified SCNR paste electrode. At a more cathodic potentials than $-1.4 \text{~V}$ the $\text{H}_2\text{O}_2^+$ cations started to reduce. Sensitivity of the 20% PB-containing SCNR paste electrode to the hydrogen peroxide in the concentration range from 0.0010 to 0.010 M was $37 \text{ mA/(M cm}^2\text{)}$ ($v = 50 \text{ mV/s}$). This is in the same range as found by us for unmodified SCNR paste electrode ($50 \text{ mA/(M cm}^2\text{)}$) [12] or by Ricci and Palleschi ($45 \text{ mA/(M cm}^2\text{)}$) for PB-modified carbon paste electrode [22]. Along with this data and that of electrode kinetics, such results indicate no real advantage of the SCNR over that of graphite.

Acknowledgments

The authors thank Estonian Science Foundation (Grant no. GLOKT 8172) and Estonian Target Financial Project SF0180002s08 for their support.

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