Electrochemical purification of carbon nanotube electrodes

Aránzazu Heras a, Alvaro Colina a, Jesús López-Palacios a, Paola Ayala b, Jani Sainio c, Virginia Ruiz c,*, Esko I. Kauppinen c, d

a Dept. de Química, Universidad de Burgos, Pza. Misael Bañuelos s/n, E-09001, Burgos, Spain
b Fakultät für Physik, Universität Wien, Strudlhofgasse 4, A-1090, Wien, Austria
b Dept. of Applied Physics, Helsinki University of Technology, P.O.Box 5100, FI-02015 Espoo, Finland
c VTT Biotechnology, P.O. Box 1000, FI-02044 VTT, Finland

A R T I C L E   I N F O

Article history:
Received 12 May 2009
Received in revised form 26 May 2009
Accepted 27 May 2009
Available online 6 June 2009

Keywords:
Single-walled carbon nanotubes
Electrochemical purification
Optically transparent electrodes
Spectroelectrochemistry

A B S T R A C T

We present a fast and effective electrochemical method to purify random networks of single-walled carbon nanotubes (SWCNTs) that leads to total removal of metal catalyst without apparent detrimental effect on the electrochemical properties of the electrodes. The efficiency of the electrochemical purification has been compared with that of conventional chemical purification (acid washing). The disappearance of the peaks corresponding to the electrochemical redox reactions of iron during electrochemical purification evidences removal of iron impurities. The efficiency of electrochemical cleaning is further corroborated by cyclic voltammetry (CV) of an iron-sensitive electrochemical reaction, hydrazine oxidation. X-ray photoelectron spectroscopy also indicates that no iron can be detected after electrochemical purification whereas some iron is still left after acid washing. Moreover, Raman spectroscopy reveals higher degree of SWCNT damage after chemical purification compared to the electrochemical one. Electrochemically purified and pristine SWCNT electrodes exhibit similar conductivity, electrochemistry and performance as optically transparent electrodes for an iron-insensitive redox probe, Ru(bipy)3 2+.

1. Introduction

Carbon nanotube (CNT) electrodes continue to receive considerable attention in electrochemistry due to their low electrical resistance, high accessible surface area, chemical stability and enhanced sensing properties [1,2]. However, a correct assessment of the performance of CNT electrodes requires high purity samples as the electrochemical properties of CNTs are strongly sensitive to the presence of metallic impurities. CNT purity is particularly critical for applications in electrocatalysis and electroanalysis, for it has been shown that the presence of metallic impurities even at trace level can dominate the electrochemical response of the CNTs [3–6], leading to misplaced claims about the superior intrinsic electrocatalytic properties of CNTs. In particular, it has been shown that residual iron impurities are responsible for the electrocatalytic activity associated with CNT electrodes toward the electrochemical reactions of important analytes in electroanalytical sensing such as the reduction of hydrogen peroxide [4,5] and oxidation of hydrazine [3,5].

Considerable progress in the purification of CNTs has been made and a number of purification methods have been proposed, including both chemical oxidation and physical separation (for a recent review on CNT purification, see [7]). So far chemical oxidation treatments, in particular direct washing of CNT electrodes with strong mineral acid have failed to remove metal impurities completely, even after prolonged treatment [8] and using high temperatures [9]. Likewise, the combination of electrochemical oxidation of SWCNT electrodes in basic solutions followed by acid washing leaves residual metal catalyst [10].

Here, we will compare the efficiency of chemical and electrochemical oxidation to eliminate metal impurities from optically transparent electrodes consisting of polyethylene terephthalate (PET) supported random networks of SWCNTs grown by aerosol chemical vapour deposition (CVD). As-grown SWCNT electrodes contain iron nanoparticles (typically <5 at.%) arising from ferrocene used as catalyst for SWCNT growth [11]. We will show that complete removal of iron impurities without apparent changes in the electrochemical properties of SWCNT films can be achieved very quickly by electrochemical stripping in mild conditions.

2. Experimental

2.1. Reagents and materials

Ru(bipy)3 2+ Cl2·6H2O (Acros Organics), HNO3, KNO3 and hydrazine (Merck) were used as received. Aqueous solutions were prepared using high-quality water (MilliQ gradient A10 system, Millipore).
SWCNT growth and preparation of the SWCNT/PET electrodes has been described in detail elsewhere \cite{11,12}.

2.2. Instrumentation

All electrochemical measurements were carried out with a PGSTAT20 potentiostat (Eco Chemie B.V.) in three-electrode arrangement using SWCNT/PET working electrodes, a Pt wire counter electrode and Ag/AgCl reference electrode. The set-up for the spectroelectrochemical measurements has been described in detail elsewhere \cite{12}.

X-ray photoelectron spectroscopy (XPS) was carried out with a Surface Science Instruments SSX-100 ESCA spectrometer using monochromatic Al Kα X-rays (1486.6 eV) in a vacuum chamber with a base pressure of about 10^{-9} mbar. Core-level spectra were recorded with a pass energy of 60 eV and a 600 μm X-ray spot size. Charge compensation with a flood gun was utilized to avoid charging of the PET support. The binding energy scale was referenced to the characteristic carbon 1s binding energy of 284.4 eV. Raman spectra were recorded in a Bruker FT-Raman spectrometer with an excitation energy of 1.16 eV using a constant 40mW laser power.

3. Results and discussion

3.1. Efficiency of the different purification methods

The recently developed press-transfer method represents a very simple, fast and reproducible strategy to prepare SWCNT/PET electrodes from SWCNT films collected directly from the gas phase of a laminar flow aerosol reactor by filtering through nitrocellulose filters. Despite its simplicity compared to methods involving SWCNT dispersions, the direct use of as-grown SWCNTs has the drawback that some iron from the catalyst precursor (ferrocene) is unavoidably present in the films. This makes essential the development of a post-assembly purification method to remove fully metallic impurities while preserving the properties of the SWCNT electrode. The amount of iron occluded in the SWCNT films can vary with the experimental conditions in the reactor. Here, we have intentionally selected three films with different thickness/opacity (Films 1 and 3 with 40%T and Film 2 with 80%T) and iron content (with Fe content decreasing in the following order: F1 ≫ F2 > F3) to demonstrate the applicability of the electrochemical purification method and compare it with the widely used chemical oxidation route \cite{3–8}. Chemical purification was done by immersing the SWCNT/PET electrode in stirred 2 M HNO₃ solution for 24 h at room temperature. Electrochemical purification was performed by cycling the SWCNT/PET electrode potential between −0.10 V and +0.60 V (a potential well below the onset of SWCNT oxidation) at 0.02 Vs⁻¹ in 1 M HNO₃. The total number of cycles required for complete iron removal varies with the metallic content and film thickness. Deliberately, the selected films cover a wide range of optical transparency values (40–80%) at 550 nm) characteristic of optically transparent electrodes (OTEs) in order to investigate the duration of the electrochemical cleaning. As an indication of the maximum duration, 10 potential cycles (700 s at 0.02 Vs⁻¹) were needed for the most opaque film investigated, F1, which has the highest iron content and a transparency (40%)T) well below typical values for OTEs.

Fig. 1a shows the first voltammetric scan for the three films in the cleaning solution (a zoom of CVs for F2 and F3 is displayed in the inset). A first anodic peak at around +0.12 V is observed only in the first cycle for all films, which can be assigned to the stripping of encapsulated iron nanoparticles from SWCNTs. The stripping current scales with the amount of iron in the SWCNT film. The reversible pair of peaks at +0.57 V and +0.47 V can be attributed to oxidation and subsequent reduction of the Fe(II)/Fe(III) ions stripped off the SWCNTs at around +0.10 V. The intensity of Fe(II)/Fe(III) peaks decreases gradually with the number of cleaning cycles, as shown in Fig. 1b for F1. These peaks are clearly observed only in thick films and hence are most likely related to the slow diffusion of Fe cations from internal SWCNT layers to the bulk solution. The intensity of the peaks corresponding to electrochemical redox reactions of iron impurities is indicative of the extent of metallic impurity removal and therefore enable determining in situ the end of the electrochemical purification, which represents an additional advantage of the method. Thus, the following cycles were required for each film: 10 (F1), 5 (F2) and 1 (F3). However, stripped iron in solution contributes to these peaks, as evidenced by the further current drop observed when the SWCNT electrode was rinsed thoroughly with deionized water and immersed in clean (Fe-free) 1 M HNO₃ solution (dashed-dotted line in Fig. 1b). The negligible currents measured in all cases after electrochemical cleaning (2 orders of magnitude lower than for the...
pristine film) indicate that no detectable iron is present in any of the SWCNT films (above the detection limit of cyclic voltammetry).

Additional evidence of total iron removal was obtained by XPS. Iron, carbon and oxygen regions were measured and results are shown for the film with the highest initial metallic content, F1. Fig. 2a shows Fe 2p photoelectron regions for SWCNT/PET electrodes prepared from sections of F1 that were purified with different methods (chemical, electrochemical and a combined chemical-electrochemical treatment) and for the pristine film. Iron in the pristine film (4 at.%) is mostly in metallic form, which further supports the mechanism suggested above that Fe removal is based on Fe stripping followed by diffusion of Fe cations from film into solution. After chemical purification, some iron (1 at.%) is still visible in the spectra whereas no iron is detected above the noise level after treatments including one electrochemical step. From the Fe/C ratios, it can be concluded that chemical purification removes ~80% of iron but treatments including an electrochemical cleaning step remove more than 95% of iron (this limit has been evaluated from the noise level).

The complete removal of iron impurities from electrochemically purified SWCNT films was further corroborated by CV in solutions of an iron-sensitive electrochemical probe, hydrazine. As surface metal oxides are known to play a role in the electrocatalytic oxidation of hydrazine, this reaction has been previously used to interrogate the content of metal impurities in CNT electrodes [3,13].

![Fig. 2](image-url)

**Fig. 2.** (a) Fe 2p photoelectron regions for a 40%T-SWCNT/PET pre- and post-treated using chemical (C), electrochemical (E) and combined chemical–electrochemical (C–E) purification. (b) Linear sweep voltammetry for a 40%T-SWCNT/PET electrode pre- (solid) and post-electrochemical purification (dotted line) in 6.9 mM Ru(bipy)₃²⁻ and 0.2 M KNO₃, 0.02 Vs⁻¹.

![Fig. 3](image-url)

**Fig. 3.** (a) Normalized Raman spectra for a 40%T-SWCNT/PET film pre- and post-treated using chemical (C), electrochemical (E) and combined chemical–electrochemical (C–E) purification. (b) CV for a 40%T-SWCNT/PET electrode pre- (solid) and post-electrochemical purification (dotted line) in 6.9 mM Ru(bipy)₃²⁻ and 0.2 M KNO₃, 0.02 Vs⁻¹.
Fig. 2b shows linear sweep voltammetry for F1 pre- and post-electrochemical purification in a phosphate buffer solution (pH 6.9) containing 6.4 mM hydrazine. A considerable decrease in hydrazine oxidation current was observed as a result of the electrochemical purification that, together with XPS data and CV in 1 M HNO₃, supports the conclusion that no iron is left after the electrochemical purification above the detection limit of the respective technique.

3.2. Impact of the purification methods on the SWCNT/PET electrodes

In order to gain deeper insight into morphological changes caused by each purification method, Raman spectroscopy was conducted on pristine and purified SWCNT films using electrochemical, chemical and combined chemical-electrochemical treatments (Fig. 3a). The increase of the D band in the Raman spectra illustrates the degree of deterioration of films subjected to different purification treatments [14]. The slight change observed for electrochemically purified films indicates that SWCNTs preserve their morphology. In contrast, spectra corresponding to treatments including one chemical step exhibit an increase of the D mode. Besides the slight increase of D/G ratio with this sampling laser wavelength, the intensity of the Raman response normalized by the laser power is half that of the pristine film, which evidences the destruction of SWCNTs by the chemical purification step.

Finally, the electrochemical performance of purified SWCNT electrodes was evaluated using a reversible redox system, Ru(bipy)_3^{3+/2+}. Fig. 3b shows CV in 6.9 mM Ru(bipy)_3^{3+/2+} solution for a SWCNT electrode with very low initial iron content pre- and post-electrochemical purification. A quasi-reversible behaviour (∆E_p = 0.10 V) and comparable peak currents were observed for both films, indicating that no apparent changes in the electrical and electrochemical properties of the SWCNT electrode were noted as a result of the electrochemical treatment. This is also corroborated by Electrochemical Impedance Spectroscopy (EIS). Moreover, the performance of purified films as OTEs was equally unaffected as no differences were noted in the spectroelectrochemical response of Ru(bipy)_3^{3+/2+} at pristine and electrochemically purified SWCNT electrodes (data not shown as is identical to previously reported for untreated SWCNT/PET electrodes [12]). Further work is currently in progress to make the method extensive to CNT electrodes modified with sensitive biomaterials, for instance using higher pH solutions compatible with the modifier.

4. Conclusions

We have demonstrated that electrochemical purification is an advantageous alternative to the commonly used acid washing for removal of metallic impurities from SWCNT electrodes. Electrochemical purification is considerably faster, more efficient and less destructive for the SWCNVs, although it cannot be regarded as a large-scale purification method. The validity of the method has been demonstrated using SWCNT films with typical thickness/ transparency values for OTEs. The possibility to follow in situ in real time the disappearance of the redox peaks of iron impurities enables using milder conditions, which contribute to reduce the extent of SWCNT oxidation and damage. Thus, electrochemically purified SWCNT electrodes exhibit identical electrochemistry and spectroelectrochemistry for Ru(bipy)_3^{3+/2+} as pristine ones. The method opens a new route for direct cleaning of CNT electrodes that could be implemented as a routine conditioning step prior to electrochemical measurements.

Acknowledgments

We thank Albert G. Nasibulin for supplying SWCNT films. Support from Ministerio de Ciencia e Innovación (MAT2006-13875), Junta de Castilla y León (GR71, BU006A09, BU012A09), COST Action D36 (WG D36-0005-06), Academy of Finland (V.R., Academy Research Fellowship, Nanoduramea and TKK-MIDE CNB-E projects) is acknowledged.

References