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Enhanced electron transfer kinetics through hybrid graphene-carbon nanotube films

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Abstract

We report the first study of the electrochemical reactivity of a graphenated carbon nanotube (g-CNT) film. The electron transfer kinetics of the ferri-ferrocyanide couple were examined for a g-CNT film and compared to the kinetics to standard carbon nanotubes (CNTs). The g-CNT film exhibited much higher catalytic activity, with a heterogeneous electron-transfer rate constant, k^0 , approximately two orders of magnitude higher than for standard CNTs. Scanning electron microscopy and Raman spectroscopy were used to correlate the higher electron transfer kinetics with the higher edge-density of the g-CNT film.

Keywords

Hybrid graphene-carbon nanotubes film; Kinetics; Electron-transfer; Edge planes; Raman spectra

1. Introduction

Electrodes made from various carbon materials are widely used in electrochemical applications. The diversity of carbon materials — graphite, activated carbon, carbon nanotubes (CNTs), graphene — illustrates the unique structures of carbon [1][2][3]. Recent studies have shown how hybrid materials can be used to combine and optimize properties of various carbon forms, as illustrated by graphene-based composites [4][5][6]. Understanding the relationship between structure and electrochemical properties is of particular interest for these hybrid carbon materials and can enable the optimization of their exceptional properties.

In this letter, we report the first study of the electrode kinetics of “graphenated CNTs” (g-CNTs), which consist of multi-walled CNTs with perpendicularly -oriented foliates growing

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from the sidewalls of the CNTs. Previously, we reported on the growth and characterization of this material [7][8][9]. Other groups have reported on CNT-graphene structures that share similarities with the present material [10][11][12][13], but have not examined the electron transfer kinetic properties of these hybrid materials for electrode applications. Herein, the electrode kinetics of g-CNTs are compared to that of CNTs. The integrated graphene-CNT structure of g-CNTs has the fundamental advantage of combining the high surface area and three-dimensional framework of CNTs with the high edge-density graphene. This is of particular interest given the high charge density and reactivity of graphene edges compared to that of the basal plane of graphene. As previously reported for pyrolytic graphite [14], the edge plane typically shows faster electron transfer (ET) kinetics than the basal plane. Recent studies involving measurements on single layer graphene [15][16] showed that its interfacial double-layer capacitance is limited by the quantum capacitance of the material, highlighting the influence of the low density of states (DOS) of the basal orientation of graphene-based materials.

Although standard CNTs expose mostly basal planes, they have been reported to exhibit fast ET for various electrochemical systems [17][18][19][20]. Banks et al. [21] suggested this was due to the presence of edge-plane-like defects in the CNTs. Correspondingly, the high edge density in graphenated CNTs should provide even faster ET kinetics. To evaluate this hypothesis, we have compared the ferri-ferrocyanide couple ($[\text{Fe}(\text{CN})_6]^{3-}/[\text{Fe}(\text{CN})_6]^{4-}$) on g-CNTs and CNTs.

2. Material and methods

2.1. CNT film growth

CNTs and g-CNTs were grown using a 915 MHz microwave plasma enhanced chemical vapor deposition (MPECVD) system (see [22] and [8] for details on the PECVD growth system and the growth of the g-CNTs, respectively.) Briefly, the films were grown on silicon substrates with 50 Å Fe catalyst. Substrates were preheated to the deposition temperature in 100 sccm NH_3 . The plasma was then ignited and stabilized at 21 torr at 2.15 kW magnetron input power. The substrates were subsequently pretreated for several minutes in the ammonia plasma to form nanoparticles by dewetting the Fe catalyst film. The gas flow was then changed to 150 sccm CH_4 and 50 sccm NH_3 for the deposition. The graphene and CNT formed simultaneously during the growth process.

2.2. Materials characterization

Raman spectroscopy was performed with a Horiba Jobin Yvon LabRam ARAMIS system operating with a 633 nm HeNe laser. The details of the calculation of the ratio of the D and G band intensities and of the nanocrystalline domain size are described elsewhere [23]. Scanning electron microscopy (SEM) was performed using a FEI XL30 SEM-FEG.

2.3. Electrochemical measurements

Electrochemical experiments [cyclic voltammetry (CV), linear sweep voltammetry (LSV), electro-impedance spectroscopy (EIS)] were performed in a three-terminal cell using a SP-300 potentiostat (BioLogic Science Instruments). A carbon nanotube or graphenated

carbon nanotube sample served as the working electrode, both samples having the same nominal area. The counter electrode was a platinum mesh. The reference electrode was a KCl-saturated Ag/AgCl electrode. Details on the cell are given elsewhere [24]. For the CV experiments, the ohmic drop was compensated by the potentiostat. A Tafel-type fit using EC-lab software was used to calculate the exchange current density.

2.4. Chemical reagents

Potassium hexacyanoferrate(II) trihydrate ($K_4[Fe(CN)_6] \cdot 3H_2O$) (purchased from Alfa Aesar) and potassium chloride (KCl) (purchased from VWR) were used to prepare the electrolyte, a solution of 5 mM ferrocyanide in 0.1 M KCl.

3. Results and Discussion

3.1. Morphology

SEM images of the standard CNTs and g-CNTs are displayed in Fig. 1. As seen in Fig. 1a and 1b, the standard CNTs have a uniform height of approximately 10 μm . The tube diameter is approximately 50 nm. Images of g-CNTs are displayed in Fig. 1c and 1d. Their height is approximately 15 μm but extends up to 30 μm for some tubes. The tubes are significantly thicker than the standard CNTs, with diameters from 200–300 nm. The g-CNTs are comprised of a high density of graphene foliates. The inset in Fig. 1d is a transmission electron microscopy (TEM) image of a foliate, showing its multi-layer graphene structure.

3.2. Electrode kinetics: Voltammetry

CV curves for both CNT and g-CNT electrodes in 0.1 M KCl containing 5 mM ferrocyanide are provided in Fig. 2. Fig. 2a is a comparison of the CV response of CNTs and g-CNTs for a scan rate of 100 mV/s. The anodic and cathodic peaks associated with the oxidation and reduction of the ferri-ferrocyanide couple are visible at both electrodes and marked with dashed lines. In order to allow for easy comparison of the different CV curves, the currents are normalized to the anodic peak current. It is clear from the CV curves that the peak potential separation (E_p) is significantly larger in the case of CNTs compared to g-CNTs (e.g., at a sweep rate of 100 mV/s, E_p is 66 mV for g-CNTs and 376 mV for CNTs). Thus, the g-CNTs exhibit a reversible behavior (i.e. $E_p = 59$ mV [25]) at low sweep rates, up to approximately 50 mV/s. This indicates much faster electron transfer kinetics for the g-CNTs.

To calculate the standard electrochemical rate constant, k_0 , we utilized the method proposed by Nicholson [26], which is applicable to quasi-reversible systems. Both samples exhibit the characteristics of quasi-reversibility [25] as shown in the CV curves at sweep rates of 10 and 500 mV/s for CNTs and g-CNTs in Fig. 2b and 2c, respectively. In particular, above a certain sweep rate, E_p is larger than 59 mV, which is the value expected for a one-electron transfer reaction that has a purely Nernstian behavior. Additionally, E_p increases with faster sweep rates. Thus, we can use the empirical method proposed by Nicholson to estimate the rate constant, k^0 , using the parameter Ψ which is associated with E_p , and is proportional to k^0 . Ψ is defined as:

$$\Psi = [(D_O/D_R)^{(\alpha/2)k_0}] / [(D_O \pi \nu F / (R T))^{0.5}] \quad [26]$$

where D_O and D_R are the diffusion coefficients of $[\text{Fe}(\text{CN})_6]^{3-}$ and $[\text{Fe}(\text{CN})_6]^{4-}$, α is the transfer coefficient, ν is the sweep rate, F is the Faraday constant and T is the temperature ($T = 295 \text{ K}$). The diffusion coefficients of $[\text{Fe}(\text{CN})_6]^{3-}$ (D_O) and $[\text{Fe}(\text{CN})_6]^{4-}$ (D_R) were taken equal to $D_O = 7.2 \times 10^{-6} \text{ cm}^2/\text{s}$ [27]. Ψ was calculated using a fitting function [28]. k_0 was calculated for scan rates where E_p was over 65 mV, given the low precision of the method for small E_p . The average values of k_0 for CNTs and g-CNTs were calculated to be $4.92 \times 10^{-4} \pm 2.5 \times 10^{-4} \text{ cm/s}$ and $231 \times 10^{-4} \pm 108 \times 10^{-4} \text{ cm/s}$, respectively. The standard rate constant is therefore approximately two orders of magnitude higher for g-CNTs compared to CNTs, indicating much faster electron transfer kinetics for g-CNTs.

3.3. Electrode Kinetics: Polarization Curves

Fig. 3 shows polarization curves for CNTs and g-CNTs, recorded at a scan rate of 5 mV/s. The current is normalized to the electrode nominal area. As seen in the figure, g-CNTs exhibit a lower reversible potential than CNTs, by approximately 65 mV. The exchange current density estimated from the curves is approximately $3 \mu\text{A}/\text{cm}^2$ and $9 \mu\text{A}/\text{cm}^2$ for CNTs and g-CNTs, respectively. Both the higher exchange current and lower reversible potential are indicative of faster electron transfer for the g-CNTs. These results are also consistent with electrochemical impedance spectroscopy (not shown) that indicated charge transfer resistances of 218 ohm and 618 ohm for the g-CNTs and CNTs, respectively.

3.4. Correlating edge density and electrode kinetics

The faster kinetics for the g-CNTs can be linked to the higher density of defects and edges for this material. The I_D/I_G ratio of the samples was calculated from Raman spectroscopy using deconvolved peaks, as described elsewhere [23]. This ratio is proportional to the nanocrystalline domain size [29] and is therefore correlated with the edge density. The lower nanocrystalline domain size of g-CNTs measured by the Raman spectroscopy indicates a smaller spacing between edges, which is consistent with the high foliate density of the material as seen in the SEM. This is summarized in Table I along with the primary parameters relevant to the study of the electron transfer rate for the two materials. This data highlights the correlation between the high edge density of g-CNTs with their fast electron transfer kinetics. This confirms the view that graphenated CNTs are a high edge density 3D material that exhibits enhanced electrode kinetics and of use as a potential catalyst.

It should be noted that electrode porosity can also influence the apparent kinetics, with a higher porosity leading to a smaller interpeak distance. However, estimating the magnitude of this effect from the literature, it is expected to account for only ten percent of the interpeak distance difference observed in the present work. Thus, the surface properties determined by the concentration of edges are expected to play the dominant role in the observed difference in kinetics.

Considering the high DOS of graphene edges and the reactivity of the unsaturated carbon bonds comprising the edges, the different surface electronic structures between CNTs and g-

CNTs could be responsible for the different ET kinetics on the electrodes. The specific mechanisms underlying the differences between CNTs and g-CNTs are not yet identified. There has been some evidence in the literature that oxygenation can impact the ferri-ferrocyanide couple [30][34]. Thus, different rates of oxygenation between the two materials may be a root cause of these differences. Further studies are underway in our laboratory to investigate the mechanisms responsible for the different ET kinetics.

4. Conclusions

In summary, using the ferri-ferrocyanide couple, we report the first study of the electron transfer kinetics of g-CNTs. Electrochemical measurements showed that the kinetics of g-CNTs are much faster than CNTs. The calculated heterogeneous electron-transfer rate constant k^0 is approximately two orders of magnitude higher for g-CNTs than for CNTs. Materials characterization techniques (Raman spectroscopy, scanning electron microscopy) were used to show the high-edge density of g-CNTs compared to CNTs. This high-edge density is correlated to the faster kinetics of the g-CNTs, with the particular mechanism responsible for the different kinetics still under investigation.

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Highlights

- Hybrid graphene-carbon nanotubes (g-CNT) films exhibit much higher catalytic activity than standard carbon nanotubes
- g-CNTs have a higher edge-density than CNTs
- The faster kinetics at g-CNTs can be correlated to their higher edge-density

Figure 1. Scanning electron microscopy (SEM) images. (a) and (b) Carbon nanotubes (CNTs). (c) and (d) Graphenated carbon nanotubes (g-CNTs). The bright features shown in (d) are carbon edges comprised of few-layered graphene as shown in the inset (TEM image).

Figure 2.

Cyclic voltammograms in a 5 mM ferrocyanide/0.1 M KCl solution. (a) Comparison of the cyclic voltammetric response of CNTs (dashed line) and g-CNTs (solid line) for a sweep rate of 100 mV/s. (b) and (c) Cyclic voltammetric response at sweep rates of 10 and 500 mV/s for CNTs and g-CNTs, respectively.

Figure 3. Polarization curves of the CNTs (dashed line) and g-CNTs (solid line) obtained in a solution of 5 mM ferrocyanide/0.1 M KCl. The potential (E) was swept at a rate of 5 mV/s.

Summary of the parameters that indicate the higher reactivity of the g-CNTs compared to CNTs, and the correlation with edge defects, including: Interpeak distance (E_p), electron transferrate constant (k_0), exchange current densities (j_0), I_D/I_G ratio, and nanocrystalline domain size of the carbon nanotubes (CNTs) and graphenated carbon nanotubes (g-CNTs).

Table 1

	E_p^a (mV)	$k_0 \times 10^4$ (cm/s)	j_0 (μ A/cm ²)	I_D/I_G	Nanocrystalline domain size ($\text{\AA}$)
CNTs	376	~ 4.9	~ 3	1.26	65.8
g-CNTs	66	~ 231	~ 9	1.84	45.1

^a For a sweep rate of 100 mV/s