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Observations of copper deposition on functionalized carbon nanotube films☆

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ABSTRACT

This research details the spontaneous electroless and electrodeposition of copper onto carbon nanotube (CNT) film from a copper sulfate electrolyte. Inhomogeneous electrodeposition was found to occur on pristine CNT film due to differences in available active nucleation sites and the hydrophobic nature of the film. In order to improve the electrochemical response of CNT films, oxidative pre-treatments such as heat treatment and anodization were investigated. These treatments were shown to increase the amount of oxygen containing defects at the surface of CNT film material. Incorporation of functional groups were shown to enhance the wetting of the aqueous electrolyte and created a highly active surface suitable for homogenous electrodeposit. Cathodic polarization curves showed that the presence of functional groups decreased the required level of polarization for copper deposition. Nevertheless, after a certain level of functionalization the polarization starts to decrease due to increased resistivity of the CNT film. Oxygen grafted CNT films were also shown to exhibit enhanced adsorption and reduction of copper without applied voltage due to redox replacement reactions, which were observed to increase with enhanced levels of functionalization.

1. Introduction

Carbon nanotubes (CNTs) used as reinforcements in composite materials have been the subject of significant research due to their unique mechanical, thermal and electrical properties. Composites formed of carbon nanotubes and metals have shown both enhanced mechanical and electrical properties including improved strength and stiffness [1] and ampacity [2]. There are a multitude of methods related to CNT-metal composite production, such as sintering [3], molten metal infiltration [4], casting, as well as electroless [5–7] and electrodeposition [8–13]. Electrodeposition is a commonly used CNT-metal composite production method that has been applied to both CNTs dispersed in the electrolyte [10,12] and with deposition directly onto CNT substrates [8,9,11,13]. Recently, electrodeposition of copper on planar CNT sheets has been reported with the resulting composite exhibiting increased specific conductivity, current carrying capacity and lifetime at elevated temperatures [13].

It has been noted that deposition of metal occurs preferentially at CNT surface defects [14,15], leading to inhomogeneous nucleation on CNTs, an effect that can be attributed to the low reactivity of pristine CNT material. A commonly used approach to make CNT material more reactive is to functionalize the surface with reactive groups via methods that include esterification, use of ionic liquids or oxidation [16]. Functionalization also improves the dispersion of CNTs in liquids while grafting groups such as atomic oxygen (-O), hydroxyl (—OH) and carboxyl (—COOH) [10,17,18]. Such treatments have a direct effect on the interfacial bonding between CNTs and metals that play an important role in determining the mechanical and electrical properties of the resulting composite [19]. Theoretical calculations have also shown that oxygen containing functional groups promote adsorption, nucleation and electron exchange between CNTs and Cu [20,21]. Nevertheless, the rationale for the use of one oxidation treatment rather than another is often not thoroughly explained and the degree of functionalization achieved is rarely related to the resultant electrochemical activity of the CNT material. Furthermore, although there have been numerous studies on the

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electrochemical deposition of copper on different carbon materials including carbon fiber [22], pyrolytic graphite [23], glassy carbon [24] and carbon nanotube fibers [9] the extent of the surface functionalization is rarely taken into consideration. As a consequence, the aim of this study was to observe how the reactivity of aligned carbon nanotube films can be adjusted through the use of different oxidation pre-treatments for copper deposition in copper sulfate electrolytes. The degree of functionalization was related to the formation of copper particles at the film surface after spontaneous electroless and electrodeposition of copper.

2. Experimental

CNT film consisting of axially oriented single- (SWNT), double- (DWNT) and multi-walled (MWNT) CNTs was drawn continuously from an aerogel onto a spinning winder as has been reported earlier [25]. The film specific surface area is about 200 m^2/g and the film consists >80% of MWNTs. CNT film samples were cut with a surgical blade into rectangle shapes with dimensions of approximately 10 mm x 25 mm. Film samples were then attached with glue (Hybrid Glue, Loctite) to a rigid frame made of PVC and electrical contact to a copper sheet was realized with a silver paste (42469, Alfa Aesar) to ensure that current could be passed to the film (Fig. 1).

Two different functionalization treatments were investigated, anodization and heat treatment. Anodization pre-treatments of CNT film prior to electrodeposition were performed under ambient conditions at potentials between 1.0 and 2.4 V vs. saturated calomel electrode (SCE) in 1 M H_2SO_4 for 60 seconds with the setup shown in Fig. 1 using a platinum counter electrode (CE) instead of copper CE. Heat treatments of the CNT films were performed with a Scandia Oven K4/PDI 40 at 400 °C, 450 °C and 500 °C in a steady oxygen flow of 150 SCCM for 20–60 minutes prior to the attachment of the film samples to the sample holder. Electrochemical deposition, polarization measurements and anodization of carbon nanotube film were performed with an Autolab 30 potentiostat, equipped with a three-electrode system (working electrode (WE) – CNT film; counter electrode (CE) – copper sheet (platinum for anodization) and reference electrode (RE) – SCE). Electrodeposition was carried out in an electrolyte containing 0.6 M $CuSO_4{}^*5H_2O$ and 0.9 M H_2SO_4 in ambient conditions.

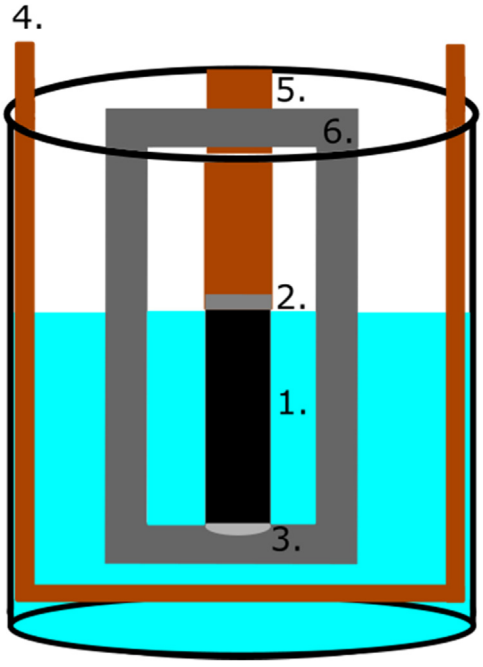

Fig. 1. Schematic drawing of the experimental setup consisting of (1) CNT film, (2) silver paste electrical contact, (3) glue, (4) Copper sheet, (5) Copper conductor sheet, and (6) PVC sample holder.

Characterization of the samples was conducted with scanning electron microscopy (SEM) in secondary electron (SE) and back-scattered electron (BSE) modes. SEM micrographs were taken with a Mira[3] and LEO 1450 VP and EDX- analysis was performed with a LEO 1450 VP attached with Oxford Instruments INCA analyzer. Analysis of copper weight percentages after immersion tests at the film surface were conducted on thoroughly DI-water rinsed samples from areas of approximately 100 μm x 100 μm, representing the typical surface morphology i.e. where no large copper particles (over 5 μm) could be observed. This was done in order to ensure that the results would be comparable and represented typical film surfaces.

Raman spectroscopy was performed with LabRAM HR UV-NIR (red excitation wavelength, λ = 633 nm) to observe changes in nanotube sidewalls i.e. the level of functionalization. Raman spectra were baseline corrected and curve fitted with the Gaussian-Lorentzian function. The reported Raman I_D/I_G-values are intensity height ratio averages of five measurements across the surface of a film sample.

In addition to electrodeposition tests, immersion tests were carried out to eliminate the effect of applied voltage by immersing the film samples in the same electrolyte used for electrodeposition for 48 hours in ambient conditions. After immersion the samples were cleaned by rinsing with DI water for 10 minutes. In this way the difference in adsorption-reduction behavior of functionalized CNT films could be determined.

3. Results and discussion

The surface features of the CNT films were studied by SEM. Fig. 2a shows the surface of a pristine i.e. “as-spun” CNT film and as can be seen the presence of extraneous carbon material leads to the formation of distinctive micron/submicron scale features of on the CNT film surface. The level of oxidation was measured by Raman Spectroscopy, which has been shown to give accurate results in terms of oxidation degree [26–28]. The Raman spectra of nanotubes exhibit two characteristic band regions, one centered at around 1350 cm^{-1} (D-band) and the other at 1590 cm^{-1} (G-band) and the intensity ratio of these bands can be used to estimate the level of functionalization i.e. the quality of CNT material [26–29]. The G-band is related to the sp^2 graphene structure of the carbon atoms at the nanotube sidewall, while the D-band is caused by the presence of sp^3 carbon atoms either at defect sites on the nanotube wall or amorphous carbon. When functionalizing CNT material there are two processes that affect this ratio, the removal of amorphous carbon by oxidation and the grafting of oxygen containing groups onto defective sites. From the I_D/I_G-ratio of 0.14 it can be stated that the CNT film quality is high with a low number of defects or functional groups at the nanotube surfaces. A mild functionalization of the CNT film by heat treatment (20 minutes at 450 °C) resulted in a noticeable change at the surface; the amorphous carbon particles were largely removed, Fig. 2a. Similarly, the decontamination by removal of amorphous carbon particles from the film surface was evident with all functionalization treatments used and is in line with previous observations in the literature [26–28].

The change in Raman I_D/I_G-ratio by various heat treatments and anodization processes is shown in Fig. 3. Heat treatment time was 1 hour and anodization was carried out for 60 seconds at potentials measured vs. SCE. Fig. 3a shows the change in I_D/I_G-ratios from pristine to highly functionalized CNT film and it can be seen that the level of functionalization achieved was higher with all