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Functionalization of super-aligned carbon nanotube film using hydrogen peroxide solution and its application in copper electrodeposition

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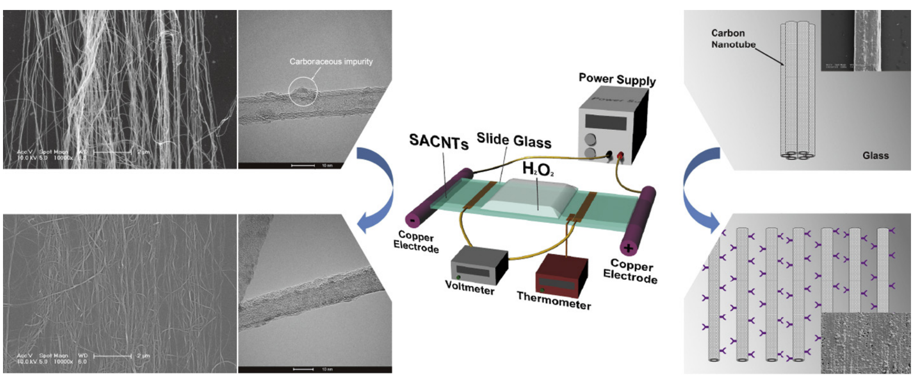

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In order to make super-aligned carbon nanotubes (SACNT) homogeneously spread in electrolytes, a swift and effective method was devised for surface functionalization of SACNT film by ohmic heating using hydrogen peroxide solution. Controllable generation of defects and notable graft of oxygen functional groups on the sidewall of SACNTs were induced as proven by X-ray photoelectron spectroscopy and Raman spectroscopy. Differently from the harsh wet chemical oxidation, the super-aligned morphology and structural integrity of carbon nanotubes in the SACNT film were found to be well preserved by electron microscopy analysis. The functionalized treatment can remove extraneous material contaminating SACNT film and improve its conductivity. The grafting of polar ionizable groups has been proved to effectively eliminate the agglomeration of SACNTs. When the oxidized SACNT film was used as host material for electrodeposition of copper, the composite film of well-bonded SACNTs and Cu was successfully prepared.

1. Introduction

Ever since the discovery of the exceptional mechanical, thermal, and electrical properties of carbon nanotubes (CNTs) [1], the research community have demonstrated many promising applications to exploit these features [2,3]. In particular, the scientific interest has been focused on exploring their potential as filling and reinforcing nanoparticles in polymer, ceramic and metal matrix composites [4–8]. The desired property improvement can only be achieved if CNTs are finely dispersed within the matrix and bond to it. However, their highly non-polar structure makes

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CNTs incompatible with most of the common matrixes or solvents. Serious agglomeration caused by strong inter-tube Van der Waals forces remains problematic. Therefore, a swift and effective functionalization of CNTs is a prerequisite for their successful application in composites. Various methods have been developed to modify their surface and to tackle this problem. The mainstream strategies to achieve this goal rely on the oxidation of CNTs, which equips them with a variety of oxygen functional groups. Such modification often involves subjecting CNTs to various conditions such as concentrated acids e.g. H_2SO_4 and/or HNO_3 [9,10], UV light [11], ozone and water mixture [12], or oxygen at high temperature [13]. Although profound changes have been achieved, these oxidation methods have some disadvantages, e.g., high temperature required, high cost, complexity of the operation process, or environmental pollution. More importantly, owing to strong oxidants and harsh conditions, severe fragmentation of CNTs structure and massive formation of defects take place. These damage will undermine excellent physical properties of CNTs, as well as their enhancement effects in the composites. In contrast, dry UV-ozonolysis can increase conductivity and meanwhile maintain the structural integrity of the nanotubes, but the level of oxidation was less than by other modification methods [14]. Since weak points such as defects to the graphitic structures comprising CNTs are the primary site of oxidation with chemical groups, a trade-off between oxidation and physical properties must be made. One of the feasible solutions is to induce controllable generation of defects and maximize the use of them.

Alternatively, hydrogen peroxide (H_2O_2) is a mild, inexpensive and green oxidant. Suzuki et al. utilized H_2O_2 to purify SWCNTs with iron particle as catalyst [15]. Datsyuk et al. studied the effect of oxidation on the structural integrity of multi-walled nanotubes through ammonium hydroxide/hydrogen peroxide mixture [10]. Recently, a novel method has been reported to modify electrical and structural properties of resistively heated CNTs by the action of hydrogen peroxide [16]. Under certain conditions, extraneous material contaminating CNT films was successfully removed and resistance of CNT films was decreased. Nevertheless, the introduced oxygen-functionalized groups and their effect on surface properties have not been fully studied. Additionally, since the CNT films were submerged in aqueous solution of H_2O_2, elevated temperatures created very vigorous conditions, which made the reaction uncontrollable. Accordingly, the oxidation process could not be accomplished sufficiently.

Super-aligned carbon nanotube (SACNT) film [17] is a continuous CNT film with highly oriented structure, in which the axes of CNTs are all lined up in one direction. High quality SACNT reinforced composites can be made only if the SACNTs can homogeneously spread in solvents (especially electrolytes). The aim of this work was to tackle this challenge by surface functionalization.

In the present work, we report a swift oxidation methodology to functionalize the super-aligned carbon nanotubes (SACNTs) on the surface of H_2O_2 solution. By absorbing joule heat, rapid evaporation of the solution can prevent its boiling and thus create a mild reaction environment, which introduces controllable amount of defects·H_2O_2 and water vapor mixture can treat SACNTs over prolonged time to use these defects efficiently and eventually functionalize SACNTs effectively. The variations of SACNT morphology before and after functionalization were observed by electron microscopes. The oxidized SACNTs were characterized by Raman spectroscopy, X-ray photoelectron spectroscopy (XPS). Conductivity of the SACNT film was improved after treatment, which investigated by four-probe measurement. Furthermore, to investigate the effect of the surface functionalization on agglomeration, the oxidized SACNTs were used as host material for electrodeposition of Cu. The agglomeration of SACNTs was effectively eliminated and the composite films of SACNTs and Cu were produced.

2. Materials and methods

2.1. Materials

The pristine super-aligned multi-walled CNT arrays on a silicon wafer were provided by Tsinghua-Foxconn Nanotechnology Research Center. When drawing CNTs from super-aligned CNT arrays, a continuous and super-aligned CNT (SACNT) film could be formed due to the Van der Waals interaction which makes the CNTs join end to end [17,18]. The thickness of the SACNT films was 0.2 μm.

2.2. Functionalization of SACNTs

The setup for the functionalization of SACNTs is schematically shown in Fig. 1. A cover glass was placed on the middle part of a slide glass, and 0.5 ml 30 wt% aqueous solution of H_2O_2 was dripped onto the cover glass. A liquid layer was formed on the entire surface of the cover glass. Owing to the surface tension of H_2O_2 solution, it would not spread to slide glass. A 25 mm × 90 mm SACNT film drawing from SACNT arrays was laid on the surface of the solution. Both ends of the film were attached to rod-like Cu electrodes which were connected to a DC Power Supply (Tradex MPS 1008). In parallel, a thermometer was used to record the temperature of SACNT film beside the cover glass. On the surface of H_2O_2 solution, DC 120 V and 140 V voltages were applied to the SACNT films separately whilst monitoring the temperature of the films. The reaction time varied from 1 to 10 min.

2.3. Characterization

Specimens were coated with a 10 nm thick gold layer and examined in a scanning electron microscopy (FEI Sirion 200). The transmission electron microscopy observations were made on a FEI Tecnai F20 microscopy to probe for the morphological variation of SACNTs and the presence of carbon impurities. The samples for TEM analysis have been prepared by dropping 5 μL of SACNTs alcohol suspension onto copper grids, letting then the solvent dry. Raman spectroscopy (Horiba LabRAM HR, λ = 632.8 nm) was used to investigate nanostructures of the samples by measuring the intensity of defect induced band (D) and the band of vibrations of graphitic structures (G). The XPS experiments were carried out

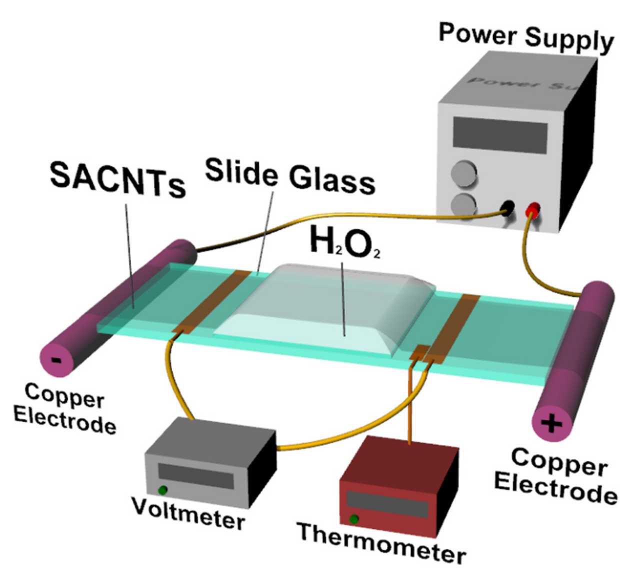

Fig. 1. Schematic diagram of functionalization of SACNTs.