

Upgrading non-oxidized carbon nanotubes by thermally decomposed hydrazine



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ABSTRACT

We found that the electrical properties of conductive thin films based on non-oxidized carbon nanotubes (CNTs) could be further improved when the CNTs consecutively underwent a mild hydrazine adsorption treatment and then a sufficiently effective thermal desorption treatment. We also found that, after several rounds of vapor-phase hydrazine treatments and baking treatments were applied to an inferior single-CNT field-effect transistor device, the device showed improvement in I_{on}/I_{off} ratio and reduction in the extent of gate-sweeping hysteresis. Our experimental results indicate that, even though hydrazine is a well-known reducing agent, the characteristics of our hydrazine-exposed CNT samples subject to certain treatment conditions could become more graphenic than graphanic, suggesting that the improvement in the electrical and electronic properties of CNT samples could be related to the transient bonding and chemical scavenging of thermally decomposed hydrazine on the surface of CNTs.

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1. Introduction

Since the growth of graphitic carbon needles ranging from 4 to 30 nm in diameter and up to 1 μm in length on the negative end of a carbon electrode by arc-discharge evaporation was reported by Iijima in 1991 [1], the research on carbonaceous materials in the forms of nanotubes (or carbon nanotubes) have attracted the interest of many scientists [2]. As carbon nanotubes (CNTs) possess unique electrical, electronic and mechanical properties, they are widely used for many technological applications [3–10]. To exploit CNTs for various technological applications, chemical treatments are frequently used to tailor CNTs' properties [6,11–14]. Among the studies on employing chemical treatments to manipulate CNTs' properties, some have shown that amine-containing compounds could decrease CNTs' electrical conductivity by donating electrons to n-dope CNTs [15–17].

Hydrazine (N_2H_4) is the simplest diamine in the azane family [18]. It is a labile compound with a nitrogen-based molecular backbone and four nitrogen–hydrogen single bonds [19,20]. Hydrazine has long been used as the major ingredient in hypergolic fuels for rockets, missiles and satellites [20,21]. It can also be used as a reducing agent, for example, to adjust post-synthesis oxidation states of polyanilines [22–26], process graphene oxides [27–30], or remove carboxyl groups on the surface of polymeric nanoparticles [31].

As hydrazine is an amine-containing compound, CNTs tend to exhibit lower electrical conductivity after being treated with hydrazine [32]. Therefore, hydrazine-treated CNTs usually would not be considered for technological applications which require CNTs with enhanced high electrical conductivity [33]. However, some studies have shown that hydrazine-treated CNTs could alternatively be used for other purposes. For example, it has been demonstrated that CNT-based field-effect transistors (FETs) could be converted from p-type devices to n-type devices by N_2H_4 treatment [34,35]. It has also been reported that organic solar cells integrated with CNTs as penetrating electrodes could give higher power conversion efficiency when N_2H_4 -treated CNTs were used [36].

In view of its molecular size, hydrazine is a relatively small diamine [20]. Upon heating, bulk hydrazine can readily decompose

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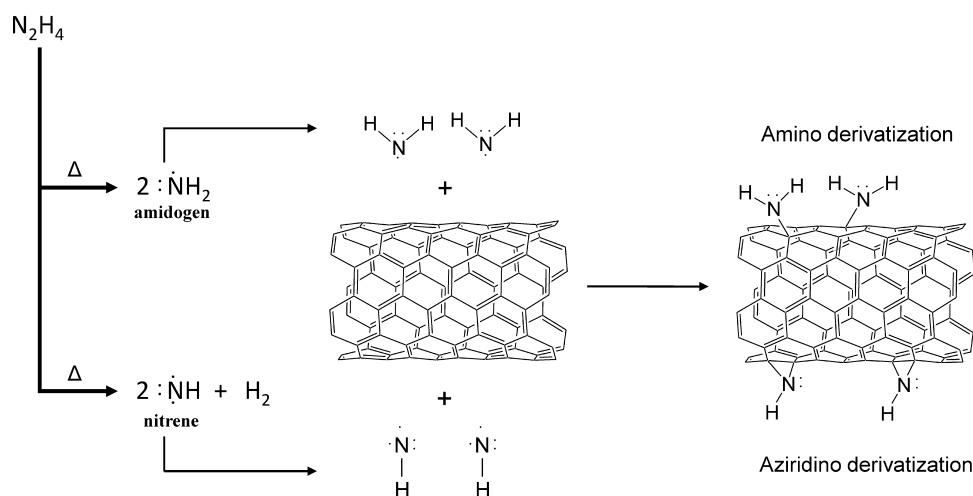


Fig. 1. Thermal decomposition of hydrazine to reactive nitrogenous radicals and the subsequent amino/aziridino derivatization of amidogen/nitrene on CNTs. Adapted from [38] with permission. Copyright 2012 Elsevier.

to N_2 , H_2 and/or NH_3 [19]. Previously, it has been reported that the decreased electrical conductivity of CNT samples caused by their exposure to the vapor of a small-molecule azane (or amine), such as trimethylamine, *n*-butylamine and monomeric 3-aminopropyltriethoxysilane, could be restored relatively easily by just blowing N_2 or leaving the samples in air for one day [16,17]. However, in one of our previous studies, we found that the n-doping effect on CNTs caused by a vapor-phase N_2H_4 treatment still persistently remained even after a thermal treatment intended to promote the desorption of hydrazine and its decomposition products was applied [37]. Specifically, the study showed that the sheet resistance of CNT samples which underwent a N_2H_4 -vapor-exposure/80 °C-baking treatment was still ~ 6 times as high as that of pristine CNT samples. In the same study, we also performed a series of experiments by synchrotron photoelectron spectroscopy and found that the CNT samples subject to the N_2H_4 -vapor-exposure/80 °C-baking treatment showed spectral signals corresponding to (i) decreased amount of sp^2 -carbons, (ii) increased amount of sp^3 -carbons, (iii) decreased degree of π -bonding, (iv) obvious appearance of C–N bonding and (v) decreased work function associated with n-doping [37]. To account for the above-mentioned changes in chemical and electronic structures, we proposed a mechanism in which chemical functionalization involving certain highly reactive nitrogenous radicals (such as nitrene and amidogen, which can be produced by thermal decomposition of hydrazine) took places on the surface of CNTs [38] (Fig. 1). As is shown in Fig. 1, the chemical functionalization can generate covalent amino/aziridino derivatization on the surface of CNTs and then n-dope CNTs. Besides, our experimental results also showed that the covalent amino/aziridino functionalization was thermally metastable and could be significantly eliminated by annealing at 350 °C [37].

In this work, we conducted a series of experiments to investigate the effect of cumulative baking on the properties of CNTs subject to hydrazine treatments under different experimental conditions (such as ambient atmosphere vs. nitrogen atmosphere and liquid hydrazine treatment vs. hydrazine vapor treatment). As was expected, the CNT samples subject to hydrazine treatments all showed an initial increase in sheet resistance and then a progressive decrease in sheet resistance upon subsequent cumulative baking. Most importantly, we found that, unlike the CNT samples treated in air by liquid hydrazine or vapor-phase hydrazine, when the CNT samples were treated with hydrazine under very mild conditions (*i.e.* treated by hydrazine vapor under nitrogen

atmosphere), the initial increase in sheet resistance was much smaller and the following progressive decrease in sheet resistance upon cumulative baking would eventually reach a sheet resistance value smaller than that of the untreated pristine CNTs. We also found that, after several rounds of hydrazine-vapor treatments and baking treatments were applied to a poor single-CNT FET device, the device showed improvement in I_{on}/I_{off} ratio and reduction in gate-sweeping hysteresis. The experimental results in this work indicate that (i) a trace amount of hydrazine vapor can be used to upgrade the electrical and electronic properties of non-oxidized CNTs and (ii) the improvement in CNTs' electrical and electronic properties could be related to the transient bonding and chemical scavenging of nitrogenous radicals thermally decomposed from hydrazine to repair certain defective sites (in particular, sp^3 -carbon sites with redundant dangling substitution) on the bulk graphitic surface of CNTs.

2. Experimental

2.1. Preparation and characterization of networked CNT thin films

Surfactant-free single-walled CNT (SWCNT) thin films were synthesized by alcohol catalytic chemical vapor deposition (ACCVD) using anhydrous ethanol (Sigma–Aldrich) as the precursor and silicon wafers with 300-nm thermal $SiO_2/3$ -nm Ni/50-nm porous SiO_2 as the growth substrate (area of the growth substrate ~ 1.5 cm \times 1.5 cm, which also defines the 2-dimensional sheet size of our SWCNT samples) [39]. The SWCNTs initially produced by ACCVD at 800 °C were partially buried in SiO_2 . To transfer the SWCNTs grown on the growth substrate to another substrate, the growth substrate covered with the ACCVD-grown SWCNTs was dipped into 6:1 buffered oxide etching, or BOE, solution (J.T. Baker). The BOE solution would etch SiO_2 to release the SWCNTs from the growth substrate. The released SWCNTs then became a free-standing SWCNT film floating on the surface of the BOE solution. The free-standing SWCNT film was subsequently transferred to deionized water to dilute residual BOE solution. For scanning electron microscopy (SEM) and sheet resistance measurement, the free-standing SWCNT film floating on deionized water (DI water) was collected by a glass substrate. For X-ray photoelectron spectroscopy (XPS), the SWCNT film was collected by indium tin oxide glass. Thickness of the obtained SWCNT films was ~ 20 nm.

The SWCNT sample prepared as described above is referred to as pristine SWCNTs (*Note:* The ACCVD method can consistently

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