



Impacts of structure defects and carboxyl and carbonyl functional groups on the work function of multiwalled carbon nanotubes



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ABSTRACT

The work function is important for achieving the desired performance of many electronic devices. Several investigations have been conducted on the work-function engineering of multiwall carbon nanotubes (MWNTs). Oxidation of carbon nanomaterials is a simple approach to increasing MWNTs' work function without introducing extrinsic metallic elements or altering the nanotubes' morphology; however, few experiments have been conducted to study the mechanism by which different types of oxygen-containing functional groups increase the work function of MWNTs. In this work, we designed and carried out systematic experiments to investigate the influence of the overall oxygen content, structure disorder, and two individual types of functional groups on work-function shifts. Our results demonstrate that the work function is not simply correlated with the overall oxygen concentration, that structure defects are unlikely to change the work function, and that carbonyl groups are the dominant contributor to the increase in the work function of MWNTs. Our results provide distinctive insights into work-function engineering of MWNTs and guide the application of MWNTs in functional devices for photovoltaic and optoelectronic devices.

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1. Introduction

Carbon nanotubes (CNTs) are a very attractive material for use in various electronic devices and optoelectronic applications because of their promising structural and electronic properties compared to those of other carbon materials [1]. CNTs have been successfully applied in field-emission displays, light-emitting diodes, and solar cells [2–4]. In these electronic or optoelectronic devices that require a modification of the junction interface to achieve a well-defined electronic energy level leading to the desired performance, the work function is a critical parameter. Organic–inorganic hybrid perovskite solar cells (PSCs), which emerged in 2009 [5], show strong potential for commercialization in the near future; researchers have therefore devoted extensive effort to reducing the cost and improving the performance and stability of PSCs. CNTs have been used in PSCs to replace the precious-metal back contact and to even eliminate the hole-transport material (HTM) [6–9]. On the basis of device simulations of HTM-free PSCs, a matching work function of the back contact material is critical for maintaining its

open-circuit voltage [10]. Thus, developing a simple and effective pathway to manipulate CNTs' work function to match diverse energy structures is a priority.

Several approaches to manipulating CNTs' work function have been proposed. Evan et al. developed a work-function tuning method by depositing various metallic nanoparticles onto a CNT network [11]. A similar idea for changing CNTs' work function was reported by Seong et al., who deposited a nanoscale thin layer of aluminum onto a CNT film [12]. An alkali-metal cation exchange through surface functional groups has also been proposed [13]. However, in devices, the interaction at the interface between these work-function-modified CNTs and a metal or semiconductor would be difficult to investigate because the aforementioned approaches to engineering the work function of CNTs involve foreign metal atoms, which function as impurities.

In fact, introducing oxygen-containing functional groups onto CNTs could effectively change the work function of CNTs without the incorporation of an extrinsic metallic element [14–16]. Functional groups could be easily decorated onto CNTs via oxidative treatments often used to purify or modify CNTs. Numerous CNT oxidation methods have been reported, ranging from early work involving gas-phase oxidation to liquid-phase reactions with solitary or mixed oxygen-containing acids [17–22]. The species of

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oxygen-containing functional groups and their proportions on CNTs strongly depend on the oxidants and reaction conditions. However, oxidation not only results in the grafting of functionalities but also transformations of the CNTs' morphology, such as cutting CNTs short or shredding their walls to graphene if a more aggressive oxidation method is used [23,24]. Although previous studies on the influence of functional groups on CNTs' work function have been reported [13,14], the effects of structure defects and particular functional groups on the electronic structure of CNTs remain inconclusive.

In this work, we elucidate the effects of carboxyl and carbonyl functional groups on the electronic structure of multiwall nanotubes (MWNTs), which is a common and economic carbon nanomaterial and the best candidate for replacing noble metal back contact in PSCs, by treating MWNTs with various solution-state chemical oxidation reagents that result in different degrees of oxidation and diverse proportions of functional groups; furthermore, annealing functional-group-containing MWNTs to a certain temperature to eliminate certain functional groups provides an opportunity to study the effects of each functional-group species. The functional groups are quantitatively analyzed and identified using both X-ray photoelectron spectroscopy (XPS) and temperature-programmed desorption (TPD). Ultraviolet photoelectron spectroscopy (UPS) is used to explore the valence-band density of states (DOS). The MWNTs' work-function values are determined by both photoelectron spectroscopy in air (PESA) and UPS. We also propose a pathway for manipulating the work function by removing surface functional groups on defective MWNTs using a chemical drilling method to create hole defects and thereby provide many more potentially active sites for functional-group implantation.

2. Experimental

2.1. Materials synthesis and preparation

The raw MWNTs were received from Showa Denko KK, Japan (VGCF-X). Their diameter and length were 10–15 nm and approximately 1 μm , respectively. For purification, the raw MWNTs were heated to 500 °C in air for 1 h, this method damages and contaminates the MWNTs to a lesser extent than other purification methods. After the heat treatment, the purified MWNTs (i.e., heat-treated MWNTs (HMWNTs)) were refluxed in a mixture of 2 M sulfuric acid and concentrated nitric acid (1:1 v/v) for 4 h, collected by filtration using deionized water, and dried overnight. During this process, the mixed acid not only grafted functional groups onto the surface of the MWNTs but also dissolved metal particulate impurities.

For the preparation of defective MWNTs (DefMWNTs), cobalt(II) nitrate hexahydrate (Wako, 99.5%) was used as a precursor. One hundred milligrams of acid-oxidized MWNTs (AMWNTs) and 10 wt % Co were dispersed in 10 mL of ethanol with ultrasonic assistance for 15 min to achieve a good dispersion. The resulting dispersion was then heated to 70 °C for 20 min to obtain AMWNTs well coated with the Co precursor; the coated AMWNTs were then transferred to a constant-temperature vacuum oven and heated at 60 °C overnight. The sample was ground into a fine powder, transferred to a well-sealed quartz cylinder-shaped electronic furnace pre-filled with argon to create an inert atmosphere, and heated for 3 h at 300 °C. The sample was then oxidized for 25 min at 270 °C under an atmosphere of flowing argon and oxygen mixed at 4:1 to create hole defects on the MWNTs. The cobalt oxide coating was removed by washing the sample with sulfuric acid diluted to 2 M to avoid damaging the MWNTs with a strong acid. More details related to the defect creation procedure are described in our previous work [25].

To acid-oxidize the DefMWNTs, the DefMWNTs were refluxed in concentrated nitric acid for 1 h, diluted with deionized water, stirred for 3 h, washed with water, and then collected by filtration using deionized water. This sample is referred to as ADefMWNTs.

To eliminate certain functional groups' effects on the work function, samples were annealed under an Ar atmosphere at 500 °C or 900 °C for 1 h to decompose different functional groups at different temperatures.

All the MWNT samples were prepared in the form of buckypaper. The buckypaper preparation were described as follows. Typically, 25 mg of samples was mixed with 1 mL Triton X-100 surfactant, 5 mL 1-propanol, and 100 mL of deionized water and using a homogenizer to obtain a well dispersed mixture. The mixture was then filtered through a 0.45 mm pore size mixed cellulose ester membrane followed by the addition of 400 mL deionized water and 100 mL of 2-propanol. The buckypaper samples then were transferred to a vacuum oven drying at 60 °C overnight then subsequently peeled it off from filter paper. Fig. S6 shows the morphology of buckypaper and its surface.

2.2. Characterization

PESA (AC-3, Riken Keiki Co., Ltd.) was conducted at atmospheric pressure using an open counter and a UV source. XPS (PHI 5000 VersaProbe III, ULVAC-PHI Inc.) equipped with an ultraviolet photoelectron spectroscopy (UPS) apparatus was used to analyze the concentrations of surface elements, characterize the valence-band structure, and determine the MWNTs' work function.

The work functions were determined from the UPS spectra; specifically, the work function represents the difference between the energy of a photon of He I radiation (21.2 eV) and the binding energy of the secondary electron cut-off edge ($\Phi = 21.2 \text{ eV}$ – (the full width of the photoelectron spectrum)). The structure defectiveness was examined by laser raman spectrometer (NRE-4100, Jasco International Co., Ltd). The oxygen content was estimated on the basis of the O 1s peak (531 eV) in the XPS spectrum. The oxygen functional groups were evaluated using temperature-programmed desorption (TPD, EMD-WA1000S, ESCO Co., Ltd.) in conjunction with a quadrupole mass spectrometer system (QMG 422) for analyzing the desorbed gases. The electrical conductivity measurement was measured by Metrohm Autolab (PGSTAT30). The measurement setup was described in supplementary information (Figs. S4 and S5).

3. Results and discussion

Fig. 1 summarizes the overall oxygen content and work functions of pristine and functionalized MWNTs used in this study. The oxygen content was estimated from the O1s peak (531 eV) in the XPS spectrum (Fig. 4). Work functions were measured by both UPS and PESA to avoid problems associated with measuring work functions using only UPS; these problems arise from the heterogeneous surface of buckypaper and from the background of degraded electrons distorting the spectrum near the work-function cut-off [27,28]. PESA was used to assist with determining the work function of the MWNTs. PESA is useful for determining the value of work functions because it enables the work function value to be read directly from its spectrum as the crossing point of the background and the yield line (Figs. S2 and S3).

Fig. 1 and Table 1 reveal that the work functions measured by PESA are normally higher than those measured by UPS because PESA is conducted in moist air, whereas UPS is carried out in ultra-high vacuum (UHV); moreover, because all of the samples were prepared in the form of buckypaper, whose porous morphology tends to absorb moisture and impurities on its surface, absorption

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