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Structural and electrical properties tailoring of carbon nanotubes via a reversible defect handling technique

Xin Li [a], Yong Cheng [a], Longze Zhao [b], Qiaobao Zhang [a], Ming-Sheng Wang [a, b, *]

[a] Department of Materials Science and Engineering, College of Materials, Xiamen University, Xiamen, Fujian 361005, China
[b] Pen-Tung Sah Institute of Micro-Nano Science and Technology, Xiamen University, Xiamen, Fujian 361005, China

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ABSTRACT

Irradiation with energetic particles has been recently demonstrated as an effective means to tailor the structures of a variety of materials with high precision, which, however, usually leading to irreversible degradation of the related properties due to defect introduction. Herein, we present a highly controllable defect handling approach, i.e. defect creation followed by their elimination in carbon nanotubes (CNTs). Technically, this can be accomplished by the alternate use of room-temperature electron irradiation and a separated heat treatment, as demonstrated here via in-situ transmission electron microscopy. The regarded CNTs thus undergo the order/disorder structural transition, which can be repeated up to at least 10 cycles with the CNT structural integrity largely retained. A temperature-dependent annealing experiment shows that the CNT recrystallization can be initiated at a surprisingly low temperature of ~300 °C, and the irradiated CNTs can primarily regain their structural perfectness over 1000 °C. This technique allows for the reversible and repeatable tuning of a number of important CNT electrical properties, such as electron transport, as well as electron field emission that has never been achieved before. Furthermore, this defect handling technique has the potential as a general route for reversible tuning of other defect-dependent properties of sp^2 carbon nanosystems.

1. Introduction

Over the past decades, sp^2 carbon has gained tremendous research interests owning to its high technological importance, as well as the fascinating structural variety of these C systems. Like no other material, sp^2 carbon systems have the unique ability to evolve into various structures by diverse C–C bond reconstruction under certain circumstances [1,2]. Such structural transformations can be readily driven by, for example, the irradiation with energetic particles (such as electrons and ions), which has proven to be an effective means to alter the structures and properties of carbon materials [3–12]. However, the irradiation of sp^2 carbon usually reported destructive effects since it irreversibly deteriorated the materials due to the introduction of defects and disorder [7–12]. The irradiation defects, for instance, even a small number of divacancies, can produce a drastic decrease in the conduction of a carbon nanotube (CNT) [7,10]. Such a property tuning route based on defect introduction, unfortunately, could hardly meet the demands in many applications where the reversible tuning of device properties is required [13,14].

From the perspective of property-defect relationship, this requires a controllable technique that allows reversible defect handling, that is, defect introduction and their elimination. Such defect handling, as presented in our recent work, can be accomplished via room-temperature electron irradiation followed by a heat treatment [14]. Although we have demonstrated the unique ability of this technique in reversible tuning of a series of mechanical properties of CNTs, some critical issues with respect to the optimal control of this defect handling technique and its effects on CNT microstructures remain unexplored. For example, is there any limitation for this irradiation/annealing cycling technique? What is the temperature threshold for defect annealing initiation or full recrystallization of irradiated CNTs? More importantly, in addition to mechanical properties tuning, we believe this useful method has the great potential to be further extended to the reversible tuning of a variety of properties of CNTs and other sp^2 carbon.

In this work, we present a systematic study of the structural evolution of CNTs during the defect-handling cycles, and

* Corresponding author. Department of Materials Science and Engineering, College of Materials, Xiamen University, Xiamen, Fujian 361005, China.
E-mail address: mswang@xmu.edu.cn (M.-S. Wang).

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demonstrate the great controllability of this technique in the reversible tailoring of the electrical properties of individual nanotubes by *in situ* transmission electron microscopy (TEM). High-temperature annealing treatments were applied by using a heating TEM stage or via *in situ* current-induced Joule heating. We explored the temperature threshold for initiating the post-irradiation defect annealing, as well as that for perfect CNT recrystallization. We further demonstrated that the structural tailoring cycles based on order/disorder transition can be repeated up to at least 10 times. Thus, some important electrical properties of individual CNTs can be reversibly and repeatedly tailored and *in situ* tested, including the CNT resistance tuning in a highly controllable way, as well as the first successful demonstration of reversible tuning of CNT field emission properties.

2. Experimental

In-situ TEM heating experiments: The MWNT and DWNT samples were first ultrasonically dispersed in alcohol and glycol respectively. A tiny drop of sample liquid was loaded on a MEMS chip that was then mounted on a TEM heating holder (FEI-NanoEx). This heating stage allows the samples to be locally heated up to 1200 °C with a temperature accuracy <4% (with 0.1 °C readout accuracy). In-situ TEM heating experiments were conducted inside a FEI Talos-F200s TEM by using this heating stage. During CNT annealing, the electron beam was sufficiently dispersed or moved away to minimize the irradiation effects.

In-situ TEM electrical probing: The CNTs were assembled onto a freshly cut gold wire (0.25 mm in diameter) before each experiment by rubbing the gold wire on the CNT flake surface. This gold wire was then transferred and fixed by inserting the wire into a tiny-diameter pipe welded to the STM sample holder frame (from "PicoFemto" company). An electrochemically etched tungsten wire (0.2 mm in diameter) was inserted into the three-dimensional movable part of the piezo-driven holder. The CNT manipulations and *in situ* electrical and field emission measurements were performed inside a JEOL-2100 TEM by using this STM holder.

3. Results and discussion

3.1. Reversible tailoring of CNT microstructures

Since the CNT property tuning is highly dependent on the structural evolution during the defect-handling process, we first investigate the defect-engineering effects on the microstructure of CNTs. The irradiation/annealing experiments were performed inside a FEI Talos F200s TEM by using a MEMS-based heating holder (FEI-NanoEx) with an accurate temperature control (≤1200 °C). The multi-walled CNTs (MWNTs) and double-wall CNTs (DWNTs) used in this work were synthesized by arc-discharge methods. Defect introduction was accomplished by irradiating the CNTs with a 200 keV electron beam of a current density of 7.2A/cm^2. As depicted in Fig. 1, the CNTs with originally perfect shells became heavily defective and even amorphorized after 5 min's irradiation. The defect formation can be well understood in terms of the aggregation of interstitials and vacancies under room-temperature irradiation. However, such defect agglomerates, once formed at room temperature, can hardly be annealed up to a very high temperature [1]. To achieve the post-irradiation annealing of these defects, the irradiated CNT was first heated at 1200 °C, during which the e-beam was sufficiently dispersed to minimize the irradiation effects. 10min later, the annealed CNT recovered from its defective state and primarily regained the structural perfection, including the shell number, as evidenced by the regular fringes in the corresponding HRTEM image that indicate the healed basal planes along the nanotube axis (Due to the difficulty in clarifying the exact nature and density of the defects that is beyond the resolution power of our electron microscope, we here only present a phenomenological description of the order-disorder transition process).

Surprisingly, the CNTs that experience a single irradiation/annealing cycle can exhibit a somewhat memory-like effect on certain structural details at atomic scale. As indicated by the black arrowheads in Fig. 1 (for the cases of 1200 °C and 1000 °C), a number of structural features of the nanotubes reappear after annealing although they seem to be lost under irradiation. This might be related to the remaining short-range ordering, i.e. the discrete graphitic fragments in the discontinuous graphene layers. They may guide the subsequent annealing process, in which the interstitial atoms tend to migrate and recombine with the vacancies along the original basal planes, resulting in the repairing of the tube shells, including many structural details. In fact, if a prolonged irradiation with the same current density is applied, this structural-memory effect will be seriously weakened (see supporting information Fig. S1). This suggests that the limited irradiation dose would be critical for the irradiated nanotubes to regain their structural integrity after annealing.

The annealing process is supposed to be retarded at a reduced temperature. Thus, it would be of particular importance to explore the lower temperature limit for post-irradiation healing of CNT defects. This, to our knowledge, has not yet been experimentally confirmed. To approach this temperature threshold, the above experiment was repeated at successively decreased annealing temperatures with an interval of 100 °C. Fig. 1 displays the representative images of different CNTs (about the same diameter) after the irradiation and annealing at the temperatures of 1200, 1000, 800, 500, 300 and 200 °C respectively. As expected, the degree of CNT crystallization decreases with the reduced temperature, as revealed from both HRTEM images and the corresponding fast Fourier transform (FFT) patterns. It is noted that at the temperature of 1000 °C, the defective nanotube can still be well crystallized, whereas at 800 °C, the tube graphitization becomes visibly incomplete with slight bending of the basal planes. Unexpectedly, the annealing effect on the tube crystallization can still be observable at the temperature as low as 300 °C, but becomes almost negligible at 200 °C (as could be more evident from the comparison of the FFT patterns before and after the annealing). As previously proposed, a few types of interstitials with relatively low migration energy of 0.8–0.9 eV could be mobile enough to recombines with vacancies above ~300 °C, such as di-interstitials and mono-interstitials bound to the graphene layers [1,15]. The increased mobility of these interstitials may account for the observed partial annealing of the CNT shells at 300 °C, since other interstitial and vacancy clusters are believed to be stable at this temperature.

As seen above, an annealing process, even at 1200 °C, does not necessarily lead to perfect healing of the irradiated CNTs. The atomic network near the vacancy may reconstruct by saturating dangling bonds to form non-six-membered rings, such as heptagon-pentagon pairs. They preserve the connectivity of the sp^2 hybridized lattice, but introduce the local bending of the annealed graphene cylinders [2]. The vacancy generation and its extension due to continuous sputtering would appear as voids or breaking of the tubular shells after annealing, as indicated by the white arrowheads in Fig. 1. Accordingly, the interstitials that fail to be recombined with vacancies have a tendency to aggregate into each other to reduce their free energy, resulting in the formation of irregular graphene-like fragments, as observed on the outer layers of the annealed nanotubes (as seen in Fig. 2 and Fig. 4b).

Because of the incomplete recovery of the microstructures mentioned above, it is necessary to study the influence of the