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Size-controllable fabrication of Cu nanoparticles on carbon nanotubes by simple heating

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ABSTRACT

In this paper, employing simple heating inside the transmission electron microscope, we demonstrated the decoration of carbon nanotubes (CNTs) by Cu nanoparticles (NPs). More significantly, the particle sizes could be effectively controlled by simply controlling the temperature and duration. It is believed that the nucleation and growth of NPs results from the deposition of generated Cu vapor as well as the surface diffusion of Cu on the CNTs at elevated temperature.

1. Introduction

As one of the most significant one-dimensional materials, carbon nanotubes (CNTs) with special tubular structure are the focal point of intense study due to their unique mechanical [1,2], optical properties [3], high thermal conductivity [4], and biocompatibility [5], etc. Unfortunately, their surface suffers from limited reactivity, making them difficult to modify or functionalize. In this light, driven by the perspective to make the surface of CNTs more flexible and thus expand the potential applications, extensive efforts have been dedicated to decorate the CNTs with different functional groups [6,7]. At the same time, many CNT-based composites have been prepared [8,9]. Among them, metal-CNT composites are of considerable technological importance. For example, the Au–CNT composites can serve as excellent catalysts in organic reactions [10] while the Cu–CNT composites can be used for interconnects [11] and sensor applications [12].

In general, plenty of methods such as the electron beam (e-beam) deposition [13], chemical reduction [14], electroless plating method [15], and thermal evaporation [16], etc., have been proposed to synthesize the CNT-based composites. However, most of the documented methods are somewhat cumbersome as they may involve a tedious assembly process and/or require pretreatment of the CNTs with surfactant or oxidation, which would inevitably affect the quality of CNTs, such as the one-dimensional electronic structure and mechanical properties [17]. On the other hand, it is well accepted that nanoparticles (NPs) with different sizes may exhibit distinct mechanical [18], optical [19,20], and catalytic properties [21], signifying that the sizes of NPs are crucial in determining the functionality of the composites [10]. As a result, realizing the size-controlled synthesis of NPs on the CNTs is a prerequisite for the full exploitation of this kind of materials, which has long been an engineering pursuit [16,22].

Herein, we report a convenient and effective approach of decorating CNTs with Cu NPs in a size-controllable manner. By directly heating the Cu grid coated with CNTs inside the transmission electron microscope (TEM), the Cu NPs were observed to nucleate on the surface of CNTs. The averaged NP size gradually increased within the heating period while the NP would retain its size without heating. Thus, assisted by the TEM images, which provide real-time feedback during the heating process, the sizes of the Cu NPs could be easily monitored and thus precisely controlled by manipulating the heating temperature and the holding time. It is believed that the diffusion of the Cu along the CNTs as well as the Cu vapor generated from the Cu grid during heating play pivotal roles in the nucleation and growth of the NPs.

2. Experimental

The heating experiment was performed inside the JEM-2010 (HT) (HT: high angle tilt) employing a Gatan 652 double-tilt heating specimen holder (model 652 with a model 901 SmartSet

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hot stage controller), equipped with the capability of raising the specimen temperature up to maximum 1000 °C. In subsequence, the Cu grid was remounted onto a double-tilt TEM holder for energy dispersive spectroscopy (EDS) and high resolution transmission electron microscope (HRTEM) characterization inside the JEM-2010 FEF (UHR) (FEF: field emission gun and in-column Ω-type energy filter; UHR pole-piece: ultra-high resolution with a Scherzer resolution of 0.19 nm). Both microscopes were operated at an accelerating voltage of 200 kV.

3. Results

Fig. 1(a) shows a bright field (BF) image of the as-fabricated CNTs coated on the Cu grid at room temperature (RT). The concentric diffraction rings presented in corresponding selected area electron diffraction (SAED) pattern (Fig. 1(b)) can be indexed based upon the typical hexagonal graphite structure (lattice parameter: $a = 0.25$ nm, $c = 0.68$ nm, space group: $p6_3mc$), indicating that the CNTs are well graphitized without noticeable contamination. In contrast, a large number of NPs were formed at the surface of CNTs after the holder was heated at more than 400 °C for approximately 100 min (Fig. 1(c)). Besides the diffraction rings originated from CNTs, there exists some extra bright diffraction spots which can be characterized by face-centered cubic structure of Cu metal (lattice parameter: $a = 0.36$ nm, space group: $Fm\bar{3}m$) (Fig. 1(d)). It is noted that the extra diffraction spots cannot be indexed by the cubic structure of Cu_2O (lattice parameter: $a = 0.43$ nm, space group: $Pn\bar{3}m$) (Fig. S1), suggesting the nucleation of Cu NPs without noticeable oxidation.

Further HRTEM image of as-prepared NP and CNT (marked by black arrows) composites is shown in Fig. 2(a) with characterized $\{111\}_{Cu}$ and $\{0002\}_C$ crystallographic planes; while the EDS spectra recorded from the NP and CNT, respectively, are illustrated by the black curves in Fig. 2(b), confirming that the product is Cu NPs and most of Cu NPs with smaller sizes (<10 nm) are single-crystallines. In the EDS spectrum taken from the CNT (curve at the lower part), the Cu Lα peaks mainly originate from the Cu grid. Thus, it is suggested that such a convenient method can be applied to effectively decorate the CNTs with Cu NPs.

In addition, the averaged NP-size demonstrates an increasing tendency accompanied with the elevated temperature. Fig. 3(a–c) present the sequential TEM images showing the deposited Cu NPs in the same local area with the temperatures of 450 (Fig. 3(a)), 560 (Fig. 3(b)), and 650 °C (Fig. 3(c)). Fig. 3(d–f) show the size distribution of the Cu NPs corresponding to Fig. 3(a–c), respectively. It is evident that the NPs are getting larger with the heating temperature, as indicated by the size statistics whereas the averaged NP size increases from 7.0 (Fig. 3(d)) to 12.6 (Fig. 3(e)) and 20.5 nm (Fig. 3(f)), corresponding standard deviation is 2.8, 4.9, and 7.4 nm. Moreover, the averaged NP-size increases with the heating time. Fig. 4(a–c) present the time-lapsed TEM images of the growth process of Cu NPs in the same local area when the temperature is above 400 °C. An enlarged view of local area in Fig. 4(a) is presented in Fig. S2 to clearly show the existence of Cu

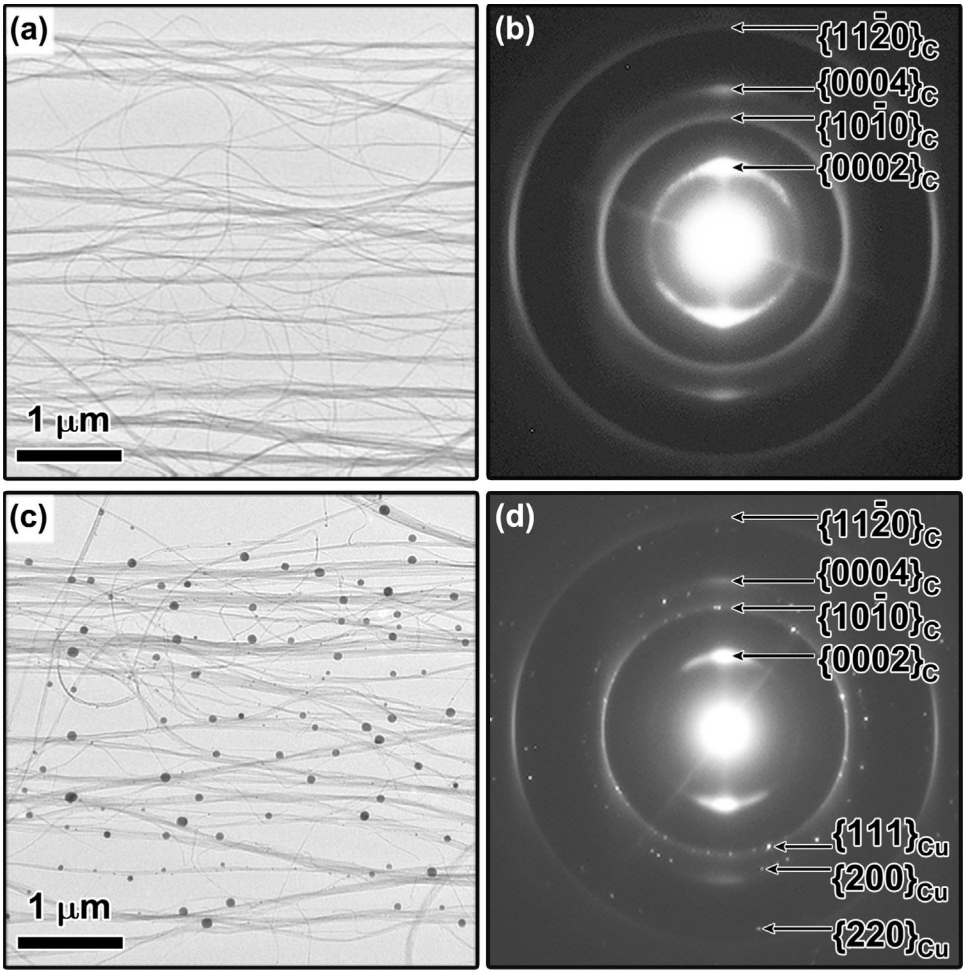

Fig. 1. (a) A BF image of as-synthesized CNTs. (b) SAED pattern corresponding to (a). (c) BF image of Cu–CNT composites after Cu grid was heated at more than 400 °C for 100 min. (d) SAED pattern corresponding to (c).