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Letter to the editor

Is the tensile strength of carbon nanotubes enhanced by supported materials?: Effect of supported amorphous alumina nanoparticles on the tensile strength of carbon nanotubes

ABSTRACT

The interfacial bonding strength between carbon nanotubes (CNTs) and the metal matrix in CNT/metal composites can be increased by depositing metal or metal oxide particles onto the CNT surface. In this study, the effect of the supported amorphous Al_2O_3 nanoparticles on the tensile strength of individual multi-walled CNTs (MWCNTs) synthesized by chemical vapor deposition has been investigated *in situ* by scanning electron microscopy. The average tensile strength of MWCNTs with supported amorphous Al_2O_3 nanoparticles was slightly higher than that of the as-grown MWCNTs, which could be attributed to the interactions between the supported materials and the CNT defect sites.

Lightweight and strong carbon nanotubes (CNTs) are widely utilized for manufacturing CNT/metal and CNT/ceramic composites. In order to fabricate robust CNT-based composite materials, the interfacial strength between the CNTs and the matrix in the designed composites must be high enough to endure the load transfer between these two components. Recently, the interfacial strength of single-walled CNTs (SWCNTs) inside a Cu matrix was improved by coating them with Ni species; as a result, the mechanical properties of the produced Ni-coated SWCNT/Cu composites were significantly enhanced [1]. In another study, the conducted molecular dynamics (MD) simulations revealed that the Young's modulus of Ni-coated SWCNT/Au composites was larger than that of uncoated SWCNT/Au [2]. Hence, the application of metal coatings characterized by the high affinity to the CNT surface significantly improved the mechanical properties of the resulting nanocomposites, and the affinity and associative interaction properties of Al [3–5], Ti [4], Fe [3,4], Ni [4], Cu [4], Pd [3,4,6,7], Pt [6,7], Au [3], and Pb [3] species deposited onto the surface of CNTs have been extensively studied both computationally and experimentally. However, Inoue and Matsumura reported that the breaking stress for Ni-coated defect free SWCNTs estimated via MD simulations was lower than that for uncoated SWCNTs; they also showed that Ni atoms had a tendency to react with C atoms to produce Ni–C bonds, which induced local distortions in the nanotube structure [8]. Song and Zha also performed MD simulations to show the decrease in the tensile strength and Young's modulus of SWCNTs after Ni coating because of the strong interactions of Ni atoms with C atoms, which ultimately changed the area of the CNT cross-section [2]. It is known that the CNTs, especially the CNTs produced by chemical vapor deposition (CVD), are not defect free. With regard to CNTs with defects, oxygen-containing functional groups (including –OH, =O, and –COOH) easily interact with surface defects (such as vacancies), where metal and metal oxide nanoparticles such as Ni [9], Pd [7], Pt [7], and TiO_2 [10] adsorb only selectively. If the adsorbate material strongly interacts with the functional groups attached to the defect sites, it can significantly affect the mechanical strength of individual CNTs, therefore to the overall strength of the CNT/metal composites. In contrast, no theoretical or experimental studies on the mechanical strength of CNT-based metal composites containing metal oxides deposited on the CNT surface as interfacial reinforcement materials have been reported. Thus, it remains unclear about the effect of coated metal oxides on the mechanical strength of an individual CNT. In this work, we investigated the effect of the supported Al_2O_3 nanoparticles on the tensile strength of individual MWCNTs, which were synthesized via CVD. It was found that the average tensile strength of the MWCNTs containing supported amorphous Al_2O_3 nanoparticles is greater than that of the as-grown MWCNTs.

Vertically aligned MWCNTs synthesized by chemical vapor deposition were used in all experiments (see the Supplementary Data). A Cu grid (F–400 mesh, Nisshin EM Co., Ltd., Japan) used for transmission electron microscopy was cut in half and then pressed to a forest of vertically aligned MWCNTs, to transfer a fraction of individual MWCNTs onto the grid surface. For making amoAl_2O_3-MWCNT, the grid was placed into a vacuum chamber followed by supported aluminum by using a radio-frequency magnetron sputtering system (JEC–SP360R, JEOL, Japan) at a sputtering power of 100 W, constant back pressure of 3 Pa, Ar gas flow rate of 30 sccm, and deposition time of 30 s. Al_2O_3 nanoparticles were prepared by oxidizing Al nanoparticles inside an electric furnace at a temperature of 50 °C for 12 h in air. The obtained Al_2O_3 nanoparticles were characterized by distorted shapes, and their sizes were estimated by aligning the longest part along the axis. Tensile testing was conducted inside the vacuum chamber of a scanning

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electron microscope (SEM) (S–4100, Hitachi, Japan) equipped with a nanomanipulator [11]. The cantilever of an atomic force microscope (AFM) (Chip CSC38, MikroMash, USA) was mounted to a piezoelectric bender on the X–Y linear motion stage, while the Cu grid attached with specimen (individual MWCNT or amoAl_2O_3-MWCNT) was mounted on the opposite Z linear motion stage. The AFM cantilever was used as a force-sensing element and force constants were obtained for each studied specimen *in situ* prior to tensile testing using a resonance method [11]. Before the test, one end of the specimen was first fixed on the Cu grid via electron beam-induced deposition (EBID) of carbonaceous materials, and then another end of the specimen was attached to the AFM cantilever and mounted there by EBID of carbonaceous material. The applied force was calculated from the angle of deflection measured for the cantilever tip. Minimum twelve tensile loading and fracturing experiments were performed for each type of individual MWCNT specimen. In order to estimate the tensile strength of each specimen, fractured cross-sectional area was obtained for each broken specimen via a transmission electron microscope (TEM) (HF–2000, Hitachi, Japan). The details of the mechanical evaluation procedure can be found elsewhere [12]. Elemental compositions of the deposited nanoparticles were estimated using a scanning transmission electron microscope (STEM) (HD–2700, Hitachi, Japan) equipped with an energy dispersive X-ray spectroscopy (EDX) module (Apollo XLT, EDAX, USA). X-ray photoelectron spectroscopy (XPS) was performed using a K-Alpha system (Thermo Fisher Scientific Inc., USA) with a monochromatic Al Kα X-ray source in order to analyze the elemental carbon compositions of the as-grown MWCNTs.

The average inner and outer diameters of the as-grown MWCNTs were 4.4 ± 1.1 and 9.3 ± 1.4 nm, respectively (see Fig. S1). The obtained nanotube structure contained more flexures, interlaminar disorders, and surface defects (Fig. 1a and b), as compared to that of the MWCNTs synthesized by an arc discharge method. The C_{1s} XPS studies of the as-grown MWCNTs (Fig. S2) revealed the presence of oxygen-containing groups on their surface. Fig. 1c and d show the bright field (BF)- and scanning electron (SE)-STEM images of the MWCNT-supported chain-like Al_2O_3 nanoparticles, which exhibited an average particle size of 3.1 ± 1.1 nm (Fig. S3) and elemental composition of C: Al: O = 97.0: 0.9: 2.1 (atom%) obtained from the STEM–EDX mapping images depicted in Fig. S4. The obtained results indicate that the deposited nanoparticles have not completely covered the nanotube surface. As indicated by the arrows depicted in Fig. 1c and d, some nanoparticles seem to be supported at the defective sites of the nanotube surface. Since the elemental composition of the as-prepared MWCNTs (determined from the STEM–EDX analysis) was C: O = 99.4: 0.6 (atom%), their defective sites were most likely functionalized with O-containing groups. After excluding the oxygen atoms related to these groups, the estimated elemental nanoparticle composition could be described by the formula $Al_2O_{3.4}$, suggesting that the Al nanoparticles have been completely oxidized to produce alumina nanoparticles with an amorphous crystalline structure (the resulting samples are referred to as "amoAl_2O_3-MWCNTs").

A typical tensile testing procedure for amoAl_2O_3-MWCNTs is illustrated in Fig. 2. After fracture, the nanotube tip, which was in contact with the Cu grid, was cut perpendicularly to the nanotube axis (Fig. 2d). During all tensile tests, MWCNT fracture of the sword sheath type was observed not only for the outer nanotube layers and but also for the other layers [11] at random positions between the Cu grid and the AFM cantilever (see a typical TEM image of the fractured cross-sectional area of amoAl_2O_3-MWCNTs depicted in Fig. S5). Fig. 3 exhibits the bar graphs of the tensile strengths measured for the obtained MWCNTs before and after the deposition of Al_2O_3 nanoparticles. The average tensile strength of

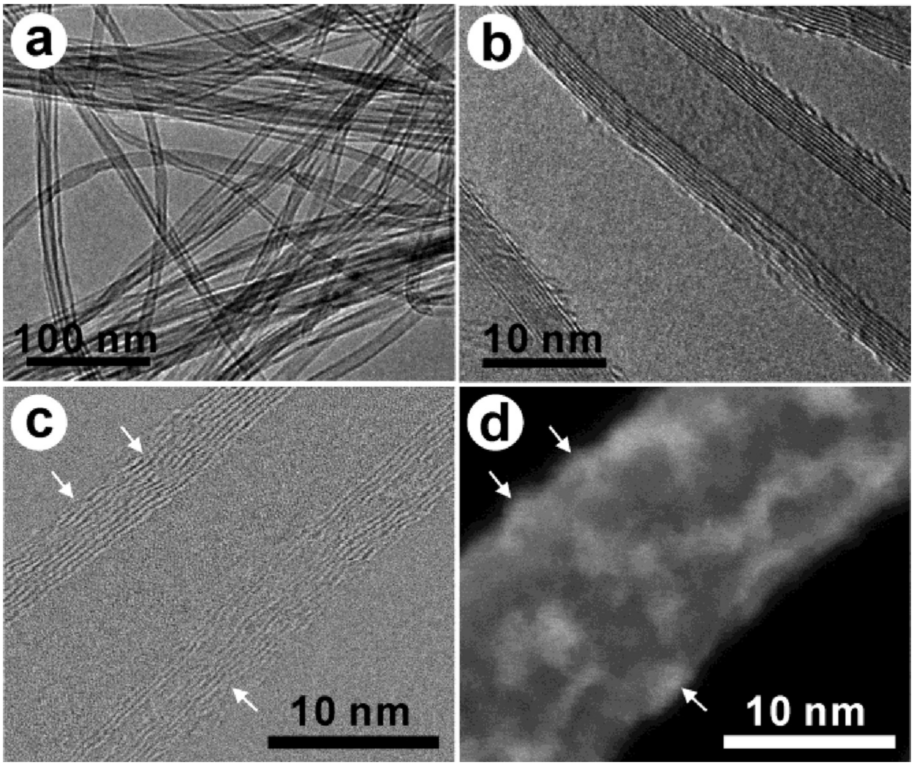

Fig. 1. (a) Low- and (b) high-magnification HRTEM images of the as-grown MWCNT. (c) BF–STEM and (d) SE–STEM images of the MWCNT-supported Al_2O_3 nanoparticles. The white arrows denote the defective sites.