Rapid formation and transfer of carbon nanotube probes: The lowest resistance from nano-bridges

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Aggregated carbon nanotubes (CNTs) are difficult to be manipulated. Various approaches have been carried out for making nanotube probes, including selection of longest protruding tube from a nanotube aggregate adhered onto substrate [1], direct synthesis of oriented CNTs on a porous surface via metal catalytic pyrolysis [2] and mechanical attachment of CNTs onto an AFM tip under dark-field optical microscope [3]. In this work, automatic attachment of CNTs onto metal tips at solvent–air interface is demonstrated. Adhered CNTs can be bridged between electrodes.

Multi-walled boron-doped carbon nanotubes (BCNTs) produced by arcing BN-containing graphite rods were used as probe formation materials [4]. Distribution of tube length is centered at 20–30 μm and their aspect ratio is greater than 1000, meanwhile, BCNTs possess lower intrinsic resistance ($10^{-5}$–$10^{-6}$ Ω m) than pure carbon tubes [4]. Fig. 1a–e depicts CNT-mounting procedure. BCNTs (50 mg) are dispersed in acetone solution (30 ml), followed by an ultrasonic stirring for 10 min (Fig. 1a–b). An electrochemically sharpened tungsten tip (ca. 1 μm) electrically connected to ground level is dipped into solution for 10–20 s (Fig. 1c–d), tip retracts (Fig. 1e). Optical microscope reveals that BCNT bundles always adhere onto tip. Our repeat procedures show successful alignment of BCNTs with tip by ca. 60–70%; a value was obtained based on 100 runs. Organic solvents such as toluene, chloroform, ethanol and benzene produce a similar result. Fig. 1f–g shows oriented nanotubes adhered on metal tips from different runs. The probe-tip configuration relies only on van der Waals binding (Fig. 1f–g), therefore a drastic vibration on tube-tip assembly often leads to tube deviation. Nevertheless, adhered BCNTs do not fall. Adhered bundle is a tapered-structure, i.e. BCNT fringes are clearly seen at tube-tip junction; becomes obscured at its free end (Fig. 1f–g). On the basis of previous data [4], the tiny bundles (Fig. 1f–g) correspond to ca. 10–25 BCNTs at tube-tip junction and ca. 3–8 BCNTs at free end respectively. Oriented tube-tip formation at sharper tips is realized and tubes mostly align with tip at solvent–air interface. Fig. 1h–j illustrates the probe transfer to another tip coated with Ag-paste. Fig. 1k displays a successful transfer. Fig. 2a–e highlights the transfer of BCNT-probe from tip to tip and corresponding sequence (Fig. 2f–j). Fig. 2f shows a tiny bundle attached by two carbonaceous aggregates (arrows A and B, Fig. 2f). Insertion of nanotube bundle into Ag-coating is facile before paste solidification (Fig. 2g). Small vibration from micro-manipulator is capable of pulling-out embedded nanotubes from Ag-paste, accompanied by a blister-like feature (arrow, Fig. 2i). The blister indicates that Ag is still in a paste form and nanotube bundle is truly embedded in Ag-coating. One of the carbonaceous aggregates has vanished after tube submergence (Fig. 2j). The length of free-standing bundle is ca. 20 μm and carbonaceous aggregates A and B locate approximately at distance of 3 and 12 μm from tube-tip junction respectively (Fig. 2f), namely, the depth of bundle insertion into paste exceeds 8 μm and remaining aggregate (arrow, Fig. 2j) is likely to be aggregate B; A has submerged into paste.

Fig. 3 displays a tiny bundle bridged between Ag-electrodes and its electrical resistance measurements were carried out at zero-bias to exclude the modification of band structure by electric field. The initial bridging resistance is ca. 10–11 kΩ between $t = 0$ and 9 min, due to wet paste (Fig. 3a–b). When paste is dried, the resistance rapidly drops to 80 Ω (Fig. 3c). This value maintains for 15 min ($t = 8–23$ min, Fig. 3c), then increases

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to 12–20 kΩ \( (t = 23–30\) min, Fig. 3d). Re-promotion of resistance at \( t = 23\) min possibly arises from the contraction of Ag-paste during solidification, thus causing a gradual pulling-out of embedded BCNTs from Ag-matrix. The nano-bridge structure shown here is similar to the device made by dipping single nanotube into liquid metal (Fig. 3c) [5], whereas our histogram of time-dependent resistance data exhibits a phonon-dominant mechanism in doped CNTs, which is consistent with report [6]. To our best acknowledge, the tube-bridging resistance recorded between \( t = 8\) and 23 min is lowest value ever reported. Two dried Ag-coatings in contact gives 0.1–0.5 \( \Omega\) only, negligible in terms of overall resistance. Accordingly, 80 \( \Omega\) truly come from bridging BCNT-bundle. The intrinsic resistance of a metallic CNT with two sub-bands intercepted at \( E_F\) level is 6.5 kΩ, corresponding to 155 \( \mu\)S [1]. The lowest resistance seen here comes from two factors. Firstly, length of bundle (ca. 20–50 BCNTs) exceeds 10 \( \mu\)m (i.e. greater than gap between electrodes), and individual BCNT resistors connected in parallel between electrodes can be expressed as \( 1/R_n = 1/R_1 + 1/R_2 + 1/R_3 + \cdots, n\) number of nanotubes [7]. When individual BCNTs within bundle is shorter than gap between electrodes total resistance is written as \( R_{tot} = R_n + 1/R_n + R_{con}\) because carrier scattering mostly occurs at tube–tube interface \( (R_{con}:\text{contact resistance})\). Secondly, BCNTs are essentially lower resistance than pure carbon nanotubes [8]. Individual BCNTs with a conductance of 500 \( \mu\)S (ca. 5–6 sub-bands crossing at the \( E_F\) level) have been detected [9]. If individual BCNT resistors are taken to be ca. 2.58 kΩ (corresponding to five sub-bands intercepted with \( E_F\) level, 12.5 kΩ/5), then BCNT resistors bridging is \( 1/R = \sum 1/R_n\), \( R = 131\) Ω and 51 Ω for \( n = 20\) and \( n = 50\) BCNTs, respectively. This number is comparable with reported value here. In summary, automatic attachment of BCNTs onto metal tip at solvent–air interface provides successful alignment of tube-tip assembly at ca. 60–70%. A lowest resistance is present when BCNTs are continuously bridging electrodes.

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**References**

Icicle-like carbon nanotubes forest at tungsten wire tip formed by high-voltage corona discharge

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Nowadays carbon nanotubes (CNTs) are produced by several methods based on various principles, i.e., arc discharge [1,2], laser ablation [3], chemical vapor deposition (CVD) [4–7], etc. The methods using arc discharge and laser ablation are suitable for production of CNTs in powdery forms. On the other hand, CVD can be applied to produce CNTs in aligned forms on substrates. When catalysts are prepared on a stable substrate surface and reaction gas was fed to the substrate at an elevated temperature, CNTs which have blush-like high-density alignments can be formed [4,5]. The formation of this morphology is caused by mutual support between CNTs one another during their growth process. In addition, if plasma is applied to assist the CVD process, the controllability of the growth of CNTs can be enhanced, and the shape and the distribution of the CNTs can be changed by varying some operational parameters [6,7]. By use of the plasma-enhanced CVD (PECVD) process, low density alignments of CNTs can be fabricated by applying high-voltage bias on the substrate to enforce the CNTs growth to straight direction. Such CNTs in controlled alignment on the surface of a substrate can be useful to fabricate excellent electric field emission devices [8]. In addition, PECVD process gives a benefit to decrease the temperature of the reaction field for CNTs growth due to the formation of reactive carbonaceous radicals. In this study, we employed a simple process using corona discharge [9,10] to provide the high-voltage bias and plasma environment to a selective CNTs growth zone at the tip of a tungsten (W) wire cathode. As a feature of this method, we can build the reactor very easily because this method requires neither vacuum systems nor high-frequency power source. This letter reports a discovery of a unique morphology of CNTs film that we refer as ‘icicle-like CNTs forest’, which were formed by such CVD process with support of the high-voltage corona discharge.

The apparatus used here is schematically shown in Fig. 1. Tungsten (W) wire (diameter = 0.3 mm) was co-axially placed in a cylindrical quartz tube (inner diameter = 20 mm) against a flat-end graphite rod (diameter = 9 mm) with a gap, 8 mm. This graphite rod was electrically earthed. Before the W wire was placed in the corona discharge reactor, the surface of the W wire was oxidized by a temperature elevation to 800 °C in air (temperature elevation rate = 46 °C/min) in the furnace, and the furnace was immediately turned off when the temperature reached this target value. After the furnace was cooled down, the W wire was coated with Ni by sputtering. After the W wire was set in the reactor, H2 was firstly fed into this quartz tube (1000 cm3/min), and the temperature of this reaction field was raised to 600 °C for 10 min to anneal the Ni film and to form nanoislands with a size ranging between 10 and 30 nm. After this annealing process, ethylene (C2H4) was admixed to this H2 flow (C2H4/H2 = 1/100), and a direct current high-voltage (1.6 kV) of negative polarity was...