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Synthesis of Single- and Double-Walled Carbon Nanotube Forests on Conducting Metal Foils

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Chemical vapor deposition (CVD) provides direct growth of carbon nanotubes (CNTs) on substrates and thus is the preferred growth method for nanoelectronic applications.[1,2] For this purpose, generally, SWNT syntheses have been implemented on insulating substrates, such as Si wafers or quartz. In many cases, growths on conducting substrates have resulted in the formation of multi-walled carbon nanotubes (MWNTs) or graphite films.[1−4] The difficulty to efficiently grow SWNTs on conducting films restricts device architectures and fabrication processes for nanoelectronic devices.

Here, we report a highly efficient growth of SWNT and double-walled carbon nanotube (DWNT) forests on conducting metal foils. We found that foils made of Ni-based alloys with Cr or Fe were excellent for SWNT (DWNT) synthesis. DWNTs grown on these substrates showed homogeneous field emission throughout the entire cathode grid, thus providing evidence of electric contact between the DWNTs and the metal foils. These results open up an economical route for the mass production of SWNT (DWNT) forests and also enable the straightforward integration of SWNTs (DWNTs) into nanoelectronic devices, such as field emission displays.

Catalytic thin films of Al_2O_3 (30 nm)/Fe (1 nm) were sequentially sputtered onto metal foils. Al_2O_3 was used to enhance growth efficiency. Electronic conduction measurements showed that the Al_2O_3 was too thin to form an insulating barrier on the metal foils, enabling the subsequently grown CNTs to have electric contact with the metal foil substrate. Highly efficient CNT syntheses were carried out using water-assisted CVD at 750 °C with an ethylene carbon source (100 sccm) and water (200−300 ppm) and He as the carrier gas.[5]

A survey of the direct syntheses of SWNTs on commercially available and economically affordable pure metal foils, such as Al, Mo, etc., showed that they suffered from a variety of difficulties in SWNT (DWNT) growth by CVD. For example, Al melted at the growth temperature; Mo, Ta, and Nb grew brittle after exposure to the oxidation−reduction CVD growth ambient; Ag and Cu foils did not support CNT growth.

Importantly, we did find that Ni-based alloys with Cr or Fe possessed both high durability to the CVD ambient and the ability to support highly efficient SWNT (DWNT) synthesis. Water-stimulated catalytic activity produced dense, catalyst-free, and vertically aligned SWNT forests with millimeter-scale heights directly grown on metal foils as demonstrated by a 1 mm tall SWNT forest on Inconel 601 foil (Figure 1A). Similarly, successful syntheses of SWNT forests were achieved on various alloys spanning many standard metals, such as Inconel 601, YEF 426, NiCr, YEF 50, and SUS 310S, covering a wide range of Ni−Fe−Cr compositions (Figure 1B and Supporting Information Table S1 for the composition of alloys). Transmission electron microscopy (TEM) analysis (Figure 1C,D) showed that the growth product was mainly SWNTs with selectivity approaching 95%, a result similar to the level achieved on Si wafers. Furthermore, the efficiencies of the water-assisted growths on these foils were very high, almost approaching the level of Si wafers, as shown in the plot of the yields in Figure 1C. The G-band/D-band ratios (Figure 1C) of the Raman spectra using 532 nm excitation wavelength (see Supporting Information Figure S2) of the forests revealed that the SWNTs grown on Ni-based foils and Si wafers were of the same quality level. These experimental results show that Ni-based alloys with Fe/Cr are excellent substrates for SWNT synthesis. The success in synthesizing similar SWNT forests, as on Si wafers, on many standard Ni-based metal foils demonstrates the generality of our approach.

In significant contrast, detailed TEM analysis revealed that CNTs grown on Ni, Fe, and two Fe−Cr alloys (SUS 430, SUS 304) consisted not only of SWNTs but also of MWNTs. The G-band/D-band ratios were low for CNTs grown on these foils in accordance with the appearance of MWNTs. We interpret the formation of MWNTs on these foils as a result of the catalytic effect of the Ni/Fe content in the foils.[4,6] The Fe and Ni contained within their respective foils seem to increase the amount of catalytic metals, resulting in MWNTs. Growth on thinner Fe catalytic films only resulted in a reduction of the yield, while the product remained a composite of SWNTs/MWNTs. We could not find a direct relationship between the SWNT selectivity and flatness of the substrates (see Supporting Information Figure S3).

To demonstrate the versatility of CNT forests as electrodes and direct electric contact of CNT forests with the foils, field electron emission from a CNT/foil cathode to anode was measured. To this end, we grew a short DWNT forest on a 1 cm diameter YEF 426 metal cathode by reducing ethylene to 20 sccm (Figure 2A). We chose YEF 426 because of its similar thermal expansion coefficient with soft glass, which is commercially used in cathode ray tubes. DWNTs were synthesized here because of their superior field emission properties[7] and were selectively grown by tuning the catalyst thickness to 1.8 nm, which also provides DWNTs on Si wafers.[8] TEM images (Figure 2B) confirmed that the majority of CNTs synthesized were DWNTs. The ability to control the selectivity of SWNTs and DWNTs highlights the controllability and reliability of Ni-based alloys for CNT synthesis. The emission current exponentially increased with increasing electric field (Figure 2C), following the Fowler−Nordheim equation.[9] The spatial

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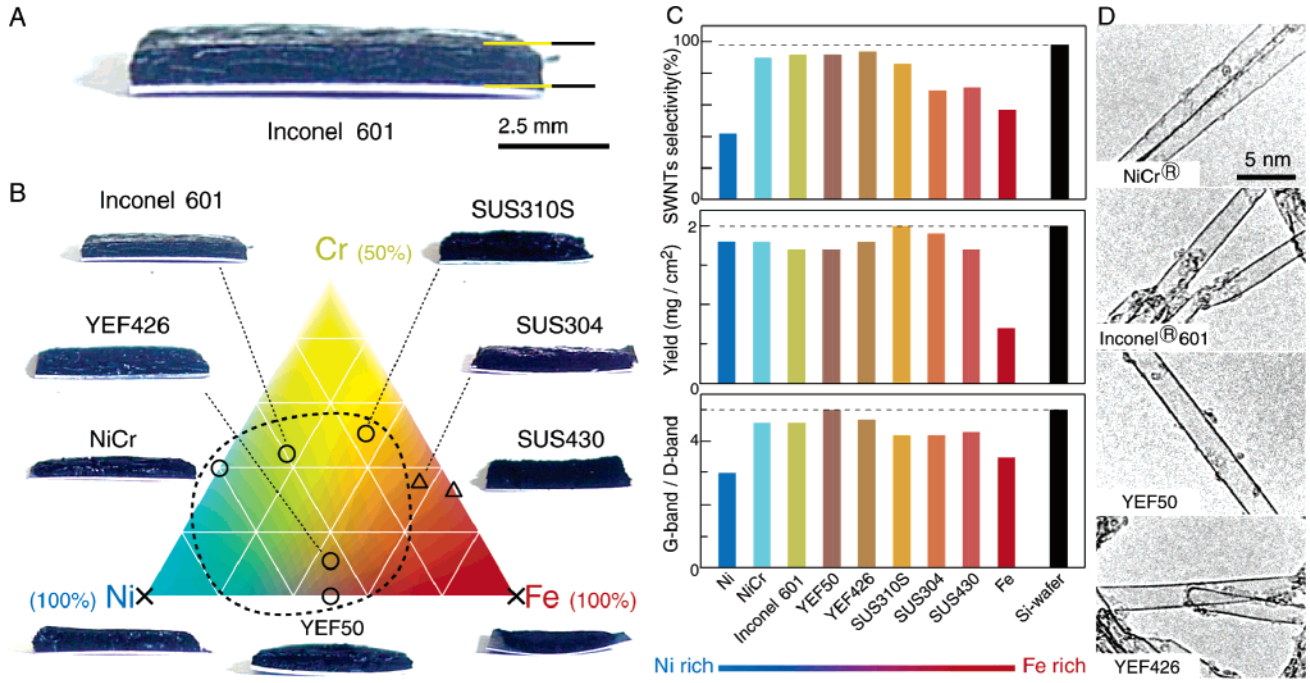

Figure 1. Direct growth of CNT forests on Ni−Cr−Fe alloys with water-assisted CVD. (A) A photograph of a SWNT forest synthesized on Inconel 601. (B) Correlation between components of Ni−Cr−Fe alloys and photographs of CNT forests grown on them. Symbols indicate the level of SWNT selectivity (○ high selectivity; Δ medium selectivity; × low selectivity). (C) A family of histograms showing selectivity of SWNTs, yield per cm^2, and G-band/D-band ratio of Raman spectra. (D) TEM images of SWNTs synthesized on Ni-based alloys.

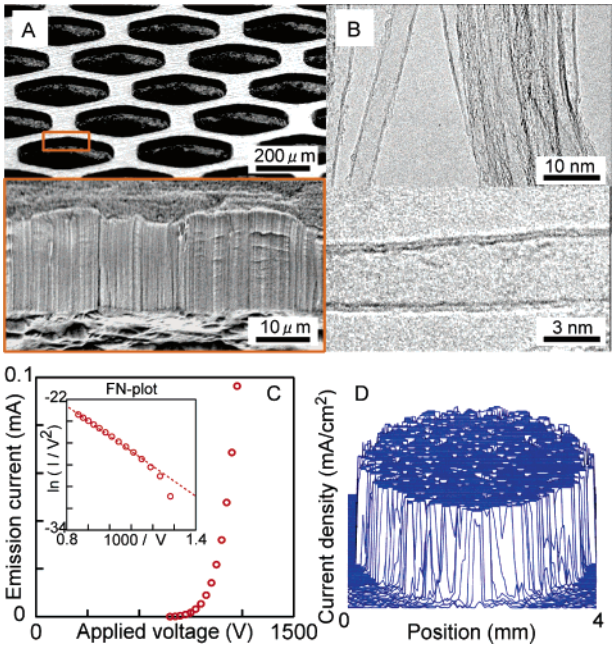

Figure 2. DWNT/YEF 426 as an electron field emitter. (A) Scanning electron microscopy images of a DWNT forest directly grown on a YEF 426 grid. (B) TEM images of the DWNTs. (C) Emission current versus applied voltage profile. (D) Emission distribution profile of an electron emitter at a display range of 0.00−1.00 mA/cm^2.

mapping of the emission current at the range of 0.00−1.00 mA/cm^2 showed an excellent homogeneity (Figure 2D), an important point for the practical application toward field emissions displays. Homogeneous emission from the DWNT electrode is direct evidence of good electrical contact between DWNTs and the grid substrate.

Metal foils are much more economical and scalable than Si wafers or quartz substrates. Therefore, we believe that our approach opens up an economical route toward mass production of SWNT (DWNT) forests and will facilitate flexible design of device architectures and fabrication processes for CNT devices.

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Supporting Information Available: Details for compositions of Ni−Fe−Cr alloys (S1), Raman spectra (S2), and AFM images of the substrate surfaces (S3). This material is available free of charge via the Internet at http://pubs.acs.org.

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