Transferable Thin Films of Pristine Carbon Nanotubes

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We describe here a simple and low-cost method to prepare ultra-thin, homogeneous, and transferable films of pristine carbon nanotubes (CNTs). The highly efficient chemical vapor deposition (CVD) growth method involves silica supported catalysts and alcohol vapor as gaseous carbon source. By varying the amount of catalysts, the thickness of synthesized films can be easily tuned from 20 nm (sub-monolayer) to 150 nm in a controlled fashion. High-resolution transmission electron microscopy (HRTEM) revealed that the films are composed primarily of single-walled and a small fraction of double-walled CNTs. A nonlinear relationship between film conductivity and thickness was observed. Our sub-monolayer (~20 nm) film, which is noticeably thinner than conductive CNT films synthesized using other methods (typically ~50 nm and up to ~100 μm), shows the highest conductivity of 400 mho·cm−1 with ~90% transparency in the visible range and close to 100% transparency in the infrared range. This ultra-thin film can also be transferred carrier-film free to a wide range of substrates including low-cost plastics for flexible electronics. Compared to CNT films prepared by filtration techniques, our films demonstrated superior stability against mechanical bending.

Keywords: Carbon Nanotube, Chemical Vapor Deposition, Transparent Conductive Thin Film, AFM, SEM, Raman.

1. INTRODUCTION

Carbon nanotube (CNT) is a class of extraordinary materials with unique optical, electrical, thermal, and mechanical properties.1 Several research groups have demonstrated the performance of devices consist of a single CNT as transistors,2 sensors,3 oscillators,4 and actuators.5 However, mass production of these devices is not yet possible simply because of the dissimilar properties of individual CNTs owing to their different cross-section and chirality.1,6,7 Although a combination of various procedures (for example, non-covalent complexation and selective precipitation,8 ion-exchange chromatography,9 AC dielectrophoresis,10 etc.) could be applied to lower the variation, isolation and assembling of CNTs with similar length, diameter and chirality on a wafer scale in a reproducible way are not yet realized. A more realistic approach, as adopted by several research groups,11,12 is to prepare thin films of purified CNTs and then use conventional lithographical procedures to make mass production of identical building units, each made of thousands of interconnected CNTs. The degree of purification depends on the nature of application and there is a trade-off between performance and time/cost of the purification processes. The property of each building unit is an ensemble of those of individual CNTs. Therefore, devices made out of the units show very consistent behavior. Apart from this, CNT films can be made thin enough to be almost transparent without sacrificing the conductive nature and have received considerable attention as potential alternatives to the expensive and fragile indium titanium oxide (ITO) coating widely used in commercial products, such as flat panel display and photovoltaic devices.13

There are several common methods to prepare CNT thin films: filtration of CNT dispersions through membranes,13,14 casting and transfer printing,15 and dip-coating.16 With these methods, CNT films can be made on a wide range of useful low-cost substrates, for example, plastics for flexible electronics, which are not compatible with the high temperature CNT growth conditions. The starting materials in these methods are typically as-produced CNTs in a powder form which could contain aggregated bundles, major concentrations of impurities like amorphous carbon and metal catalyst particles. Prior to film preparation, stringent post-synthesis purification and dispersion protocols involving strong sonication and/or harsh chemical treatments are often necessary to achieve high quality CNT films and consequently CNT film devices with consistency.1,13,17 These procedures, however, shorten CNTs and add defects (by attaching polar groups, for example COOH, and thereby converting the sp2 hybridized carbon into sp3). So the resulted films consist of...
relatively pure but short and defected CNTs that have considerably lowered optoelectromechano-thermal properties. In addition, films from most of these methods are comparable to those of ordinary organic polymers in terms of mechanical strength\(^1\) and suffer from inhomogeneity primarily because of the flocculation due to the van der Waals interactions among the CNTs.\(^{18,19}\) Polymers are sometimes used as binders to increase the mechanical strength of the films. But phase separation is very common due to poor miscibility, and the distribution of CNTs varies largely across a film. The formation of different micro features during the drying process could lead to additional inhomogeneity in the final film.\(^{20}\) Furthermore, the composite films generally become fragile if the CNT content exceeds 20%.\(^{21}\) At low CNT concentrations, though, CNTs are not continuous and the property (for example, conductivity) of the binder becomes the bottleneck. Here we describe a simple method to prepare pristine CNT films that are pure, homogeneous, continuous, and can be scaled down to near monolayer thickness, yet strong enough to be transferred to a wide selection of substrates of interest.

2. SYNTHESIS

Figure 1(a) shows a schematic diagram for the synthesis and transfer of the CNT film. Initially, a cocktail of catalysts: iron(III)acetylacetonate (3.1 mg, Aldrich), molybdenum(II)acetate (0.7 mg, Aldrich) and cobalt(II)acetate (4.5 mg, Aldrich), is sonicated with silica nanoparticles (7 nm in diameter, 50 mg, Sigma) in an ethanolic solution (10 ml, anhydrous) for one hour and then spin-coated (5000 rpm, 1 min) on a SiO\(_2\) (3.5 micron)/Si substrate. Subsequently, the substrate is placed into the CVD chamber (a horizontal 1" quartz tube furnace) and the temperature is ramped to 850 °C at a gradient of 50 °C/minute under a constant flow of carrier gases, namely...
300 standard cubic centimeter per minutes (sccm) of Ar and 9 sccm of H$_2$. When the CVD chamber stabilizes at 850 °C, the carrier gases are switched to bubble through an ethanol reservoir (kept at $-1$ °C) and carry alcohol vapor to the CVD chamber for CNT growth. After 20 minute of growth time, carrier gases are then switched to bypass the ethanol reservoir and the CVD system is cooled down to room temperature. The silica nanoparticles act as support/template for the formation of isolated nanosized catalyst particles during the ramp-up (calcination). Also the porosity of the silica film allows the carbon source gas to penetrate deep and enables the synthesis of multilayers of CNTs.

Next, the substrate with the as-grown CNTs is placed in a 1% hydrofluoric (HF) acid aqueous solution for 5 minutes. During this step, the supporting silica particles and the underneath SiO$_2$ layer dissolve. The substrate is then carefully immersed in water, the CNT film lifts-off completely and floats on water. The film remains suspended (for days) on water due to its natural hydrophobicity and can be transferred to a variety of substrates (see Fig. S1 of the Electronic Supplementary Information, ESI). As revealed by the scanning electron microscopic (SEM; Leo1530, Jeol) image (Fig. 1(c)), the transferred film is very homogeneous, compact and made of long CNTs entangled to each other. The relative carbon content of the as-prepared CNT film is much higher (>99%, as revealed by the energy-dispersive X-ray, EDAX spectra, Fig. 1(d)) compared to those made otherwise.$^{19,22}$ Moreover, film thickness is observed to be linearly correlated to the amount of catalysts deposited (Fig. 2). Films ranging from 20 nm to 150 nm thick (Figs. 2(a), (b)) are made in a controlled fashion by simply varying the number of drops of catalyst-silica solution spin coated. Sub-monolayer films are achievable that still consist of long interlinked CNTs and are strong enough to be handled and transferred (Fig. 2(c)).

### 3. RESULTS AND DISCUSSION

It should be pointed out that the quality, including purity, tube diameter distribution, and average tube length, of the film is very sensitive to the ratio of the catalyst precursors and silica particles in the ethanolic solution, and the amount of the alcohol vapor during the CNT growth step. We believe that the optimized catalyst recipe described in this report yields homogeneously distributed and similarly sized catalyst nanoparticles (∼2 nm in diameter, Fig. S2 of ESI) after calcination, which leads to narrow tube diameter distribution and high catalytic activity. The amount of alcohol vapor (i.e., carbon source) during CVD growth is controlled through the flow rate of carrier gases and the temperature of the alcohol reservoir. Elevated level of alcohol vapor in the growth chamber would yield amorphous carbon coating, while deficiency of alcohol vapor would lead to shorter tube length and less growth yield. We also optimized the growth temperature using the minimum amount of catalysts and the maximum yield of CNTs. From the EDAX spectra (Fig. 1(d)), it can be seen that...
the amount of catalyst is negligible (<1%) in the as-grown CNT film and this remains virtually constant after lift-off. This indicates that almost all the catalyst particles participate in CNT growth and could be trapped inside the CNT tips according to the tip-growth mechanism. Our protocol bypasses the unavoidable and extensive post-synthetic purification procedures that remove excess metal particles and carboneous by-products, but also consequently introduces defects in other methods of preparing CNT films.

The diameter of the CNTs varies from 0.8 to 2.4 nm as revealed by the height profiles of atomic force microscopic (AFM) measurements (Fig. 3(a)). In addition, high-resolution transmission electron microscopy (HRTEM) confirmed the presence of both single-wall (SW) and double-wall (DW) CNTs (Fig. 3(b), (c) respectively). The samples were prepared by sonicating films of CNT in 1,2-dichlorobenzene and casting the dispersion on Si substrates (for AFM; Nanoscope IIIa, Digital Instruments) and copper grids (for HRTEM; Titan 80-300, FEI).

Raman spectra (excitation at 514.5 nm, 0.57 mW, HORIBA Jobin Yvon) of the films show a stronger G-band (tangential C–C stretching) at ~1580 cm\(^{-1}\) (with a splitting at 1560 cm\(^{-1}\) indicating the presence of both metallic and semiconducting CNTs\(^{24}\) compared to the D-band (at ~1330 cm\(^{-1}\)) commonly interpreted to be related to the amorphous and/or defected sp\(^2\) carbons\(^{25}\) (Fig. 4(a)). The G/D intensity ratio (2.8–5.7) is lower than those SWCNT films reported in the literature\(^{26}\), which is expected due to the presence of DWCNTs.

A crude estimation of the CNT diameter can be obtained from the radial breathing mode (RBM) frequencies.

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Fig. 3. (a) The AFM image and the corresponding height profile (inset) of a CNT. The samples were prepared by sonicating the films in 1,2-dichlorobenzene and spreading the dispersion on Si substrates. More than 30 individual CNTs were checked by height profiling for each sample. (b, c) HRTEM of a SW and DW-CNT, respectively.

Fig. 4. (a) The G- and D-bands (at ~1580 and 1330 cm\(^{-1}\), respectively) in the Raman spectra (excitation at 514.5 nm, 0.57 mW) of CNT films prepared by different number of depositions. (c) The corresponding radial breathing mode (RBM) frequencies.
following the relation \( d \text{ (nm)} = \frac{223.75}{\omega_r} \text{ (cm}^{-1}) \).\textsuperscript{27, 28} For the thickest film (50 \times deposition), the RBM frequencies are primarily centered at 173 cm\(^{-1}\) corresponding to a diameter of 1.29 nm (although the peak could be a convolution due to CNTs that are very close in diameter, Fig. 4(b)). The RBM peaks of thinner films show more clearly the diameter distribution, since less bundling and intertube interactions are present. Primarily three different kinds of CNTs in terms of diameter emerge (\( \Delta \omega_r \approx 18 \text{–} 23 \text{ cm}^{-1} \), equivalent to 1.1–1.8 Å difference). The weak peaks at \( \sim 235 \) and 250 cm\(^{-1}\) (0.95 and 0.90 nm, respectively) could be related to the presence of a minor fraction of smaller SWNTs and/or the inner tube of the DWCNTs.\textsuperscript{28}

The conductivity of the films (on quartz substrates, two-probe, DC, 20 \pm 1 °C) shows a non-linear relationship with film thickness (Fig. 5(a)). Compact monolayer film (thickness = 20 nm, 5 \times deposition) persists the highest conductivity of 400 mho \cdot cm\(^{-1}\). This observation could be a direct consequence of the insufficient degree of connectivity among the metallic CNTs in the sub-monolayer films (from less than 5 \times deposition) and lower compactness (therefore higher contact resistance) in the thicker ones. The nonlinear behavior of the film conductivity makes it difficult to compare our CNT films with those made by solution deposition methods, which are typically much thicker. In the literature, the conductivity of CNT films, prepared by different methods, varies in a wide range\textsuperscript{13, 19, 22, 26} and it is a complex function of compactness,\textsuperscript{22} experimental procedures.\textsuperscript{13, 17} In addition, the presence of polar groups (may be in the salt form) and different amounts of metallic impurities (which are hard to remove even after extensive purification\textsuperscript{17, 19}) may further complicate the data in this regard. Worth noting is that our CNT films are pristine. The conductivity of our \(~20 \text{ nm} \) film (400 mho \cdot cm\(^{-1}\)) is comparable to that of the best “dedoped” 50 nm thick CNT film (666 mho \cdot cm\(^{-1}\)).

![Fig. 5. (a) The conductivity (on quartz substrates, two-probe, DC, 20 \pm 1 °C) versus the thickness. (b) UV-Vis and IR spectra of the CNT films.](image-url)

![Fig. 6. (a) The change in the conductivity of the 5x deposited (20 nm) film (on PET substrates, two-probe, DC, 20 \pm 1 °C) upon different degrees of bending. (b, c) SEM images of our film and a CNT film (on PET substrates) prepared by the “filtration technique,” respectively, upon bending. Note the damaged pattern in the later.](image-url)
reported in literature.\textsuperscript{13} We further characterized the optical transparency of our CNT films. The film (20 nm thick, 5 × deposition) shows ∼90% transparency in the visible range and close to 100% transparency in the infrared range (Fig. 5(b)).

We also characterized the stability of our CNT films under elastic bending. A 20 nm thick film (5 × deposition) was transferred onto a poly(ethyleneterephthalate) (PET) substrate. The PET substrate was then fixed between a pair of micromanipulators and bent against a metallic rod with a minimum bending radius of 4 mm, which corresponds to a maximum strain of 1.25%. The electrical conductivity of the film is highly stable under elastic bending (Fig. 6(a)). After repeated bending, the film showed no evidence of damage (as confirmed by SEM, Fig. 6(b)). As a comparison, we also prepared films on PET from commercially available CNTs (purified SWNTs, CheapTube.com) by following the “filtration technique”.\textsuperscript{13,14} After a couple of bending, the films showed significant amount of damage (Fig. 6(c)). In both cases, the CNTs are randomly oriented (Figs. S3 and S4) and the better mechanical resilience of our film is most likely due to the entangled nature of long and structurally intact CNTs (Fig. S3).

4. CONCLUSION

In summary, we report here a simple and cost effective method to synthesize and transfer ultra-thin (∼20 nm), homogeneous, conductive, and highly transparent pristine CNT films, which consist of primarily SWCNTs with a small fraction of DWCNTs (∼5% as determined by random sampling in HRTEM). The films are also highly durable against extreme mechanical bending. The CNT films are synthesized using CVD method without oxidative acid treatments and free of surfactants or “carrier” film commonly used in other methods\textsuperscript{13} for CVD film transfer. Our method is optimized to minimize defects, impurities, and undesirable absorbents on CNT surface which not only affect the film optoelectronic properties\textsuperscript{29,30} by introducing scattering centers and charge trap sites but also limit the tunability and applications of CNT films. The growth gas used here (alcohol vapor) is the cheapest compared to other carbon source gases and the silicon oxide substrates could be reused multiple times after cleaning and renewed after thermal growth of oxide layer. Film size is currently limited by the size of our CVD chamber, which can be extended to wafer scale in the future. Incorporation of liquid bed could make it possible to synthesize large areas of CNT films continuously using this method, which is to be explored soon.

\textbf{ELECTRONIC SUPPLEMENTARY INFORMATION}

\textbf{Fig. S1.} Transferred CNT films on different substrates: (a) PET, (b) glass slide and (c) metallic needle for SPME.

\textbf{Fig. S2.} TEM images of the catalyst particles embedded inside the CNTs.
Fig. S3. SEM image of the edge of a CNT film (5 × depositions) showing the entangled nature of the CNTs.

Fig. S4. SEM images of the CNT films (on PET substrates) prepared by the "filtration technique," before (left) and after (right) bending. Note that the CNTs are randomly oriented.

Fig. S5. TEM of the CNTs.

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References and Notes

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