



Direct synthesis of graphene/carbon nanotube hybrid films from multiwalled carbon nanotubes on copper

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ABSTRACT

Graphene and carbon nanotube (CNT) (G/CNT) hybrid films have recently attracted great attention due to their potential of combining the merits of both one-dimensional (1D) and two-dimensional (2D) nanostructures. Here, we report a facile approach to form G/CNT hybrid films by thermal annealing of multiwalled carbon nanotube (MWNT) networks on copper foils. At elevated temperature and in the presence of hydrogen, MWNTs are partially etched to form active carbon species which then nucleate and grow graphene on copper until the formation of a continuous G/CNT hybrid film. We find that copper plays an important role in catalyzing the etching of MWNTs by hydrogen, as no etching has been observed for MWNTs on Si/SiO₂ substrates under similar conditions. The obtained G/CNT hybrid films exhibit enhanced electrical stability under mechanical stress compared to CVD-grown graphene films.

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1. Introduction

Carbon based nanomaterials exhibit unique size- and structure-dependent properties. In particular, CNTs and graphene are low-dimensional allotropes of sp² carbon with distinctive band structures. Both CNTs and graphene have demonstrated attractive electrical and mechanical properties that are useful for many applications, such as flexible displays [1,2], sensors [3–5], and energy-storage [6–9]. The integration of CNTs and graphene into a hybrid film [10–31] or a three-dimensional (3D) hierarchical structure [32–44] offers an attractive means to combine the merits of both nanostructures. In particular, G/CNT hybrid films have been demonstrated and shown improved mechanical [12,15,21,22], electrical [10,11,13,17,18,20,22,24–26,30], optoelectrical properties [16,19,27], and catalysis capability [14,31] owing to a synergistic effect of graphene and CNT.

Various methods have been applied to fabricate G/CNT hybrid films, among which the post-synthesis assembly approach was initially employed. Routes including solution mixing and film casting of graphene oxide (GO) nanosheets and CNTs

[10,11,23,24,28,30,37,45], layer-by-layer self-assembly of positively charged CNTs and negatively charged reduced GO nanosheets, and mechanical stacking of CVD-grown graphene and CNT layers [12,15,21,27], have been previously demonstrated to produce G/CNT or GO/CNT hybrid films. The post-synthesis routes offer the advantage of low-cost and scalable fabrication of large-area G/CNT hybrid films. However, they cannot provide effective structural connection between graphene and CNTs, which limits the electrical and mechanical connection within the hybrid films. For example, the mechanical strength of physically stacked G/CNT hybrid films degrades under bending tests due to weak interaction and ineffective load transfer between graphene and CNTs [29,46]. In addition, GO/CNT hybrid films prepared by solution methods suffer from extensive lattice defects of both GO and CNTs from oxidation by strong acids or high-power ultrasonication, which seriously limits their electrical and mechanical performance [11,28].

Recently, chemically hybridized G/CNT films have been realized through chemical vapor deposition (CVD) process. Chemical methods for the preparation of G/CNT hybrid films usually involve the CVD growth of graphene on catalytic substrates that are pre-coated with CNTs [16,18,19,26] or simultaneous growth of CNTs and graphene [13]. A variety of solid precursors have been applied to prepare the graphene component of the hybrid films, including organic molecules functionalized on the surface of single-walled CNTs (SWNTs) [18] and polymethyl methacrylate (PMMA) containing self-assembled SWNT arrays [26]. Gaseous precursors have

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also been used for the chemical preparation of G/CNT hybrid films, in which SWNTs or SWNT networks were pre-coated onto Cu foil and graphene films were subsequently grown by the catalytic decomposition of methane to form a hybrid film [17,20,22,25]. Chemically synthesized G/CNT hybrid films have shown improved electrical conductivity and mechanical strength owing to the strong connection between graphene and CNTs [18,22,25,29].

Chemical synthesis of G/CNT hybrid films without additional carbon precursor can greatly simplify the fabrication process. In this study, we present a new strategy for the direct synthesis of G/CNT hybrid films by thermal annealing of MWNT networks on copper foils. MWNTs were used as both the solid carbon precursor for graphene growth and the host component for joining with graphene to produce continuous G/CNT hybrid films. Compared to previous studies, no additional carbon precursor was added for the preparation of the hybrid G/CNT films in our approach. In addition, the strong interactions between graphene and CNTs in the chemically hybridized films lead to their high electrical stability under cyclic bending tests, which makes the hybrid G/CNT film a promising candidate in flexible devices.

2. Experimental section

2.1. Preparation of MWNTs coated copper foils

MWNTs (0.1–0.4 mg) with a purity of 95% (Nanjing XFNANO Materials Tech Co., Ltd) were dispersed in ethanol (10 mL) by ultrasonication. A droplet of the MWNT suspension was then deposited onto the surface of deionized (DI) water. The ethanol with MWNTs quickly spread on the water surface as a result of the Marangoni effect [47]. Then MWNTs interacted with each other via π - π interactions as ethanol evaporated, forming a large-area MWNT film on the surface of the water. The thickness of the MWNT film can be easily controlled by adjusting the concentration of the MWNT dispersion or the volume of the ethanol deposited onto the water surface. To transfer a MWNT film spreading on water surface, a rinsed Cu foil was immersed in water and then raised slowly out of water to scoop up the MWNT film. Finally, the MWNT coated Cu foil was dried on a hot plate at 60 °C for 10 min.

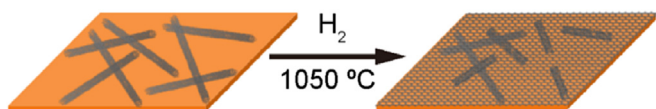


Fig. 1. Schematic of the direct synthesis of a G/CNT hybrid film by thermal annealing of a MWNT-coated copper foil. (A colour version of this figure can be viewed online.)

2.2. Direct growth of G/CNT hybrid films

In a typical synthesis, a Cu foil coated with MWNTs was loaded into a quartz tube. The quartz tube was then inserted into a horizontal tube furnace (Lindberg/Blue, Thermofisher Scientific). The furnace was gradually heated to 550 °C under air atmosphere. The temperature of the sample was maintained at 550 °C for 1 h for the removal of the amorphous carbon on the MWNTs. The system was then evacuated to a base pressure below 80 mTorr, and H₂ (99.999%, 20 sccm) was introduced into the furnace. The temperature was increased to 1050 °C, and the MWNTs were annealed for 5 min to grow graphene until a continuous G/CNT hybrid film was formed.

2.3. Characterizations

The morphology of MWNTs and G/CNT hybrid films was characterized with scanning electron microscope (SEM, Hitachi S8220) and transmission electron microscope (TEM, Tecnai G2 F20 U-TWIN, FEI). X-ray photoelectron spectroscopy (XPS) was collected in ESCALAB 250Xi. Thermogravimetric analysis (TGA) was carried out with Diamond TG/DTA (PerkinElmer). Raman Spectra (excited at 514.5 nm) were obtained with a micro-Raman microscope (Renishaw inVia plus). To investigate the mechanical properties of G/CNT hybrid films, hybrid films of 2 cm × 0.3 cm were transferred onto 80 μ m thick PET substrates by using a PMMA-assisted transfer technique. The resistance of the G/CNT hybrid films or CVD-graphene films was monitored (Keithley semiconductor parameter analyzer, 4200 Source Meter) upon cyclic bending strains.

3. Results and discussions

Fig. 1 shows a schematic for the direct growth of a G/CNT hybrid film by thermal annealing of MWNT networks coated on a copper foil in the presence of hydrogen. The MWNTs were covered with amorphous carbon shells (**Fig. S1a**). XPS and TGA of the as-received MWNTs show no sign of metal catalyst residue (**Figs. S2 and S3** and **Table S1**). To remove the amorphous carbon, the MWNT networks were firstly calcined at 550 °C under air atmosphere. After calcination, the amorphous carbon shells of the MWNTs were completely removed by selective oxidation (**Fig. S1b**). The purified MWNTs have an averaged diameter of about 21 nm and length of 1.5 μ m.

After a further annealing process at 1050 °C in the presence of hydrogen, a continuous G/CNT hybrid film was formed (**Fig. 2a** and **b**). The transformation from MWNTs to G/CNT films was monitored with Raman spectroscopy measurements. In the Raman spectra of the as-received and purified MWNTs (**Fig. 2c**), the peak at 1575 cm^{-1} is the G band that can be attributed to the in-plane

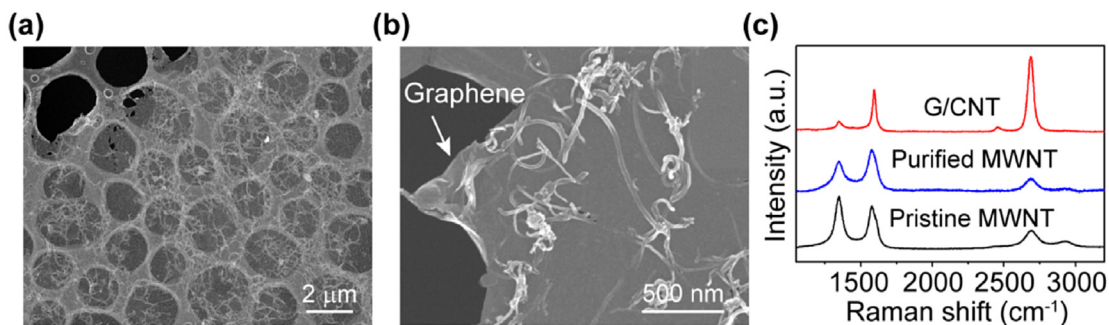


Fig. 2. (a, b) SEM images of a G/CNT hybrid film supported on a Cu micro grid; (c) Representative Raman spectra of the as-received and purified MWNTs and G/CNT hybrid film. (A colour version of this figure can be viewed online.)

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