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One-step growth of graphene-carbon nanotube hybrid materials by chemical vapor deposition

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Abstract:

Graphene-carbon nanotube (CNT) hybrid materials were synthesized by simple one-step chemical vapor deposition (CVD) using ethanol as precursor. On a copper foil decorated with silicon nanoparticles (Si NPs), a graphene film grows uniformly on the substrate while CNTs sprout out from Si NPs to form a network on top. The density of CNTs can be controlled by the CVD growth temperature. As measured by scanning and transmission electron microscopy, the obtained CNTs exhibit bamboo-like multiple-wall

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structures. Electrical characterization shows that the graphene-CNT hybrids exhibit p-type field-effect characteristics and a significantly higher conductivity compared to a CVD grown pure graphene film.

1. Introduction

Graphene, a 2D carbon material comprised of a single sheet of hexagonally packed carbon atoms, has attracted tremendous attention due to its unique electrical, physical and optical properties [1-4]. It has been demonstrated great potentials in various applications, such as field-effect transistors [5-8], transparent electrodes [9-10], energy-storage materials [11-12], composites [13-14], chemical and biosensing [15-20], and many other areas [21-23]. In order to combine the merits of the 2D graphene and 1D carbon nanotube (CNT) nanocarbon materials, many attempts have recently been made to obtain graphene-CNT hybrid materials or composites. For example, Tung et al. reported a nanocomposite comprised of chemically converted graphene oxide (rGO) and CNTs for high-performance transparent conductors [24]. Using a self-assembly method, Yu and Dai [25] fabricated rGO-CNT hybrid films with interconnected networks, which were used as supercapacitor electrodes. By chemical vapor deposition (CVD), Fan et al. prepared a three-dimensional (3D) rGO-CNT-rGO sandwiched structure where the CNT pillars grow between two rGO layers, used for electrodes in supercapacitors [26]. Recently, the graphene-CNT hybrid has also been obtained using a solid-phase layer-stacking approach with ethanol wetting [27]. However, these nanocarbon hybrids require multiple fabrication/synthesis steps or use rGO as the non-ideal substitute of graphene. The density of CNTs in the hybrid materials is difficult to control. Here we

report a simple approach to synthesize highly conductive graphene-CNT hybrid materials by one-step CVD growth on Si nanoparticle (Si NPs) coated copper foil. The electrical conductivity of the graphene-CNT hybrids is significantly higher than that of pure graphene films.

2. Experimental

2.1 Preparation of graphene-CNT hybrid materials

The graphene-CNT hybrids were grown by CVD on a copper foil coated with Si NPs under atmospheric pressure using ethanol as precursor. Briefly, after 70 or 100 nm Si NPs (Aldrich) dispersed in ethanol were spin-coated on the surface of copper foil, the sample was loaded into a quartz tube furnace with a temperature gradually increased to 800 or 900 °C in the H₂/Ar environment (20% H₂, 100 sccm) to reduce the native copper oxide on the surface of copper foil. Then, the ethanol vapor was introduced into the tube by H₂ flow (40 sccm) for growth of graphene-CNT hybrids. The schematic of the process is shown in Fig. 1. In control experiments, using the same CVD, the pure graphene film was grown on the copper foil without coating Si NPs.

Fig. 1. Schematic of one-step growth of graphene-CNT hybrid materials by CVD on Si NPs pre-coated copper foil.

2.2 Characterization

The morphology of graphene-CNT hybrids was characterized with scanning electron microscope (SEM) and transmission electron microscope (TEM). Raman spectra were obtained with a WITec CRM200 Confocal Raman microscopy system (laser wavelength 488 nm and laser spot size about 0.5mm). The Si peak at 520 cm^{-1} was used as a reference for wavenumber calibration. The as-grown pure graphene and graphene-CNT hybrid films were transferred onto SiO_2/Si substrate [28], which was then covered with a hard mask. The Au source and drain electrodes (30 nm thick, channel length 50 μm) were deposited on top of the graphene or graphene-CNT films by thermal evaporation. The electrical measurements were performed in ambient condition using a Keithley semiconductor parameter analyzer (model 4200-SCS).

3. Results and discussion

The morphology of Si NPs and graphene-CNT hybrids grown on copper foils were observed by SEM. Fig. 2a is a typical SEM image of 100 nm Si NPs spin-coated on a copper foil substrate. It is well known that the graphene films are easily grown on copper foil by CVD [5]. In our CVD, CNT network was simultaneously obtained on top of the graphene film and firmly attached on the surface of graphene *via* strong π - π stacking, as shown in Fig. 2b. The magnified image indicates that the density of CNTs is high (top inset in Fig. 2b), and the CNTs were stemmed from Si NPs (bottom inset in Fig. 2b). It have been reported that the CNTs can grow in the metal catalyst-free CVD [29,30]. But the size of the non-metal particles must be small enough (several nanometers). Our Si NPs are much bigger (70 nm or 100 nm) than this size limit. To investigate the role of Si NPs, the same CVD was applied to SiO_2/Si substrates spin-coated with 100 nm Si NPs.

CNT growth was not observed (Fig. S1 in Supporting Information (SI)), indicating that the copper foil is essential for the growth of CNT and large Si NPs alone cannot serve as catalysts for CNTs growth. It is conceivable that, at high temperature (800 °C), Cu may

Fig. 2. (a) SEM image of Si NPs pre-spun-coated on copper foil. (b) SEM images of graphene-CNT hybrids grown on copper foil at 800 °C. Inset: (top) magnified SEM image of (b) and SEM image of CNTs grown from single Si NP (bottom). (c) SEM image of graphene-CNT hybrids with a lower CNT density. (d) Raman map of the graphene-CNT hybrids film constructed by plotting peak width of G-band (1500-1700 cm⁻¹) as the map height. (e) Raman spectra of CVD grown graphene (bottom),

CNTs (middle) and graphene-CNT hybrids (top) on SiO₂/Si substrate. (f) Fitting spectra of graphene-CNT hybrids Raman G band.

evaporate, precipitate, and aggregate on Si NPs to serve as the nano-catalysts for growth of CNTs. This hypothesis is consistent with a previous report in which Si spheres pre-soaked in metal catalyst solution can initiate the growth of CNTs [31].

The Raman map of the graphene-CNT hybrid materials constructed by integrating the G band area (1500-1700cm⁻¹) allows us to identify the coexistence of graphene films and CNTs. A region of a relatively low CNT density is chosen for Raman mapping (Fig. 2c), in which the lighter regions indicate the graphene film and the brighter regions indicate the CNT bush on graphene film (Fig. 2d). The Raman spectrum of the graphene regions is similar to that of the graphene films grown on Cu foils using alcohol CVD without putting Si NPs (Fig. 2e). The two characteristic peaks at ~1570 and ~2700 cm⁻¹ can be assigned to the G and 2D band of graphene, respectively [32]. The peak width of 2D band and the ratio of 2D/G (~0.6) suggest that the graphene film is few-layered. In comparison, the Raman spectrum of graphene-CNT region exhibits broadened G and 2D bands, a weak G' peak, and a prominent D band due to the existence of CNTs. To confirm this, CNTs from the hybrid materials were detached by sonication and casted onto fresh SiO₂ substrates for Raman measurements. As expected, the Raman spectrum of CNTs presents a large defect peak (D band) at ~1350 cm⁻¹ and a weak G' peak at ~1615 cm⁻¹, in addition to G and 2D bands with a slight shift to lower vibration frequencies. Interestingly, the G and 2D band shifts disappeared in the graphene-CNT hybrids. As shown in Fig. 2f, the G-band of graphene-CNT hybrids can be fitted into three major peaks corresponding to

G' band (1615 cm^{-1}) and G band (1576 cm^{-1}) [33] from CNTs and G band (1588 cm^{-1}) from graphene. These results confirm that graphene film has grown simultaneously by the CVD and formed graphene-CNTs hybrid materials in one-step.

At a higher CVD growth temperature ($900\text{ }^{\circ}\text{C}$), the graphene-CNT hybrids can also be obtained. But, the CNT density on the surface of graphene film is significantly decreased (Fig. S2 in SI), indicating that the density of CNTs can be controlled by the growth temperature. Our experimental results also demonstrate that graphene-CNT hybrids can be obtained using the smaller Si NPs (70 nm) coated on copper foil (Fig. S3 in SI).

Fig. 3. (a) TEM image of CNTs grown on a Si NP surface. (b) A magnified TEM image of a single bamboo-like CNT. (c) High-resolution TEM image of crystalline bamboo node of a CNT. (d) TEM image of the edge of the grown graphene film.

Fig. 3a shows the TEM image of a Si NP with grown CNTs on its surface. The Cu NPs (dark dots) with outgrown CNT on the Si NP can be clearly identified. It can be concluded that the role of Si NPs is to condense Cu vapor from Cu substrate at high temperature to form Cu NPs, which, in turn, catalyze the growth of CNTs. We have attempted CVD growth by spin-coating or drop-casting small Fe nanoparticles, which can directly catalyze CNT growth, on Cu foil. But, only graphene film without CNTs was resulted, presumably due to melting of metal particles into Cu substrate at high temperature. We noticed a recent report on synthesis of 3D graphene-CNT nanostructure [34]. In this study, 5-nm-thick film of Fe catalysts was uniformly evaporated on Cu substrate using e-beam and dense vertical CNTs were obtained on a simultaneously grown graphene film underneath. This is distinct to the thin-film CNT network on graphene layer demonstrated here.

The magnified TEM image (Fig. 3b) demonstrates that the CNT exhibits bamboo-like structure with a Cu nanoparticle at its end. As reported previously, the formation of bamboo-like CNTs arise from the simultaneous vertical and lateral growth of CNTs in the presence of mixed gas (H_2 and ethanol in our case) [35]. The hollow core of CNTs is approximately 10-20 nm in diameter. The high-resolution TEM image of the bamboo node reveals that the thickness of multilayered CNT wall and the node is about 7 and 4 nm, respectively (Fig. 3c). The measured graphitic interlayer spacing is about 0.34 nm (Fig. 3c), which is consistent with the previous report [35]. Fig. 3d presents a typical TEM image at the edge of the CVD grown graphene film, confirming a few layer graphene is formed [28].

To evaluate the electrical property of the obtained graphene-CNT hybrid materials, field-effect transistors (FETs) with graphene-CNT or pure graphene films were fabricated on SiO₂ (300 nm)/Si substrate, as shown in Fig. 4a. Fig. 4b and 4c show the I_d - V_g (drain current versus back-gate voltage) and I_d - V_d (drain current versus drain voltage) curves of the pure graphene and graphene-CNT hybrid devices, respectively. The I_d - V_g curves show that both the pure graphene and graphene-CNT hybrid FETs exhibit p-type characteristics (Fig. 4b). The I_d - V_d curves indicate that the electrical conductivity of the graphene-CNT hybrid grown at 800 °C increase greatly as compared to the pure graphene film (about fivefold) (Fig. 4c). In comparison, graphene-CNT hybrid grown at 900 °C gives lower CNT density and thus lower conductivity. The synergistic effects arising from CNT-graphene interaction has been previously reported [27, 36, 37]. Although mechanistic investigations are required, it is conceivable that the conjugation of the 2D graphene and the percolating network of 1D CNTs results in a quasi-3D conduction network with exceptionally high conductivity at low carbon mass. It postulates the potentials of graphene-CNT hybrid materials as superior and transparent electrical conductors.

It is arguable that spin-coating multi-walled CNTs on graphene film may alternatively be used to obtain graphene-CNT hybrid. But surfactants are needed to disperse CNTs for spin-coating, which are known to severely compromise the CNT network conductivity. In addition, uniform CNT networks by spin-coating often rely on pre-functionalization of the surface (e.g., APTES coating). Such coating, however, would adversely affect the interaction between the graphene film and the CNT network. We have tried both spin-coating (Fig. S4 in SI) and dip-coating to deposit multi-walled carbon nanotubes

(dispersed by 4-dodecylbenzenesulfonic acid surfactant) on CVD grown graphene film. But we were not able to obtain uniform and continuous CNT network. As demonstrated here, our one-step synthesis is a simple procedure that can reproducibly generate a highly conductive nanocarbon hybrid without any use of surfactants, solvents or chemical treatments. Other nanoparticles may be used instead of Si NPs, as long as they can survive through the high temperature growth process without melting or reduction, for example, Al_2O_3 and MgO particles which have been used as the support for CNT growth [38, 39].

Fig. 4. (a) Schematic of a pure graphene or graphene-CNT hybrid FET. (b) I_d - V_g and (c) I_d - V_d curves of pure graphene and graphene-CNT hybrid (grown at 800 or 900 °C) FETs.

4. Conclusions

Highly conductive graphene-CNT hybrid materials have been synthesized on Si NP-coated copper foil by a one-step chemical vapor deposition. The SEM and TEM characterizations indicate that the CNTs sprouted out from Si NPs distribute on the surface of graphene uniformly and have bamboo-like structures. This simple method provides a novel route to obtain nano-carbon hybrids. The shape and property of the hybrids could be tuned by the growth conditions (e.g., temperature and growth time), and the size, density and patterns of Si nanoparticles.

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