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Constructing 3D CNTs-SiO_2@GNP structures by using GO sheets as template

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Abstract

A three-dimensional carbon nanotube-graphene oxide hybrid (CNT-SiO_2@GO) was synthesized by floating-catalyst chemical vapor deposition (CVD), in which ferrocene was used as catalyst precursor, acetylene as carbon source, respectively. graphene oxide (GO) was pre-treated by tetraethyl orthosilicate (TEOS) to deposit a SiO_2 layer on both side of the platelet surface. The morphology, structure and component were investigated by scanning electron microscope, transmission electron microscope and thermogravimetric analysis. The obtained hybrid has a uniform structure with a platelet sandwiched by aligned CNTs vertical to its surface. The length of CNT can be well controlled by the variation of growth time. The growth mechanism was also elaborated by comparing the GO substrates before and after TEOS treatment.

Keywords: CVD, SiO_2@GO, CNT-GO@SiO_2 hybrid

1. Introduction

Graphene has received tremendous attention from both the experimental and the theoretical scientific communities due to its unique electrical, thermal and mechanical properties. It provides an ideal fillers to prepare functional materials for a wide range of applications [1]. However, their applications have been limited by its industrial production, both in quality and quantity. Due to the ultra-high specific surface, graphene tends to form aggregation and reduce its pristine performance. Many methods have been developed to prepare graphene. Among them, the oxidation and reduction of graphite is one of the most effective methods in mass production of graphene [2]. However, the reduction of GO leads to irreversible agglomeration and precipitation [3]. As a result, the unique 2D feature of graphene would be lost. Besides, due to the thin thickness, graphene tends to aggregate in the matrix when fabricating into composites which reduces its pristine performances. Thus, large amounts of works have been focused on better using excellent properties of graphene by exploiting 3D structures of graphene based hybrids.

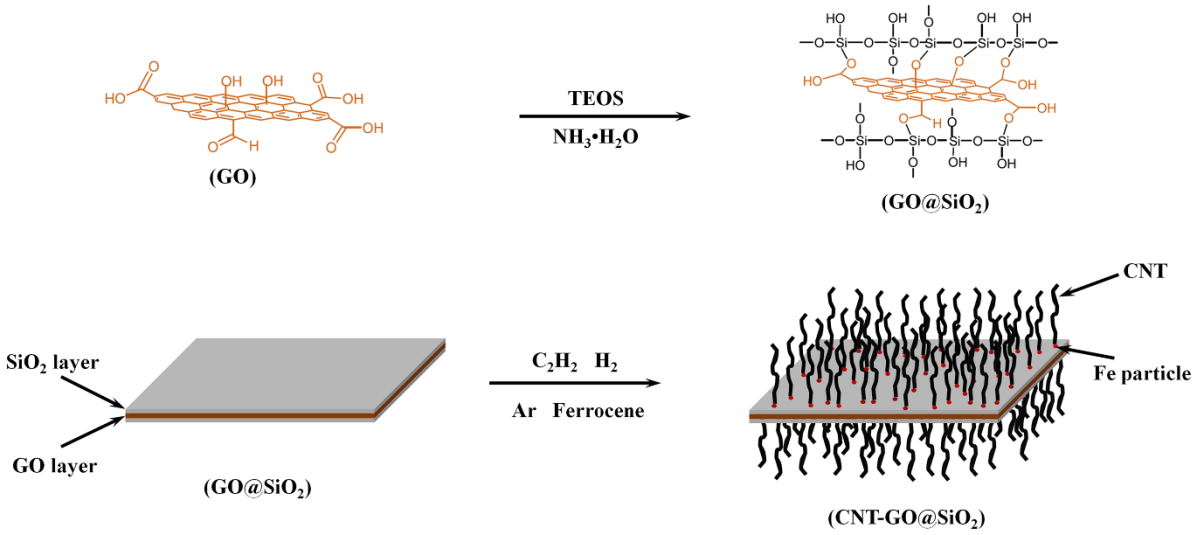
Attentions to combining CNTs and graphene have been attracted to prepare graphene-CNT reinforced composites for different applications [4, 5]. Significant property enhancement has been achieved in these materials with the existence of CNTs which are believed to bridge the defects for electron transfer and, in the meantime, to increase the basal spacing between graphene sheets. In recent years, a 3D carbon material, consisting of parallel graphene layers stabilized by vertically aligned CNTs on the graphene planes (CNT-GNP), has been fabricated by CVD method. The CNT-GNP has been used as reinforced fillers in various kinds of materials [6, 7]. However, experimental investigation has demonstrated that most cases of growing CNTs on graphite substrates is not uniform due to the poor wettability between graphite surface and catalyst

particles, which results in aggregation. Meanwhile, coalescence of the catalyst particles always happens on the graphite substrate during sintering which also affects the homogeneous distribution of CNT on graphite substrates.

Therefore, how to improve the wettability between graphite surface and catalyst particles as well as avoiding coalescence as much as possible become a crucial point to prepare CNT-GNP hybrid. In this work, a uniform layer of SiO_2 was first covalently bonded to the GO surface by a typical sol-gel method. Then, the CVD process was conducted to grow CNT on the SiO_2@GO surface. (In this work, oxide graphene (GO) with a layer of SiO_2 prepared by sol-gel method will be uses instead of graphite as a substrate to grow CNT by CVD.) The length and density of CNT array growing on the SiO_2@GO will be controlled by the synthesis time and the morphology and component will be investigated by electron microscope and TGA, respectively.

2. Experiment

2.1 Samples preparation



Scheme 1 Illustration of the formation of CNT-SiO_2@GO hybrid.

SiO_2@GO was prepared by a typical sol-gel method [8], as shown in Scheme 1. 100 mg GO (GO-V50, GRAPHENE STANDRAD) was loaded in a 400 mL flask, to which ethanol (210 mL) and distilled water (30 mL) were added. After ultrasonic agitation for 1h, several drops of ammonium hydroxide (30%, Aladdin) were added to the dispersion under stirring to adjust the pH to 9.0. Then, 1 mL of tetraethyl orthosilicate (TEOS, Aladdin) was added dropwise and stirred for 16h at room temperature. Finally, the product was centrifuged and further washed with 96% ethanol solution three times, respectively. The resulting precipitates were dried in a vacuum oven at room temperature for 6h to obtain SiO_2@GO powders. The hybrids were synthesized by the floating-catalyst CVD method. Acetylene was selected as carbon source, and ferrocene was served as catalyst precursor for the growth of CNTs. The synthesis temperature was fixed at 650 °C and the synthesis time were varied from 5 min to 10 min.

2.2 Characterization

The microstructure of hybrids and GO derivatives was observed by scanning electron microscope (SEM) (ZEISS, LEO 1530 Gemini) at 20 kV. Scanning transmission electron microscope (STEM) imaging was performed using a Titan^3 G2 (FEI) with a bright field emission gun (XFEG) operating at the accelerating voltage of 200 kV. Energy-dispersion X-ray microscopy (EDX) was carried out on the same equipment and operated at 200 kV in a STEM mode. The EDX maps were acquired for 10min. Thermogravimetric analysis (TGA, NETZSCH STA 443 F3) was used to evaluate the mass fraction of CNTs grafted on the SiO_2@GO surface. Around 4 mg sample was heated from 30 °C to 800 °C at a rate of 10 °C/min. The atmosphere was a mixture of oxygen and nitrogen, with a flow rate of 20 mL/min. Raman Spectrometer (LabRAM HORIBA Jobin Yvon, Edison, NJ, USA) excited by the 633 nm coherent line of a He:Ne laser was used to evaluated the carbon structure of the samples at room temperature.

3. Results and discussion

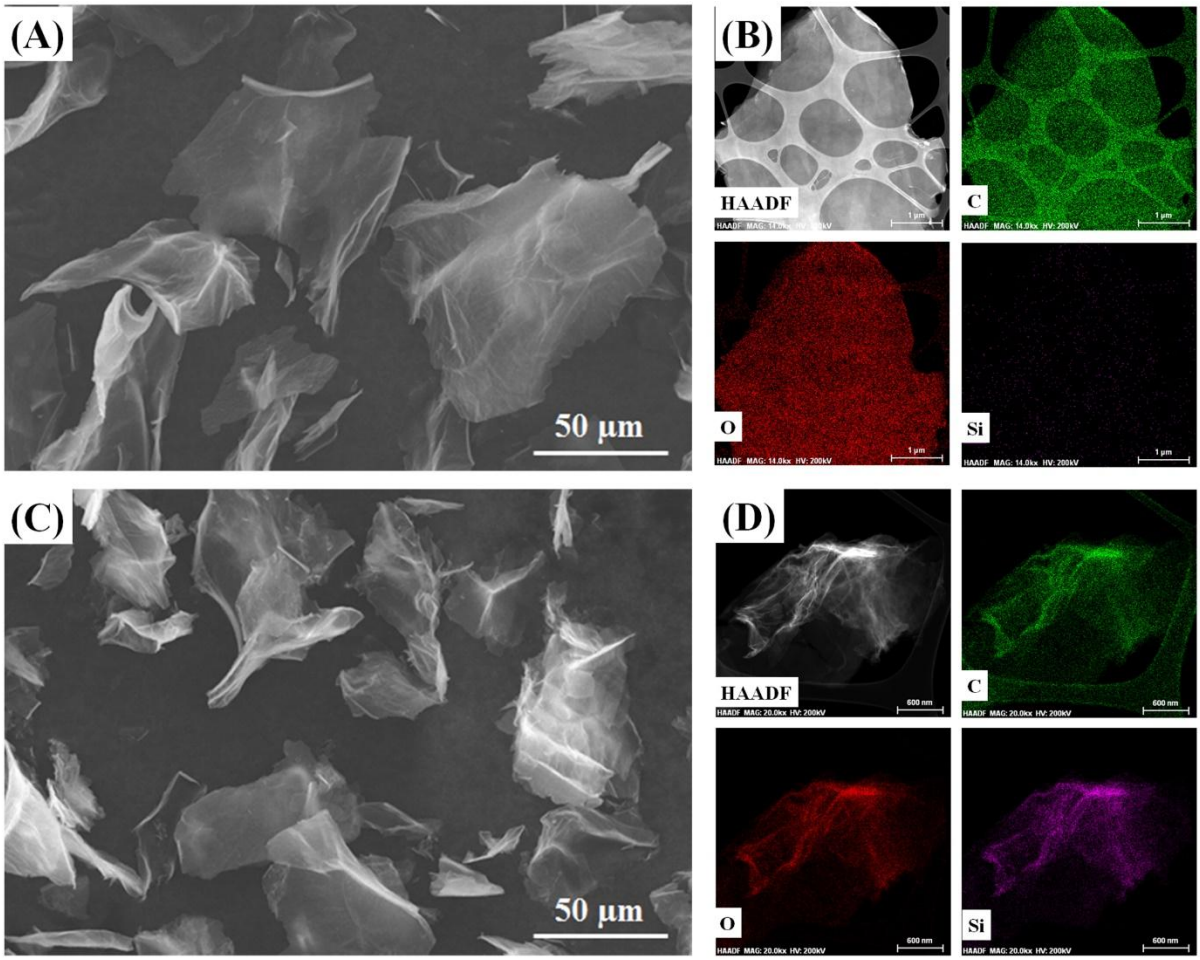


Figure 1 SEM images of (A) original GO and (C) SiO_2@GO; HAADF-STEM image of (B) original GO and (D) SiO_2@GO, and their corresponding EDX element maps of C, O and Si, respectively.

First, SEM and STEM measurements have been carried out to identify the morphologies of the original GO and the SiO_2@GO. Figure 1(A) shows the pristine GO with a mean lateral size of 50 µm and ultra-thin thickness. Figure 1B presents the HAADF image of pristine GO and the corresponding EDX elemental maps. As presented in Figure 1 (C), EDX has provided evidence that the SiO_2@GO has been successfully prepared in a water-alcohol mixture with sol-gel technique. SiO_2

can be coated on the surface of GO, which is ascribed to the covalent reaction between TEOS and the functional groups (e.g., -OH, -COOH, -COH) of GO [9]. Moreover, the morphology of SiO_2@GO does not change a lot compared with GO without SiO_2. EDX results indicate that before deposited SiO_2, in pristine GO, the elemental mass ratio of C: O: Si is 80.35:19.58:0.07, while after deposited SiO_2 layers, the elemental mass ratio of three elements became 49.00:32.39:18.61. Such an increase of Si ratio confirms the existence of Si in the SiO_2@GO and as shown in Figure 1 D, SiO2 has been homogeneously deposited on the surface of GO.

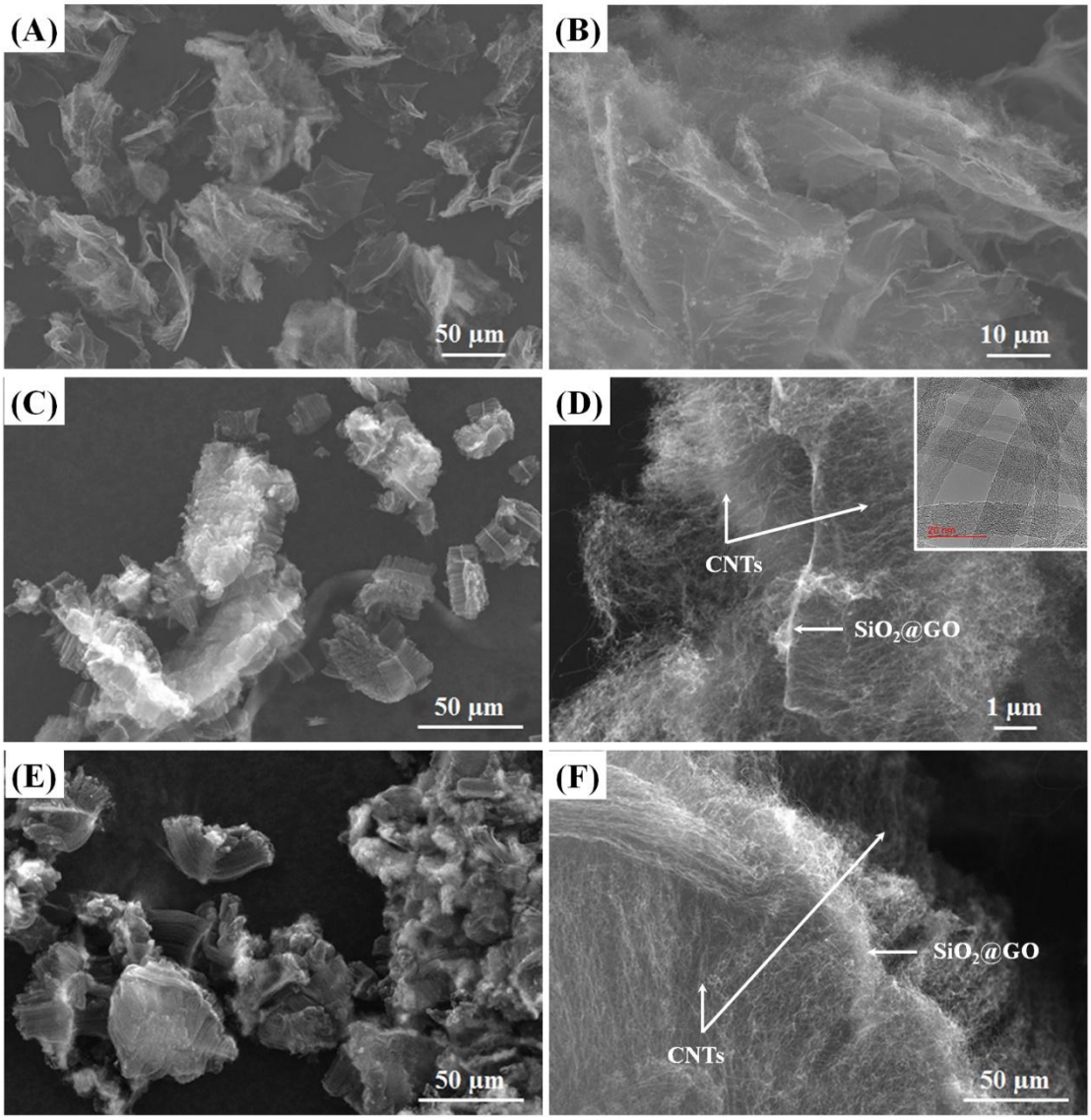


Figure 2 Morphological characterization of particles by using SEM and TEM: (A) and (B) shows the 5 min growth of CNTs on pristine GO; (C) and (D) shows the growth of CNTs on SiO_2@GO for 5 min, the insert image presents the diameter of CNTs; (E) and (F) shows the growth of CNTs on SiO_2@GO for 10 min.

The growth of CNTs on different substrates has been achieved by a one-step CVD method using metalorganic compound ferrocene as catalyst precursor. Figure 2A presents the growth of CNTs on GO after 5 min. The major part of GO has no CNTs on the surface, only a small part of GO is covered by sparse CNTs. The enlarged region in Figure 2B shows the

inhomogeneous CNTs growth, which is due to the poor wettability between graphite surface and catalyst particles. It is noteworthy that the CNT clusters grow perpendicularly onto the surface of individual SiO_2@GO (Figure 2C). The length and diameter of CNTs grown on the platelet surface are uniform with the length of about 5 μm and the diameter of about 10 nm, respectively. Figure 2D shows the high magnification image of hybrids. The edge and surface of SiO_2@GO platelet can be well distinguished in the hybrids, which indicates the array of CNTs on the platelet is very sparse synthesis for 5 min. Figure 2E and 2F show the hybrids synthesized for 10 min. Comparing to the hybrids grown for 5 min, the grown CNT has longer length and much denser array on the platelets. Due to dense CNTs covered on the platelet, the edge and surface of the platelet is not obvious.

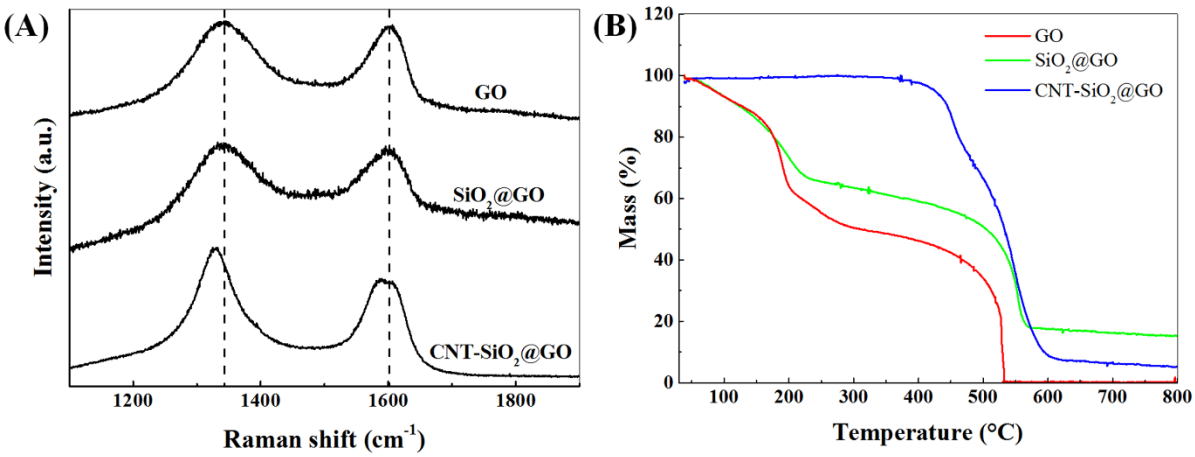


Figure 3 Basic characterization of GO, SiO_2@GO and CNT-SiO_2@GO: (A) Raman spectra and (B) TGA analysis.

To get more precise structure and composition information about the pristine GO, the SiO_2@GO and the hybrids, Raman spectroscopy and TGA have been conducted and the results are presented in Figure 3. As shown in Figure 3A, the pristine GO and the SiO_2@GO display two characteristic peaks around 1343 and 1601 cm^{-1}, corresponding to the typical D and G bands of the carbon species, respectively. The intensity ratio of D band over G band is usually used to quantify the graphitic ordering degree. After deposition of SiO_2 layers, the I_D/I_G value has no obvious change comparing to that of the pristine GO. However, the D band has shifted to 1328 cm^{-1} for the hybrids, which is due to the growth of CNT on the platelet surface. As illustrated in Figure 3B of TGA, the curve of pristine GO is also displayed in Figure 3B. The pristine GO and SiO_2@GO exhibit a remarkable weight loss below 500 °C, which is due to the decomposition of oxygen-containing groups on GO and the related disordered carbon atoms in the platelets. The weight loss of the pristine GO is 100% when the temperature is beyond 630 °C. But after the deposition of SiO_2 layers, the completely decomposition of GO structure has shifted to higher temperature, around 650 °C and the mass ratio of SiO_2 in the hybrids is 18%. Moreover, after CVD process, the GO has been completely reduced to RGO (reduced graphene oxide), which can be confirmed by the TGA curve since there has no noticeable weight loss below 400 °C. The hybrids begin to decompose at 450 °C, which is possibly corresponded to the decomposition of CNTs. A remarkable weight loss stage from 500 °C to 600 °C is corresponded to the decomposition of RGO structure and the rest CNTs. It is known that during the CVD synthesis process of hybrids, the high temperature in the

furnace can not only offer the energy for chemical reaction but also accompany a thermal reduction effect which changes GO into RGO. Thus, the specific surface area of fillers and the conductivity (？) of final hybrids can be increased effectively.

4. Conclusion

In summary, the SiO_2@GO hybrids have been first synthesized by a typical sol-gel method. Then, the CNT array has been grown on the surface of SiO_2@GO hybrids with uniform length by CVD method to form a 3D structure. The length and density of CNT array can be well controlled by the synthesis time. The strategy of the 3D structure design and optimization will contribute to achieving composites with higher performances and further drive the fabrication process to industrial scale.

Acknowledgements

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