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A novel synthesis of graphene nanoscrolls with tunable dimension at a large scale

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Abstract
Graphene nanoscrolls which could overcome the chirality dependence of metallic or semiconducting behavior in carbon nanotubes have been recently investigated and proposed for a wide variety of applications. In order to further improve their practical applications, a variety of synthetic approaches have been widely explored but with various limitations. For instance, it remains challenging to produce graphene nanoscrolls with tunable dimensions and high quantity, which greatly hinders their potential applications. Herein, we report a new and general approach to synthesize graphene nanoscrolls with accurately tunable widths and lengths at a large scale. The resulting high-quality graphene nanoscrolls show promising applications in a wide variety of electronic devices.

(Some figures may appear in colour only in the online journal)

1. Introduction

Graphene nanoscrolls which could overcome the chirality dependence of metallic or semiconducting behavior in carbon nanotubes have been recently investigated and proposed for a broad spectrum of applications [1, 2]. In order to further improve their practical applications, a variety of synthetic approaches have been widely explored but with various limitations [3–11]. Lithography had been used to synthesize wide ribbons from graphene sheets, but their quality was limited by the lithographic resolution [3, 4]. Chemical and sonochemical methods have been developed to produce narrow graphene nanoscrolls, however, the yield was low and the width distribution was broad [5–8]. Nanoscrolls have also been produced by unzipping carbon nanotubes, but the resultant quality and yield needed to be improved [9–11]. In addition, there remains a common challenge in all the above approaches, i.e., the difficulty in producing the graphene nanoscrolls with tunable widths and lengths at a large scale, which greatly hinders their potential applications. New approaches capable of producing large amounts of high-quality graphene nanoscrolls with a controlled dimension are therefore required. Herein, we report such a general and easy route to prepare tunable graphene nanoscrolls by using Fe_3O_4 nanoparticles as the catalyst precursor based on a chemical vapor deposition process [12–14].

2. Experimental section

2.1. Materials

$Fe(acac)_3$ (99%) was received from Acros Organics, 1,2-dodecanediol (90%) and oleylamine (95%) were received from Tokyo Chemical Industry, oleic acid (chemically pure) and diphenyl ether (chemically pure) were received from Sinopharm Chemical Reagent, *N*-hexane (97%) was received from Shanghai Lingfeng Chemical Reagent, and ethyl alcohol absolute (99.7%) was received from Shanghai Zhenxing No. 1 Chemical Plant. De-ionized water was produced by the Millipore water purification system Elix35 + Tank200.

2.2. Synthesis of graphene nanoscrolls

Fe_3O_4 nanoparticles were synthesized by a typical thermal decomposition. Typically, 2 mmol $Fe(acac)_3$, 10 mmol

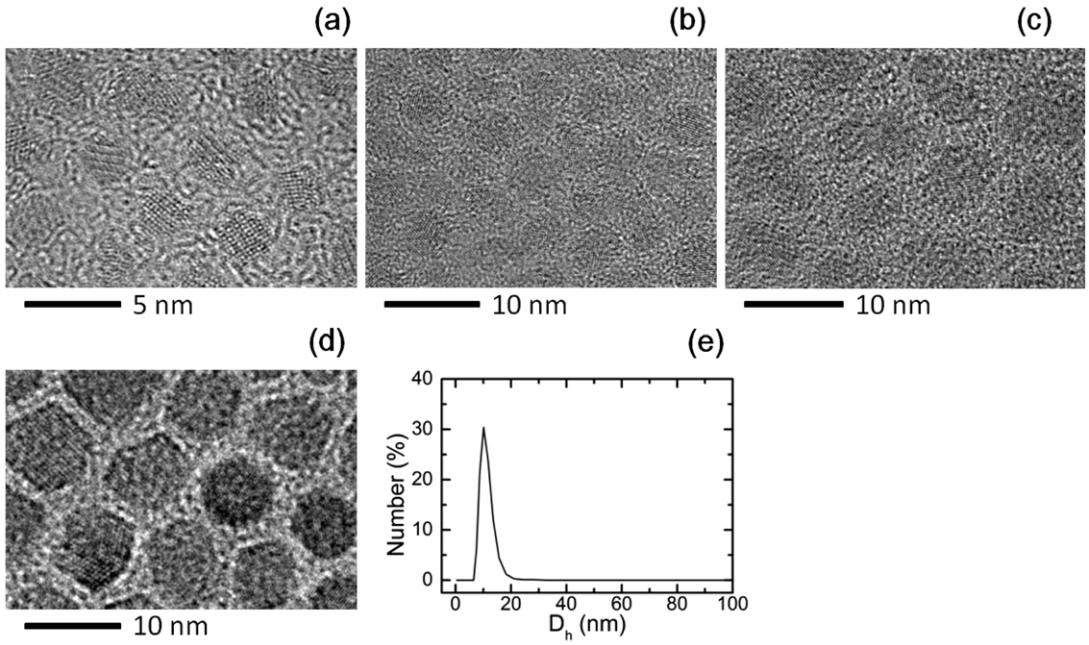

Figure 1. Fe_3O_4 nanoparticles with tunable diameters characterized by high-resolution transmission electron microscopy (HRTEM) and dynamic laser light scattering (DLS). (a) HRTEM image with an average nanoparticle diameter of ∼2 nm. (b) HRTEM image with an average nanoparticle diameter of ∼4 nm. (c) HRTEM image with an average nanoparticle diameter of ∼6 nm. (d) HRTEM image with an average nanoparticle diameter of ∼8 nm. (e) A typical DLS graph of the Fe_3O_4 nanoparticles in (d).

1,2-dodecanediol, 20 ml diphenyl ether, 6 mmol oleic acid, and 6 mmol oleylamine were mixed in a 150 ml flask while vigorously stirring with N_2 bubbling. This mixture was heated to 200 °C, kept at that temperature for 30 min, followed by a further increase to 265 °C, and then kept at that temperature for another 30 min. The reaction solution was allowed to cool to room temperature, and then 40 ml of ethyl alcohol (absolute) was added to produce precipitates of Fe_3O_4 nanoparticles. The nanoparticles were further purified according to previous studies [15, 16]. Subsequently, the purified Fe_3O_4 nanoparticle solutions were coated onto silicon substrates through the Langmuir–Blodgett method and used as a catalyst to grow graphene nanoscroll arrays in a tube. A mixture of Ar (560 sccm) and H_2 (35 sccm) was pumped into the tube reactor, the temperature of which was increased to 500 °C in 15 min and kept at this temperature for various lengths of time, i.e., a few minutes to 2 h, to reduce Fe_3O_4 into Fe. The tube reactor was further heated to 760 °C in 7 min and stabilized for 2 min. Finally, ethylene as the carbon source was pumped into the reactor for 13 min. The resulting products were dispersed in DMF under an ultrasonic treatment to prepare graphene nanoscrolls.

2.3. Characterization

Dynamic laser light scattering, scanning electron microscopy, transmission electron microscopy (TEM), and atomic force microscopy (AFM) were performed on a Zetasizer Nano (Malvern), an FE-SEM S-4800 (Hitachi, operated at 1.0 kV), a JEM-2100F (JEOL, operated at 200 kV), and an SPM-9500J3 (Shimadzu), respectively. The TEM and AFM samples were prepared by dispersing the graphene nanoscrolls in ethanol or dimethyl formamide, followed by coating onto copper grids and silicon substrates, respectively.

3. Results and discussion

The Fe_3O_4 nanoparticles were stabilized by a thin layer of oleic acid on their outer surfaces and could be well dispersed in non-polar solvents such as hexane. The diameters of the Fe_3O_4 nanoparticles could be accurately controlled from several to tens of nanometers by varying the experimental conditions such as the heating condition, speed of stirring, speed of centrifugation, and quantity of seeds [15, 16]. Figures 1(a)–(d) show high-resolution transmission electron microscopy (HRTEM) of four representative samples with controlled average diameters of about 2, 4, 6, and 8 nm. In addition, the nanoparticles for each sample are very uniform with a diameter fluctuation of ±4.4%. The uniform size of the Fe_3O_4 nanoparticles was further confirmed by dynamic laser light scattering (DLS). For instance, figure 1(e) shows a typical DLS graph for the Fe_3O_4 nanoparticles in figure 1(d) with an average hydrodynamic diameter of 10.9 nm and a low polydispersity of 0.22. The average diameter measured by DLS seems a little larger than that obtained from HRTEM as the outer layer of oleic acid in the Fe_3O_4 nanoparticles could not be observed under HRTEM due to the low contrast.

For the synthesis of the graphene nanoscroll arrays, Fe_3O_4 nanoparticles were coated onto silicon substrates through a Langmuir–Blodgett method and used as the catalyst in a tube reactor. A mixture of Ar and H_2 was first pumped into the tube reactor to reduce the Fe_3O_4 to Fe on the outer surfaces

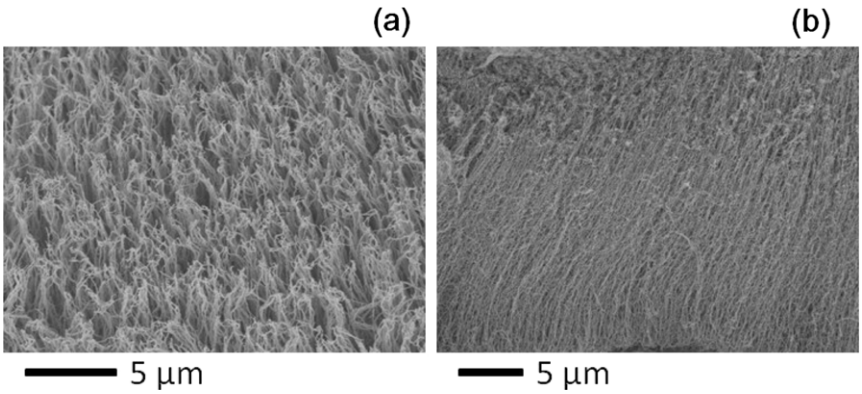

Figure 2. Characterization of a graphene nanoscroll array by scanning electron microscopy (SEM) from (a) a top view and (b) a side view.

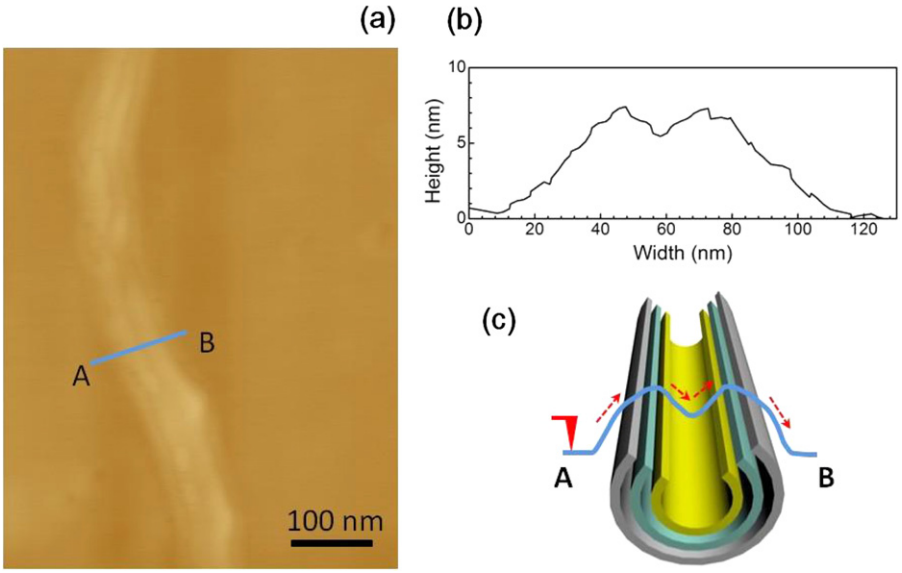

Figure 3. A scrolled graphene nanoscroll. (a) Atomic force microscopy (AFM) image. (b) Dependence of the height on the width in the scrolled graphene nanoscroll. (c) Schematic illustration of (a).

of the nanoparticles. Then ethylene as the carbon source was pumped to grow scrolled graphene nanoscroll arrays. Figure 2 shows scanning electron microscopy images of a typical array. No impurities were observed in either the top or side views. In other words, high-purity graphene nanoscrolls could be obtained by this route. Figure 2(b) further indicates that the scrolled graphene nanoscrolls are highly aligned with an average number density of 10^{11} cm^{-2} in the array. Therefore, this approach also exhibits a high productivity in the synthesis of graphene nanoscrolls.

The scrolled graphene nanoscrolls were further confirmed by atomic force microscopy (AFM). Figure 3(a) represents a typical AFM image of a scrolled nanoscroll synthesized from the Fe_3O_4 nanoparticle. Figure 3(b) shows the change in the height with the width of this nanoscroll in a dynamic mode, and two height peaks are generally observed. These two peaks correspond to the two scrolled ends of the nanoscroll. The detailed structure is schematically shown in figure 3(c). The scrolled graphene nanoscrolls were opened after dispersion in the solvent under ultrasonic treatment. It should be noted that no carbon nanotubes were unzipped under the same conditions.

The widths of these nanoscrolls could be easily controlled by varying the experimental conditions. Here we focus on the preparation of narrow graphene nanoscrolls. It was found that the nanoscroll widths increased with increasing sizes of the Fe_3O_4 nanoparticles. Their widths increased from (11.3–13.2), (14.3–15.4), (16.4–18.5), to (19.6–20.2) nm when the diameters of the Fe_3O_4 nanoparticles increased from 2, 4, 6, to 8 nm, respectively. Their numbers of layers varied between 4 and 6. Figure 4 shows HRTEM images of four typical nanoscrolls, and the inset in figure 4(a) indicates a high quality of the graphene nanoscrolls with smooth sides. The nanoscroll width also depends on the other growth parameters such as the reduction time of Fe_3O_4 nanoparticles and the rate and composition of the gases. For instance, a short reduction time of the Fe_3O_4 nanoparticles by which only a fraction of their outer surfaces can be reduced into Fe produces narrow ribbons, while a long reduction time favors the formation of wider nanoscrolls. If the reduction time were increased beyond a critical point such as a few hours, seamless

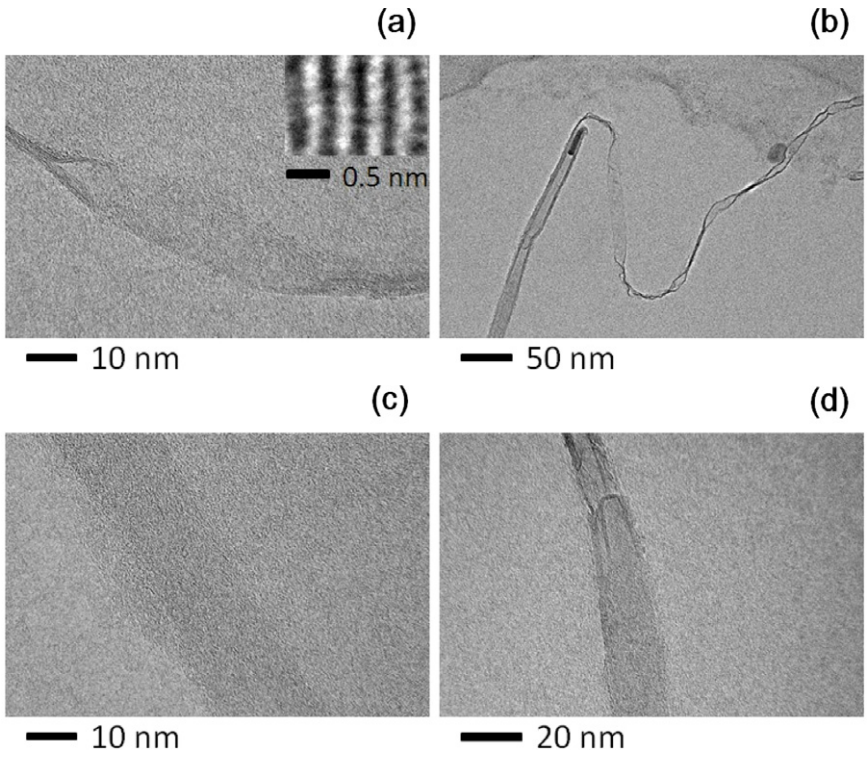

Figure 4. HRTEM images of the graphene nanoscrolls with tunable widths of (a) ∼12.5 nm, (b) ∼15 nm, (c) ∼17.5 nm, and (d) ∼20 nm. The inset in (a) shows the side of a graphene nanoscroll.

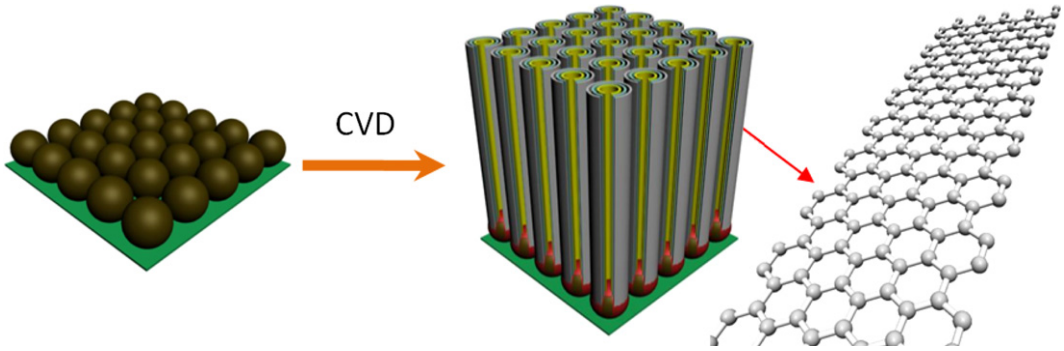

Figure 5. Schematic illustration of the growth of a graphene nanoscroll array by using metal oxide nanoparticles as the catalyst precursor. The outer surfaces of the metal oxide nanoparticles are partially reduced to grow the scrolled graphene nanoscroll array during a chemical vapor deposition process.

carbon nanotubes would be produced instead of the graphene nanoscrolls. The nanoscroll length is mainly tuned by varying the growth time during the synthesis, e.g., in our experiments, the nanoribbons showed lengths of 0.5, 2.2, 5.2, 6.6, 10.8, 22.3, and 24.8 μm for growth times of 1, 3, 5, 7, 8, 10, and 13 min, respectively. The nanoribbon length did not further obviously change after the growth time of 13 min.

The synthetic mechanism of the graphene nanoscroll array may be summarized as follows. Metals such as iron have been widely explored to grow high-quality carbon nanotubes with a tunable diameter and length by a chemical vapor deposition process [17]. Generally, complete reduction on the outer surfaces of the iron oxide nanoparticles produces iron nanoparticles to induce the growth of carbon nanotubes. If the reduction time is less than that required to completely reduce the outer iron oxide in the nanoparticles, it is difficult to grow seamless nanotubes. The areas which have not been reduced will not induce growth and will produce seams in the resulting carbon nanostructures. In other words, scrolled graphene nanoscrolls are produced (figure 5). The sizes including the widths and lengths of the graphene nanoscrolls can be controlled by varying the diameters of the catalytic nanoparticles and the growth parameters such as the gas-flow rate, temperature, and time.

4. Conclusion

In summary, a new and general approach has been developed to synthesize high-quality graphene nanoscrolls at a large

scale by chemical vapor deposition. The widths and lengths of the nanoscrolls can be accurately tuned to tens of nanometers and up to tens of micrometers, respectively. More efforts are underway to further understand the mechanism, control their size, and explore their electronic applications.

Acknowledgments

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