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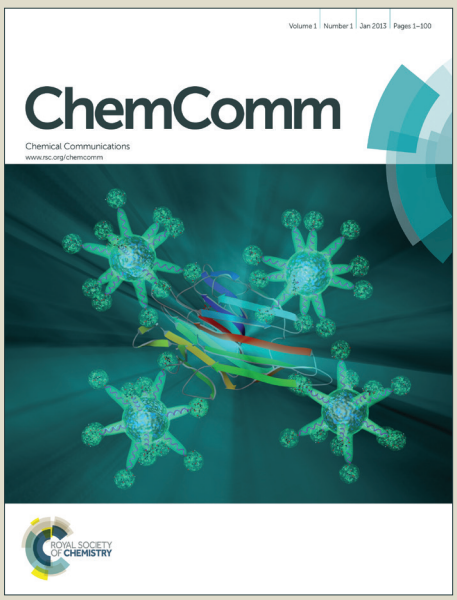

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Graphene/graphite sheets assisted growth of high-areal-density horizontally aligned carbon nanotubes†

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We report a facile graphene/graphite sheet assisted CVD process for the synthesis of high-areal-density HACNT arrays. Besides, some metal nanoparticles could eat the graphene/graphite sheets, forming serpentine holes on the sheets in the early stage, and finally leading to the precipitation of CNTs without additional carbon source.

Carbon nanotubes (CNTs) have drawn persistent attentions due to their extraordinary properties resulted from unique geometry and electronic structures.[1-5] Many great successes on the controlled synthesis of CNTs have been achieved during the past 20 years.[6-14] Depending on the preparation methods, the morphologies of the as-prepared CNTs vary a lot. Particularly, ultralong horizontally-aligned CNTs (HACNTs) grown by chemical vapor deposition (CVD) draw significant interests due to their macroscale length, atomically perfect structures and superior properties.[15, 16] Individual HACNTs with length of more than a half-meter have already been successfully prepared.[17] However, the areal density of ultralong HACNTs is extremely low, which greatly hinders their practical applications. Effective methods to improve the areal density of ultralong HACNTs are desired.

It has been proposed that one of the main reasons for the low density of HACNTs is that small catalyst nanoparticles (NPs) agglomerate into large ones at high temperature,[18] implying that the methods and substrates to load catalysts have great influence on the areal density of the as-prepared HACNTs. Substrates with coarse surfaces, which should be stable enough to sustain high temperature of CVD, are expected to suppress the agglomeration of catalyst NPs. In our previous study, silica NPs have been deposited on substrates to obtain coarse surfaces and improved areal-density of ultralong HACNTs have been achieved.[19] However, the deposition of catalysts on the silica NP modified surface is uncontrollable, and the silica NPs are potential obstacles for the further use of the CNTs. Graphene/graphite (GP) sheets, which can suffer high temperature in inert environment, are potential 2-dimentional materials to suppress the agglomeration of metal NPs. Besides, they contain the same element as CNTs. Moreover, they are electrical conductive and can be used as electrodes for fabrication of CNT devices. However, although graphene has been studied extensively in the past several years, the potential of GP sheets to assist the growth of HACNTs has not been explored. In this work, we used GP sheets to assist the growth of CNTs and observed obviously improved areal-density of ultralong HACNTs.

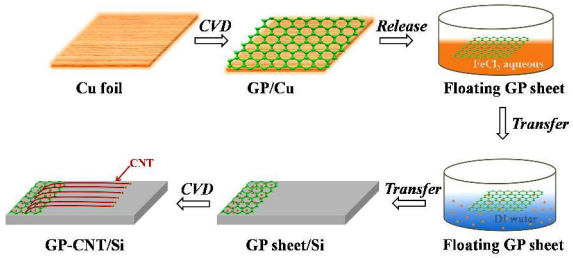

Fig. 1 Schematic illustration for the process of GP sheets assisted growth of HACNTs.

A schematic illustration for the synthesis process of ultralong HACNTs with the assistance of GP sheets is shown in Fig. 1. GP sheets and HACNTs were both grown in an atmospheric pressure CVD system. The GP sheets grown on copper foils were released by etching copper in $FeCl_3$ aqueous (Fig. S1a) and were transferred onto one end of the substrates for growth of CNTs. The GP sheet was washed with deionized water for several times to remove most of the residual metal ions (Fig. S1b and Fig. S2). With the above process, the GP sheets would carry trace amount of metal ions, which could serve as catalysts for the growth of HACNTs in the following process.[12, 20-22] Finally, the substrates with GP sheets were used directly to grow HACNTs by CVD as reported before.[19]

The as-prepared GP sheets were small few-layer graphene flakes connected with thick graphite films, which were found to be good choices to fulfill the requirements of this study. For a thin graphene film with large size, it is too fragile to sustain the hash transfer process.[23, 24] A polymer film is usually used to support the thin graphene film during the transfer process, which will leave some organic contaminations on the surface of graphene films[25] and protect graphene flakes from the etchant solution (Fig. S3). For a thick graphite film, the interaction between the film and the substrate is not strong enough and the film is usually detached from the substrate after the CVD process (Fig. S4). Fig. 2a shows a typical scanning electron spectroscopy (SEM) image of a GP sheet

deposited onto a substrate. The graphene flakes with different layers have different contrast on silicon substrates in SEM, where the bright areas are thin while the dark ones are thick.[26-29] Areas with different contrast were characterized by Raman microscopy (Fig. 2b) and atomic force microscopy (AFM) (Fig. S5), which revealed that some parts of GP sheets were single-layer or bilayer graphene, while some parts contain more than ten layers. The disorder band (D-band) was also observed in the Raman spectra of GP sheets, resulted from defects located in the joint between graphene flakes with different thickness or the transfer process. Transmission electron microscopy (TEM) images (Fig. 2c) further affirmed that the GP sheets consist of GP flakes with different number of layers, and transitional areas between flakes with different layers could be observed.

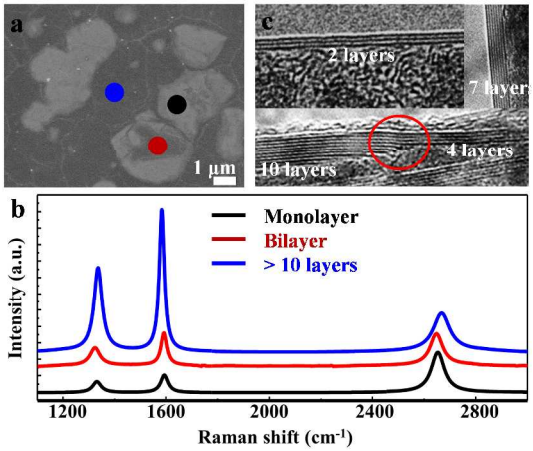

Fig. 2 Characterization of GP sheets. a. SEM image of a GP sheet on a silicon substrate. b. Raman spectra of the GP sheet obtained from the corresponding colored spots in (a) with 633-nm laser. c. TEM images of GP flakes with different layers. The circle shows the transitional areas between flakes with different layers.

As shown in Fig. 3, obviously improved areal density of ultralong HACNTs was observed with the assistance of GP sheets. Fig. 3a and Fig. S6 show the ultralong HACNTs grown with the assistance of GP sheet without additional loading of catalysts. Fig. 3b shows result with the catalysts loaded through the typical microcontact printing method[19] in identical growth conditions. In Fig. 3a and b, horizontally long lines in white on the substrates were HACNTs, and the slots on the substrates were marks to facilitate characterization. Obviously, the HACNTs in Fig. 3a were denser than that in Fig. 3b.

To understand the process growing HACNTs, catalyst zone before and after were characterized (Fig. 3c and 3d). As mentioned in the above, the residual metal ions on the GP sheets from the etchant solution, such as Fe^{3+} and Cu^{2+}, would be reduced and serve as catalysts for the growth of CNTs. The main catalysts precursor for the growth of HACNTs were also investigated by using GP sheet with just only Cu metal ions (Fig. S7). It is deduced that there are few HACNTs grown out of GP sheets with Cu metal ions as the condition to grow CNTs was optimized based on Fe catalyst precursor.[18-20] Moreover, The size and the distribution of catalyst NPs are crucial factors for the growth of ultralong HACNTs.[30, 31] In order to know the size and the distribution of catalyst NPs on the GP sheets, the GP sheets were annealed in Ar/H_2 flow and characterized by SEM. Backscattering electron mode (BSE mode) of SEM could detect the difference of element composition on substrates,[32] which could be used to distinguish the metal NPs on the GP sheets. The left images in Fig. 3c and 3d were SEM images obtained in BSE mode, from which we can see that the NPs on the GP sheets were small and uniformly distributed on the surface, while the catalysts patterned by microcontact printing method were agglomerated into big ones and non-uniformly distributed. After the CVD process, the GP sheets were covered by CNTs (The right image in Fig. 3c). In contrast, there were mainly short and curly CNTs in the right image of Fig. 3d. The above results show clearly density of HACNTs. However, the areal density of HACNTs clearly decreased with the increased distance from the edge of GP sheets (the left side in Fig. 3a). To understand this phenomenon, we characterized the HACNTs near the GP sheets with SEM (Fig. 3e), and found that many CNTs twisted with each other along the gas flow direction. It indicates that the strong interactions between nearby floating HACNTs, leading to the formation of bundles which are hard to grow into ultralong ones, are responsible for the above observation. An optimized CVD condition with a stable gas flow is expected to eliminate the above phenomenon. We also used Raman spectroscopy to characterize the as-prepared HACNTs grown from GP sheets (Fig. 3f), which showed no observable disorder induced Raman band, indicating perfect structures of the HACNTs.[33, 34] Noted that most of the as-prepared HACNTs are few-walled CNTs, showing no RBM peaks in the low at lower wavenumbers.

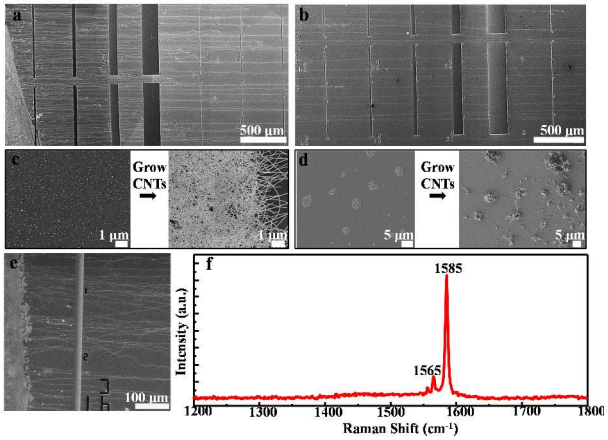

Fig. 3 Comparison of HACNTs grown with different catalyst loading methods and the characterization of HACNTs. a. Grown with the assistance of GP sheets. b. Grown with catalysts loaded by microcontact printing. c. SEM images of catalyst zone on the GP sheets before and after the growth of HACNTs. d. SEM images of catalyst zone loaded with microcontact printing method before and after growing HACNTs. e. SEM image of HACNTs near the edge of GP sheets. f. Raman spectrum (with 633-nm laser) of an individual HACNT. The gas direction in (a, b, e) was from the left to the right.

To better understand the role of GP sheets in the above process, we investigated the status of catalyst NPs during the CVD. Fig. 4a shows there were many NPs anchored by the wrinkles on the GP sheet. Then SEM image of a GP sheet transferred onto a substrate. It is clear that we characterized the GP sheet experienced the reduction phase in the growth process of CNTs, as shown in Fig. 4b. We observed that there were curve tracks on the GP sheet with a catalyst NP on one end (marked by arrows in the left SEM image in Fig. 4b). AFM image showed that the tracks were serpentine holes and their widths were smaller than the diameters of the corresponding NPs (the right image in Fig. 4b). These results indicate that, during the reduction process, catalyst NPs would eat carbon of GP sheets, leaving serpentine holes on their behind, which is in consistence with a previous report.[35] In this way, the GP sheets effectively hindered the aggregation of catalyst NPs into large ones. Moreover, the pre-taken of carbon in catalyst NPs by eating GP sheets might promote the following precipitation of ultralong CNTs.

Based on the above observation, we further tried to grow CNTs with the existence of GP sheets without adding other carbon precursors. We observed that there were none HACNTs grown out

of GP sheets (Fig. S8) and only some short CNTs grown on the GP sheets (Fig. 4c), indicating the GP sheets could serve as carbon precursor for CNTs. Meanwhile, many dents could be seen on the GP sheet after the growth of CNTs. In a typical synthesis process for ultralong CNTs, water has added to remove amorphous carbon covering the catalyst and thus to increase the growth rate of HACNTs.[36] In this study, the water could not only help to keep the activity of catalyst NPs, but also etch the GP sheets and form CO, which might serve as precursor for the growth of CNTs. Fig. 4d shows the SEM image of a GP sheet after growing CNTs with adding gas carbon source (methane). Many CNTs on the GP sheet were observed. As seen in Fig. 4d, some CNTs could extend out of the GP sheet and potentially grow into ultralong ones. These observations show that, the efficiency of the catalysts for the catalytic growth of ultralong CNTs, with the support of GP sheets and with additional carbon precursor, is significantly improved

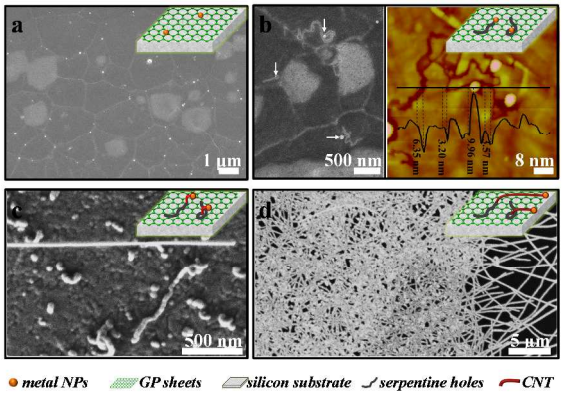

Fig. 4 Evolution of catalyst NPs and GP sheets during the CVD process. a. GP sheet with catalyst NPs transferred onto silicon substrates. b. SEM image (left) and AFM image (right) of the GP sheet with catalyst NPs treated with reduction process. The arrows indicate metal NPs etched the GP sheet and led to the formation of serpentine holes. c. SEM image of a GP sheet treated in the condition of growing HACNTs without adding carbon source. Some short and thick CNTs were grown on the GP sheets. d. SEM image of a GP sheet after growing HACNTs with adding of methane. The insets in (a-d) are corresponding illustrations.

Conclusions

We developed a facile approach for the synthesis of high-areal-density HACNTs, where GP sheets were used to suppress the agglomeration of catalyst NPs. The GP sheets were synthesized on copper foil, and then released in $FeCl_3$ aqueous and transferred on to substrates for growth of CNTs. The residual metal ions on the GP sheets, including Fe^{3+}, Fe^{2+}, and Cu^{2+}, would be reduced and serve as catalysts for the growth of CNTs. Therefore, the GP sheets could be directly used without further loading of catalysts. It is found that the catalyst NPs could eat the GP sheets with serpentine holes left behind, indicating that the GP sheets could hinder the moving and the agglomeration of catalyst NPs, which is crucial for the efficiency growth of ultralong HACNTs. Moreover, we found that the GP sheets could also serve as carbon source for the growth of CNTs. This approach might also represent a promising method for the integration of CNT devices with graphene/graphite electrodes, which is important for the development of all-carbon electronics.

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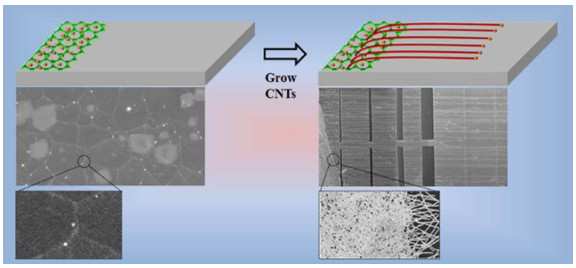

Graphene/graphite sheets produced by chemical vapor deposition and released by chemical etching were directly used for the synthesis of high-areal-density horizontally aligned carbon nanotube arrays.