Graphene Oxide as a Carbon Source for Controlled Growth of Carbon Nanowires

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Graphene, a one-atom-thick two-dimensional sheet of sp^2-hybridized carbon atoms, has attracted increasing interest due to its unique structure and properties.[1] The large-scale production of graphene, via reduction of graphene oxide (GO), facilitates the synthesis of graphene-based materials.[2] The synthesis of various graphene-based materials with controlled structures and properties shows great importance, not only in fundamental research, but also in its extensive applications in various areas.[3] In particular, graphene composites with other carbon materials, such as carbon nanotubes (CNTs)[4] and fullerenes[5] are extremely promising. For example, it has been revealed that there are synergistic effects between graphene derivatives and CNTs, which facilitates the diffusion of ions from electrolytes to a graphene/CNT electrode.[6] Until now, approaches to the synthesis of graphene-based carbon composites have been mainly based on directly mixing graphene with other carbon materials in solution.[4] However, to achieve a well-dispersed solution without aggregation while avoiding damage to the original structures of the carbon materials remains a challenge.

Chemical vapor deposition (CVD) is a versatile and promising method for directly producing high-quality graphene-based materials on a large scale.[7] The high temperature of CVD can also convert GO to the conductive reduced graphene oxide (rGO).[8] The graphene-based materials recently synthesized by CVD are based on gaseous carbon precursors, such as hydrocarbon[7a–c] and carbon dioxide.[7d] However, the obtained structures of carbon materials greatly rely on the species, feeding rate, decomposition temperature, and pressure of the gaseous carbon precursors.[9] To achieve the controlled synthesis of graphene-based materials, it is essential to investigate the experimental parameters used in CVD. In addition, the gaseous precursor requires extreme caution in handing and transportation.

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In this Communication, we present a simple method to synthesize a novel rGO/carbon-nanowire (rGO/CNW) composite by simply annealing GO sheets that have been pre-coated with $CoCl_2$ in a CVD chamber. By using this method, without additional carbon precursor, only GO itself serves as the carbon source for growth of the rGO/CNW composite. This method significantly simplifies the previous CVD process and minimizes the experimental parameters, thus facilitating easy control of the synthesis of rGO/CNW composites, such as control of the diameter and position of the CNWs on rGO. The mechanism of synthesis of rGO/CNW composites is also investigated. Moreover, as a proof of concept, a chemical sensor based on the rGO/CNW composite micropatterns is demonstrated that is capable of excellent detection of dopamine.

Before deposition of GO and catalyst, the Si/SiO$_2$ substrate was cleaned by piranha solution (see Experimental Section for details), followed by O$_2$-plasma treatment to remove the organic contaminants. The quartz tube of the furnace was cleaned by annealing in air at 950 °C for 30 min, followed by rinsing with aqua regia and Milli-Q water and then drying with N$_2$. The GO substrate was prepared by spin-coating GO aqueous solution on the cleaned Si/SiO$_2$ wafer, on which the CoCl$_2$ aqueous solution was subsequently spin-coated. The obtained substrate was annealed at 900–1000 °C under a protective atmosphere of premixed gas of H$_2$ and Ar at a pressure of ≈150 Pa (**Scheme 1**). As a comparison, the control experiment with only CoCl$_2$-coated Si/SiO$_2$ substrate (without GO) was also conducted, where only Co nanoparticles (NPs) (obtained from thermal decomposition of CoCl$_2$)[10] were formed under the same experimental conditions.
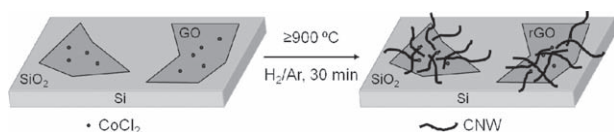
Figure 1A shows the GO substrate coated by CoCl$_2$. After annealing at 950 °C for 30 min, the GO was thermally reduced to rGO,[11] which was also confirmed by Raman spectroscopy, as shown in Figure S1 of the Supporting Information (SI), and its morphology dramatically changed, on which some fiber-like materials were formed (Figure 1B). If the concentration of CoCl$_2$ solution, which was spin-coated on the GO substrate, was lower, less-dense fiber-like materials were obtained (Figure 1C).

Transmission electron microscopy (TEM) was used to characterize the structure of the fiber-like materials. As shown in Figure 1D, it reveals that they are carbon nanowires (CNWs) with a diameter of 11.9 ± 1.3 nm. A high-resolution TEM (HRTEM) image (Figure 1E), together with the

Scheme 1. Schematic illustration of the procedure for synthesis of rGO/CNW composites by simply annealing the GO sheets, precoated with $CoCl_2$, on Si/SiO$_2$ in a CVD chamber.

selected-area electron diffraction (SAED) pattern (inset in Figure 1D), confirmed those CNWs are amorphous.

Based on the aforementioned results, it is clear that a novel graphene-based composite material, that is, rGO/CNW, has been successfully synthesized through a simple annealing process without additional carbon precursor.

The mechanism for synthesis of rGO/CNW composites by annealing alone is investigated. One key question concerns the nature of the carbon source and the manner in which it supplies the growth of CNWs. As we have taken extra precautions to prevent additional carbon sources and any organic contaminants during the sample preparation, the only carbon source should be the GO itself.

Previous studies on the CVD growth of carbon nanotubes (CNTs) suggest that the catalyst NPs can dissolve carbon from graphite and nucleate the CNTs.[12] Therefore, we believe that the Co NPs, obtained from the high-temperature thermal decomposition of $CoCl_2$,[10] can also dissolve carbon from the GO substrate to form CNWs in our experiments.

Recently, it has been revealed that the catalyst NPs can etch graphene to form graphene trenches if annealed at high temperature with hydrogen.[13] The formation of trenches is believed to follow the catalytic gasification reaction,[13a,13c] where the catalyst NPs absorb carbon from graphene and convert it to hydrocarbon species such as CH_4. In this case, CNTs were also sometimes observed as a byproduct of the trench.[13c] In our experiments, similar trenches were observed in rGO (Figure S2 of the SI). Therefore, we believe that a similar catalytic gasification reaction[13a,13c] might also occur in our experiments and the generated carbon species could be a part of the carbon source.

Based on the above speculation, in order to confirm that some carbon species are released from GO and serve as a supplementary carbon source for the growth of CNWs, we intensively placed a Si/SiO$_2$ substrate spin-coated with $CoCl_2$ behind the $CoCl_2$-coated GO substrate (Figure S3A in the SI). As expected, after annealing at 950 °C for 30 min, short CNWs were observed on the $CoCl_2$-coated Si/SiO$_2$ substrate (Figure S3B in the SI). This suggests that some carbon species, released from GO substrate, moved and accumulated on the $CoCl_2$-coated Si/SiO$_2$ substrate for growth of CNWs. As a comparison, the same annealing process was performed on a $CoCl_2$-coated Si/SiO$_2$ substrate without any GO present. As expected, no CNWs were founded on the Si/SiO$_2$ substrate. According to the results mentioned above, we conclude that the highly dense CNWs are generated not only by the carbon from the GO sheets underneath Co NPs but also by the carbon species released from GO during high-temperature annealing.
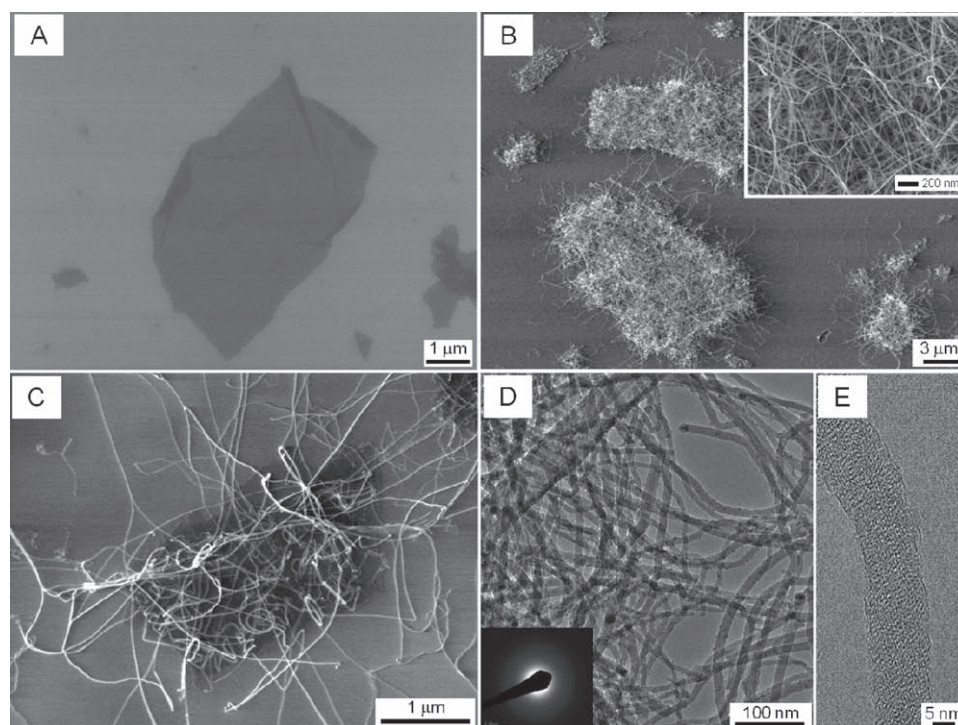

Figure 1. SEM images of 0.5 mm $CoCl_2$ spin-coated on GO substrate A) before and B) after annealing at 950 °C for 30 min. Inset in (B): magnified scanning electron microscopy (SEM) image of CNWs grown on rGO. C) SEM image of 0.1 mm $CoCl_2$-coated GO on Si/SiO$_2$ substrate after annealing at 950 °C for 30 min. D) Transmission electron microscopy (TEM) image of the formed CNWs. Inset: selected-area electron diffraction (SAED) pattern of CNWs. E) High-resolution TEM image of a single CNW.
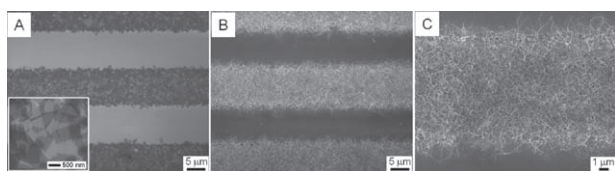
Figure 2. SEM images of A) micropatterned parallel GO arrays, B) rGO/CNW composite arrays, and C) a magnified image of the rGO/CNW composites in (B). Inset in (A): GO micropatterns consisting of single- or few-layer GO sheets.

To control the synthesis of rGO/CNW composites, different synthesis conditions in the CVD chamber were investigated in detail. We found that the annealing temperature, CVD chamber pressure, thickness of GO films, and H_2 concentration are crucial for the formation of rGO/CNW composites, as summarized in Table S1 in the SI. The diameter of CNWs grown on GO substrates can be controlled by varying the annealing temperature. As shown in Figure S4 of the SI, the diameters of the CNWs increase with the annealing temperature, being 8.6 ± 0.8, 11.9 ± 1.3, and 18.3 ± 3.2 nm at 900, 950, and 1000 °C, respectively.

In order to control the position of CNWs on Si/SiO$_2$ substrates, a parallel GO array containing single- or few-layered GO sheets with a patterned size of 10 μm and an interfeature distance of 10 μm was fabricated by our previously reported method,[3d] as shown in **Figure 2**A. After the patterned GO substrate was coated with CoCl$_2$ and annealed at 950 °C for 30 min, the rGO/CNW composite patterns were formed (Figure 2B and C and Figure S5 in the SI). The uniform and dense rGO/CNW patterns indicate that our method is capable of controlling the position of rGO/CNW composites on solid substrates.

As a proof of concept, a front-gated (solution-gated) field-effect transistor (FET), based on the synthesized rGO/CNW composite patterns (left inset of **Figure 3**), is demonstrated

for the real-time detection of dopamine (DA). The channel materials are parallel rGO/CNW composite patterns (the size of micropatterned rGO/CNW composite thin film is fixed at 0.5×0.5 cm^2). Silver paint was deposited as the source and drain electrodes and silicone rubber was used to insulate the Ag electrodes and define the sensing chamber. Figure 3 shows that the drain-to-source current (I_{ds}) increases significantly with each addition of DA. The right inset of Figure 3 gives the plot of the change of I_{ds} versus the concentration of DA. Our experimental result shows that the patterned rGO/CNW-composite-based chemical sensor can detect dopamine at levels as low as 0.5 mM, which is comparable to that obtained in our previous report.[3d]

In summary, we have synthesized novel rGO/CNW composites by a simple, one-step annealing process. It is found that GO itself can serve as a carbon source to efficiently support the growth of CNWs. Without using additional carbon precursor, the experimental setup and procedure are significantly simplified, which facilitates not only control of the synthesis but also the potential for practical large-scale production of rGO/CNW composites. This method also opens up a new pathway for synthesis of other graphene-based carbon materials, such as rGO/CNT composites. Moreover, as a proof of concept, micropatterned rGO/CNW composites used as channel materials for an FET exhibit excellent sensing properties in detection of dopamine. We believe that these novel rGO/CNW composites may have potential applications in field emission, sensing, and so on.

Experimental Section

Substrate Preparation: After the Si/SiO$_2$ wafer (with a 300-nm SiO$_2$ layer) was ultrasonicated in a mixture of acetone, water, and ethanol (1:1:1 by volume) for 10 min and rinsed with Milli-Q water, it was immersed in a piranha solution (H_2SO_4:H_2O_2 = 7:3, v/v) at 100 °C for 30 min, followed by rinsing with Milli-Q water, and drying with N$_2$. (CAUTION: Piranha solution is a vigorous oxidant and should be used with extreme caution). The O$_2$-plasma cleaning process was operated under a pressure of 140 mTorr with a power of 6.8 W for 5 min to remove organic contaminants on the Si/SiO$_2$ wafer.

Graphene oxide (GO) was prepared by a modified Hummers method.[14] The GO substrate was prepared by spin-coating of GO aqueous solution (0.1 mg mL^{-1}) onto the cleaned Si/SiO$_2$ wafer. Next, CoCl$_2$ aqueous solution (0.1–0.5 mM) was spin-coated on the prepared GO substrate, which was immediately moved into a CVD chamber for growth of rGO/CNW composites.

Synthesis of rGO/CNW Composites: Before synthesis of rGO/CNW composites, the quartz tube of the furnace was cleaned by annealing in air at 950 °C for 30 min, followed by rinsing with aqua regia and Milli-Q water, and then drying with N$_2$. To synthesize rGO/CNW
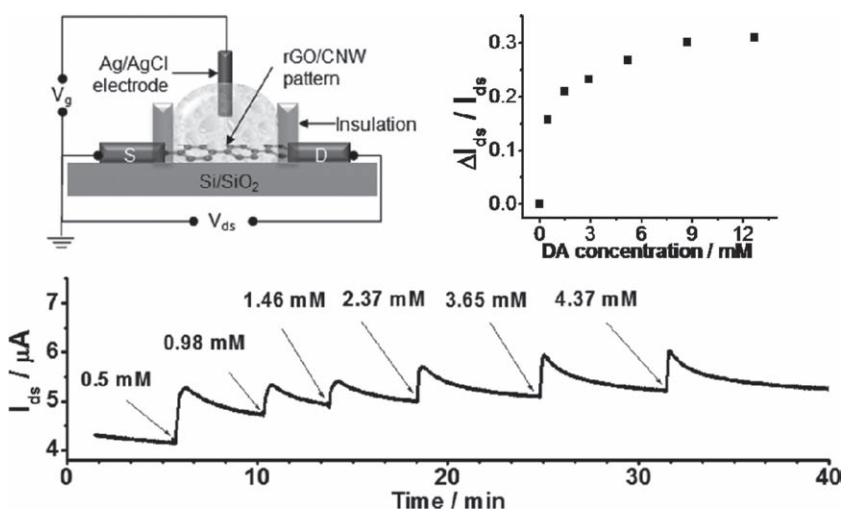

Figure 3. Typical real-time recording of I_{ds} with addition of dopamine on the patterned rGO/CNW-composite-based FET device at $V_g = -0.1$ V. Each step represents the gradual addition of dopamine. Left inset: schematic illustration of the experiment setup, a front-gated rGO/CNW-composite-based FET, for sensing experiments. Right inset: change of I_{ds} with increase of dopamine concentration.

composites, the $CoCl_2$-coated GO substrates in the CVD chamber were annealed at 900–1000 °C for 30 min under a mixture of Ar/H_2 (190 sccm/ 10 sccm) gas flow with a pressure of ≈150 Pa.

Sensing Application: The sensing experiments were carried out on the front-gated (solution-gated) FETs. The left inset in Figure 3 shows the typical set-up of a front-gated FET based on the rGO/CNW micropatterns. The channel materials were parallel rGO/CNW composite patterns (the size of the micropatterned rGO/CNW composite thin film was fixed at 0.5 cm × 0.5 cm). Silver paint was deposited on both sides as the source and drain electrodes. Silicone rubber was used to insulate the Ag electrodes and define the sensing chamber. 200 µL of phosphate buffer solution (PBS; pH 7.2) was used as buffer solution. The source–drain current (I_{ds}) was biased at 400 mV and the gate voltage (V_g) was applied at −0.1 V through the top gate (Ag/AgCl electrode).

Supporting Information

Supporting Information is available from the Wiley Online Library or from the author.

Acknowledgements

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