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Mechanism of graphene oxide as a growth template for complete reduced graphene oxide coverage on SiO₂ substrate

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Reduced Graphene Oxide (rGO) has the distinct advantage of an aqueous and industrial-scalable production route. However large deviation in the electrical resistivity of fabricated rGO devices, caused by inhomogeneous coverage of rGO on the substrate, prevents its practical application in electronic devices. This critical problem could be solved by using an ethanol chemical vapour deposition (CVD) treatment on the graphene oxide (GO). With the treatment, not only GO was reduced to rGO, rGO new growths preferentially grow outwards from the edges of the existing GO template and enlarge in size until rGO completely covered the substrate. The growth sequence was presented and our results indicate that the growth support the free radical condensate growth mechanism. After the ethanol CVD treatment, the standard deviation in electrical resistivity decreased significantly by 99.95% (1.60E+06 to 7.72E+02 Ω/square) in comparison to hydrazine-reduced rGO substrates. As no carbon signatures on the substrate were observed if no template was used; this work indicate that GO could act as template for subsequent formation of rGO.

1 Introduction

Graphene consists of a single planar layer of sp² hybridised carbon. Its large carrier mobility and extraordinary optical, thermal and chemical properties had been in the spotlight¹ since its exfoliation from graphite in 2004². However, the zero-band gap and semi-metal electronic structure of graphene confines its use in optical, electronic and sensing applications^{3, 4}. Therefore, approaches have been made to open the band-gap, such as breaking inversion symmetry in bi-layer graphene⁵, lateral confinement^{6, 7}, strain engineering⁸, oxidation⁹ and usage of reduced graphene oxide (rGO)¹⁰.

One of the methods to obtain the band-gap is to use rGO. This method is inexpensive and has an aqueous-processable route, thus making it compatible with many chemical processes and industrial-scalable. Despite these advantages and a substantial interest in rGO research in recent years¹¹, synthesis of rGO on substrates with good homogeneity and conductivity for practical application has not been reported¹². For device fabrications, rGO flakes have been spin-coated or attached electrostatically by (3-Aminopropyl)triethoxysilane (APTES) to silicon dioxide (SiO₂) substrates. APTES's electrostatic attraction to graphene oxide (GO) is a common technique used to obtain mono or few-layer GO on the substrate¹³⁻¹⁶. However, the surface coverage ranges from 60-80%^{13, 17-19}. This is due to the cross-linked APTES²⁰ and varying sizes of rGO flakes¹⁰; posing a problem to work with rGO fabrication.

Large sized thin-films of single and few-layered graphene have

recently been synthesized using atmospheric pressure ethanol chemical vapour deposition (CVD) on copper²¹. Carbon nanotubes were synthesized using atmospheric pressure ethanol CVD using catalysts such as iron²². However, the metal catalysts used in these processes pose a problem to be removed later and sheets grown with metal catalysts do not have extensive applications because of the undesirable characteristics of residual catalyst material.

Most of these metal catalysts form metastable metal carbides at high temperature which has (i) high carbon solubility and (ii) high carbon diffusion rates. The principle in catalytic reaction is that the metal catalyst can act as both an electron donor and acceptor. Metal catalysts are required in graphene²¹ and carbon nanotube²² growth which allows ready exchange between the metal surface and carbon molecules. From computation studies, it has also been reported that the minimum energy growth mechanism of graphene sheets is by the sequential addition of carbon hexagons at the edges of the graphene sheet²³.

Thus it is reasonable to hypothesize that GO, with its 2D electron gas properties¹¹, is also comparable with metal surfaces and could act as a catalyst for the growth of rGO, thus producing rGO on substrate with good homogeneity and conductivity for practical applications.

2 Experimental

Large GO flakes in aqueous solution were synthesized as reported^{10, 24} and electrostatically attached to the APTES-functionalized SiO₂ substrates. Thereafter, these substrates were

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Fig. 2 Scanning electron microscope image of (a) before ethanol CVD treatment GO flakes with *ca.* 60% coverage and (b) after 30-minutes ethanol CVD treatment rGO flakes with *ca.* 80% coverage [GO flakes highlighted in purple and new growth highlighted in yellow, please refer to online version for colour] (c) High-magnification image on the new growths.

Fig. 1 An atmospheric pressure CVD setup with alcohol vapors for growth of rGO.

placed on quartz holder and into the CVD tube. The furnace was first purged with argon gas at 300sccm for 40 minutes to remove oxygen gas that might oxidise rGO into gaseous products. Argon gas was then adjusted to 100sccm; hydrogen gas turned on and set at 20sccm. The gases passed through an ethanol bubbler which was kept at 0°C while the furnace was set at 950°C for 2 hours. After 2 hours, the furnace was switched off and the tube was left to cool slowly to room temperature.

The ethanol CVD-treated chips were then characterized by (1) a JEOL JSM-7600F Field Effect Scanning Electron Microscope (SEM) instrument operating in gentle beam mode at 1KV; (2) a FEI Tecnai F20 Transmission Electron Microscope (TEM) instrument operating at 200kV for bright field imaging and JEOL 2000FX TEM operating at 200kV, beam size 130nm, for SAED imaging; (3) a Keithley 4200-SCS semiconductor parameter analyser with 20nm titanium and 100nm gold electrodes; (4) a Renishaw Invia Ultra Violet (UV) Raman of 325nm, spot size 1µm with an aperture of 40x; (5) an Asylum Research AFP-3D

Atomic Force Microscope (AFM) in tapping mode using Olympus AC240TS Silicon tip under ambient condition with scanning rate of 0.2Hz and (6) an Advanced Instrument Technology 4-Point Probe CMT-SR2000N using 1mm probe spacing and 100g spring constant.

3 Results and Discussion

The experiment used an alcohol CVD setup as shown in **Figure 1**. In theory, any hydrocarbon source such as methane, ethylene and ethanol could be used. However, liquid carbon sources such as ethanol are a safer alternative than gaseous hydrocarbons, which are extremely flammable and may form explosive mixtures with air. Thus ethanol was used for the carbon source.

During the deposition phase, the gaseous hydrocarbon is thermally pyrolyzed: each of the C-C and C-H bond could break to form two free radicals with each fragment keeping one electron. The presence of radical in the molecule allows rapid rearrangement of carbon bonds. Though the reaction is more complicated for alcohols, the possible cracking of carbon radical species to form carbon deposition in the basic form could be expressed as **Equation 1** and the catalytic hydrogenation²⁵ process of solid carbon in which H₂ forms CH₄ as **Equation 2**.

According to Le Chatelier's principle and Equation 1, the growth rate of carbon will decrease with decreasing hydrocarbon concentration and increasing hydrogen gas. From Equation 2, increasing the ratio of hydrogen gas increases the dissociation rate of carbon and hydrogen into gaseous hydrocarbons. Thus the addition of hydrogen gas could help to etch away amorphous or excess carbon formed²⁶. In the experiment, by increasing the hydrogen to argon gas ratio from 0.17 to 0.34 while maintaining

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Fig.3 (a) I_d - V_d (drain current- drain voltage) output graph under different applied gate voltages and (b) I_d - V_g (drain current-gate voltage) transfer curve under sweeping gate voltages; of the CVD-processed rGO device under vacuum and room temperature. [Please refer to online version for colour]

Fig. 4 Ultra-violet Raman spectra of diamond, GO, different ethanol CVD processed rGO and HOPG. The intensities of diamond and HOPG are scaled down to allow fitting into graph.

the total flow volume of gas mixture, no deposition of carbon occurred even after 1 hour. With the ethanol precursor removed from the system for only 1 hour, no carbon Raman signature was detected on the substrate; the entire GO template was etched away. Thus, the deposition of rGO in the experiment obeys the Le Chatelier's principle as depicted in Equation 1 and occurs in direct competition with the catalytic hydrogenation process as depicted in Equation 2.

In **Figure 2**, existing rGO flakes are highlighted in purple and the new growths are highlighted in yellow. **Figure 2a** shows the GO coverage of ca. 60% after a typical APTES-functionalization and GO incubation on SiO_2 . However, after a partial ethanol

CVD treatment of 30 minutes, the coverage increased to ca. 80% as shown in **Figure 2b**. A high magnification of the new growth is shown in **Figure 2c**. A lighter contrast was observed for the new growths compared with the existing GO flakes after the ethanol CVD treatment. The contrast difference could be due to the e-beam induced surface potential between graphene of different band gaps²⁷. The different thickness of the graphene could also be observed as different contrast, with darker sections indicating more layers²⁴. Thus SEM imaging allows efficient identification between the flakes and extensions after ethanol CVD treatment.

It is shown in the high-resolution SEM image that the new rGO new growth can continue to act as a catalyst for subsequent growth, subsequently covering more of the gap between existing rGO flakes. To prove the role of GO as an effective catalyst, substrates in the same conditions (clean and APTES-functionalized) without GO were processed under the same CVD conditions for up to 2 hours. Neither carbon deposits nor carbon spectrum were detected by SEM and Raman respectively. Obviously the initial GO flakes act as crystal nucleus for the subsequent growth of these flakes²⁴.

Since rGO can be a template for subsequent growth of rGO, this work supports the free radical condensate concept in which metal catalysts only help to initiate carbon precipitation and rearrangement at the nucleation stage: once the carbon structure is created, e.g. cloning of 1-Dimensional carbon nanotube²⁸, the metal catalyst becomes non-functional. The carbon radicals from the pyrolysis of ethanol could then catenate into longer chains by forming covalent bonds directly on the existing edges of rGO template resulting in the growth observed²⁹.

The 2-hour ethanol CVD processed film is then transferred onto lacey-carbon copper grids for TEM analysis. From the bright-field TEM image (**Figure S1a**), the new grown rGO, existing rGO and the boundary between these two regions is

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Table 1 D/G Raman spectrum peak intensity, AFM height profile and 4-point probe sheet resistance for GO and rGO reduced under different conditions.

		GO	15 mins CVD	30 mins CVD	1 hour CVD	2 hour CVD	12 hour hydrazine ¹⁰
UV Raman Spectroscopy	Peak intensity of D/G	0.42	0.35	0.32	0.17	0.09	NA
	Flake thickness (nm)	1.4	1.5	2	4	4	NA
AFM Height Profile	New growth thickness (nm)	0	0	0.8	1	2	NA
	Average Resistance ($\Omega/\square$)	NA	6.10E+04	2.87E+04	2.23E+04	4.68E+03	1.99E+06
4-point probe Sheet Resistance (n=5)	Standard Deviation ($\Omega/\square$)	NA	4.43E+04	1.25E+04	7.16E+03	7.72E+02	1.60E+06
	Relative Standard Deviation (%)	NA	72.6	43.6	32.1	16.5	80.5

shown. The existing rGO region is characterized by the area with straight edges and darker contrast (thicker layers), while the new grown rGO have rounded edges and lighter contrast.

Selected area electron diffraction imaging (**Figure S1b**) on the film shows strong spots with a hexagonal pattern, confirming the three-fold symmetry arrangement of carbon atoms. There are weaker spots beside this set of hexagonal pattern forming a distinct weak ring-like pattern indicating that there are a few domains of crystalline graphene overlapped in the examined area. The first hexagonal ring pattern arises from the (100) plan while the second from the (110) plane.

To test the ethanol CVD processed rGO electrical properties, back-gated Field-Effect Transistors based on 1 hour CVD processed GO sheets were fabricated and their electrical properties tested under vacuum at room temperature. The channel length was 100 μm to ensure transport is bulk-limited and role of the all contacts minimized. **Figure 3a** shows the drain current (I_d) versus drain voltage (V_d) curve at six discrete gate voltages (V_g). The figure shows linear output behaviour indicative of a good ohmic contact between the GO film and electrodes. **Figure 3b** illustrates the same transistor I_d under sweeping V_g at fixed $V_d=0.1\text{V}$. The threshold voltage is shifted to the positive side due to p-doping from persistent moisture and oxygen. The CVD treated rGO device showed a clear increase in conductance as the V_g deviates from 0V, indicating that the rGO films behaved as ambipolar semiconducting material with stable electrical characteristics up to $\pm 100\text{V}$.

Hole mobility is obtained from the linear regime of the transfer curve using **Equation 3**, where L and W are the channel length and width; C_{ox} is the gate capacitance; V_d , V_g and I_d are the drain-source voltage, gate voltage and drain-source current respectively.

$$\mu = (L/WC_{ox}V_d)(\Delta I_d/\Delta V_g) \quad (3)$$

The hole mobility of a typical 2-hour ethanol CVD processed device under vacuum at room temperature is 124 cm^2/vs . It is considerably more than the rGO samples studied previously^{30, 31}, thus validating that the CVD new growth could extend the pre-existing 2-dimensional network and allows π -electron charge percolation.

The UV Raman spectra were obtained and fitted with Lorentzian to obtain the positions and intensities of the peaks for the 15 mins, 30 mins, 60 mins, 120 mins ethanol CVD processed samples with diamond, GO, HOPG as comparison as shown in **Figure 4**. UV Raman is used because in visible Raman, the sp^2 sites have such a high cross section that they dominate the spectra. The presence of G peaks in UV excitation of GO, rGO and HOPG showed that the sp^2 vibrations still dominate even in the UV Raman excitation. The diamond sample exhibited a characteristic diamond peak at 1330 cm^{-1} . For CVD processed rGO, the D peak was measured at 1409 cm^{-1} and G peak at 1584 cm^{-1} in agreement with existing literature^{24, 33, 34}.

We then investigate whether the grown carbon is rGO-like carbon or diamond-like carbon (DLC). RGO is defined generally as sp^2 regions in a sp^3 matrix whereas DLC is defined as amorphous carbon with sp^3 and trans-polyacetylene bonds³³. The T peak³³ that is due to C-C sp^3 vibrations occurs only with UV Raman excitation at wave number of $\sim 1060\text{cm}^{-1}$. It is due to a resonant enhancement of the σ states and it directly probes the sp^3 bonding. As the sp^3 content falls, the sp^3 vibrational density of states peak 1060 cm^{-1} will shift upwards to that of sp^2 VDOS at 1400 cm^{-1} . In both GO and CVD processed rGO spectra, no T peak was observed, indicating that the CVD processed samples

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Fig. 5 Schematic showing the growth sequence of rGO from a GO template during ethanol CVD treatment.

sp^3 percentage was small and non-diamond like. It is also observed that the D peak decreases as the CVD processing time increases, indicating increasing graphitic order in the rGO structure³⁵.

The I_D/I_G ratio of the UV Raman (Table 1) can be used to estimate the sp^2 domain size using the Tuinstra-Koenig empirical formula³⁶ in UV conditions³³. The ratio decreases continuously from 0.42 in the GO sample to 0.09 in the 2 hour CVD treated samples indicating increased ethanol CVD treatment results in increased sp^2 domain size in the rGO samples. Thus from Raman spectrums and I_D/I_G , we confirm the carbon growth to be rGO, that the CVD treatment increases graphitization and that the sp^2 domain size increases with increasing processing time. The Raman mapping of the intensity peaks of D, G and D/G are presented in Figure S2. The I_D/I_G ratio of the new grown rGO is lower than that of existing rGO flakes indicating that the new grown rGO has larger sp^2 domain size.

The AFM is performed on the 15 mins, 30 mins, 60 mins, 120 mins ethanol CVD processed samples. From 0 to 15 minutes of CVD treatment, the AFM height profile indicates that the thickness of pre-existing GO template had negligible increase in height and no growth from the edges was observed²⁶. However,

as the process time increases to 30 minutes, new growths appear and the thickness of the GO template also increases slightly by 0.5nm. With increasing process time to 2 hours, the new growths continue to extend outwards and completely cover the gaps in between the pre-existing rGO flakes. The new growth thickness after 2 hours of growth is 2nm and this corresponding to ~2-3 layers of rGO¹⁰. The AFM image and corresponding height profile between existing rGO and the new grown rGO of a 2 hour CVD treated sample is shown in Figure S3.

From the 4-point probe measurement, the average electrical resistance of the chips decreased from $1.99E+6$ to $4.68E+3$ Ω /square (99.76% reduction) while the relative standard deviation decreased from $1.60E+06$ to $7.72E+02$ Ω /square (99.95% reduction) after a 2 hour ethanol CVD treatment as compared to 12 hour hydrazine vapor reduction. The decrease in electrical resistivity in the ethanol CVD treated samples could be attributed to the increased percolation pathways between flakes due to the new growth completely filling up gaps between pre-existing rGO flakes. Due to the more uniform and increased coverage of the rGO on the substrate, the reported growth method had decreased the standard deviations between chips, thus solving a critical problem for the practical use of rGO in electronic devices.

Having considered the data from the experiment, we arrived at the following growth sequence of rGO schematic (**Figure 5**). Ethanol CVD treatment of up to 15 minutes on the GO lead to an improved graphitization from the free radicals produced from pyrolysis of gaseous ethanol. After 30 minutes, a thin graphitic shell is formed around the GO catalyst. Due to the lower growth activation energy at the edge of graphene sheets for sequential addition of carbon hexagons²³, rGO preferentially grows out from the edges. Finally, rGO completely covers the substrate after 2 hours of the ethanol CVD growth process.

Our data suggest that rGO could be grown via the free radical condensate mechanism. The mechanism of carbon nanotube carbon growth has been debated and two different mechanisms have been proposed: the dissolution of elemental carbon into metal nano-clusters followed by precipitation³⁷ or the free radical condensate that carbon can act as reaction medium for production of nanotubes²⁵. In the experiment, no metal catalyst was used, but rGO growth was observed, thus supporting the free radical condensate growth theory. After the pyrolysis of ethanol, free radicals preferentially condensate at the edges of the pre-existing GO flakes and thus rearrange itself into a new carbon skeleton until a local minimum has been reached.

4 Conclusions

Complete coverage of rGO on SiO₂ substrate was achieved using GO template under ethanol CVD at ambient pressure without any metal catalysts. GO edges preferentially act as a catalyst for further growth of rGO. The growth sequence proceeds by the free radical condensate growth mechanism. After a 2 hour ethanol CVD treatment, the electrical resistivity decreased by 99.76% and its relative standard deviation decreased by 99.95% compared to hydrazine treated samples. The results and proposed mechanism show that the use of 2 hour ethanol CVD treatment on GO is a promising way towards a better and homogenous rGO for practical, high-yielding preparation of novel functional biosensors^{38, 39}, catalysts⁴⁰, electronics⁴¹, batteries⁴² or crystal growth templates⁴³.

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Notes and references

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- [†] Electronic Supplementary Information (ESI) available: [AFM image with corresponding height profile; optical microscope image with Raman mapping of the intensities of D,G and D/G peaks; and bright-field TEM image with SAED pattern of the 2-hour ethanol CVD processed sample]. See DOI: 10.1039/b000000x/
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