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Growth of Reduced Graphene Oxide

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ABSTRACT

Reduced graphene oxide (RGO) has the advantage of an aqueous and industrial-scalable production route. However, one of the main limitations that prevent the use of RGO in electronics is the high electrical resistance deviation between fabricated chips. In this article, we present the novel growth of RGO which can bridge the gaps in-between existing flakes and thus reduce the electrical resistance standard deviation from 80.5 % to 16.5 %. The average resistivity of the treated RGO of ~ 3.8 nm thickness was 200 Ω /square. The study uses an atmospheric-pressure chemical vapour deposition (CVD) system with hydrogen and argon gas bubbling through ethanol before entering the furnace. With a treatment of 2 hours, 100 % of the silicon dioxide substrate was covered with RGO from an initial 65 % coverage. This technology could enable large-scale application of RGO use in practical electronic devices.

INTRODUCTION

Reduced graphene oxide (RGO) or chemically derived graphene (CDG) can be used as an alternative to graphene in electronics because it has a tunable band gap and that it has the advantage of a scalable and solution processable route[1-4]. However, current RGO devices have high variation in the electrical resistivity because the varying coverage of RGO flakes that can range from 60-90%. For this reason, 100% coverage like CVD grown graphene[5-8] is necessary. In this paper, we report a post-treatment process to graphene oxide (GO) to simultaneously reduce, grow it and extend the coverage to 100% in 2 hours.

To grow graphene, a catalyst such as copper[5] or nickel[9] is needed. The high carbon solubility of nickel film allows the diffusion of carbon into the film at growth temperature and precipitate out of the substrate upon cooling; whereas the low carbon solubility of copper catalytically decomposes alcohol into radicals and allows adsorption of the carbon on the surface[6].

Recently, the extended growth of carbon nanotube without any additional catalyst has been reported[10]. The extended growth followed the configuration and structure of the original nanotube template. A convincing model is still lacking on how the carbon is nucleated and

grown from this template. There had been reports of using ethanol CVD to repair both graphene and GO[11, 12]; but no growth was observed. Herein, our group proposes a hypothesis that extended growth of GO by ethanol CVD is possible.

EXPERIMENT

Synthesis of Large GO flakes

A modified Hummers method[13-16] to obtain large GO sheets was used. Concisely, 2 grams of graphite flakes (3-5 mm, NGS) were mixed with H_2SO_4 (12 ml) for 4 hours at 80 °C. The flakes were then washed over a filter and dried overnight. The pre-oxidized graphite powder were then added to H_2SO_4 (120 ml) and KMnO_4 (15 g) and stirred for 2 hours. DI water (250 ml) was then slowly added to the mixture in an ice bath and stirred for another 2 hours. Thereafter, DI water (700 ml) and H_2O_2 (20 ml) was added to stop the reaction. The obtained mixture was centrifuged and used as stock GO solution.

GO on substrate

Silicon dioxide substrates were RCA cleaned 2 times and then functionalized in 1% v/v 3-APTES ethanol solution for 1 hour to make the surface electrostatically positive. Stock GO solution (negatively charged) was then drop-casted on the substrates and left to react for 1 hour. The substrates were then rinsed and kept under ambient conditions.

Ethanol CVD Growth of GO

The quartz tube of the CVD was first purged with argon for 30 minutes. Then, 5 prepared substrates were placed into the quartz tube of an ethanol CVD setup per batch. The temperature ramp was set at 40 °C per minute and the final temperature at 950 °C. The hydrogen and argon gas were set at 20 and 100 sccm respectively. These parameters are the optimized conditions to produce carbon nanotubes in this ethanol CVD setup.

DISCUSSION

Figure 1. SEM image of ethanol CVD treatment of GO flakes after 1 hour. The GO coverage increased from 65% to 80%. The GO flakes are highlighted in purple and the growth in yellow. SiO_2 substrate remain grey in colour.

Figure 1 shows the SEM images of the GO flakes before and after ethanol CVD growth. The high magnification image shows the new growth islets between the gaps of two flakes. The ethanol precursor provides the carbon radicals for deposition; in direct competition with the hydrogen in the gas precursor which etches away amorphous carbon thus allowing controlled monolayer growth. The competition between these two precursors can be written in the form of the Le Chatelier's equation.

Figure 2. AFM height profile and corresponding height of GO at different stages of ethanol CVD.

From Figure 2, as the ethanol CVD treatment time proceeds up to the first hour, both the height of the original GO and new growth increases. In the second hour, only the new growth continue to increase and it eventually forms a continuous layer with 2nm thickness, corresponding to ~2 layers of GO[17].

Table 1 shows that average sheet resistance of RGO decreased 3 orders of magnitude from $1.99\text{E}+06$ (12 hours hydrazine) to $4.68\text{E}+03$ (2 hours ethanol CVD) $\Omega/\square$. The corresponding relative standard deviation also decreased from 80.5 % to 16.5 %. The decrease in electrical resistivity could be due to the increased percolation pathways between flakes from the new growths. The complete coverage of RGO on the substrate decreased the standard deviation of between measurement sites significantly, thus solving a critical problem for the practical use of RGO in electronics such as the development of biosensors[18-20] and microelectronics[14, 21].

Reduction Method	Hydrazine vapor	Ethanol CVD			
Processing Time	12 hours	15 mins	30 mins	1 hour	2 hours
Average Resistance ($\Omega/\square$)	1.99E+06	6.10E+04	2.87E+04	2.23E+04	4.68E+03
Relative Standard Deviation (%)	80.5	72.6	43.6	32.1	16.5

Table 1: Four-point probe sheet resistance for GO reduced under different conditions

Future work on these results include (1) study of the conduction mechanism, (2) optimization of the growth time and (3) application of the post-treated GO to sensing of molecules[22] such as Interleukin-6 bio-molecule [23] and hydrogen sulphide gas[24, 25].

CONCLUSIONS

In summary, the lateral size of GO could be grown up to 100 % coverage on silicon substrate (from ~60-85 %). This growth not only reduced the electrical resistance deviation between chips due to variable coverage, but also reduced the overall electrical resistance (80.5 % to 16.5 %). This technology could enable large-scale application of RGO to be used in practical electronic devices.

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