ORIGINAL ARTICLES

Rectangular Graphene Synthesis by CVD Method


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ABSTRACT

Inspired by the recent concentric interest towards the graphene, this study is concerned to optimize the large scale synthesis with specific shape of this exciting nanomaterial. Few layered graphene of uniquerectangular shaped were synthesized by chemical vapor deposition (CVD) method using a catalyst of specific combination. The produced graphene was characterized by various techniques to know the aspect ratio, number of layers and purity. This study is suggestive to extend work for easy scale up production method of themost potent emerging nanomaterial.

Key words: Graphene, CVD, Catalyst, TEM, Raman, EDX, Electronics

Introduction

Graphene is a single atom thin two dimensional lattice of carbon atoms which has been attracting intense research efforts owing to its superior electronic, mechanical, and thermal properties (Novoselov, K.S., et al., 2005; Zhang, Y., et al., 2005; Lee, C., et al., 2008; Baladin, A.A., et al., 2008). Graphene exhibits interesting electronic transport properties such as high carrier nobilities and the half-integer quantum Hall effect ((Novoselov, K.S., et al., 2005; Zhang, Y., et al., 2005) and displays a high Young’s modulus (Lee, C., et al., 2008).

Graphene embodies a range of unique properties leading an exciting electronic character, described as a zero-gap semiconductor (Castro Neto, A.H. et al. 2009), unparalleled strength (breaking strength ~40 N/m, Young’s modulus ~1.0TPa) (Lee, C., et al. 2008), and record thermal conductivity (Balandin, A.A. et al. 2008). Charge carriers, described as massless Dirac fermions, exhibit ballistic movement across submicron distances approaching relativistic speeds, with intrinsic carrier mobilities up to 200,000 cm$^2$ V$^{-1}$ s$^{-1}$ (Geim, A.K., K.S. Novoselov, 2007; Novoselov, K.S. et al. 2005; Hwang, E.H. et al. 2007).

Chemical vapor deposition (CVD) is an attractive approach to graphene synthesis due to its capability of producing large area deposition and the lack of intense mechanical and/or chemical treatments. It is believed that carbon is then adsorbed and absorbed into the metal surface at high temperatures, where it is then precipitated out in the lowest free energy state (graphene) during the cool down to room temperature (Reina, A. et al. 2009; Kim, K.S. et al. 2009; Arco, L.G.D. et al. 2009; Chae, S.J. et al. 2009; Reina, A. et al. 2009; Li, X. et al. 2009).

2. Experimental:

Initially, the catalyst of specific combination of transition metals was prepared through conventional wet chemistry involvement. More specifically 5g Iron nitrate (III) nonahydrate [Fe(NO$_3$)$_3$.9H$_2$O] and 5g Cobalt (II) nitrate hexahydrate[ Co(NO$_3$)$_2$.6H$_2$O ] were mixed in 50 ml ethanol. The solution was added in to 190 gm Magnesium Oxide [MgO] in 500 ml ethanol with stirring. These chemicals were procured from Sigma Aldrich. The mixture was viscous and in order to facilitate the mixing process 50 ml ethanol is again added. It was then stirred for another two hours. The resultant mixture was again left for two hours on probe sonication. The catalyst mixture was then kept in the oven at 130°C for overnight. The dried light greenish cake was grinded to obtain powder.

Graphene samples were grown in a quartz boat ( 100 mm X 25 mm ) centrally placed inside the quartz tube ( 800 mm length and 74 mm inner diameter ) furnace system using CVD ( Catalytic chemical vapor deposition ) method using methane and argon gas (Li, X.S. et al, 2009).

The grinded powder of the mixed catalyst was taken as thin layer on the quartz boat inside the quartz boat. The set up was connected to gas inlet and outlet. The tube was evacuated by running vacuum pump. Argon gas...
was in flowed at the rate of 200 ml/minute while temperature kept on rising at the rate of 10 °C/min. Once the furnace temperature reaches the niche temperature (1050 °C) methane gas was purged into the CVD reactor tube along with argon gas. The flow rate of the methane gas (500 ml/minute along with 200 ml/minute of argon) was maintained for a period of time corresponding to the amount of catalyst loaded in the CVD reactor. The methane gas purged inside the CVD reactor was reduced to the pure carbon form, i.e., Graphene, by the alkaline and transition metal catalyst.

Followed by the completion of reaction the flow of methane gas into the tube was stopped and then the system was cooled under argon gas atmosphere. Fast cooling is achieved by continued argon gas flow at 500 ml/minute for another 2 hours. The nanomaterial thus formed were purified by one-step Hydrochloric acid (HCl)(35%) demineralization process. Further repeated washing with DM (demineralized) water and ethanol were performed using shear stirring. The Graphene cake was finally dried in an oven at 120 °C for 12 hours and then grinded into fine powder using mortar and pestle. Thus ultrafine powder of very fine grayish-black, randomly aggregated powder was obtained. On characterization it revealed that product was few layered thin rectangular Graphene sheet. The percentage yield calculated was found to be 69%.

![Figure 1A: TEM image](image1a.png)

![Figure 1B: TEM image](image1b.png)

![Figure 1C HRTEM image](image1c.png)

![Figure 1D TEM image](image1d.png)

**Fig. 1:** TEM images
Result And Discussion

The structural analysis and characterization of the Graphene were performed using the transmission electron microscopy (TEM) and Raman spectroscopy. The transmission electron microscopy (TEM) studies were carried out to determine the exact size of as-manufactured Graphene rectangular structure using Philips, TECHNAI FE 12 microscope (TEM) at an accelerating voltage of 120 kV. Figure 1A, 1B, 1D and Figure 1D show the (TEM) images. Figure 2 shows a typical Raman spectrum of Graphene thus formed in the present study. The three intense peaks were observed as the D band at 1350 cm\(^{-1}\), the G band at 1580 cm\(^{-1}\) and the 2D band at 2650 cm\(^{-1}\). The elemental analysis of the Graphene rectangular structure thus synthesized shows the carbon content of 91.67 atomic percentages in table 1.

![Fig. 2: Raman Spectra of Graphene](image)

<table>
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<tr>
<th>Table 1: Elemental analysis</th>
<th>Weight %</th>
<th>Atomic %</th>
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<tbody>
<tr>
<td>C K</td>
<td>84.41</td>
<td>91.67</td>
</tr>
<tr>
<td>Mg K</td>
<td>14.45</td>
<td>7.85</td>
</tr>
<tr>
<td>Co K</td>
<td>2.14</td>
<td>0.48</td>
</tr>
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Graphene deposition was uniformly formed few layered as defect free flakes. The uniform layer can be caused due to a surface adsorption growth mechanism. The nucleation caused during the growth process due to presence of metallic entities in catalyst.

TEM images are clearly exhibiting the uniformity and morphology without any defects at surface. HRTEM (High resolution TEM) is explaining the growth pattern. At the same time some impurities are seen in EDX spectra depicted in figure 3, which are remaining during the purification process. EDX spectra (Quantization method, Cliff Lorimer thin ratio section Number of iterations = 1) are revealing the purity level of the obtained product. Further purification steps can give absolute pure product.
The results obtained from Raman spectroscopy are in favor of uniform growth of the graphene sheet. The spectrum has large symmetrical G and 2D peaks indicating the presence of few layered graphene (Malard, L.M. et al., 2009).

There are many reports regarding the synthesis of graphene sheet but synthesis of rectangular graphene has been rare. The rectangular graphene seeks many electronic applications because of its unique electronic properties (Nikolaev, A.V., Barone, V., et al., 2001). Thus, this work is unique in regard to controlled synthesis of this particular structure of graphene.

Conclusion:

Few layered graphene flakes of rectangular structure obtained, have average particle size of 45nM, and thickness of less than 6nM. The catalyst combination in these experiments is capable of giving uniform rectangular Graphene sheet with high purity and defect free surface by CVD method at the current parameter. Further study is suggestive to scale up the synthesis method taking current study in consideration. A facile and scalable production method of specific shaped graphene is reported herein.

References

Li, X. et al. Science, 2009, 324: 1312-1314