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CVD synthesis of graphene nanoplates on MgO support

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Synthesis of graphene directly on MgO has been carried out and the structural properties of the obtained material have been investigated. Few-layered graphene was produced by simple thermal decomposition of methane over MgO powder at 950 °C in a CVD reactor. The samples were purified by 10 N HNO_3 treatment, and studied by TEM, Raman spectroscopy, EDAX and SEM. TEM clearly indicated the formation of graphene. EDAX showed that the purified sample contained only carbon and no traces of MgO. The characteristic Raman features of graphene were also seen as D-band at 1316 cm^{-1}, G-band at 1602 cm^{-1}, and a small 2D-band at 2700 cm^{-1} in the Raman spectra. The strong D-band suggests that the graphene possess large number of boundary defects. The small 2D-band indicates the formation of few-layered graphene.

Keywords: *graphene; magnesium oxide; nanographene*

1. Introduction

Graphene has been extensively studied in the last several years even though it was only isolated for the first time in 2004 [1]. The fast growth of interest in graphene is due primarily to a number of exceptional properties that it has been found to possess. There have been several reviews discussing the topic of graphene in recent years. Many are theoretically oriented, with a special emphasis on electronic properties [2] whereas the other ones are particularly focused on the review of its electronic transport properties [3]. Experimental reviews include detailed discussions of synthesis [4], Raman characterization methods [5], transport mechanisms [6, 7], relevant applications of graphene such as transistors and the related bandgap engineering [8] and optoelectronic technologies [9].

Various methods such as exfoliation [1], thermal decomposition of SiC [10], chemical vapour deposition (CVD) on nickel [11] and copper [12] substrates, molecular beam deposition [13], unzipping carbon nanotubes [14], sodium ethanol pyrolysis [15], electron beam irradiation of PMMA nanofibres [16], arc discharge of graphite [17], thermal fusion of PAHs [18] and conversion of nanodiamond [19] have been reported and reviewed.

Among all these methods, chemical vapour deposition on nickel and copper substrates are the most common and popular methods of graphene synthesis. However, CVD-grown graphene on metals has the drawback that the graphene needs to be transferred onto a wafer after synthesis. Routes to deposit graphene or few-layer graphene on dielectric surfaces are intensively studied. A possible alternative route is the use of dielectric surface itself to directly form graphene layers via CVD. This is attractive because most of today's transistor technologies use complementary metal-oxide semiconductor (CMOS) technology in which an oxide layer insulates the transistor gate from the channel. Hence, the ability to synthesize graphene directly on an oxide eliminates the need to transfer the graphene after synthesis and the necessity for large-area synthesis as required with metal substrates. Rummeli et al. [20] suggested MgO as the support material for graphene synthesis. Also, efforts have been made to synthesize carbon nanotubes on silica and zirconia support materials [21, 22]. Basing on

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this idea, we have planned to synthesize graphene on MgO.

2. Experimental

2.1. Apparatus

Graphene synthesis was carried out using a thermal CVD system (First Nano ET2000, shown in Fig. 1), under variable conditions of gas flow rate, reaction time, cooling rate etc. The product obtained was purified with 10N HNO_3 to remove the support material. The purified graphene sample was analyzed by Raman spectroscopy, transmission electron microscopy (TEM), high resolution transmission electron microscopy (HR-TEM) and scanning electron microscopy (SEM). Elemental analysis was carried out by energy dispersive X-ray analysis (EDAX).

Raman spectra were recorded on a Horiba JY LabRAM HR800 micro-Raman spectrometer equipped with 17 mW 632.8 nm laser excitation (He–Ne laser, $E_{laser} = 1.96$ eV) in the backscattering mode.

TEM studies were carried out using an FEI Technai F20 electron microscope operating at 200 kV with EDAX facility while HR-TEM studies were carried out using an FEI Technai F30 electron microscope operating at 300 kV. SEM micrographs were obtained using an FEI Quanta 200 3D with EDAX facility.

2.2. Chemicals

All the chemicals used were of AR grade and obtained from Sigma-Aldrich and Merck.

2.3. Procedure

100 mg of nanocrystalline MgO was accurately weighed and transferred to quartz plate. It was loaded on a substrate holder of the CVD system. Experimental conditions were as follows:

Step 1: Heating the reactor to attain the reaction temperature
(argon flow rate: 1000 sccm, time: 14 min, temperature: RT to 950 °C);

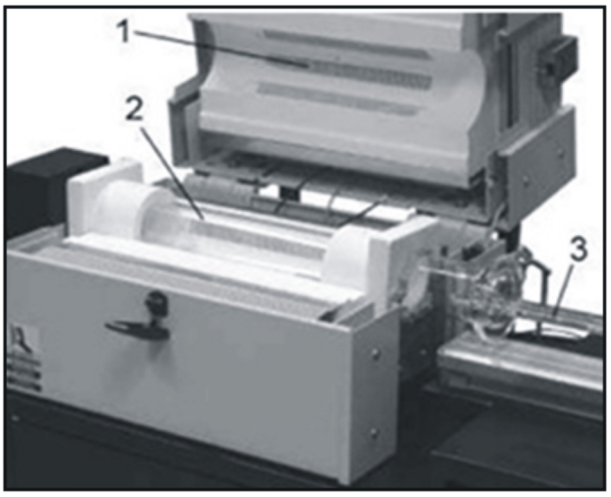

Fig. 1. Process unit of First Nano Easy Tube ET 2000 thermal CVD system (1) heating coils, (2) quartz tube reactor and (3) substrate loader.

Step 2: Methane decomposition on the substrate (methane flow rate: 1000 sccm, time 30 min, temperature: 950 °C);

Step 3: Cooling the product to room temperature (argon flow rate: 2000 sccm, temperature: 950 °C to RT).

In order to remove MgO from the sample, it was kept stirring in 10 N HNO_3 overnight. The solution was then diluted 10 times and filtered through 10 micron PTFE membrane filter under suction. It was dried under IR lamp and preserved in a desiccator.

3. Results and discussion

3.1. Elemental analysis

The elemental analysis data as obtained by EDAX is shown in Fig. 2. The sample contains only carbon and small amount of oxygen. It clearly shows that the MgO has been completely removed by nitric acid treatment. Carbon is the major element, indicating formation of graphene or graphene-like material.

3.2. Raman spectroscopy

Raman spectrum is shown in Fig. 3. It shows the D-band at 1316 cm^{-1} and G band at 1602 cm^{-1}.

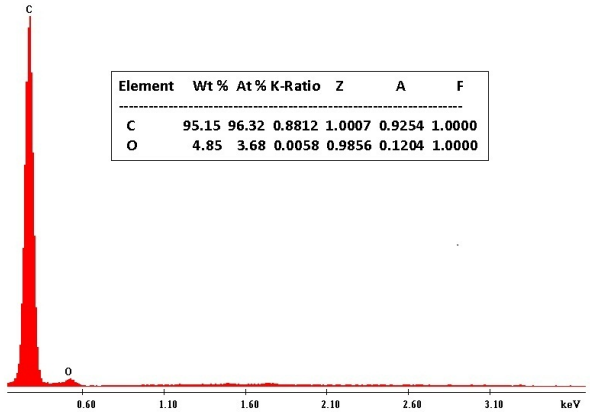

Fig. 2. EDAX spectrum of graphene synthesized on MgO substrate.

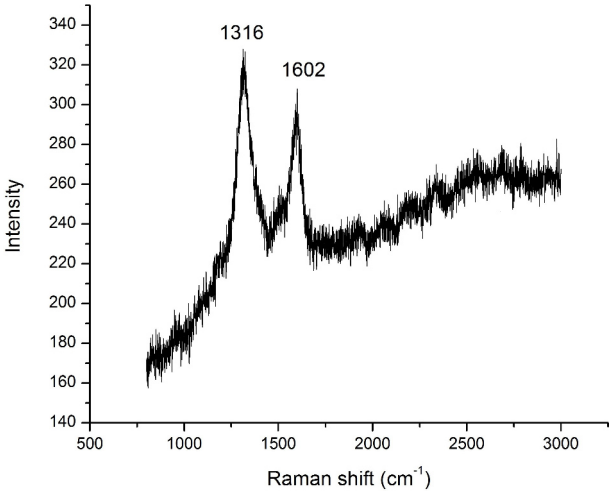

Fig. 3. Raman spectrum of graphene synthesized on MgO substrate.

The D-band is attributed to the disorder in the graphitic carbon. The graphene formed on MgO nanocrystals is nanographene with large number of boundary defects. This leads to a strong D band as reported by Rummeli et al. [20]. Small 2D band (G-band) around 2700 cm^{-1} clearly shows the formation of few layered graphene. However, the band is not distinctly visible due to background noise.

3.3. Transmission electron microscopy (TEM)

TEM and high resolution TEM images obtained at different magnifications are shown in Fig. 4. These images clearly indicate the formation of graphene or Q-graphene [23]. The high resolution TEM clearly shows formation of layered graphene.

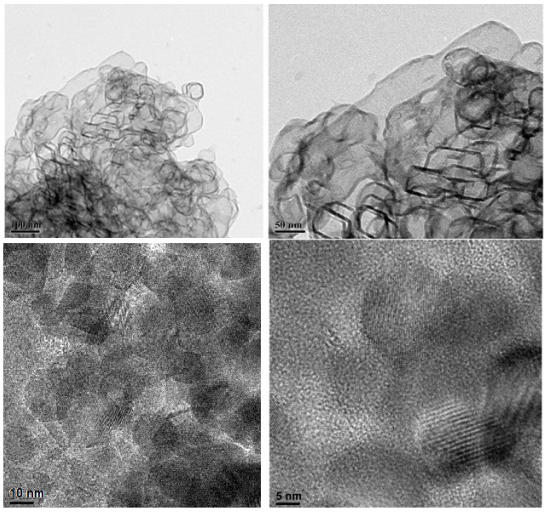

Fig. 4. TEM images of nanographene synthesized on MgO support.

3.4. Scanning electron microscopy (SEM)

The SEM images of graphene are shown in Fig. 5. It shows the bundles of graphene layers forming a packet-like structure.

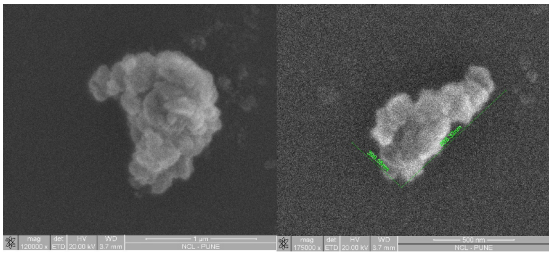

Fig. 5. SEM images of nanographene synthesized on MgO support.

4. Conclusion

It has been found to be possible to synthesize nanoplates of graphene on MgO as a support material. MgO support material can be completely dissolved in nitric acid thereby it was possible to obtain the nanomaterial in pure form. TEM images

have clearly shown that the nanoplates of graphene formed a layered structure. An important advantage of this method is that the nanographene can be directly used without post-synthesis transfer from metal surface onto insulator surface.

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References

[1] NOVOSELOV K., GEIM A., MOROZOV S., *Science*, 306 (2004), 666.
[2] CASTRONETO A., GUINEA F., PERES N., NOVOSELOV K., GEIM A., *Rev. Mod. Phys.*, 81 (2009), 109.
[3] DAS SARMA S., ADAM S., HWANG S., ROSSI E., *Rev. Mod. Phys.*, 83 (2011), 407.
[4] CHOI W., LAHIRI I., SEELABOYINA R., KANG Y., *Crit. Rev. Solid State*, 35 (2010), 52.
[5] NI Z., WANG Y., YU T., SHEN Z., *Nano Res.*, 1 (2008), 273.
[6] AVOURIS P., *Nano Lett.*, 10 (2010), 4285.
[7] GIANNAZZO F., RAINERI V., RIMINI E., *Nanosci. Technol.*, 2 (2011), 247.
[8] SCHWIERZ F., *Nat. Nanotechnol.*, 5 (2010), 487.
[9] BONACCORSO F., SUN Z., HASAN T., FERRARI A., *Nat. Photonics*, 4 (2010), 611.
[10] BERGER C., SONG Z. , LI T., *J. Phys. Chem. B*, 108 (2004), 19912.
[11] YU Q., LIAN J., SIRIPONGLERT S., LI H., CHEN Y., PEI S., *Appl. Phys. Lett.*, 93 (2008), 113103.
[12] LI X., CAI W., AN J., *Science*, 324 (2009), 1312.
[13] ZHAN N., OLMEDO M., WANG G., LIU J., *Carbon*, 49 (2011), 2046.
[14] KOSYNKIN D., HIGGINBOTHAM A., SINITSKII A., *Nature*, 458 (2009), 872.
[15] CHOUCAIR M., THORDARSON P., STRIDE J., *Nat. Nanotechnol.*, 4 (2009), 30.
[16] DUAN H., XIE E., HAN L., XU Z., *Adv. Mater.*, 20 (2008), 3284.
[17] SUBRAHMANYAM K., PANCHAKARLA L., GOVINDARAJ A., RAO C., *J. Phys. Chem. C*, 113 (2009), 4257.
[18] WANG X., ZHI L., TSAO N., TOMOVIĆ Z., LI J., MÜLLEN K., *Angew. Chem. Int. Edit.*, 47 (2008), 2990.
[19] SUBRAHMANYAM K., VIVEKCHAND S., GOVINDARAJ A., RAO C., *J. Mater. Chem.*, 18 (2008), 1517.
[20] RUMMELI M., BACHMATIUK A., SCOTT A., BORRNERT F., WARNER J.H., HOFFMAN V., LIN J., CUNIBERTI G., BUCHNER B., *ACS Nano*, 4 (2010), 4206.
[21] HUANG S., CAI Q., CHEN J., QIAN Y., ZHANG L., *J. Am. Chem. Soc.*, 131 (2009), 2094.
[22] STEINER S., BAUMANN T., BAYER B., BLUME R., WORSLEY M., MOBERLYCHAN W., SHAW E., SCHLOEGL R., HART A., HOFMANN S., WARDLE B., *J. Am. Chem. Soc.*, 131 (2009), 12144.
[23] RANDVIIR E.P., BROWNSON D.A.C., GÓMEZ-MINGOT M., KAMPOURIS D., INIESTA J., BANKS C.E., *Nanoscale*, 20 (2012), 6470.

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