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Planer nano-graphenes from camphor by CVD

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Abstract

Next to conducting polymers and carbon nanotubes (curved, closed graphenes), the material that can bring revolution in electronics is planer graphene (PG)/planer few layer graphenes (PFLG). Synthesis of PG and PFLG by simple, economical and re-producible method was a challenge. We synthesized PFLG films from camphor pyrolysis on nickel substrates by simple, cost effective thermal CVD method and studied using HR-TEM, visible Raman spectroscopy, XRD and FE-SEM. This opens the possibility that the controlled and large area synthesis of PGs and PFLGs is possible by CVD based methods, for possible large area electronic applications.

1. Introduction

Graphene is a single layer of carbon atoms densely packed into a benzene ring structure. Graphene can be made by extracting individual plane (s) of carbon atoms from graphite crystals and are generally used to describe properties of many carbon nanomaterials, including graphite, large fullerenes and nanotubes. Carbon nanotubes can be thought of as graphene sheet (s) rolled up into nanometer sized cylinders. Many of the applications that are thought for carbon nanotubes, can be considered for graphenes. Planer graphene has been presumed not to exist in free-state, being unstable with respect to formation of curved structures such as soot, fullerenes and nanotubes. The first attempt to produce individual graphene sheet by exfoliation dates to the work done by Brodie [1] in 1859. Since then, different attempts were made for the synthesis of planer single layer graphenes and PFLGs [2–5], with little success. To our knowledge, Novoselov et al. reported recently the most successful method for the synthesis of PFLG [6,7]. They have made planer few layer graphene (PFLG) films and are observed to be metallic in nature. Ballistic charge transport, linear current–voltage (I–V) characteristic and huge sustainable currents ($>10^8$ A/cm^2) makes them an interesting candidate for applications in electronic devices. Graphene transistors show modest on-off resistance ratio (less than $\sim$30 at 300 K) which is sufficient for logic circuits. It is also possible to increase this ratio by using p–n junctions, local gates or point contact geometry. Further, the transistor fabricated using PFLG is the 'first metallic transistor' made in which the active material was a metallic graphene, i.e. the channel was made from a metallic material [6,7]. The transistor application of graphene is very exciting, in analogy to carbon nanotubes. Planer graphenes have many unique properties [8–13]. The application of single sheet graphenes in nanocomposites as a filler is demonstrated by Schniepp et al. [14]. Application of nano-graphenes for the storage of molecular hydrogen is also suggested [15,16]. Single graphene sheet has been detected by Horiuchi et al. in a carbon nanofilm [17]. Jang et al. obtained US patent for a complex process for the fabrication of nano-scaled graphene plates [18]. Controlled, easy and low cost synthesis of graphene/PFLG is still a challenge and not much efforts have been made in this direction. The chemical approach developed by Prof. Mullen for synthesis of 'graphene molecules' is very interesting and important [19]. However, in the last 10 years, chemical vapor deposition (CVD) based methods are developed to synthesize curved closed graphenes (i.e.

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carbon nanotubes) with a good success, worldwide. It will be interesting and important if these methods can ultimately produce planer graphene/PFLGs – that can be used for fabricating electronic devices. Considering these facts, we are looking for the possibility of synthesis of planer graphenes/PFLGs by CVD methods. Via this communication, we disclose our important observation that, indeed, planer graphenes/PFLGs film can be synthesized by simple thermal CVD method. We obtained PFLG film on Ni substrates from pyrolysis of camphor by thermal CVD. Large amount of camphor yielded pyrolytic graphite (PG) films. Our experiments indicate that PFLGs can be directly synthesized by CVD method and that its controlled synthesis, patterning and manipulation should be possible in the near future. Further, the method has good prospects to be scaled up.

2. Experimental

A one-meter long quartz tube (diameter 50 mm) serves as a CVD reactor kept horizontally inside two horizontal furnaces. Camphor (0.1–0.5 gm) is evaporated in the first furnace (180 °C) and pyrolyzed in the second furnace (700–850 °C) with argon as carrier gas. In each experiment, 3–4 samples of Ni sheets ($2 \times 2\ cm^2$, NILACO Corporation, Japan) are kept on the alumina boat in the centre of the second furnace. The substrates are used as received and were cleaned ultrasonically with acetone and methanol. No other special pre-treatment is given to them. When the experiment is complete, the two furnaces are opened and allowed to cool naturally. The material collected on the Ni substrates is scrapped using a sharp blade and the powder collected is studied using high-resolution transmission electron microscope (HR-TEM, JEOL:JEM-2100F equipped with field emission source operated at 200 kV along with EDAX) and visible Raman spectroscopy. Various experiments by changing the experimental parameters were performed. The composition of the Ni substrate is: C (5.78 at.%), O (4.64 at.%), Si (0.5 at.%), Ni (89.08 at.%) – as determined by EDAX.

3. Results and discussions

Fig. 1 shows TEM image of PFLG film. In the top left corner of the image, a PFLG sheet is visible which is folded a bit at the places marked by arrows. In the region marked by two arrows, graphitic structure with interlayer spacing of about 0.34 nm is clearly visible, corresponding to graphite 0002 spacing. Centre of the image shows yet another PFLG film edge. Fig. 2 shows the high resolution image of this central PFLG film edge. Inset shows the intensity pattern along the line marked in Fig. 2. From this intensity pattern, an interplaner spacing of about 0.34 nm is estimated which again corresponds to graphite 0002 spacing. Number of graphitic layers in this film are about 35. Tilting experiments unambiguously proves that its a planer structure and not carbon nanotubes. In situ

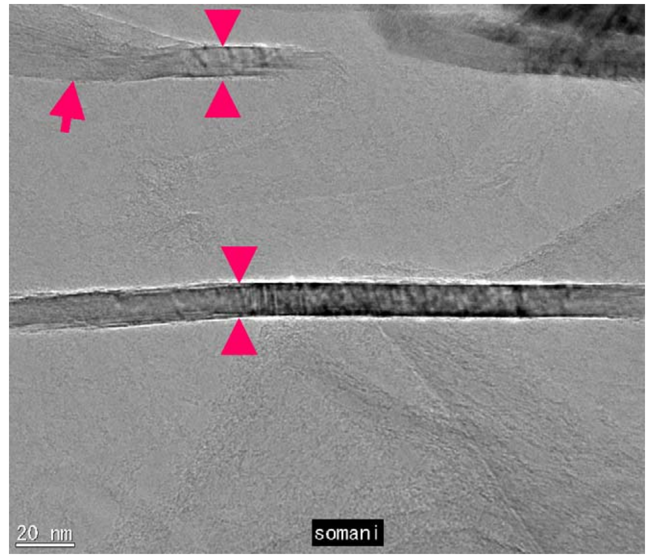

Fig. 1. HR-TEM image of PFLG film. In the top left corner of the image, a PFLG film is visible which is folded a bit at the arrows shown. In the region marked by two arrows, graphitic structure is visible. Centre of the image shows yet another PFLG film edge. Graphatic structure is visible.

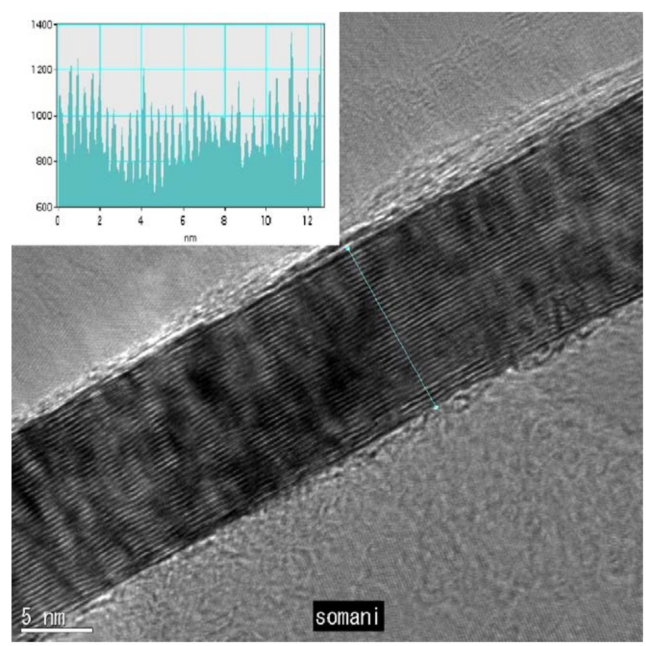

Fig. 2. High magnification TEM image of the PFLG film shown in the centre of Fig. 1. Inset shows the intensity pattern along the line marked.

EDAX analysis shows the presence of carbon only, indicating that the structures are made of carbon only. In order to confirm, independently, the presence of PFLGs in the samples, the samples were also tested at the company 'Ion Engineering Research Institute Corporation Limited, Japan' on a payment basis by HR-TEM. Results given by company are fully consistent with our observations by HR-TEM at Chubu University. In contradictory to the earlier view that PFLGs will be unstable; our observations indicates that PFLG film is stable. In majority of the TEM observations we observed that PFLG film gets folded. TEM gives direct insight into the structure of the carbon nanomaterials and is widely used tool to get structural understanding of carbon nanomaterials. However, due to such folding behaviour of PFLG film, it is quite difficult to focus at the edge in order to give direct structural evidence. We feel that the film gets folded at the time of evaporation of the solvent while putting it on TEM grids. Some of these observations are consistent with the observations reported by Novoselov et al. [6,7].

Fig. 3 shows the visible Raman spectra of the carbon film on Ni substrate obtained by 532 nm green laser excitation source using JASCO-NRS 300 system. A broad D-peak is centred at about 1343–1349 cm^{-1} and a comparatively sharp G-peak is centred at about 1578–1581 cm^{-1}. This indicates that there are defects in the PFLG films. Defects may arise from the incorporation of the pentagons, heptagons etc. in the planer graphitic planes. Larger amount of camphor pyrolysis yielded 'pyrolytic graphite' films on Ni substrates. The SEM and XRD of one such pyrolytic graphite film is shown in Fig. 4. A sharp and intense XRD peak at about $2\theta = 26.68°$ indicates good graphitic nature of the film.

Camphor is a natural hydrocarbon source which is regenerative, low cost and environmental friendly. Camphor has an unique structure consisting of hexagonal, pentagonal rings and methyl carbons. During pyrolysis, methyl carbon can be easily detached whereas breaking of the 3D-carbon skeleton is less probable. Moreover, mass spectra of camphor vapour have shown high abundance of hexagonal and pentagonal carbon rings. A sketch of molecular structure of camphor is shown in Fig. 5. Also presented is the cartoon of how pentagonal and hexagonal carbon rings can be formed from the breaking of camphor molecule. We would like to mention here that when the evaporated material is insufficient to form a continuous carbon film on the Ni- substrates over a larger area, carbon nanocapsules (CNCs) are detected in the samples. CNCs are thought to be formed from the addition of pentagons in the hexagonal lattice. It is well known that pentagons give curvature – as in fullerenes. The other possibility is that the planer graphene sheets of very small area gets curved and closed and forms CNCs. We feel that a carbon precursor giving only hexagonal carbon rings will be a better candidate rather than camphor – which yields both pentagons and hexagons [20]. This will also help in reducing the number of defects formed while formation of the planer graphene

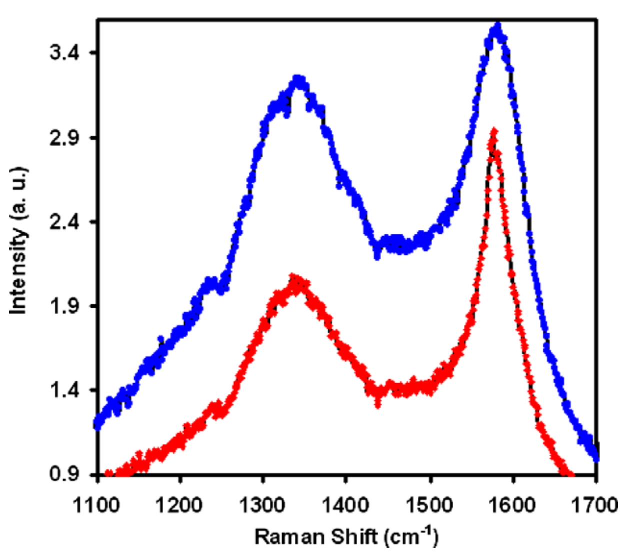

Fig. 3. Visible Raman spectra of a PFLG film on Ni substrate.

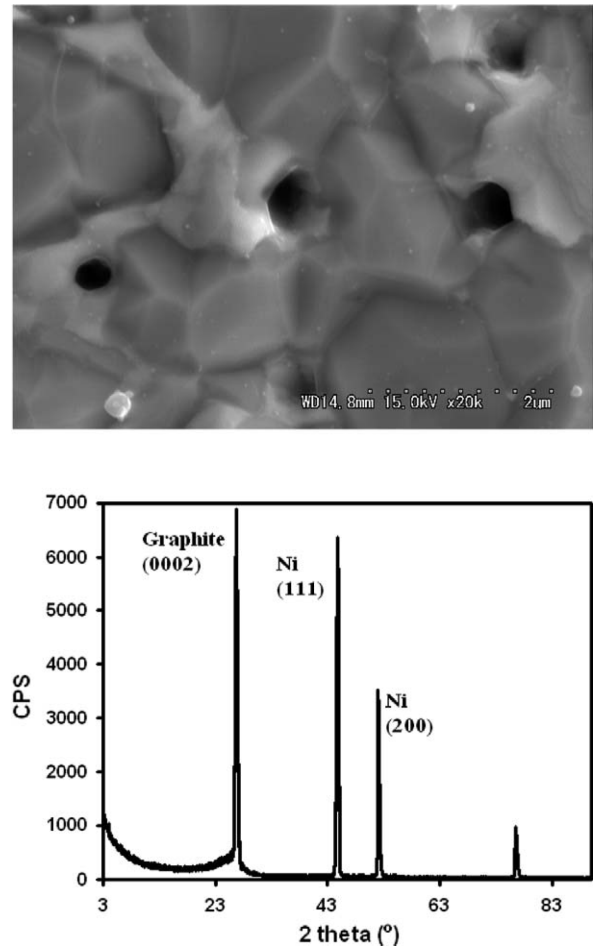

Fig. 4. SEM and XRD of Pyrolytic Graphite film on Ni substrate.

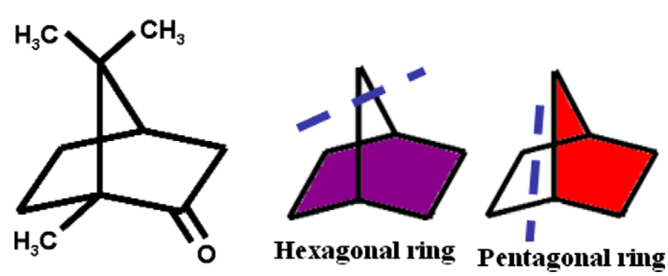

Fig. 5. Sketch of molecular structure of camphor and cartoon of its breakdown to yield hexagonal and pentagonal rings.

sheets on Ni-substrates. The role of the Ni substrate is yet to be fully understood.

In past, atomically thin graphite films (single layer graphenes) have been produced by thermal decomposition of the (0001) face of a 6H-SiC wafer [21]. However, such synthesis was carried out in ultra-high vacuum (UHV) conditions. The present experiment reported by us is advantageous in the sense that it does not require vacuum system. In an another effort, diamond nanoparticles were converted to single nano-graphenes at 1600 C [22]. However, such very high synthesis temperature is a serious drawback. In the present experiments, we have been able to get PFLG films at about half the temperature of this (i.e. 800 °C). In yet another experiment, formation of very small (about 20–30 Å in diameter) graphitic islands were observed and studied by scanning tunnelling microscopy (STM). Such graphitic islands were formed by hydrocarbon decomposition on Pt (111) surface [23]. It should be noted here that the formed structure was in the form of very small islands and not a continuous film. Although, at present, we have not got single layer graphene; we have been able to get PFLG down to about 20 graphene layers. Efforts are underway to synthesize single layer graphene film by this method. Even though, the present PFLG films are deposited on Ni (conducting) substrates and are not much directly useful for fabricating electronic devices like FET, we believe that this is the first experiment for the successful synthesis of PFLG films by CVD method.

4. Conclusions

In conclusion, for the first time, we experimentally demonstrated that planer few layer nano-graphenes (PFLGs) can be synthesized by simple thermal CVD method. Method is simple, cost effective and has capability to scale-up. Further, such synthesis has been carried out from a natural, environmental friendly, low cost precursor – Camphor. Efforts are now directed towards understanding the growth mechanism of the PFLG film and to synthesize defect free films over a silicon wafer size area.

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Appendix A. Supporting information

HR-TEM pictures of PFLG films. Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.cplett.2006.06.081.

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