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One-step synthesis of bulk quantities of graphene from graphite by femtosecond laser ablation under ambient conditions

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ABSTRACT

Bulk synthesis of few-layer graphene (FLG) for industrial applications still remains a challenge for researchers. Here, we report a very simple technique for bulk synthesis of FLG by femtosecond laser ablation of graphite powder suspended in ethanol without the requirement of a controlled environment. Graphite powder, with an average particle size <20 μ m, was suspended uniformly in ethanol and ablated at room temperature using fs pulses (wavelength ~800 nm and an input beam diameter ~8 mm) followed by ultrasonication to obtain FLG with a lateral size of ~1 μ m. Raman spectroscopy and high-resolution transmission electron microscopy data confirmed the nature and morphology of the FLG. The quality and number of layers in the FLG could be controlled by tuning the laser parameters.

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Carbon materials; few-layer graphene; surfaces; laser ablation; ultrasonication; Raman spectroscopy HRTEM

1. Introduction

Few-layer graphene (FLG) [1] has emerged as a unique material in various fields owing to its outstanding mechanical, electrical and optical properties. However, bulk synthesis of high-quality FLG remains a challenge. Recently, researchers have attempted the utilisation of lasers to pattern FLG on metallic and non-metallic substrates [2–5]. Highly ordered pyrolytic graphite has been exposed to laser irradiation to produce porous graphene, graphene quantum dots from graphite [6–8] and graphene nanoribbons from graphite [9]. However, previously reported studies [6] used a complicated experimental set-up, which required a vacuum chamber for growing graphene on substrates, rendering it unsuitable for large-scale production of graphene, while others [7] used very high-energy (12 J) nanosecond (ns) laser pulses. Russo et al. [8] obtained porous graphene and graphene quantum dots through ablation of highly oriented pyrolytic graphite. Here, we describe a very simple procedure to produce free-standing FLG (2–10 layers with a lateral size of ~ 1 μ m) in bulk from a simple configuration of graphite powder suspended in ethanol with the aid of femtosecond laser ablation utilising very low input energies (200–400 μ J). The mechanism of formation of FLG from graphite in the present study is explained.

2. Experimental work

A suspension of RE TO HERE graphite powder (99.5% pure with an average particle size <20 μ m) and ethanol was prepared with a concentration of 0.03 g/ml. The suspension was constantly stirred using a magnetic stirrer and the femptosecond laser pulses (~50 fs duration, 800 nm, 1 kHz repetition rate and input beam diameter 8 mm) were simultaneously focused on to the suspension. Two different laser energies of ~200 and ~400 μ J were used. The laser energy of ~200 μ J was applied for 1 h, while that of ~400 μ J was applied for 1, 1.5 and 2 h in separate experiments. Following this, the laser-processed solutions were ultrasonicated for 1 h followed by probe sonication for 15 min with an amplitude of <60%. The suspensions were then allowed to settle down for 24 h under room conditions. The resultant samples are named S1, S2, S3 and S4, respectively. The samples S1–S4 were characterised using transmission electron microscopy (TEM) for morphology and crystallinity, and micro-Raman scattering for phase information. TEM was carried out using a FEI Technai G2 S-Twin microscope operated at 200 kV. Raman scattering from the S1–S4 samples was recorded with a spectral resolution of ~1 cm⁻¹ using an Alpha 300 of WiTec Raman spectrometer equipped with a 532-nm laser as excitation source.

3. Results and discussion

Figure 1 shows TEM images along with the corresponding electron diffraction patterns of the samples S1–S4. It is very clear from the TEM images that in all cases the final product is transparent to electrons indicating that S1–S4 are very thin. Figure 1 also shows that the samples S1–S4 had lateral dimensions in the range $0.8-1 \mu m$. Representative electron diffraction patterns (insets in Figure 1) clearly demonstrate the six-fold symmetry of graphene in S1–S4 [10].

Figure 2a shows the Raman spectra in the wavenumber range 1000–3000 cm⁻¹ of S1–S4 in comparison to the starting material, that is graphite. In all the cases, three signature peaks, namely D, G and 2D bands, appeared around 1350, 1580 and 2700 cm⁻¹, respectively [7–9]. Furthermore, the I_G/I_{2D} ratios of S1, S2, S3 and S4 are 1.84, 1.73, 1.84 and 1.4 (all >1), respectively, indicating the presence of several graphene layers in S1–S4 [11–13]. From Figure 2b, it can be clearly observed that the 2D band in the case of S1 and S3 is more symmetric than that in S2 and S4. This indicates that S1 and S3 samples probably had better quality in terms of the arrangement of carbon atoms in the graphene layers.

High-resolution TEM images of the samples S1 and S3 are shown in Figure 3, which shows that both S1 and S3 have a stack of 2–10 graphene layers (corresponding to a FLG particle thickness of 0.7-3.5 nm). From the high-resolution TEM images a spacing of ~0.35 nm between graphene layers could be measured. This is representative of the interlayer spacing between basal planes along the *c*-axis of graphite. Taken together, electron microscopy and Raman scattering clearly show the formation of FLG, which can be understood as arising from a force-induced physical exfoliation of the graphite crystal resulting from the formation of a plasma and associated high temperature and



Figure 1. TEM images of (a) S1, (b) S2, (c) S3 and (d) (S4) with lateral dimensions. Insets in (a)–(d) show the representative electron diffraction patterns.

pressure conditions during the interaction of the laser pulses at the solid–liquid interface. Subsequently, the probe sonication [14] helped in further exfoliation. Earlier studies [6] which demonstrated graphene formation from highly oriented pyrolytic graphite utilised nanosecond pulses at 532 nm and with laser fluences from 0.8 to 20.0 J/cm² and an ablation performed at 45° angle with respect to the incident laser pulses. It was claimed that a photon energy of 2.3 eV was insufficient for direct photochemical bond breaking and that the photothermal mechanism played a key role in the laser exfoliation process. In the present case, the photon energy used was even lower (1.55 eV). However, since the pulses are ultrashort (~50 fs), multi-photon absorption, resulting from large fluences (peak intensities) of ~100 J/cm² (~10¹⁴ W/cm²), is possible leading to direct photochemical bond breaking.

We believe that three parallel phenomena occur during the fs laser–graphite powder interaction: (a) reduction of particle size of graphite, (b) exfoliation of graphite to form FLG and (c) restacking of graphene at various time scales. We believe that the last two factors determine the number of layers present in the final product. It has been well established that



Figure 2. (a) Raman spectra of S1–S4 in comparison with that of graphite and (b) magnified view of 2D band of S1–S4 samples.

the restacking tendency of graphene is higher as the number of graphene layers decrease [15]. At 400 μ J, sample S3 provided the optimum condition where exfoliation was higher and, therefore, the number of layers obtained for S3 was low. However, for S2 the exfoliation time was insufficient and in the case of S4 the phenomenon of restacking was predominant, leading to a higher number of layers. At 200 μ J only one condition was used for S1. The results show similar product formation as for S3 with comparable Raman spectra. It could be considered that the optimum condition could be 200 μ J energy but further detailed studies at this energy level need to be carried out. Systematic studies are essential, and will be taken up in future, for conclusive observation on the (a) the yield, (b) the number of layers formed with respect to the input laser energy and (c) the quality (with regard to defects) of the formed layers.



Figure 3. High-resolution TEM images of the samples (a) S1 and (b) S3.

4. Conclusions

FLG has been prepared under room conditions by ablating graphite powder suspended in ethanol using femtosecond laser pulses. The FLG had a lateral size of $\sim 1 \,\mu m$ and contained 2–10 graphene layers. Electron microscopy and Raman scattering clearly indicated the formation of FLG, which is explained on the basis of force-induced physical exfoliation of the graphite crystal resulting from the formation of a plasma and associated high temperature and pressure conditions. The quality and number of layers in FLG could be controlled by tuning the input laser parameters. Both the fluence and the exposure time affected the graphene layer formation. The laser energy used in this study was probably sufficient to ablate the graphite into graphene sheets. However, further detailed studies are 6 😔 G. R. KIRAN ET AL.

needed to completely understand the mechanism of graphene formation by laser ablation of suspended graphite.

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Disclosure statement

No potential conflict of interest was reported by the authors.

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