



High pressure transformation of graphene nanoplates: A Raman study



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ARTICLE INFO

Article history:

Received 12 April 2013

In final form 20 August 2013

Available online 29 August 2013

ABSTRACT

High pressure Raman study on graphene nanoplates, graphite and micro-graphite has been carried out in a diamond anvil cell. A phase transformation has been observed in graphene nanoplates at 15 GPa in the experiments with or without pressure medium, which can be explained by the interlayer coupling with sp^3 bonds formed in the material. For graphite and micro-graphite, the transition pressure is 19 GPa. Different transition pressures for them are attributed to the thickness difference. The lower transition pressure in graphene nanoplates has been discussed in the framework of the special limited-number layer structure and nucleation process in phase transition.

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1. Introduction

Graphene, since its discovery in 2004 [1], has been a superstar on the horizon of materials science and condensed-matter physics. It is the experimental realization of a truly two-dimensional material and exhibits many remarkable physical and electronic properties. Graphene has been suggested as a candidate for a large number of potential applications in electronics and multi-function advanced materials [2]. Especially, there are huge interests in the mechanical properties of graphene due to its possible applications in nanodevices [3]. Graphene is very strong with a Young's modulus as high as 1.0 TPa [4], but on the other hand, it also exhibits flexible features that can crinkle and bend [5]. The possibility of using graphene as an ultrasensitive strain sensor has also been suggested [6]. High pressure is a useful way to study mechanical properties and to search for new structures of materials [7–9]. Carrying out high pressure experiments on graphene has the potential to become a significant component in characterization and understanding of this extraordinary material, as well as create new carbon structures. Up to now the reported studies are mainly focusing on the monolayer, bilayer, and few-layer graphene [10–13]. Proctor et al. [10] studied graphene (a mixture of monolayer, bilayer, and few-layer graphene) in DAC up to 8 GPa by using Raman spectroscopy and found that the Raman behaviors of graphene under compression are intrinsically similar to graphite. Nicolle et al. [12] also explored the pressure-mediated doping effect of different pressure transmitting mediums (PTMs) in graphene with 1–3 lay-

ers under pressure up to 7 GPa. Clark et al. [13] further investigated a few-layer graphene sample with the grain size of 100–300 nm in a larger pressure region by Raman and X-ray diffraction studies. They concluded that few-layer graphene still remains the local sp^2 hybridization in the layer even up to 50 GPa and no phase transition occurred. This is quite different from the phase transformations of graphite under pressure. For graphite upon compression, a phase transformation into a transparent and hard phase with hardness comparable to diamond has been experimentally observed [7] and many theoretical studies have been involved to propose various structures for this phase [7,14–17]. It is generally accepted that this hard phase is formed by the appearance of sp^3 bonds between graphite layers during compression. Why the graphite and few-layer graphene have so different high-pressure behaviors and which factors affect the high-pressure transformations, however, are still not well understood. Considering the similar layer-structure in both graphite and few-layer graphene, it is suggested that the nano-scale size in thickness of few-layer graphene plays an important role on its high pressure transitions. Furthermore, we point out that understanding the transition process in the 'nanographene' with layer number between that of graphite and the previous studied few-layer graphene could give further insight on this aspect. Performing high pressure experiments on this intermediate counterpart between graphite and few-layer graphene is thus important to clarify the size effect and understand the transformation mechanism in the 'nanographene' with known layer number. Furthermore, Raman spectroscopy is a powerful tool to characterize carbon materials and it has been widely used to recognize phase transformations of graphite and carbon nanotubes under pressure [17–22]. Especially, the linewidth change of G-band in graphite under pressure has been considered as an important signature for the structural phase transition at room temperature

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[17,18,20]. Thus we believe that if phase transition happens in the graphene with a larger layer number when submitted to high pressure, it can be traced from its Raman signals evolution.

In this letter, we carried out high pressure Raman studies on two graphene nanoplates samples with a thickness of 1–5 nm or 5–20 nm, and the results are further compared with that of graphite and micro-graphite. Irrespective of using a PTM or not, we found that graphene nanoplates exhibit a phase transformation at around 15 GPa, which is featured by the sudden broadening of their G-band linewidth. This can be explained by the interlayer coupling and sp^3 bonds formation in the samples under pressure. While for the graphite and micro-graphite, the phase transition pressure is around 19 GPa. We suggested that the thickness difference in graphene nanoplates and graphite should be responsible for the different phase transition pressures in our experiments. The mechanism for the reduction of transition pressure in graphene nanoplates is further proposed.

2. Experimental

The graphene nanoplates and micro-graphite samples are bought from XianFeng Nano Material Technology Inc. (Nanjing, China). Two graphene nanoplates samples (1–5 nm and 5–20 nm in thickness) are investigated in our letter and the micro-graphite with a grain size similar to the graphene nanoplates is also studied for comparison. Transmission electron microscopy (TEM) and Raman spectroscopy characterizations on the samples reveal a good quality and a high degree of purity. The natural high purity graphite powder (purity 99.9999%) was purchased from Alfa AESAR.

High pressure experiments were carried out in a diamond anvil cell either with or without PTM. The hole in a stainless steel gasket served as the compression chamber. The R1-line emission of a tiny ruby chip was used for pressure calibration. In the experiment using PTM, liquid argon was used as the PTM. For the experiments without PTM, we manually pressed the sample into the gasket hole until it was fully filled. Raman spectra were measured at room

temperature using a spectrometer (Renishaw inVia) with double-notch filtering and air-cooled charge-coupled CCD detector. The spectral resolution of the Raman system was about 1 cm^{-1} . A $50\times$ long focal length microscope objective was used to focus the beam on the sample and the laser beam size was approximately $1\text{ }\mu\text{m}$. We excited the Raman spectra with the 633 nm laser. The samples before and after pressure treatments were characterized by TEM operated at 200 kV (JEOL, 2200FS).

3. Results

Figure 1 shows the TEM images of graphene nanoplates and micro-graphite. We can see that the graphene nanoplates (1–5 nm) are nearly transparent and with some visible wrinkles, suggesting that the samples are mainly composed of few-layer graphene. For the graphene nanoplates (5–20 nm), they are less transparent due to the higher thickness. The micro-graphite has the similar grain size of $\sim 1\text{ }\mu\text{m}$ with graphene nanoplates, but its thickness is nearly the same as the bulk graphite. From Figure 1d we can see that the average grain size of the graphite flakes is around $20\text{ }\mu\text{m}$, which is much bigger than that of graphene nanoplates and micro-graphite.

The Raman spectra of graphene nanoplates (1–5 nm) at ambient conditions is shown in Figure 2 and it consists of three major bands, the most intense G-band, the D-band (representing the disordered band), and the second harmonic 2D-band. The principal Raman active mode of graphite is the G-band at 1582 cm^{-1} which originates from the sp^2 carbon atoms vibrating in-plane with E_{2g} symmetry. A very weak D-band in the spectra indicates good quality of our samples, which is consistent with our TEM observations. The weak D-band might be mainly from the edge effect of the nanoplates.

In the high pressure experiments, it is difficult to observe the variation of D-band and 2D-band under pressure because of the strong overlapping of Raman signals from the diamond anvil. Thus we mainly focus on the evolution of G-band of graphene nanoplates in this work. Figure 3a shows the Raman spectra in the G-

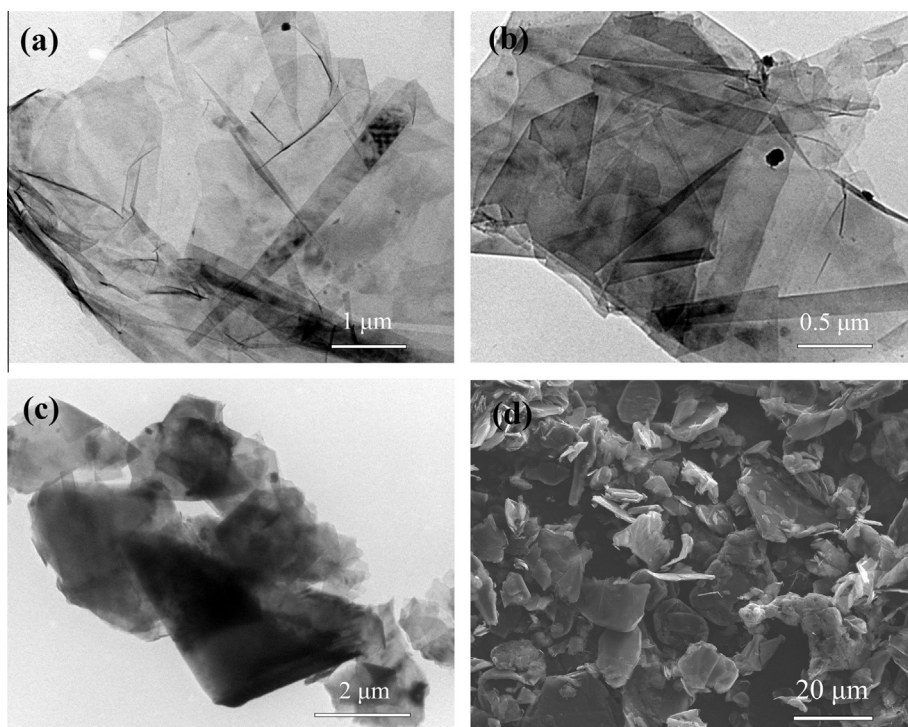


Figure 1. TEM images of (a) graphene nanoplates (1–5 nm), (b) graphene nanoplates (5–20 nm), (c) micro-graphite and (d) SEM image of natural graphite.

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