PRODUCTION OF LOW-COST, HIGH QUALITY GRAPHENE AND FEW LAYERED GRAPHENE (FLG) ON CONDUCTIVE SUBSTRATES

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This perspective attempts to describes an effective method for producing homogeneous graphene nanosheets using solvothermal exfoliation of graphite in dichlorobenzene (DCB). Sonication/centrifugation of graphite material results in stable homogeneous dispersions. The graphene sheat was prepared from DCB-graphene dispersion. The atomic structure and the electronic properties of few-layer graphene on HOPG conductive substrate was characterized using STM and CITS techniques. The produced facile, low-cost graphene flakes show good quality in terms of its fewer defects and high conductivity.

1. Introduction

Graphene is a monoatomic layer of sp^2 bonded carbon atoms forming a honeycomb structure. As a 2-dimensional crystal, graphene was supposed to be unstable at ambient temperature and pressure conditions, nevertheless it has been produced in the form of single-layer, double-layer and few-layer flakes by Novoselov and Geim in 2004 [1]. Despite their small thickness (a few Angstroms) these flakes display promising properties (mechanical strength and stiffness, high electron mobility) that make them promising candidates for new kinds of carbon based nano-devices.

Recently, different techniques have been developed to prepare graphene including epitaxial growth, mechanical and chemical exfoliation of highly oriented pyrolytic graphite or graphite oxide [2-6]. Substantial progress was made by exfoliating graphene directly from graphite, which would produce a facile, low-cost graphene with fewer defects [6]. However, problems arise because although graphene chemically exfoliated requires strong interactions between graphene and solvents, the stronger interaction may bring about great difficulties in subsequent separation processes. Moreover, in graphene, it is well known that the charge carriers are exposed and highly sensitive to environmental disturbances that can interact with charged impurities associated with the substrate material, adsorbed molecules, and electrical contacts. In this regard, it is important to explore ways to isolate the graphene flakes from random potential caused by defects and trapped charges usually present when using insulating substrates. The best way to overcome this is to replace the insulating substrate with a conducting substrate, pristine and lattice matched to graphene such as HOPG graphite.

This work deals with graphene and few-layer graphene produced by modified chemical exfoliation method of graphite using dichlorobenzene (DCB) based on combination of

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solvothermal method [2-10]. The main goal was to characterize the graphene flakes prepared by this technique by studying the morphology, the atomic structure, and the electronic properties of few-layer graphene on HOPG substrate using STM and CITS techniques.

2. Materials and methods

We have produced dichlorobenzene-separated graphene using solvothermal method. In this method firstly, an expanded graphite was heated in a microwave for few minutes to form expanded graphite. Secondly, in order to obtain pre-intercalated graphite the expanded graphite was treated by stirring in hydrochloric acid for 48 hours. Afterwards, 200 mg of pre-intercalated graphite was dispersed in 40 mL of DCB solvent, which was then heated in an autoclave at 180°C for 48 h. The autoclave was cooled naturally, and the graphene solution (40 mL) was gently sonicated for 90 min in a sonication bath. The produce graphene dispersion was centrifuged at 2 krpm for 30 min to remove the macroscopic aggregates. A dark suspension of graphene was obtained. After centrifugation, a homogeneous dark suspension of graphene formed that are stable for long periods of few months with no aggregation.

An extensive STM was employed to characterize the graphene sheets deposited onto the HOPG surface at room temperature using a home-built, low-drift STM head interfaced with a home-developed controller and software [11]. A drop of a solution containing graphene sheets suspended in DCB was deposited onto a freshly cleaved HOPG substrate. After deposition, the drop covered the entire 1 cm^2 area of the HOPG substrate. The HOPG was then left in air for approximately 24h. All topography images were recorded in constant current mode. Typically, for the STM measurements, tunneling currents between 5 and 100 pA were employed. The bias voltage was ± 50 mV to ± 100 mV for topography measurements. The scan frequency was varied between 2 and 5 Hz. CITS measurements were performed simultaneously with topographic imaging, using the interrupted feedback loop technique [12]. This was achieved by opening the feedback loop at a fixed separation of tip and sample, and ramping the bias voltage over the range of interest. I/V curves were acquired at every pixel of the topography image. This produces a three-dimensional map of the current as a function of position and voltage. The data set is then usually decomposed into a set of current maps, i.e. current I vs. position, for any measured value of the bias voltage. The scan range of voltages was typically from -0.4 V to +0.4 V relative to the tip potential for approximately 100 discrete voltage steps. Typically, tunneling resistances of the order of 2 GΩ were set.Pt-Ir (90/10) tips used in this study were mechanically cut from wires with a diameter of 0.25 mm. WSxM software was used to both acquire and analyze the STM images [13].

3. Results and discussion

Figure 1 shows typical large area STM scans of the graphene sample. There is a clear evidence of deposited graphene sheets on a freshly cleaved HOPG surface. The STM images reveal a complex morphology that depends somewhat on the deposition conditions. Regions of continuous binding to the surface as well as regions in which the sheet wrinkle and fold back onto themselves can be observed.
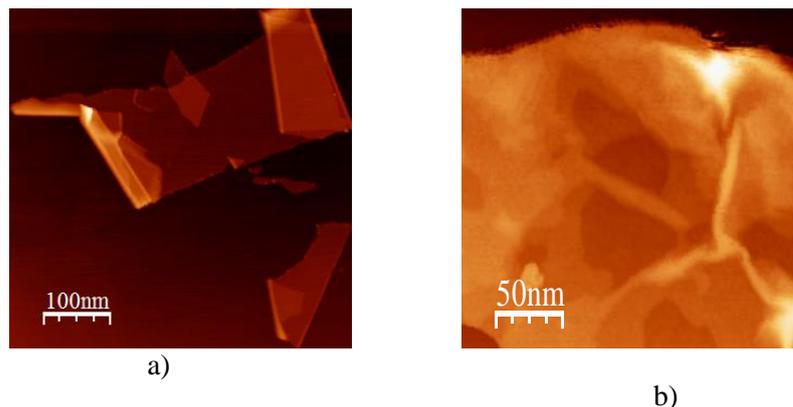
Figure 1: a) and b) STM topography images of graphene on a HOPG substrate. The images show folds and wrinkles in the deposited graphene sheets.

Figure 1a illustrates a topography image with flat regions that conform to the underlying HOPG substrate plus an evidence for folds. The minimum height of the graphene sheets was approximately 0.35 nm (relative to the HOPG substrate) while the overlapping areas of two or more graphene sheets or the folded regions of a single sheet exhibited heights that are integer multiples of this value. This fits well with the reported distance of 0.335 nm for the interlayer spacing of graphite [14]. Wrinkle structures are shown in Figure 1b. These wrinkles have variable heights that are in average approximately 2.5 nm above the graphene sheet. The formation of these wrinkles can be explained by the non-planar deposition of the graphene sheet onto the HOPG substrate. It appears more prevalent as the size of the graphene sheet increases.

Figure 2 presents a high magnification STM image of a three layers graphene sheet folded back onto itself two times and creating a multi-layer graphene sheet. It can be seen that the folding does not happen in a sharp line; the sheet is rather curved in the shape of a nanotube, which has been observed in previous studies [15,16]. A cross-section perpendicular to the axis of the structure shows that the height of the structure is about 1.6 nm (Figure 2b) which corresponds to the minimum height of a single-wall carbon nanotube. The formation of this type of structure at the fold axis may be attributed to the strain induced in the sheet close to the folding axis [16].
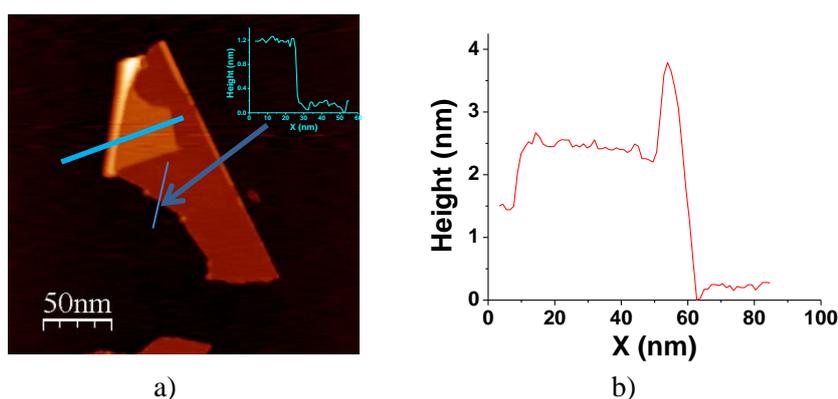

Fig. 2: a) Folding morphology of a graphene monolayer, The inset shows the profile taken along the edge of the graphene flake. b) profile taken along the line in a.

Atomic resolution topography is the first step to identify coupled and decoupled graphene flakes on the surface of graphite. Figure 3a shows a graphene flake on a graphite surface. Figure 3b presents a profile of the STM image taken along the line in Figure 3a. Interestingly, the flake has height a of 5 Å while the height of double-layer graphene is known to be more than 7 Å.

Therefore, one can assume that this flake corresponds to an isolated single-layer graphene. with a honeycomb structure. In contrast, the atomic resolution image shows a triangular structure with one atom per unit cell (see Figure 3c and d). These observations indicate that there is coupling between the graphene flake and the underlying graphite surface which breaks the symmetry, leading to two inequivalent carbon atoms per unit cell. Therefore, only one out of two carbon atoms is mapped by STM of this monolayer graphene flake.

a)   b)

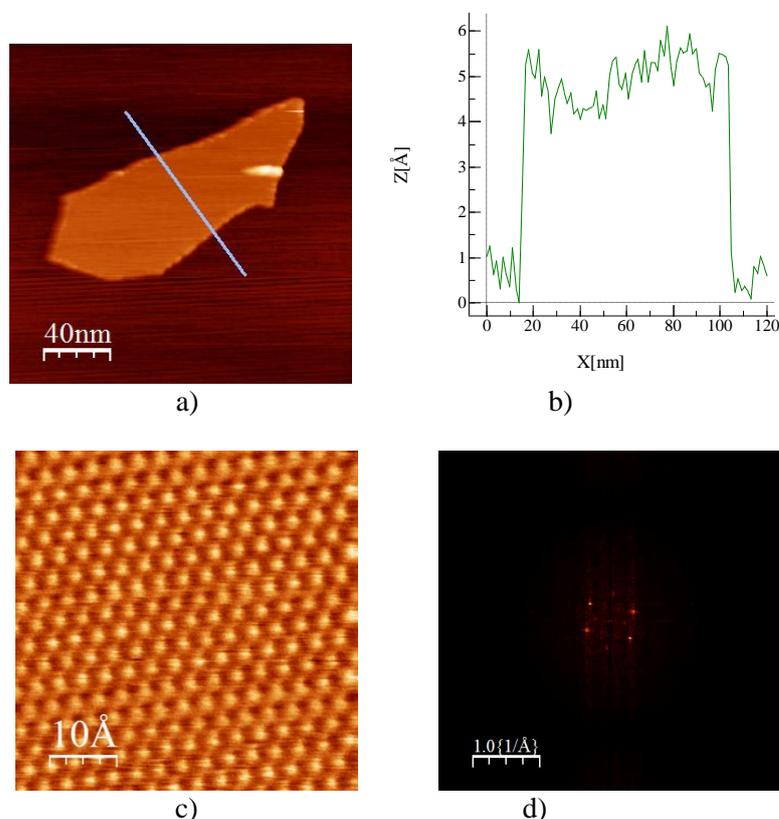c)   d)

Fig. 3: a) STM topography of a monolayer graphene flake on HOPG substrate, b) profile taken along the line in a. c) Atomic resolution topography of the graphene flake. d) The FFT image of the atomic structure.

To further clarify the electronic nature of the graphene we obtained a more detailed electrical mapping of the graphene flakes using current image tunneling spectroscopy (CITS). Figure 4b represents current-voltage (*I-V*) characteristics recorded at two different positions as marked in Figure 4a. The figure shown that the graphite substrate and the graphene flake both having the same electrical conductivity. The similarity in the conductivity can be explained only by assuming that the π electrons on the graphene flake are involved in the binding between the layers and hence would have same conductivity. Moreover, the STM experiments reported here illustrate that graphite is well fit as a substrate for supporting graphene flkes. Because graphite offers support without interference, it facilitates studying the intrinsic properties of the charge carriers in graphene.
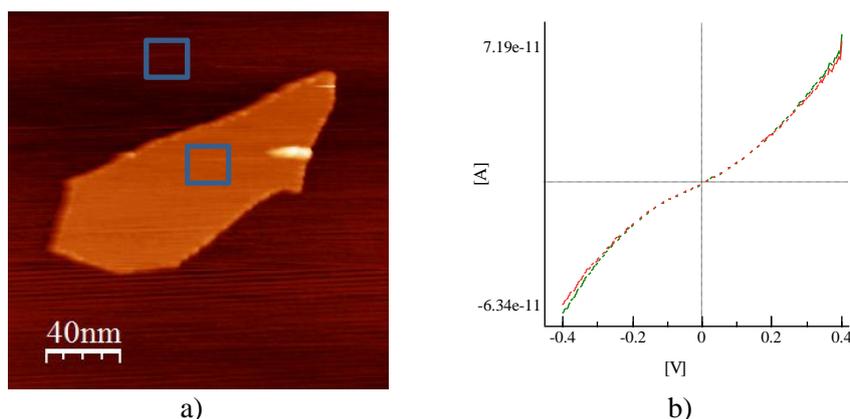
Fig. 4: a) Simultaneously recorded high resolution STM topography and b) I-V characteristics recorded at two different positions marked in Figure 5a.

4. Conclusion

We have demonstrated a method for synthesizing graphene and few layered graphite based on the exfoliation of graphene directly from graphite using the solvothermal method. The produced graphene sheets have fewer defects and more conductive than those generated using other chemical methods and can be directly fabricated by drop-casting of their solutions. The investigation of the produced FLGs gave insight in the precipitation of the flakes on HOPG surfaces. Small flakes were found to lie perfectly flat on the surface. Their mobility seems to be sufficient to achieve perfect lattice matching with the substrate, indicated by the atomic resolution images and the I-V characteristics. The produced STM images indicate a coupling between the deposited flakes and the HOPG like it exists between the layers of HOPG. Larger flakes tend to crumple and fold during the deposition process. They also have less mobility, leading to a lattice mismatch, observable in the Moiré patterns in larger area scans. High-quality graphene sheets prepared in this work may find their application in many areas from various devices to electrical fillers for conducting composite materials. However, to obtain high quality and high yield graphene sheets in the free state without any modifiers or stabilizer is still a great challenge.

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