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Adsorption and manipulation of carbon onions on highly oriented pyrolytic graphite studied with atomic force microscopy

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Abstract

Carbon onions produced by DC arc discharge method were deposited on highly oriented pyrolytic graphite (HOPG) surface and their adsorption and manipulation was studied using an atomic force microscopy (AFM). Well-dispersed adsorption of carbon onions on HOPG surface was obtained and aggregations of onions were not observed. The van der Waals interaction between the onion and HOPG surface and that between two onions, were calculated and discussed using Hamaker's theory. The manipulation of adsorbed onions on HOPG surface was realized using the AFM in both the raster mode and the vector mode. The controllability and precision of two manipulation modes were compared and the vector mode manipulation was found superior, and is a useful technique for the construction of nano-scale devices based on carbon onions.

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Keywords: Atomic force microscopy (AFM); Carbon onions; Adsorption properties; Nano-scale manipulation

1. Introduction

Since the discovery of fullerene molecules [1] and subsequent carbon nanotubes [2], carbon nanomaterials with curved surface have gained great interests because of their novel mechanical and electronic properties. Carbon onions, which consist of concentric spherical graphitic sheets, are one important member of the fullerene family. In 1992, Ugarte observed carbon onions after intense electron irradiation of carbon soot in a transmission electron microscopy (TEM) [3]. After that, many works were devoted to the synthesis methods of carbon onions and several different methods, such as arc discharge [4], ion implantation [5], annealing of diamond nanoparticles [6], etc., have been reported. Among these methods, DC arc charge method [4] is an economical method to produce carbon onions in bulk quantities. Although carbon onions have some fascinating structures and properties due to their high degree of symmetry [7], studies dealing with carbon onions still remain low in comparison to the intense research on single-layer fullerenes or nanotubes, partly because of the complicated spherical multi-layer structures and the broad size distribution of produced onions. Nevertheless, the potential scientific and technical application of carbon onions still attract many attentions, and their structures and electronic properties were investigated using high resolution transmission electron microscopy (HRTEM) [7,8], scanning tunneling microscopy (STM) [9] and electron energy-loss spectroscopy (EELS) [10] method. However, the study of the adsorption properties of carbon onions on the surface of other materials, which is important for their application in nano-device fabrication, is still scarce.

Atomic force microscopy (AFM) is a powerful and versatile tool for atomic and nanometer-scale characterization of the surface topography and mechanical properties. The interaction applied by an AFM tip in the imaging process can also be used to push or move nanometer-scale objects on a surface, and this capability makes AFM a useful tool for nano-scale manipulation and nano-device fabrication. Fullerenes and carbon nanotubes have been successfully manipulated on various surfaces [11,12] using this technique and novel nano-electronic

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devices based on carbon nanotubes have been fabricated [13]. Nevertheless, there is no report about the manipulation of carbon onions yet.

In this paper, we investigate the adsorption and manipulation of carbon onions on highly oriented pyrolytic graphite (HOPG) using an AFM. The van der Waals interactions of onions and HOPG substrate are evaluated using Hamaker's theory to understand the well-dispersed adsorption of carbon onions on HOPG surface. The manipulation of adsorbed onions on HOPG surface is realized using the raster mode as well as the vector mode. The controllability and precision of two manipulation modes are compared and discussed.

2. Experimental details

Carbon onions were produced by the DC arc discharge method [4] using an YNi_2 catalyst. The anode was an extremely pure graphite rod with a hole filled with graphite and YNi_2 powder. The cathode was a graphite rod that was shaped into a sharp tip. The arc was generated by a current of 40–100 A in a helium atmosphere at a pressure of 500 Torr. The obtained cloth-like soot contained carbon nanotubes, carbon onions, metal catalyst clusters and amorphous carbon.

The process of purification was as follows: 200 mg raw-soot was heated in an air current with a flow rate of 70 sccm at 350 °C for 2 h. The remaining soot without amorphous carbon was soaked in 36% (w/w) hydrochloric acid for one day and centrifuged in order to remove metal YNi_2 catalyst clusters. The sediment was washed three times with de-ionized water, ultrasonically dispersed into 200 ml of 0.2% benzalkonium chloride solution and filtrated with Ø 1 μm porous polytetrauoroethylene (PTFE) membrane disc filters under vacuum. The processes of dispersion and filtration were repeated twice, thus carbon nanotubes were almost removed. The filtrate obtained was again refiltrated with Ø 0.2 μm Super Membrane Disc filters under vacuum. Thus, pure carbon onions on the filter were obtained.

Carbon onions were ultrasonically dispersed in ethanol and drop-deposited onto freshly cleaved HOPG surface. After the solvent drop had evaporated, a commercial atomic force microscopy (Solver P47, NT-MDT, Russia) was used to image and manipulate the carbon onions. The AFM worked in tapping mode, and an ultrasharp Si tip (NT-MDT, Russia) with a radius of curvature of about 10 nm was used.

3. Results and discussion

3.1. Adsorption of carbon onions on HOPG surface

The adsorption of carbon onions was characterized using the AFM operated in tapping mode. Fig. 1(a) shows a typical large area (10 μm × 10 μm) topography image of adsorbed carbon onions on HOPG surface. Fig. 1(b) is a small area image (2 μm × 2 μm) of the surface with a better resolution. It can be seen that most of adsorbed carbon onions appear in a spherical shape in AFM images, agrees with their concentric spherical structures. The diameters of carbon onions were measured from the height of AFM cross-sectional profile of adsorbed onions, as shown in Fig. 1(c). The values are in the range of 10–60 nm, but most of them are concentrated into 15–35 nm. It can be found in Fig. 1 that carbon onions adsorbed in a well-dispersed form on HOPG surface. Different surface areas were characterized by AFM in our experiments and aggregation of carbon onions was not found. Usually, aggregation of surface adsorbates occurs when the interaction between the adsorbates is stronger than that between the adsorbate and the underlying surface. In our case, the interactions between the onion and HOPG surface and that between two onions are similar to the interaction of two graphite layers, which originates from van der Waals interaction. The well-dispersed adsorption of carbon onions on HOPG surface indicates that the attractive van der Waals interaction between the onion and HOPG surface is stronger than that between two onions. The van der Waals attraction between C_{60} molecules and that between a C_{60} molecule and the surface of graphite or other substrates has been discussed in ref. [14]. In that report, the van der Waals interactions between two C_{60} molecules and that between C_{60} molecule and graphite were simulated using a discrete dipole formalism in which C_{60} was viewed as a rigid cluster of 60 polarizable, interacting carbon atoms and the substrate was treated as a continuous dielectric medium. Their results showed the van der Waals attraction between C_{60} and graphite substrate is stronger than that between two C_{60} molecules. Carbon onions can be seen as multi-layer fullerenes, and have the analogous molecular and geometrical structures with C_{60}. So their adsorption properties and van der Waals attraction between each other should have qualitative consistency with C_{60}. Considering the relatively larger sizes of carbon onions, we evaluated the related van der Waals interactions using Hamaker's theory, which are used widely to calculate the van der Waals force and adhesiveness between various materials [15,16]. The van der Waals force between two similar sphere particles [17] is $F = AR/12z_0^2$, and that between a sphere particle and a plane surface is $F = AR/6z_0^2$, respectively. A is the Hamaker constant, and the value of graphite, $A_{cg} = 23.8 \times 10^{-20}$ J was used in our calculations; R is radius of the sphere; and z_0 is the contact distance, minimally at the value of an atomic radius, we used 0.16 nm [17] in our calculation. Our calculation found that for a typical carbon onion with the diameter of 30 nm, the van der Waals attraction was 11.6 nN between two onions and 23.2 nN between the onion and HOPG surface. This result is consistent with our previous analysis. Hence, the well-dispersed adsorptions of carbon onions on HOPG surface can be understand with the relatively stronger interaction of carbon onions with HOPG surface.

3.2. Manipulation of carbon onions on HOPG surface

When manipulating the adsorbed carbon onions with the AFM tip, samples with onion's coverage of about 5 μm^{-2} were prepared. The manipulation of onions was realized by the tip lateral interaction that was exerted on onions in the process of scanning, as shown schematically in Fig. 2. Two manipulating mode, namely raster mode and vector mode according to the

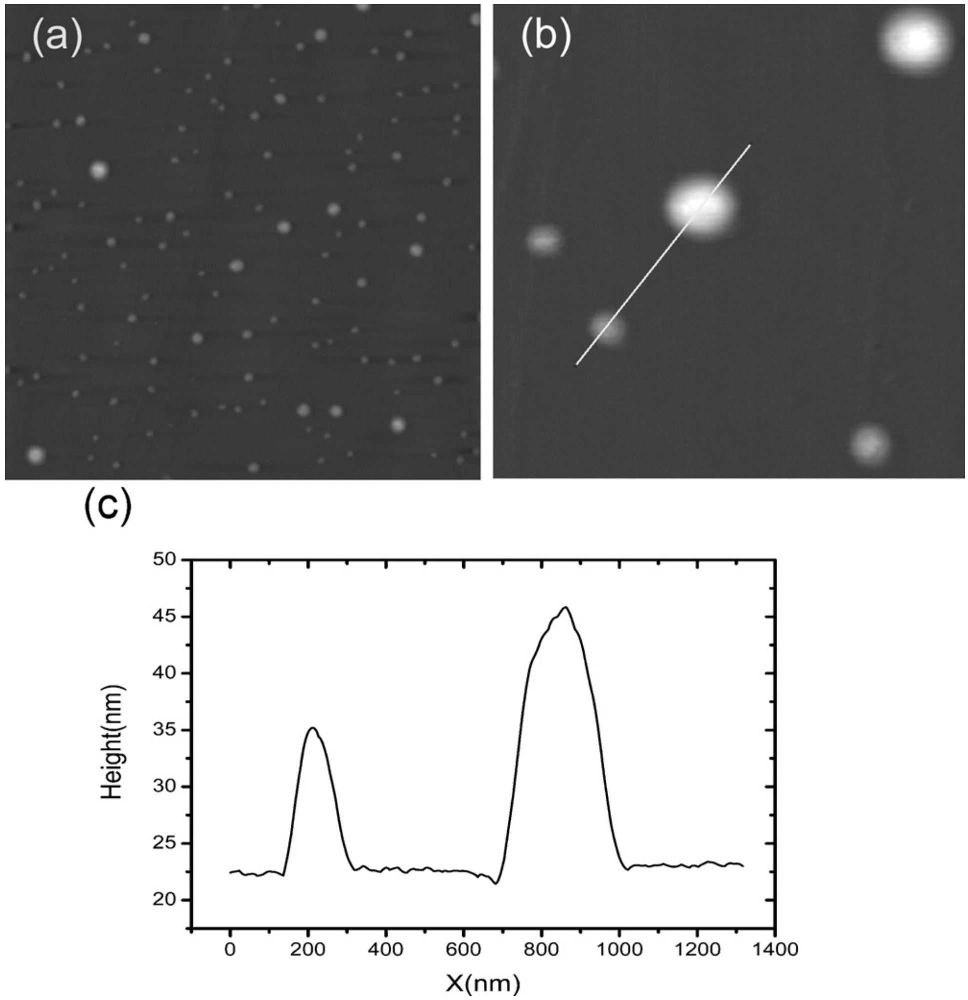

Fig. 1. AFM topographic images of carbon onions adsorbed on HOPG surface, (a) image size: 10 μm × 10 μm, (b) image size: 2 μm × 2 μm, (c) the cross-section profile of adsorbed onions made along the line shown in image (b).

different scanning manners of the AFM tip, was used in our experiments. We found that the adsorbed onions could be pushed and moved successfully on the surface of HOPG with both manipulation modes, but the controllability and precisions of two manipulation modes were different.

In raster mode, typically a 3–4 μm^2 area was imaged firstly in tapping mode of AFM. Then, the target onion and the expected location were chosen. After setting the expected scan direction and scan size, the tip was approached towards the sample surface step by step until the swing of the tapping tip was equal to zero, where the tip just contacted with the surface of the substrate. Afterward, the feedback loop was switched off and the driving voltage of tip vibration was turned off. Then the tip made a raster scanning on the predefined area as that in the normal imaging process. The target onion would be moved under the lateral force exerted by the tip when the tip encountered the onion in the scanning trace, as shown in Fig. 2(b). Fig. 3 demonstrates the manipulation of several carbon onions with the raster mode. Fig. 3(a) is the AFM topographic image of adsorbed onions before the manipulation. The onions labeled A, B and C are the selected target onions, which will be moved along the direction indicated by white arrows. Fig. 3(b–d) gives the results of manipulation. The onion A and B were moved in the opposite directions and both onions were moved ~1 μm from their original locations. Each manipulation of onion A or B was completed in just one manipulating process. The onion C was moved twice along the same direction (Fig. 3(c and d)). With the manipulation in raster mode, we found that the target onion did not always move along the predefined direction precisely, like onion A in Fig. 3. We thought this was caused by the raster scanning of the tip. In raster mode, the tip scanned in a line-by-line manner and the step of each line was determined by the scan size as well as the

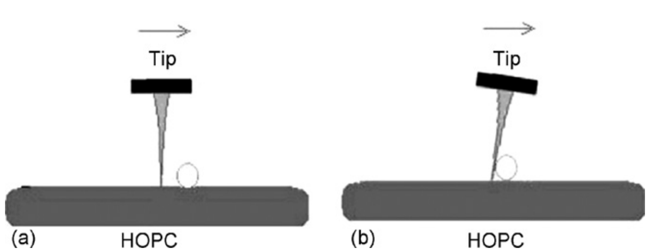

Fig. 2. Illustration of the manipulation of carbon onions by the AFM tip, (a) before and (b) during the manipulating process.

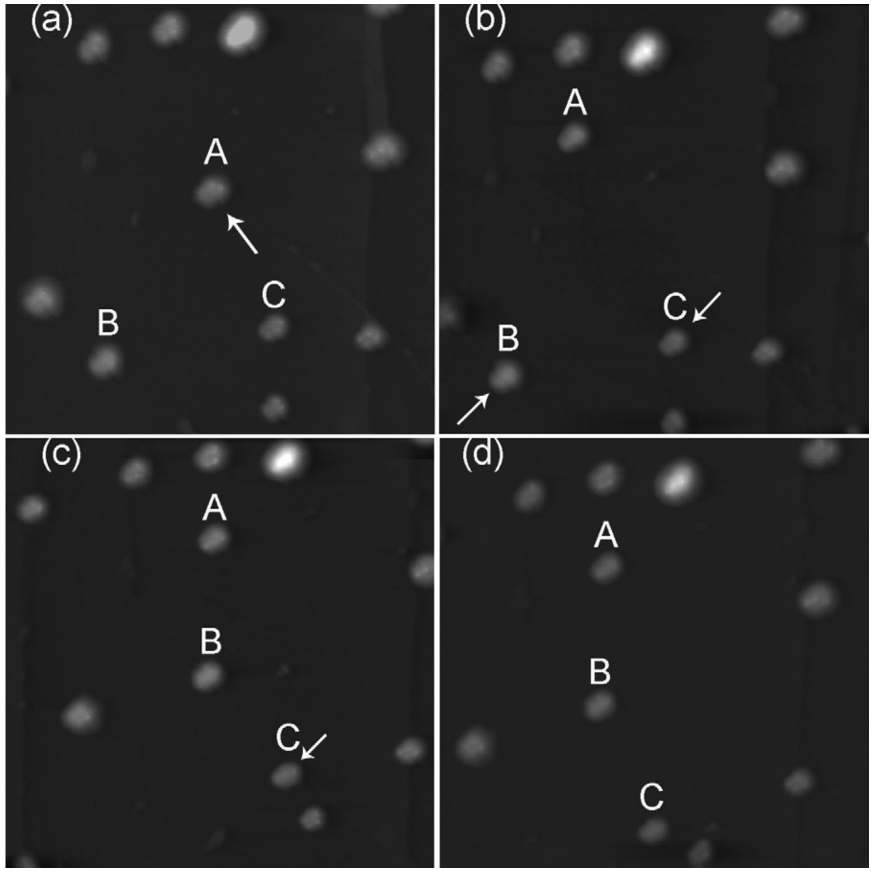

Fig. 3. (a) AFM topographic image of adsorbed carbon onions before the manipulation. The image size was 3.3 μm × 3.3 μm. Onions labeled A, B and C was selected target onions. The white arrow beside the labeled onion indicated the predefined direction of the manipulation. Correspondence results were shown in (b–d).

number of scan points on each line. If the target onion did not locate right on the scan lines, the contact of the tip with the onion would not be a head-on contact, but occur at the side of the tip and the onion. As a result, the onion would be pushed aside. The same condition was also possible when the tip encountered the onion on the subsequent scan lines. In such case, the moving distance and direction of the target onion would deviate from the predefined values significantly. This problem in the raster mode limits the controllability and precision of the manipulation. When the target onion needs to be moved in a long distance or along a complicate track, the whole process should be divided in several simple steps to insure the considerable precision of the manipulation.

To further improve the precision of the manipulation, the vector mode was used. The AFM tip was approached in the same way as in the raster mode, and the vector-scanning mode of the tip was used to insure that the tip moved along the predefined direction just once instead of a raster scanning in the

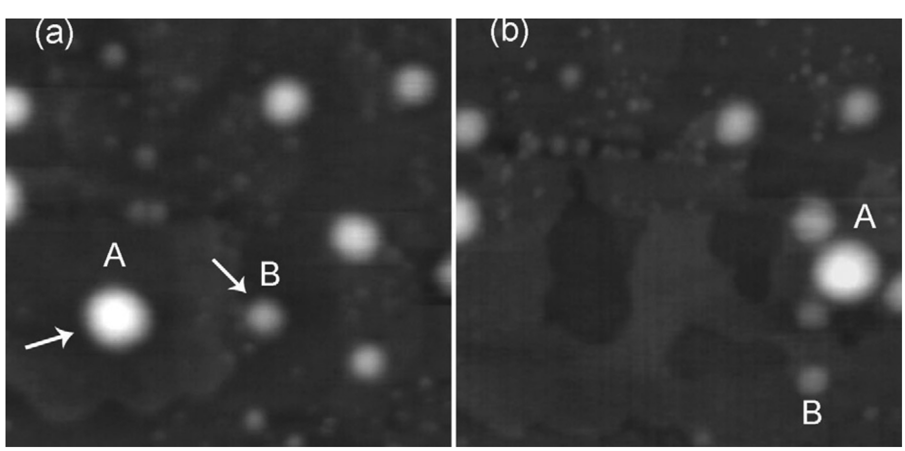

Fig. 4. (a) Before and (b) after the moving of the onion A to the location just in the middle of three other onions using the vector mode manipulation. The image size was 1.5 μm × 1.5 μm. The onion B was moved aside firstly because it was on the way of the moving trace of onion A.

rectangle area. The direction and moving distance of the target onion could be defined precisely by setting the direction and the length of the tip moving trace. Fig. 4 shows how to move the onion A with the size of about 20 nm to the location just in the middle of three less ones. In the manipulating process, the onion B was first moved aside because it was just on the way of the moving trace of onion A. The result in Fig. 4 demonstrates that carbon onions can be manipulated with considerable precision using the vector mode, and this technique is useful for the construction of two- and three-terminal nano-devices based on carbon onions.

It can also be found in Fig. 4(b) that the manipulating process indeed had some effects on the surrounding onions. There are some factors that limit the precision of the vector mode manipulation of carbon onions. Above all, the most important factor is the definite size of the AFM tip. The radius of curvatures at the tip apex is given to be around 10–30 nm. Therefore, the error brought by the size of the tip apex must be considered when setting the manipulating distance of the target onion, which is at least around 5–15 nm. Another factor that influences the precision of manipulation is the drifts of the tip, which are caused by the fluctuation of environment temperature and humidity, scanner oscillations, etc. To reduce the effect of tip drifts, the moving distance should be chosen carefully. In our experiments, we found that the drifts of the tips could be nearly omitted when the moving distance in one manipulation cycle was set below 1 μm.

4. Conclusions

In summary, the adsorption of carbon onions on HOPG surface was studied using an AFM and well-dispersed adsorption of onions was observed. The van der Waals attractive forces between the onion and HOPG surface and that between two onions were calculated using Hamaker's theory. Our results indicated that the van der Waals interaction between the onion and HOPG surface was stronger than that between two onions. The adsorbed onions were manipulated successfully using the AFM tip in the raster mode as well as in the vector mode. However, the raster mode manipulation has a less controllability due to its line-by-line scan manner of the tip. On the contrary, the vector mode manipulation shows well controllability and high precision, is a more suitable method for the construction of nano-scale devices based on carbon onions.

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