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ScienceDirect
Applied Surface Science 253 (2007) 3237–3241
applied surface science
www.elsevier.com/locate/apsusc

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

Jianfeng Zhou [a], Ziyong Shen [a,*], Shimin Hou [a], Xingyu Zhao [a], Zengquan Xue [a], Zujin Shi [b], Zhennan Gu [b]

[a] *Key Laboratory for the Physics and Chemistry of Nanodevices, Department of Electronics, Peking University, Beijing 100871, PR China*
[b] *College of Chemistry and Molecular Engineering, Peking University, Beijing 100871, PR China*

Received 13 April 2006; received in revised form 29 June 2006; accepted 4 July 2006
Available online 14 August 2006

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.

PACS: 61.48.+c; 68.65.−k; 81.16.Ta; 68.37.Ps

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

* Corresponding author. Tel.: +86 10 62762444; fax: +86 10 62759444.
E-mail address: zyshen@pku.edu.cn (Z. Shen).

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doi:10.1016/j.apsusc.2006.07.012

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