Ultrahigh vacuum scanning probe microscopy studies of carbon onions

ARTICLE *in* PHYSICA E LOW-DIMENSIONAL SYSTEMS AND NANOSTRUCTURES · FEBRUARY 2001

Impact Factor: 2 · DOI: 10.1016/S1386-9477(00)00273-3

Zhonghui Xue
Henan Polytechnic University

Zujin Shi
Peking University

Zhennan Gu
Peking University

Physica E 9 (2001) 300–304
PHYSICA E
www.elsevier.nl/locate/physe

Ultrahigh vacuum scanning probe microscopy studies of carbon onions

S.M. Hou[a,*], C.G. Tao[a], G.M. Zhang[a], X.Y. Zhao[a], Z.Q. Xue[a], Z.J. Shi[b], Z.N. Gu[b]

[a] *Department of Electronics, Peking University, Beijing 100871, People's Republic of China*
[b] *College of Chemistry and Molecular Engineering, Peking University, Beijing 100871, People's Republic of China*

Received 22 June 2000; accepted 17 August 2000

Abstract

Carbon onions were prepared by DC arc charge method. The behavior and electronic properties of carbon onions on highly oriented pyrolytic graphite (HOPG) substrate were studied by ultrahigh vacuum atomic force microscopy and scanning tunneling microscopy (UHV AFM/STM). UHV AFM/STM images showed that these ellipsoidal carbon onions tended to aggregate into clusters on the surface of HOPG. The scanning tunneling spectroscopy indicated that the electrical properties of carbon onions were between graphite and single-shell fullerenes.

Keywords: Carbon onions; Scanning probe microscopy; Scanning tunneling spectroscopy

1. Introduction

C_{60}, a new allotrope of carbon besides graphite and diamond, has gained extensive attention because of its many novel properties. The subsequent discovery of carbon nanotubes and carbon onions led to a wealth of experimental and theoretical studies of carbon having curved planes. Scientific interests are more focused on C_{60} and carbon nanotubes including characterization of their structures and studies of their electronic properties, for example, alkali-metal doping makes C_{60} superconductive [1], the electronic properties of carbon nanotubes depend on their diameter and chirality [2]. C_{60} and carbon nanotubes also have many potential applications [3,4]. By contrast, studies of carbon onions were only carried on the preparation methods [5,6], the growth mechanism and the structure analysis [7–9]. These giant fullerenes were first observed by Iijima with high-resolution transmission microscopy (HRTEM) [10]. Later, Ugarte was able to produce carbon onions by an intense electron irradiation of soot particles in a transmission electron microscope (TEM); thus, he could directly image the growth process of carbon onions [11,12]. However, this technique cannot be applied to the macroscopic production of carbon onions, the size of carbon onions cannot be controlled, either. Carbon onions have not yet found technological applications due to the lack of

* Corresponding author. Tel.: +86-10-62751769; fax: +86-10-62751762.
E-mail address: smhou@ibm320h.phy.pku.edu.cn (S.M. Hou).

1386-9477/01/$ - see front matter
PII: S1386-9477(00)00273-3

knowledge about their physical properties such as their electronic properties [13,14], their electro-optical properties, etc. In this letter, we present the DC arc charge preparation method, study their electronic properties by ultrahigh vacuum atomic force microscopy and scanning tunneling microscopy (UHV AFM/STM).

2. Experiment

Carbon onions used in this study were first produced by the DC arc discharge method [15]. The anode was an extremely pure graphite rod of diameter 6 mm, into which a hole of diameter 3 mm was drilled and filled with graphite and YNi_2 powder in a molar ratio of 1:1. The cathode, which was a graphite rod of diameter 10 mm, was shaped into a sharp tip so that the evaporation of cathode could be minimized. 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 $\phi 1$ μm porous polytetrafluoroethylene (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 $\phi 0.2$ μm Super Membrane Disc filters under vacuum. Thus pure carbon onions on the filter were finally fabricated.

Carbon onions were ultrasonically dispersed in ethanol and drop-deposited onto freshly cleaved highly oriented pyrolytic graphite (HOPG) substrates. Once the solvent drop had evaporated, the samples were transferred into an ultrahigh vacuum chamber equipped with an STM and an AFM [16]. The Needle-sensor AFM was used to study the morphology of carbon onions on HOPG substrate [17], STM and scanning tunneling spectroscopy (STS) were used to study the electrical properties of carbon onions.

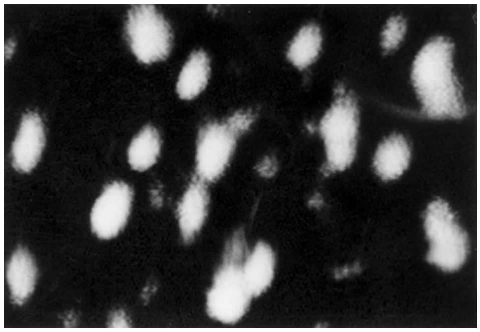

Fig. 1. An AFM topography image of carbon onions on the surface of HOPG.

3. Results and discussion

Carbon onions tend to aggregate into clusters on HOPG substrate, which indicates a strong attractive interaction between the onions and a relatively weaker interaction between the onions and the HOPG substrate. A typical AFM topographic image of carbon onions is shown in Fig. 1, the scan size is 140 nm × 100 nm. The resonance frequency of the Needle-sensor was $f = 999.4$ kHz, the phase shift setpoint was $\varphi_{\text{setpoint}} = -6.888^\circ$. The section analysis revealed that the carbon onions were ellipsoidal and the diameter was about 15–18 nm, which was consistent with the HRTEM analysis [18]. The HRTEM analysis revealed that these carbon onions were hollow ellipsoids composed of 11 fullerene shells, the long axis of the outermost shell was about 16 nm and the short axis was about 13 nm. The intershell distance was 0.336 nm, approximately equal to the interlayer spacing of turbostratic planar graphite.

Fig. 2 shows an STM image of carbon onions on HOPG, which was taken at a sample bias voltage of 0.288 V and a tunneling current of 155 pA. The scan size was 85 nm × 45 nm. It could be seen that two onions formed a cluster and the diameter of an onion was about 13 nm. In order to study the electronic structure of carbon onions, STS data were obtained on single onion molecules at the same condition as the STM image. STS of HOPG at atomic resolution was also obtained so that the effect of graphite sub-

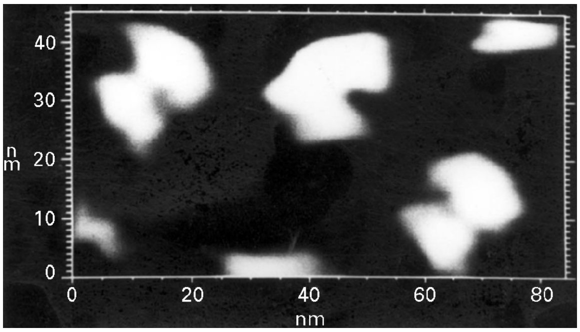

Fig. 2. An STM topography image of carbon onions on the surface of HOPG.

strate could be investigated; the data were acquired after stabilizing the tip with a 0.13 V bias voltage and 0.5 nA tunneling current. STS depends on the distance between the tip and the sample, so different STS data cannot be directly compared because the bias voltage and tunneling current were set differently. Fortunately, the normalized conductance ($\mathrm{d}\ln I/\mathrm{d}\ln V$) eliminated this dependence, and the normalized conductance is proportional to the density of states (DOS) of the sample [19]. As can be seen in Fig. 3(b), the normalized conductance of graphite was approximately parabolic at both the negative and positive voltages and there were no characteristic peaks, which is consistent with the theoretical calculations done by Kilic [20]. While the energy gap between the occupied and unoccupied bands is ~ 6 eV at the Γ point of the first Brillouin zone of graphite, it diminishes at the K point and along the KH direction where the bonding and antibonding bands join. Accordingly, graphite is a semimetal, and its DOS is a featureless parabola within 2 eV above and below the Fermi level. This also indicated that ethanol had completely evaporated and there were no effects on the electronic structure of HOPG and carbon onions. Thus, all of the characteristic peaks in the normalized conductance of carbon onions (Fig. 3(a)) can be attributed to carbon onions themselves. Three narrow, occupied state peaks were measured at -0.70 eV, -0.54 eV and -0.18 eV; the DOS at the Fermi level of carbon onions was relatively small; above the Fermi level empty electronic state peaks lay at 0.30 eV, 0.50 eV and 0.80 eV.

Theoretical calculations on the electronic structure of giant carbon onions have not been reported because the atomic number of carbon onions is very large; there are no experimental data of ultraviolet photoemission spectroscopy (UPS) and inverse photoemission spectroscopy (IPS) about carbon onions, either. So it is difficult to interpret STS results quantitatively. We know that, due to the intershell interaction, the states of one shell mix with those of another to form the eigenstates of the composite system. In this way, the states of inner shells should be presented on the outermost shell fullerenes. However, only the local density of states (LDOS) at the tip position is important for determining the tunneling current, and the LDOS on the outermost shell is not changed even if the electrons delocalize from shell to shell. Furthermore, similar to MWCNTs [21], the single-shell fullerene electron wave functions also decay very quickly away from the fullerene surface. Thus, the electronic structure of carbon onions is qualitatively between graphite and single-shell fullerene. There are characteristic peaks in the DOS similar to that of single-shell fullerene [22], which indicates that carbon onions are giant molecules; the DOS at the Fermi level of carbon onions is not zero more similar to that of graphite, one reason may be that the diameter of the outermost shell fullerene is much larger than that of small single-shell fullerenes such as C_{36}, C_{60} and the effects of the curvature of the graphitic shells are decreased, another reason may be that carbon onion molecules dimerized as shown in Fig. 2 and the gap disappears similar to appropriate C_{36} dimers [22].

4. Conclusion

Carbon onions prepared by the DC arc charge method were uniform, which was confirmed by the HRTEM analysis. UHV AFM/STM revealed that carbon onions on the surface of HOPG tended to aggregate into clusters. The normalized conductance of carbon onions had six characteristic peaks between -1 V and $+1$ V and was not zero at the origin, indicating that the electronic structure of carbon onions was between that of graphite and single-shell fullerenes.

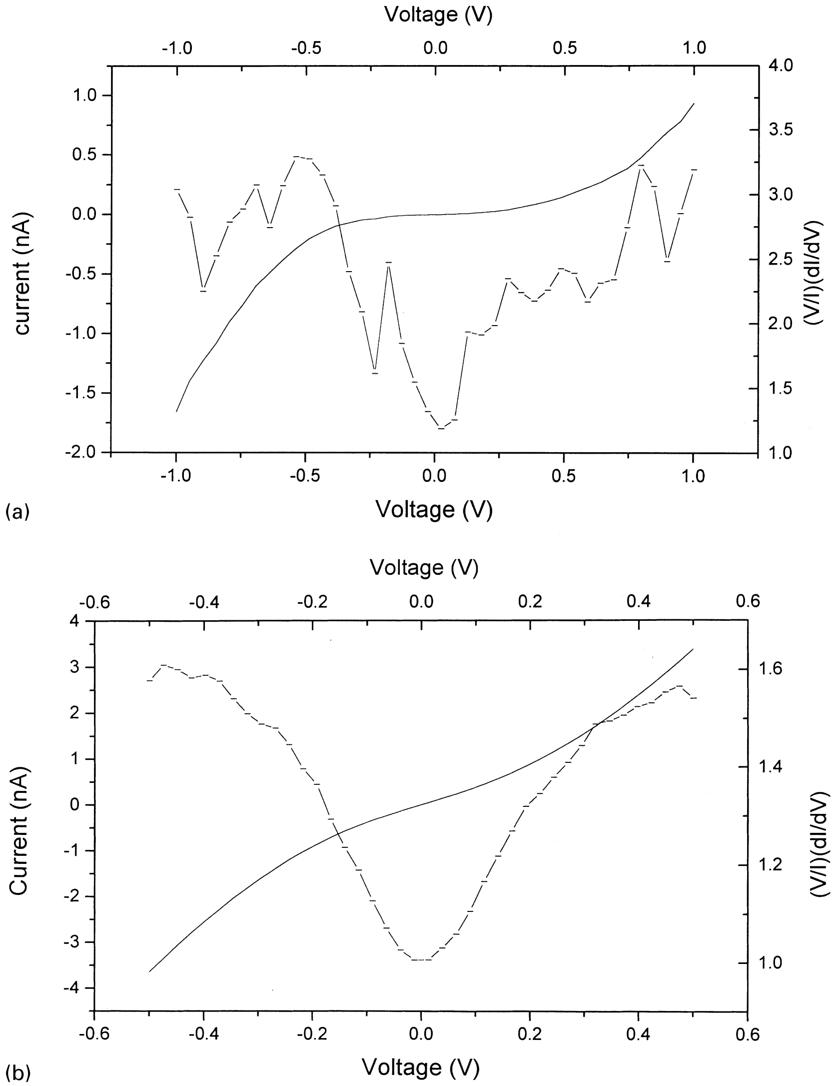

Fig. 3. Local tunneling spectra I–V and $(V/I)(\mathrm{d}I/\mathrm{d}V) - V$ measured on carbon onions and HOPG: (a) carbon onions; and (b) graphite.

Acknowledgements

This work is partially supported by National Science Foundation of China (No. 69701001) and the Ministry of Education of China.

References

[1] A.F. Hebard, M.J. Rosseinsky, R.C. Hddon, D.W. Murphy, S.H. Glarum, T.T.M. Palastra, A.P. Ramirez, A.R. Kortan, Nature 350 (1991) 600.
[2] N. Hamada, S. Sawada, A. Oshiyama, Phys. Rev. Lett. 68 (1992) 1579.
[3] D. Porath, Y. Levi, M. Tarabia, O. Millo, Phys. Rev. B 56 (1997) 9829.
[4] C. Dekker, Physics Today 52 (1999) 22.
[5] T. Cabioch, J.P. Riviere, J. Delafond, J. Mater. Sci. 30 (1995) 4787.
[6] N. Hatta, K. Murata, Chem. Phys. Lett. 217 (1994) 398.
[7] D. Ugarte, Chem. Phys. Lett. 207 (1993) 473.
[8] Q. Ru, M. Okamoto, Y. Kondo, K. Takayanagi, Chem. Phys. Lett. 259 (1996) 425.
[9] Lu-Chang Qin, S. Iijima, Chem. Phys. Lett. 262 (1994) 252.

[10] S. Iijima, J. Crystal Growth 50 (1980) 675.
[11] D. Ugarte, Nature 359 (1992) 707.
[12] D. Ugarte, Europhys. Lett. 22 (1993) 45.
[13] T. Stöckli, J.-M. Bonard, A. Châtelain, Z.L. Wang, P. Stadelmann, Phys. Rev. B 57 (1998) 15999.
[14] T. Stöckli, J.-M. Bonard, A.Châtelain, Z.L. Wang, P. Stadelmann, Phys. Rev. B 61 (1998) 5751.
[15] Z.J. Shi, Y.F. Lian, F.H. Liao, X.H. Zhou, Z.N. Gu, Y.G. Zhang, S. Iijima, Solid State Commun. 112 (1999) 35.
[16] Instruction Manual VT STM, Omicron, Germany.
[17] W. Clauss, J. Zhang, D.J. Bergeron, J. Vac. Sci. Technol. B 17 (1999) 1309.
[18] S.M. Hou, C.G. Tao, H.W. Liu, J.C. Li, X.Y. Zhao, W.M. Liu, Z.L. Zhang, L.-M. Peng, J. Shi, Z.N. Gu, Vac. Sci. Technol. (China) 20 (2000) 47.
[19] D.A. Bonell, Scanning Tunneling Microscopy and Spectroscopy – theory, Technology and Application, VCH Publishers Inc, New York, 1993.
[20] C. Kilic, H. Mehrez, S. Ciraci, Phys. Rev. B 58 (1998) 7872.
[21] P. Delaney, M. Di Ventra, S.T. Pantelides, Appl. Phys. Lett. 75 (1999) 3787.
[22] P.G. Collins, J.C. Grossman, M.Côté, M. Ishigami, C. Piskoti, S.G. Louie, M.L. Cohen, A. Zettl, Phys. Rev. Lett. 82 (1999) 165.