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Nanoscale Ordered Structure of Fullerenes on the Surface of Highly Oriented Pyrolytic Graphite

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The formation of an ordered arrangement of C_{60} molecules as path-like structures on the surface of highly oriented pyrolytic graphite (HOPG) is reported for the first time with theoretical implementations. Fullerene nucleation and deposition from solutions with different concentrations of C_{60} is performed under ambient conditions without electrochemical processes. Scanning tunneling microscopy (STM) is used to study the surface topography. The results reveal new aspects of fullerene deposition that can potentially aid in modeling with theoretical simulations.

Keywords: Fullerene, Nanowires, HOPG, STM

INTRODUCTION

The study of ordered structures of nanoparticles lies at the heart of nanotechnology and molecular systems and can resolve many problems in the design of molecular devices [1-5]. The initiation of deposition at step edge dislocations (Fig. 1) and defects in the electrode surface is the essential feature in the formation of ordered structures like meso- and nanowires in nanoelectronic and nanophotonic applications [10,11]. Several controllable and reproducible ordered nanoparticle structures have been studied based on the atomic interaction of metallic and non-metallic particles from the point of nucleation up to self assembly [6-8]. These studies undoubtedly give rise to many challenges both in industrial research and pure scientific theory.

Highly oriented pyrolytic graphite (HOPG) surfaces have been used as electrode substrates for the electrodeposition of silver, gold, molybdenum, palladium and platinum nanostructures [9]. Table 1 shows several different applications of nanoparticle depositions on the surface of HOPG as a template substrate. The formation of nuclei on

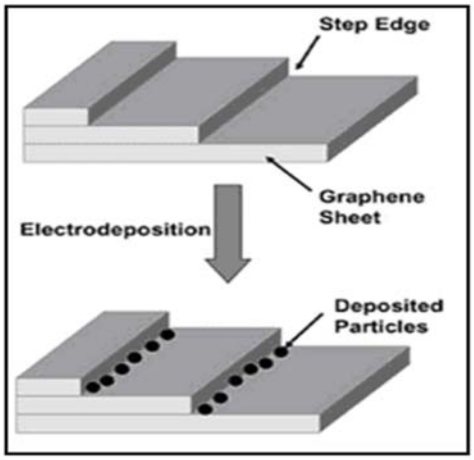

Fig. 1. A schematic diagram for synthesis of nanoparticle arrays in step edges in a graphite surface [9].

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Table 1. Various Applications of HOPG as a Template Substrate Used for Electrodeposition of Metallic Nanostructures [9]

Template substrate	Elements deposited	Size and shape of nanostructures
Highly oriented pyrolytic graphite (HOPG)	Ag	Flat island of diameter 0.29 nm
		Clusters of 10 nm diameter
		Disc (diameter 20-60 nm and height 1.5-5 nm)
	Ag	Aggregate (size 500 nm and height 70 nm)
	Mo	Nanowire of 15 nm diameter
	Pd	Island of 200-300 nm grain size range
		Two-dimensional branched island (100-160 nm)
		Mesowires of grain size 50-300 nm

surfaces has been studied from the perspective of equilibrium and non-equilibrium thermodynamics [12-13].

In recent years, some attention from the scientific community has been focused on the study of thin film solutions of passivated nanocrystals during the irreversible evaporation of solvent without electrochemical processes. In these experiments, the assembly of nanocrystals into ordered structures is an advanced approach in material science and an area of fundamental research by itself, involving various interactions between nanocrystals, substrates and solvents [14]. In the present work, the experimental formation of ordered sets of C_{60} molecules, arranged as path-like structures, based on the theoretical nature of nucleation under ambient conditions, is reported. The deposition of fullerenes at the step edge of the HOPG surface and the surface morphology is studied using scanning tunneling microscopy (STM).

EXPERIMENTAL

In order to show the probable deposition patterns of fullerenes on the surface of HOPG, C_{60} molecules were deposited onto a cleaved HOPG surface in air under ambient conditions from two solutions with different concentrations of C_{60}. We suspended 5 mg C_{60} (98%; Aldrich) in 1 ml toluene (99.8%; Fluka) in one solution, according to the supersaturation deposition method of Christensen *et al.* [15], and 2 mg C_{60} in 1 ml toluene in another solution, and placed each in a separate test tube that was subsequently closed with a rubber stopper. The mixtures were sonicated at room temperature for 1 h and allowed to settle for 15 min. One drop of each solution was deposited onto a freshly-cleaved HOPG substrate surface, which had a surface area of 0.5×0.5 cm^2. Each sample was left in a fume hood for 10 min to allow the toluene to evaporate, and then each sample was mounted onto an easyScan E-STM (Nanosurf AG, Liestal, Switzerland). STM measurements were performed in air at room temperature and atmospheric pressure using commercially-available, unmodified easyScan E-STM equipment, with mechanically-cut Pt-Ir (90/10) tips. The examinations were conducted in the constant current mode, with a current of 1 nA and a positive sample bias of 0.01-0.05 V. The experiments were carried out several times with this procedure to account for the problem of reproducibility.

RESULTS AND DISCUSSION

In Fig. 2, the paths of the fullerene structures (both single- and multi-rowed) are imaged on the surface of the HOPG. From the image, the length of the single path (Fig. 2a) is up to 405 nm.

The reproducible formation of these structures, observed as fixed patterns for the nucleation of fullerenes, occurs mostly at the step edges, as shown in Fig. 3. These step edges, where the van der Waals (VDW) attractions are greater than at other flat areas of the terraces, are thermodynamically favored with lower nucleation barriers. The mean height of the step is 0.37

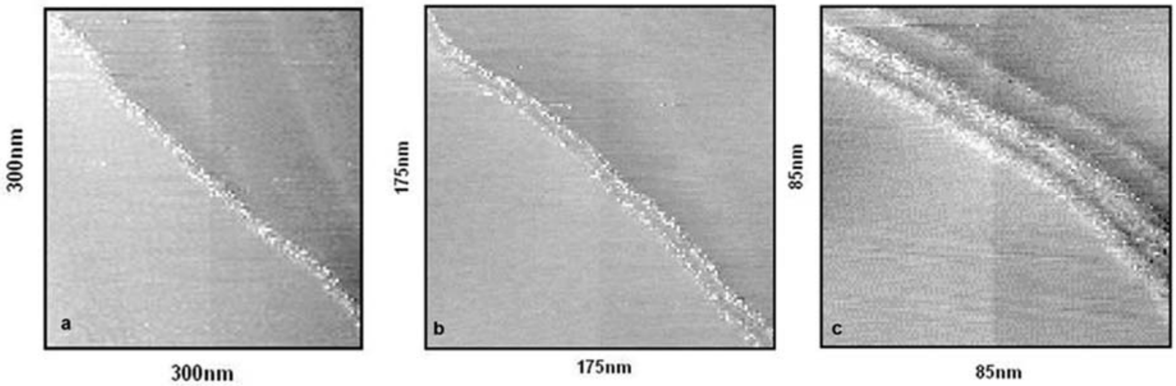

Fig. 2. Typical STM images of single-rowed (a), double-rowed (b) and multi-rowed paths (c) of fullerene deposited from a 5 mg ml $^{-1}$ solution on the HOPG surface. The diameter of an individual fullerene molecule is approximately 1 nm.

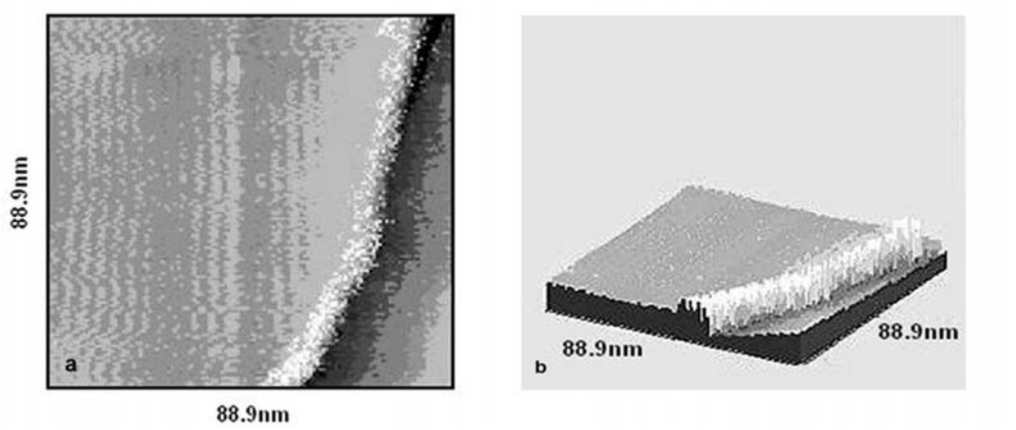

Fig. 3. Typical STM images of the path formation of fullerenes deposited from a 5 mg ml^{-1} solution on the edge steps in planar (a) and 3D (b) views. The mean height of the steps is 0.37 nm. Standing waves of electron density can be observed in the terrace.

nm, which is the step height for graphite terraces.

In Figs. 2 and 3, single molecules of fullerenes are obvious in the terrace; a remarkable note for theoretical simulations. It is possible to simulate this process by considering a hopping parameter, which indicates the capability of fullerenes to escape from the potential field of the terrace. As time passes, evaporation will render this parameter ineffective in a non-linear manner.

The start point of a double-rowed path is shown in Fig. 4 in both planar and 3D views. It is obvious from the image that the first row is formed in a step edge and the second row is placed at a distance where the VDW interactions of the first row and the surface are in fine balance. This matter is clearer when a mean line-roughness calculation gives a value of 0.34 nm for the height difference of the first row and a value of 0.098 nm for the second one.

Among the reproducible structures observed, a λ-branch path as an interesting pattern is imaged in Fig. 5. The

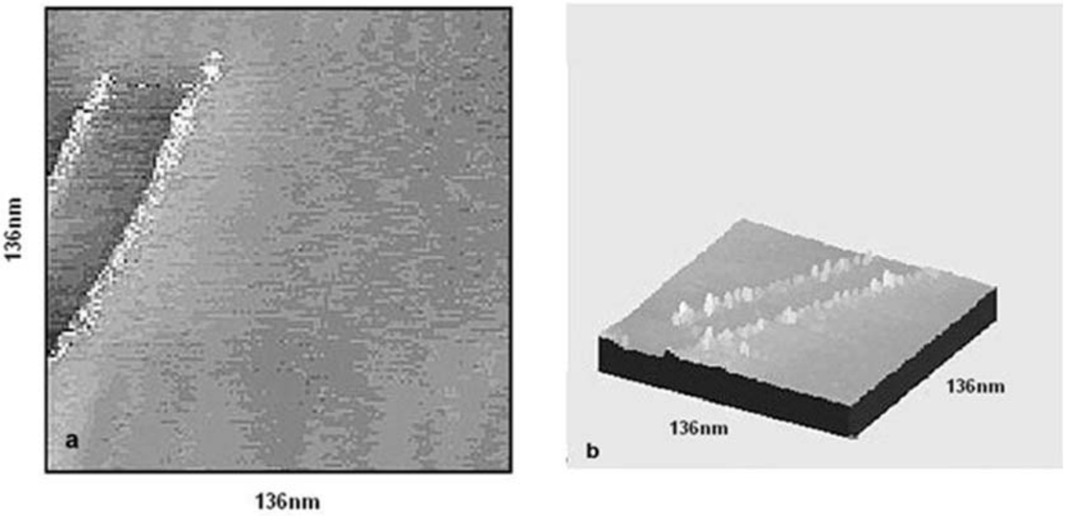

Fig. 4. Typical STM images of the start point of a double path of fullerene deposition from a solution of 5 mg ml^{-1} C_{60}. (a) Planar view, the two paths are separated about 22 nm. (b) 3D view, the first path is located on the edge, which has a mean height of 0.34 nm.

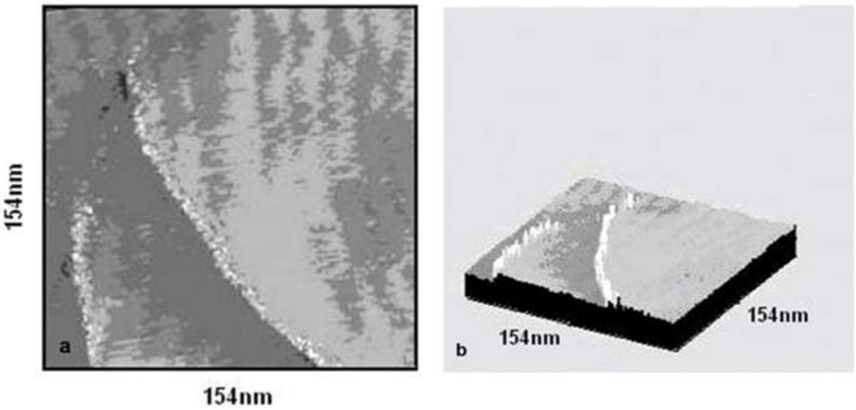

Fig. 5. Typical STM images of the deposition of fullerenes from a solution of 5 mg ml^{-1} C_{60} onto λ-branching paths in planar (a) and 3D (b) views.

nucleation of the fullerenes on this form reveals a kind of step-like defect on the surface that can be used as an intersection pattern in molecular systems, especially nanoelectronics.

Experimental evidence of the nucleation and growth processes of fullerene deposition is more easily observed if we perform these experiments using a toluene solution with a C_{60} concentration below the 3 mg ml^{-1} saturation point.

Figure 6 presents the deposition of fullerenes from a solution of 2 mg ml^{-1}. As seen in the image, a valley-type defect is presented with a low density of fullerenes. It is clear that fullerene nucleation is greater in the step edges. More

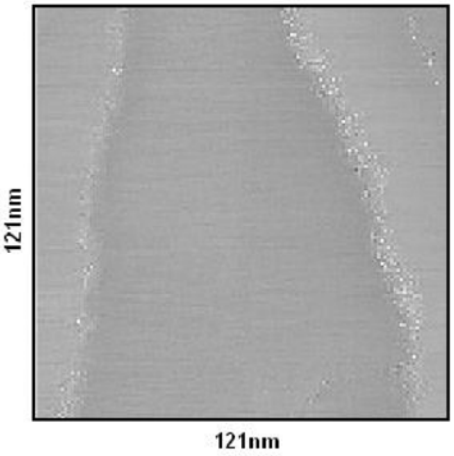

Fig. 6. STM image of the deposition of fullerenes from a solution of 2 mg ml^{-1}.

fullerenes will be deposited on the nuclei by a growth process.

CONCLUSIONS

In conclusion, although the fullerene islands and clusters have been observed under ambient conditions upon the evaporation of the solvent of supersaturated solutions of C_{60} in previous studies at areas away from cleavages in the HOPG surface [16-17], this study reveals new aspects of fullerene deposition at step edges in HOPG surfaces, and can lead to further experimental and theoretical research.

A fully theoretical investigation including molecular dynamic simulations for this process is needed. The terrace of graphite can be modeled with a 2D alternative potential field, and a hopping parameter can be considered for the role of the solvent, which can be dealt with using non-linear dynamics as the evaporation proceeds.

Such research will aid in the manufacture of nanoelectronic devices, including nanocircuits in general, specifically send and receive devices, junctions and switches.

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REFERENCES

[1] P.L Anelli, N. Spencer, J.F. Stoddart, J. Am. Chem. Soc. 113 (1991) 5131.
[2] A.P. de Silva, H.Q.N. Gunaratne, C.P. McCoy, J. Am. Chem. Soc. 119 (1997) 7891.
[3] J. Otsuki, J. Am. Chem. Soc. 119 (1997) 789.
[4] A.P. Alivisatos, Adv. Mater. 10 (1998) 1297.
[5] T.L. Breen, J. Tien, S.R.J. Oliver, T. Hadzic, G.M. Whitesides, Science 284 (1999) 948.
[6] A.K. Boal, F. Ilhan, J.E. DeRouchey, T. Thurn-Albrecht, T.P. Russell, V.M. Rotello, Nature 404 (2000) 746.
[7] A. Milchev, Electrocrystallization Fundamentals of Nucleation and Growth, Kluwer Academic Publishers, Boston, 2002.
[8] G.M. Whitesides, B. Grzybowski, Science 295 (2002) 2418.
[9] D. Bera, S.C. Kuiry, S. Seal, JOM 56 (2004) 49.
[10] M.S. Gudiksen, L.J. Lauhon, J. Wang, D.C. Smith, C.M. Lieber, Nature 415 (2002) 617.
[11] S. Banerjee, A. Dan, D. Chakravorty, J. Mat. Sci. 37 (2002) 4261.
[12] W.M. Gelbart, R.P. Sear, J.R. Health, S. Chaney, Farad. Disc. 112 (1999) 229.
[13] J.A. Venables, G.D.T. Spiller, M. Hanbucken, Rep. Prog. Phys. 47 (1984) 399.
[14] C.P. Collier, T. Vossmeyer, J.R. Heath, Annu. Rev. Phys. Chem. 49 (1998) 371.
[15] Christensen *et al*., Surface Science 601 (2007) L35.
[16] H. Yu, J. Yan, Y. Li, W.S. Yang, Z. Gu, Y. Wu, Surface Science 286 (1993) 116.
[17] J.L. Wragg, J.E. Chamberlin, H. Wkratschmer, D.R. Huffman, Nature 348 (1990) 623.