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Controllable Growth of Fullerene Nanostructures

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One-dimensional fullerene nanostructures with well-defined morphology have been prepared by a controllable method. Fullerene molecules, such as C_{60} derivatives and endohedral metallofullerenes, are introduced into the pores of anodic aluminum oxide (AAO) templates under a direct current (DC) electric field. Then several nanostructures such as porous-wall and solid-wall fullerene nanowires and nanotubes were fabricated in the pores. The morphology of the fullerene nanostructures is well controllable, and the fullerene nanotubes can be further fabricated through filling nickel atoms inside to form fullerene-metal composite structures. The results provide, in principle, a step toward broader applications of fullerene-related materials in nanoscience and nanotechnology.

Keywords fullerenes, metallofullerenes, nanowires, nanotubes, template synthesis

Introduction

Endohedral metallofullerenes are constructed by encaging one or several metal atoms inside fullerene cages, and the electronic properties of them determined by both the encaged metal atoms and the parent fullerenes. Because of their unique structure and many novel electronic properties, fullerenes and endohedral metallofullerenes have been intensely investigated because of their unique structural and electronic properties and promising applications in many fields (1–3). Recently, great effort has been made to construct fullerene nanostructures by a variety of nanofabrication techniques (4). Among them, one important approach is to build one-dimensional (1-D) nanostructures such as fullerene nanotubes and nanowires (5–8). In these references, several nanostructured fullerene materials such as C_{70} nanowires, C_{60} nanotubes and C_{60} nanowires were produced and reported, revealing the potential to build more complicated fullerene nanostructures. In this paper, we show a simple way to produce 1-D fullerene nanotubes, nanowires and fullerene-metal composite nanowires. The structural features, e.g., length, density, alignment, diameter, and wall-thickness of the tubular structures etc., are all manageable by controlling the experimental parameters.

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Experimental

A toluene/acetonitrile electrolyte solution containing 40 μM fullerene was transferred to a small Teflon cell, in which the porous anodic aluminum oxide (AAO) template coated with a layer of evaporated Ag serves as anode and a platinum counter electrode were set at a distance of 5 mm using a Teflon spacer. The AAO templates (Anodise®, Whatman Inc. Co.) with nominal pore diameter of 270 nm were chosen and the DC voltage for fullerene deposition was set at 40-100V. The morphology of fullerene nanostructures can be controlled by adjusting the deposition time.

The removal of fullerene nanowires or nanotubes from the AAO support was carried out by dissolving the AAO template in 2 M NaOH at 25°C for 2 h. For TEM and SEM observation, the nanostructures were detached from the Ag substrate and ultrasonically dispersed. A Philips CM200 FEG TEM operated at 160 kV and a JEOL JSM-6700F field emission SEM were employed in the study of the morphology and structure of the fullerene nanowires and nanotubes.

Results and Discussion

The method we employed to produce fullerene nanostructures is through a template method with electrochemical deposition strategy. It has been reported several years ago that C_{60} and its derivatives could form optically transparent microscopic clusters in some mixed solvents at room temperature, and the clusters would be negatively charged and deposited on the anode surface to form a fullerene film while a dc electric field was applied. If a porous anodic aluminum oxide (AAO) template was attached to the electrode surface, it's natural that the fullerene clusters would be deposited into the pores of AAO in the electrochemical process and form 1-D fullerene nanostructures. Since C_{60} nanowires have been successfully produced by this method (5), we attempted to use some stable fullerene derivatives and endohedral metallofullerenes, e.g., TC_{60} (monofunctionalized methanofullerene derivative) and $Sc@C_{82}$ (fullerene C_{82} molecule with encapsulated Sc atom) (Figures 1a, b), to construct fullerene nanostructures. In general, fullerene derivatives and metallofullerenes have more versatility than fullerenes in both structures and electronic properties, so the nanostructures constructed by fullerene derivatives and metallofullerenes are expected to find more applications.

The TC_{60} and $Sc@C_{82}$ were synthesized and isolated up to 99.9% purity, as confirmed by the time-of-flight mass spectrometry technique. The samples were dissolved in a mixed solvent of acetonitrile/toluene (4:1). AFM measurements, as shown in Figures 1c and 1d, show that both TC_{60} and $Sc@C_{82}$ molecules form clusters with narrowly-distributed diameters 30–55 nm.

Similar to those of C_{60}, the clusters of TC_{60} and $Sc@C_{82}$ would also be negatively charged and deposited on the anode surface under a suitable dc electric field (>30 volt). We took an ordered nanoporous AAO template (pore size: ca. 270 nm) with Ag substrate as the anode, and a dc voltage of 40-100 volts was applied to electrophoretically deposit the TC_{60} and $Sc@C_{82}$ clusters into the pores of AAO. The as-prepared 1-D nanostructures of TC_{60} and $Sc@C_{82}$ show versatile morphologies, e.g., solid wires, solid-wall tubes, porous wires and porous-wall tubes, depending on the applied voltage V and the deposition time T.

Since TC_{60} and $Sc@C_{82}$ behave similarly in forming the four types of nanostructures mentioned above, we took the 1-D TC_{60} as an example to show how the nanostructures can be managed by controlling the experimental conditions. First, the applied voltage and deposition time were set at $V = 65$ volt and $T = 3$ min. The resulting 1-D nanostructures

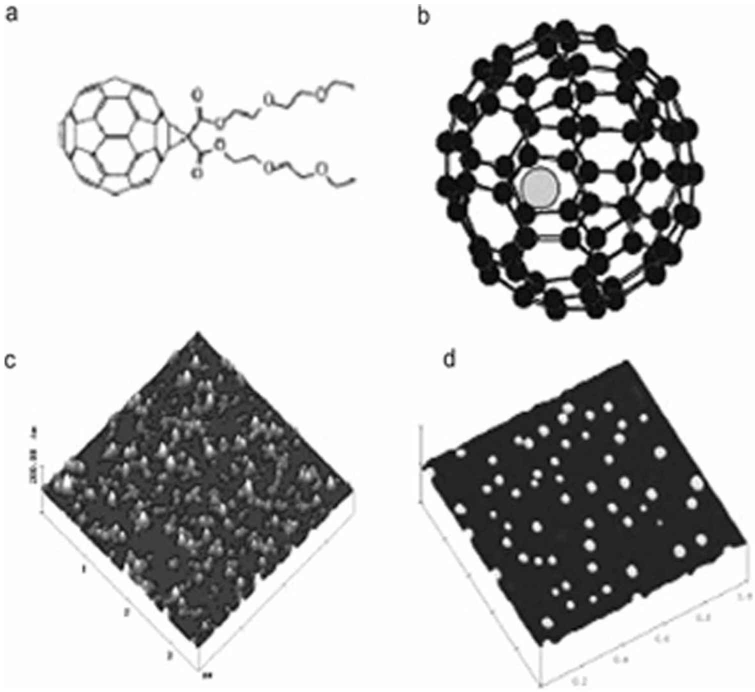

Figure 1. (a) TC_{60}, (b) $Sc@C_{82}$, (c) AFM of TC_{60} clusters in a mixed solvent of acetonitrile/toluene (4:1), (d) AFM of $Sc@C_{82}$ clusters in the same solvent.

were studied by SEM and TEM, as shown in Figure 2 (a and b). The nanostructured fullerenes were solid-wall tubes with a wall-thickness round 40 nm. The lengths and diameters of the nanowires were ca. 5.5 μm and 270 nm, corresponding to the thickness and pore size of the AAO template, respectively.

We then maintained the applied voltage at $V = 65$ volt and increased the depositing time to $T > 7$ min. As shown in Figure 2(c), the SEM images indicate that solid-wall nanowires were formed.

If we maintained the deposition time at $T = 7$ minutes but decreased the applied voltage to $V = 40$ volt, SEM and TEM studies reveal a new type of porous nanowires, as shown in Figures 2 (d and e). The wall of the porous nanowires is composed of irregular nanoclusters whose sizes are comparable to those of the clusters in acetonitrile/toluene solvents observed by AFM, as shown in Figure 1(c).

The above experiments indicate the applied voltage determines the density of the fullerene nanostructures (solid or porous) and the deposition time is related to the structural morphology (wire-like or tubular structures). Considering that the negatively charged fullerene clusters would acquire higher kinetic energies under larger dc electrical field, it is understandable that a denser packing of fullerene clusters is formed under larger dc voltage. In fact, the phenomenon that higher deposition voltage leads to denser packing of C_{60} clusters had been observed by Barazzouk et al. (5). in an experiment without the AAO. For illustrating the influence of the deposition time on the morphology of fullerene nanostructure, we suggest that the negatively charged fullerene clusters would preferentially deposit on the pore wall and grow from wall to center gradually, as shown in Figure 3. Thus, as shown, the fullerene nanostructures transit from thin-wall

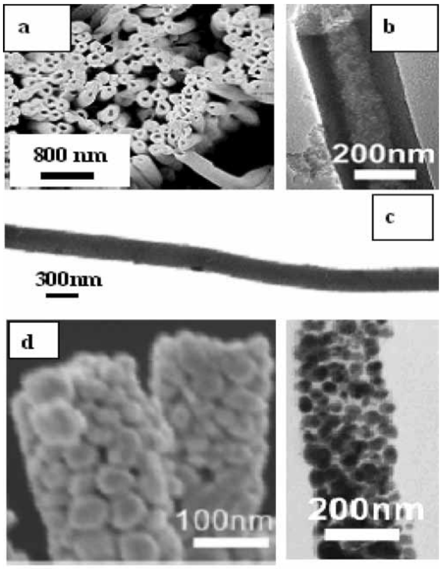

Figure 2. (a) and (b) SEM and TEM images of TC_{60} nanotubes formed at $V = 65$ volt and $T = 3$ min; (c) TEM images of TC_{60} nanowires formed at $V = 65$ volt and $T > 7$ min; (d) and (e) SEM and TEM images of TC_{60} nanowires formed at $V = 40$ volt and $T = 7$ min.

tubes to nanowires along with the increase of deposition time. Since both the applied voltage and the deposition time can be managed precisely, the morphology of fullerene nanostructures is then controllable experimentally.

The fullerene nanostructures are all flexible (Figure 4 (a)) and usually show high strength. The non-crystalline structure of these nanowires and nanotubes was revealed by XRD spectroscopic study since no diffraction lines were observed, and was confirmed by a high-resolution TEM (HRTEM) study. As shown in Figure 4(b),

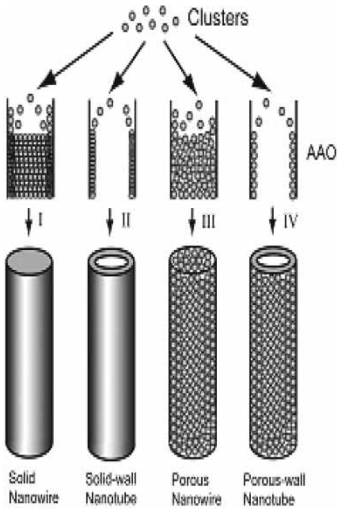

Figure 3. The model for fullerene nanostructure formation.

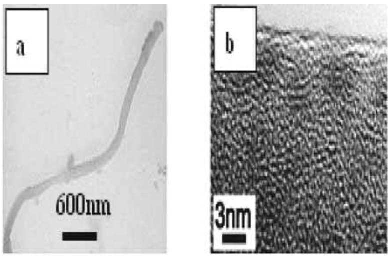

Figure 4. (a) SEM image of a Sc@C_{82} solid-wall nanorod showing the flexibility of the fullerene structure, (b) HRTEM image of a Sc@C_{82} solid-wall nanorod.

a typical HRTEM image of the solid-wall Sc@C_{82} nanotube shows that the endohedral fullerenes were irregularly packed.

The fullerene nanostructures are expected to find various applications in nanotechnology. For examples, the porous-wall nanowires and nanotubes may be used as chemical sensors due to their hollow and highly porous structure; and the hollow nanotubes can even be further functionalized through filling with other atoms or molecules to form composite nanostructures.

As an example of fullerene composite nanostructures, we studied Ni/Sc@C_{82} rods by depositing nickel atoms inside Sc@C_{82} fullerene nanotubes. We first produced thin-wall Sc@C_{82} nanotubes, as shown in Figures 5a and b, and then constructed a

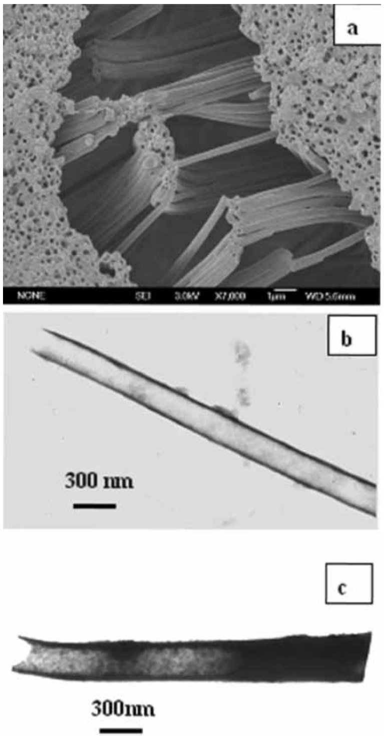

Figure 5. (a) SEM images of Sc@C_{82} nanotubes formed at V = 100 volt and T = 2 min; (b) TEM images of Sc@C_{82} nanotubes formed at V = 100 volt and T = 2 min; (c) TEM images of a nickel/ Sc@C_{82} composite rod.

three electrode system by taking the Sc@C_{82} nanotubes as the working electrode, a platinum plate as the counter electrode, and a saturated calomel electrode (SCE) as reference. A potential value of −1.4 V was applied between the working electrode and to SCE and a solvent mixture of $NiSO_4$ (2 M) and H_3BO_3 (0.5’M) as the electrolyte solution.

After 10 min of deposition of nickel atoms at room temperature, nickel/Sc@C_{82} composite rods were prepared. A typical Sc@C_{82} nanotube containing nickel atoms is shown in Figure 5(c). Due to the strong magnetic property of nickel atoms, the formation of Ni/Sc@C_{82} composite rods was first confirmed through measuring their magnetic feature. As shown in Figure 6, the Ni/Sc@C_{82} composite rods show a coercivity as high as 210 Oe, in comparison to that of bulk Ni (ca. 0.7 Oe). Additional studies, such as EDAX, also supported the formation of Ni/Sc@C_{82} composite rods.

As demonstrated by this example, template-electrophoretic deposition of fullerene should have an outstanding protential in providing customized nanotubes for a broad range of applications in nanoscience and fullerene science.

Conclusions

In summary, fullerene nanowires and nanotubes have been prepared in a controlled way. The fullerene nanotubes can be further functionalized through filling with other

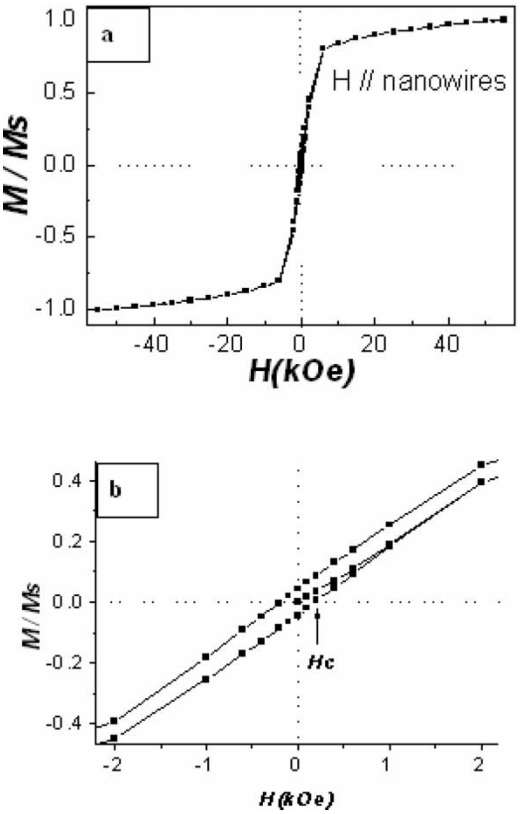

Figure 6. (a) and (b) Hysteresis curves of nickel/Sc@C82 composite nanorods at 5 K.

molecules or atoms to form composite structures. This method opens a new way for applying fullerenes in various nanotechnologies.

Acknowledgments

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References

1. Shinohara, H. (2000) *Rep. Prog. Phys.*, 63: 843.
2. Ginzburg, B.M. and Tuichiev, S.J. (2005) *Macromol. Sci. Phys.*, 44: 517.
3. Chubarova, E.V., Melenevskaya, E.Yu., Sudareva, N.N., Andreeva, O.A., Malachova, I.I., and Ratnikova, O.V. (2005) *J. Macromol. Sci. Phys.*, 44: 455.
4. Hou, J.G., Yang, J.L., Wang, H.Q., Li, Q.X., Zeng, C.G., Yuan, L.F., Wang, B., Chen, D.M., and Zhu, Q.S. (2001) *Nature*, 409: 304.
5. Cao, H.Q., Xu, Z., Wei, X.W., and Xue, Z.L. (2001) *Chem. Comm.*, 541.
6. Liu, H.B., Li, Y.L., Jiang, L., Luo, H.Y., Xiao, S.Q., Fang, H.J., Li, H.M., Zhu, D.B., Yu, D.P., and Xiang, X.B. (2002) *J. Am. Chem. Soc.*, 124: 13370.
7. Guo, Y.G., Li, C.J., Wan, L.J., Chen, D.M., Wang, C.R., Bai, C.L., and Wang, Y.G. (2003) *Adv. Funct. Mater.*, 13: 626.
8. Li, C.J., Guo, Y.G., Li, B.S., Wang, C.R., Wan, L.J., and Bai, C.L. (2005) *Advanced Materials*, 17: 71.