SIZE CONTROLLABLE PATTERNED GROWTH OF QUASI-SPHERICAL CARBON PARTICLES

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Abstract

In this paper, a novel method to synthesize size controllable patterns of quasi-spherical carbon particles, using anodic aluminum oxide as templates, was proposed. Appropriate flow rate of acetylene and reaction time helped the formation of size controllable patterns of quasi-spherical carbon particles. Both anodic aluminum oxide templates with cobalt catalyst and anodic aluminum oxide templates without any catalyst were used. The samples were characterized by field-emission scanning electron microscopy. The results showed that size controllable patterns of quasi-spherical carbon particles were obtained by controlling the reaction time and flow rate of acetylene using AAO template with cobalt catalyst.

Introduction

In recent years, various carbon materials, such as carbon nanotubes (CNTs) and spherical carbon particles, have received a great deal of attention because of their special atomic configurations and important applications. To synthesize these new carbon materials, many methods, such as arc discharge, high-energy electron irradiation, high-dose carbon ion implantation into metals, chemical vapor deposition (CVD) and plasma-enhanced CVD, have been developed. Among these methods, CVD, which usually employs transition metal (Fe, Co, Ni, Cu and so on) as catalysts, is considered to be efficient for the production of these advanced carbon materials. As a member of new carbon materials, spherical carbon particles, which can be potentially used in many aspects, such as single-electron devices, magnetic refrigerators, nanodiodes, nanotransistors, nanoball bearings and insulator lubricants, have been one of the important subjects of new carbon materials.

In recent years, photonic crystals (PCs) have attracted both theoretical and experimental attentions. The PCs with 2D structure, which are constructed by periodic dielectric materials, show the property of electromagnetic wave propagation similar to that of electron propagation in crystal. If the wavelength is of the dimensions of the periodic structure, a photonic band gap, that is, a frequency spectrum where no electromagnetic modes exist, can open up in two or three dimensions and lead to interesting phenomena of great theoretical and practical importance and potential applications in new optical devices. Our previous research revealed that fullerene based networks could be good candidates for absolute inhibition of transmission in the near infrared range for given orientations. Therefore, the fabrication of 2D PCs by periodically arranging onion-like fullerenes or carbon microspheres onto a substrate with different dielectric constant is of much research interesting.

It is well-known that CNTs have come to the growth of ordered arrays with controllable dimensions using anodic aluminum oxide (AAO) templates by CVD. However, there are few, if any, reports about the preparation of size controllable spherical carbon patterns up to now. Therefore, a reliable preparation method to control the dimension and location of spherical carbon particles is highly desirable for most applications as well as fundamental studies.

In this paper, a novel method to synthesize size controllable patterns of quasi-spherical carbon particles using AAO templates was proposed based on the consideration that the shape of a CNT with the length to diameter of 1 approaches sphere. To obtain size controllable patterns of quasi-spherical carbon particles instead of CNTs, it is essential to control experimental parameters, such as the flow rate of carbon source and reaction time. It is well known that the ways of using AAO templates to synthesize aligned CNTs can be classified into two categories. One is that hydrocarbon is deposited on the pore surface of an AAO template. In this case, CNTs were formed by the catalysis of an AAO template itself. The other approach is that hydrocarbon is deposited on the AAO template with Co catalyst. Considering the lower cost of AAO template itself, in addition to AAO templates embedded with Co catalyst, AAO templates without any metal catalyst were also used. The samples were characterized by JSM-6700F field emission scanning electron microscopy (FESEM). The results showed that size controllable patterns of quasi-spherical carbon particles were obtained by controlling the reaction time using AAO template with Co catalyst.

Experimental

In our experiments, commercial AAO templates with the pore diameters of about 50 nm were used. SEM image of AAO template was shown in Figure 1. It can be seen that the pore size was very uniform. Co catalyst nanoparticles were deposited in the bottom of the pores of the AAO templates by impregnation method. In order to make Co particles fully deposited in the bottom of the AAO template, the vessel, where an AAO template was placed, was vacuumed at first. Then 5 wt.% of cobalt acetate ($(CH_3CO_2)_2Co\cdot4H_2O$) aqueous solution was added into the vessel by peristaltic pump. After immerging in the solution for 20 min, the AAO template was taken out and dried.

The synthesis reactions were carried out in a tubular furnace, using acetylene as carbon source and Ar as carrier gas. First, AAO templates with Co catalyst were used. A quartz boat with an AAO template embedded with Co catalyst was placed in a horizontal quartz tube reactor at the isothermal zone. The AAO template with Co catalyst was reduced at 650 ℃ in a mixture of H_2 (20 $ml\cdot min^{-1}$) and Ar (180 $ml\cdot min^{-1}$) for 1 h after the tube was heated up to 650 ℃ in a steady flow of argon with 100 $ml\cdot min^{-1}$. Then, H_2 was turned off and the products were prepared by introducing C_2H_2 at a flow rate of 1 $ml\cdot min^{-1}$ for 30 min and 20 $ml\cdot min^{-1}$ for 3 min, respectively. Then the furnace was cooled to room temperature in Ar atmosphere. When AAO templates without any metal catalyst were used, the same process was repeated. The products were characterized by JSM-6700F field emission scanning electron microscopy (FESEM).

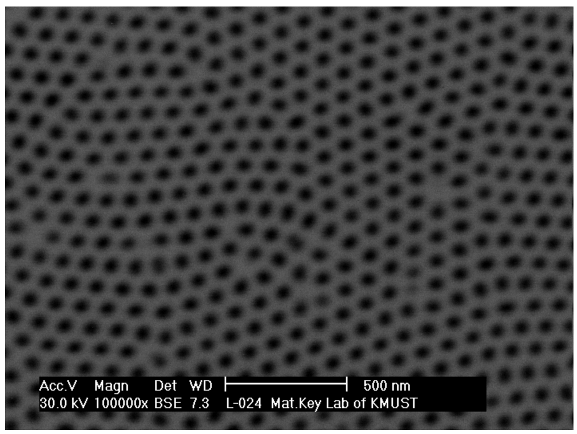

Figure 1. SEM image of an AAO template

Results and discussion

When the flow rate of acetylene was 1$ml\cdot min^{-1}$ and the reaction time was 30 min, the observation show that no products were deposited in the pores of both AAO templates without any metal catalyst and AAO templates with Co catalyst. Figure 2 shows FESEM images of products prepared with acetylene flow rate of 1 $ml\cdot min^{-1}$ and reaction time of 30 min. For the AAO templates with Co catalyst, only a few CNTs were observed on the surface of the AAO templates, and no carbon deposits were found in the pores, as shown in Figure 2(a). For the AAO templates without any metal catalyst, some amorphous carbon deposits and a few CNTs were found on the surface of AAO templates, no carbon deposits were observed in the pores of AAO templates either, as shown in Figure 2(b). These observations revealed that when the flow rate of acetylene was too low, it was very difficult for carbon to deposit in the pores by the two paths. On the other hand, these results also provided the information that it was not plausible to control the growth of aligned CNTs to synthesize size controllable patterns of quasi-spherical carbon particles by controlling the flow rate of carbon source.

When the flow rate of acetylene was raised to 20 $ml\cdot min^{-1}$ for a reaction time of 3 min, the results changed a lot. Figure 3 shows FESEM images of the samples at the reaction condition. It is important to know that CNT growth from a hydrocarbon precursor within an AAO template is always accompanied by overgrowth of CNTs from the pores or deposition of amorphous carbon on the surface of AAO templates. Figure 3(a) shows the overgrowth of CNTs from the pores of AAO templates with Co catalyst. In order to observe the carbon deposition in the pores, it is necessary to avoid the overgrowth of CNTs from the pores. In this experiment, the surface of AAO templates was cleaned by O_2 plasma. Figure 3(b) depicts FESEM image of the top surface of O_2 plasma cleaned AAO templates. The image showed that the overgrown CNTs on the surface were ablated successfully. And the patterned carbon particles were obviously observed. These particles were uniform in diameter of about 50 nm, close to the pore size of AAO templates. However, under the same reaction conditions, when AAO templates without any metal catalyst were used, only a few CNTs were observed on the surface and no carbon deposition was found in the pores. These observations proved that AAO templates with Co catalyst played a strong catalytic role, compared with AAO templates with any metal catalyst. At the same time, the observations, based on the AAO templates with Co catalyst by controlling the reaction time, revealed that quasi-spherical carbon particles would be obtained if the reaction time was further shorten. The research work is on-going and the detailed results will be reported later.

Conclusions

In summary, the size controllable patterns of quasi-carbon particles were obtained using AAO templates with Co catalyst by controlling reaction time and flow rate of acetylene, which will provide a new method to synthesize the periodic quasi-carbon particles.

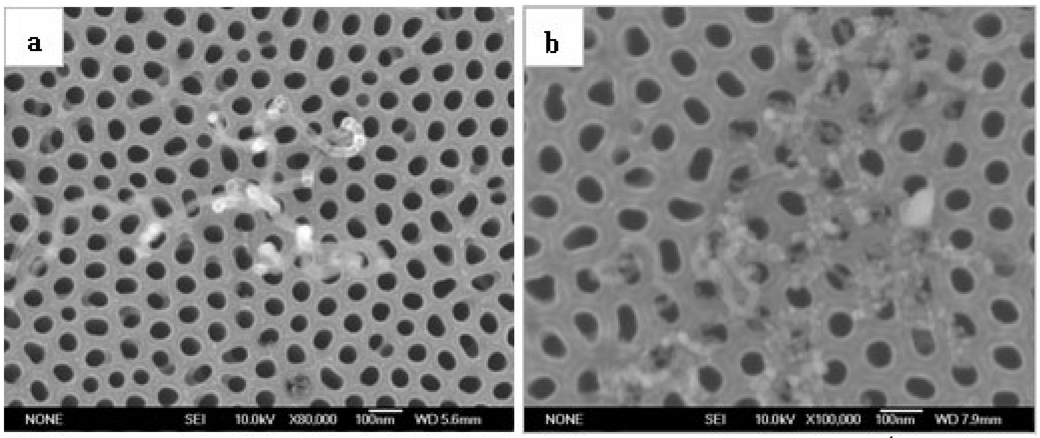

Figure 2. FESEM images of samples prepared when the flow rate of acetylene was 1 ml min^{-1} and the reaction time was 30 min. (a) using AAO templates with Co catalyst; (b) using AAO templates without any catalyst.

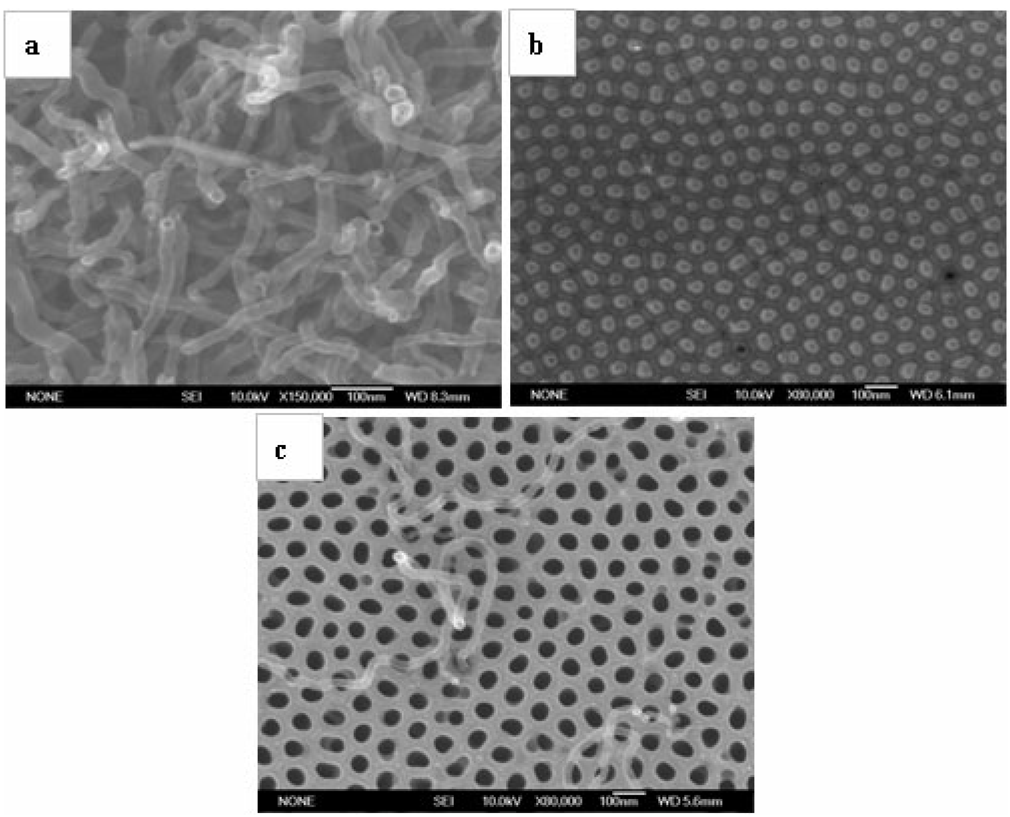

Figure 3. FESEM images of samples prepared when the flow rate of acetylene was 20 ml min^{-1} and the reaction time was 3 min. (a) the overgrowth of CNTs from the AAO template with Co catalyst; (b) the surface of the AAO template with Co catalyst after being cleaned; (c) using AAO templates without any catalyst.

Acknowledgements

This research work was supported by National Natural Scientific Foundation of China (GrantNo. 20471041, 20676086，20673072), Natural Science Foundation of Shanxi Province (Grant No.20051018,) and Shanxi Research Fund for Returned Scholars (Grant No. 200428). The authors gratefully acknowledge the support of K. C. Wong Education Foundation, Hong Kong.

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