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Nanoscale carbon tubules deposited in anodic aluminium oxide template: a study of soft x-ray transmission*

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Well-aligned, catalyst-free nanoscale carbon tubules array was prepared by organic compound vapour deposition method using anodic aluminium oxide (AAO) as a template. The experiment of soft x-ray channelling in such carbon tubules array deposited in AAO template was performed at Beijing Synchrotron Radiation Facility. The transmission of x-rays in carbon tubules array with AAO template support was found even higher than that in bare AAO template at high-energy part of energy spectrum though the porous area of the former was smaller than that of the latter. A qualitative explanation is presented to interpret our results.

Keywords: nanoscale carbon tubules, vapor deposition polymerization, optical properties
PACC: 6148, 8115J, 7865V

1. Introduction

Carbon nanotubes have been extensively investigated since their discovery in 1991 by Iijima,[1] not only because of their significance for fundamental researches but also for the potential applications in nanoelectronics,[2,3] nanodevices[4–7] and nanocomposites.[8,9] The hollow structure is an outstanding feature of carbon nanotubes, which provides a room for confined chemical reactions[10,11] and gives a good chance for transportation of matter,[12] propagation of waves[13] and channelling of high-energy charged or neutral particles in it.[14] Klimov and Letokhov[15,16] first pointed out that a carbon nanotube can emit hard x-rays or monochromatic γ-rays when high-energy charged particles pass through it. Zhevago and Glebov[14] have simulated the behaviour of charged and neutral particles (x-rays and neutrons) channelling in carbon nanotubes, which is similar to the channelling in crystals. Bellucci and Dabagov[17] have given a common theory about x-rays channelling in micro-capillary systems and nanotubes, as well as the contrast of the difference of these two cases. However, almost all efforts are dedicated to the theoretical aspect, whereas to our best knowledge no experiments have been carried out until now.

The experimental realization of channelling x-rays in carbon nanotubes may encounter the following difficulties. First, the carbon nanotubes produced by the common methods, such as arc-discharge, laser ablation and chemical vapour deposition (CVD), are generally disordered and entangled each other. Furthermore, extracting an individual carbon nanotube and

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performing x-ray transmission with it is difficult experimentally. In contrast, channelling x-ray through ordered, well-aligned carbon nanotubes array is easily realized. Second, most carbon nanotubes contain catalysts even after purification, and the catalysts whether located in carbon nanotubes or at the end of them will hinder the transportation of photons. So catalyst-free carbon nanotubes are desired.

Recently, we have successfully prepared well-aligned, catalyst-free nanoscale carbon tubule (NCT) array by using anodic aluminium oxide (AAO) as a template, and the as-prepared carbon tubules embedded in the channels of AAO are open at both ends. Compared with the generally referred carbon nanotubes, which roll up from one or several layers of two-dimensional graphite sheets with a less than 100nm inner diameter, the carbon tubules we prepared are made of amorphous carbon and have larger inner diameters (nearly 200nm). Furthermore, the carbon tubule array can overcome the difficulties in the soft x-ray channelling experiment mentioned above. In this article, we report the preliminary results of channelling soft x-rays in such a carbon tubule array. We have measured the transmission of soft x-rays through such a nanoscale carbon tubule array with an AAO template support and found that the transmission of the AAO/NCTs composite is higher than that of bare AAO template at the high-energy part of energy spectrum, though the porous area of AAO/NCTs composite has been decreased after NCTs growth.

2. Experiment

2.1. Sample preparation

AAO templates were purchased from Whatman (Anodisc13, 200nm diameter pores, 60μm thickness). The details of fabrication of well-aligned nanoscale carbon tubules were described in Ref.[18]. In brief, the AAO template was impregnated with 1M ethanol solution of paratoluene sulfonic acid (PTSA) for 1h, and dried at 90°C. Afterwards, the template was washed in alcohol for 30–50s to obtain the NCT which was open at both ends, then dried at the same temperature. Next the template was exposed to furfuryl alcohol vapours at 40°C for 3h. The AAO membrane was pressed between two quartz plates to ensure the flatness during heating in furnace. The polymerization of the deposited furfuryl alcohol and its subsequent carbonization in the channels of the alumina template were carried out by heating the impregnated sample under N_2 atmosphere up to 800°C (5°C/min) and holding it for 1h at this temperature. A typical scanning electron microscope (SEM, Philips XL 30 FEG) photograph of the as-prepared NCT array is shown in Fig.1.

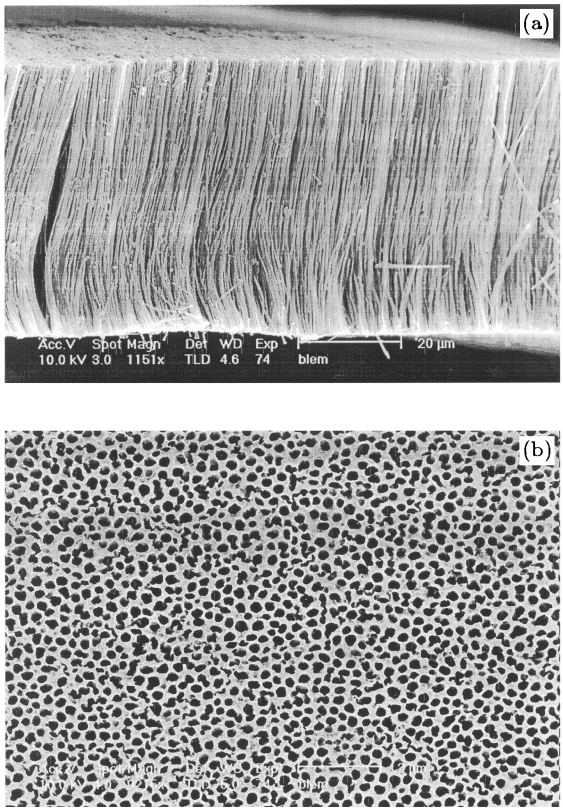


Fig.1. (a) NCT array released from AAO template. (b) Top view of NCT array with AAO template support.

2.2. Soft x-ray channelling in carbon tubule array embedded in AAO template

The soft x-ray channelling experiment was performed on the microfocused beamline 3W1B at Beijing Synchrotron Radiation Facility (BSRF). The schematic of the set-up is shown in Fig.2. The electron energy of store ring was 2.2GeV, and the intensity of beam flow was in the range of 60–100mA during the experiments. The pressure in the sample chamber was kept below 10^{-5} Pa. A circular diaphragm was placed at a distance of 280mm before the measured sample to confine the size of incident beam and ensure x-ray passing through the centre of the sample. A silicon photoelectronic diode detector (AXUV-100G, IRD, USA), which provided with a detected area of 10mm×10mm, was mounted 240mm behind the sample. The plane and rotary motions of the sample stage were controlled by a computer. The carbon tubule ar-

ray with the AAO template support was placed on the sample stage and kept perpendicular to the incident beam. Before each measurement, the sample stage and the detector were microadjusted so as to make the intensity received by the detector the strongest. In this state, we think the incident x-ray beam, the axes of carbon tubules and the detector are co-line.

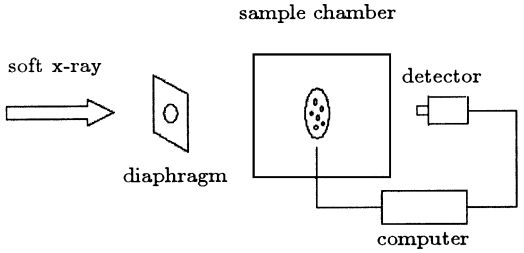


Fig.2. The schematic of the set-up of soft x-ray channelling in NCTs array embedded in AAO template.

3. Results and discussion

The incident photon energy was changed from 100 to 1520eV and the transmission spectra of the AAO/NCTs composites as well as bare AAO templates were measured. At first, to demonstrate that the microstructures of various AAO templates are resembled, three bare templates were scanned and their energy spectra are found to be almost the same. A typical curve of the transmission of the AAO/NCTs composite versus the incident photon energy is given in Fig.3 (a). It can be seen that the transmission of the AAO/NCTs composite increases with the increase of incident photon energy on the whole, which is intelligible because penetrability of x-ray will enhance when the photon energy increases. The decline of the transmission curve at about 1500eV can be attributed to the absorption edge of aluminium (1559.6eV), which resulted from the blocked channels of alumina template. The peak at about 700eV arises from the second-order harmonious wave of soft x-ray source itself. The transmission curve of the bare AAO template is also given in Fig.3 (a) as a contrast. The shapes of the two curves are similar, except that a higher transmission value is revealed in the curve of bare AAO template when the photon energy is less than 1300eV, and there is a peak at about 300eV in this curve. The origin of the peak at 300eV is not clear now.

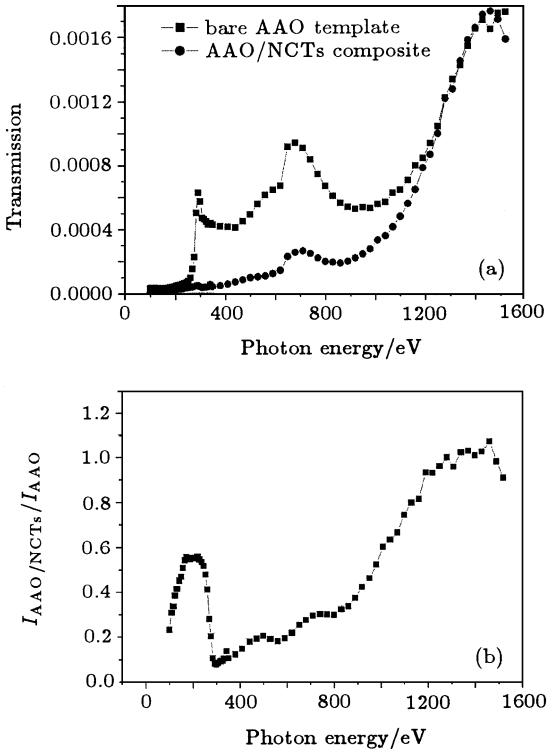


Fig.3. (a) The transmission spectra of AAO/NCTs composite and bare AAO template. (b) The ratio of transmission of the AAO/NCTs composite to that of the bare AAO template.

Figure 3 (b) shows a curve that represents the ratio of transmission of AAO/NCTs composite to that of bare AAO template. As shown in Fig.3 (b), the ratio first goes up and then falls down to a small value at about 300eV, which arises from the peak of the transmission curve of the bare AAO template at the same energy spot. Then the curve climbs gradually and at the high-energy part of the energy spectrum the ratio is even higher than unity. One should note that the average pore diameter of the bare AAO template is about 220nm,[1)] and the average wall thickness of the as-prepared NCTs is nearly 30nm. So after NCT growth, the porous area diminishes by more than forty percent on average. Figure 3 (b) describes such a fact that though the porous area of the AAO/NCT composite is smaller than that of the bare AAO template after NCT growth (so that the number of x-ray photons directly-passing through the nanochannels decreases), the transmission of soft x-ray within the range of 1300–1500eV channelling in the former is higher than that of the latter.

Here, a simple qualitative explanation is presented to interpret our results. We have mentioned above that the incident x-ray beam, the axes of the

[1)]The quoted pore diameter by Whatman Company is 200nm, however the actual pore diameter is 220nm on average according to SEM analysis.

channels and the detector were adjusted to be coline before each measurement. However, this does not mean that all the x-ray photons propagate along the axis of the channel. Instead, most of the x-ray photons will travel in a manner of multi-reflection between the inner walls of the channels due to all kinds of factors, just like the behaviour of electromagnetic waves in a cylindrical waveguide. X-rays impinging on the inner walls of the channels will experience total reflection provided that the incident angle is less than the critical angle. In addition, a portion of x-ray photons will be multi-reflected by the walls of the channels and absorbed eventually. Thus, the incident x-ray photons can be divided into the following three parts: (1) Very few photons pass through the channels directly, that is, without any reflection. (2) Some x-ray photons incident at a small glancing angle will be totally reflected by the inner walls of the channels with little loss of the photons if the channels are straight and the inner walls are smooth enough. (3) If the channels are serpentine and the inner walls are rough, some photons will be multi-reflected and eventually be absorbed by the inner walls before emerging from the channels.

As is known, the refractive index of matter for x-ray can be described as $n = 1 - \delta - \mathrm{i}\beta$, where δ and β are given by

$$\delta = \frac{n_{\mathrm{a}} r_{\mathrm{e}} \lambda^2}{2\pi} f_1; \quad \beta = \frac{n_{\mathrm{a}} r_{\mathrm{e}} \lambda^2}{2\pi} f_2. \tag{1}$$

Here, n_{a} is the atomic density and r_{e} is the classical electron radius, while f_1 and f_2 are the real and imaginary parts of the atomic scattering factor respectively. When x-ray photons are multi-reflected in the channels, the degree of refraction and absorption is tightly related to refractive index n, that is, the incident wavelength λ according to Eq.(1). So the detected intensity of x-ray from (2) is influenced by the values of n, while the intensity from (1) is only correlated to the dimension of the channels because this portion of photons does not interact with the inner wall of the channel. One can see clearly the dependence of transmission on the incident photon energy (i.e. incident wavelength) from Fig.3 (a). The transmission of bare AAO template is higher than that of AAO/NCTs composite when the photon energy is less than 1300eV, which indicates that the emerging x-ray photons mainly come from the contribution of (1) in this spectral range because the porous area of the bare AAO template is larger than that of the AAO/NCTs composite. If increasing the photon energy to more than 1300eV, the emerging photons due to the contribution from (2) begin to increase because the absorption coefficient of carbon is smaller than that of alumina for x-rays. Meanwhile, some photons which are absorbed (case (3)) in the case of bare AAO template may be emitted after NCTs growth just because of the decrease of absorption during the propagation. Therefore, the decrease of absorption of soft x-ray when channelling in the carbon tubule array can compensate the influence of transmission decrease due to the diminishing of porous areas of the channels of the template after NCT growth. Thus, the transmission of AAO/NCTs composite can be comparable or even higher than that of the bare AAO template at the high-energy part.

According to Fig.3, one also can see that the value of the transmission is very small. We note that 60μm is thick enough for alumina or carbon to hinder the soft x-rays to pass through, so the x-rays received by the detector are those completely coming from the hollow channels. We also investigate the SEM images of the surface of AAO template and find that the porous area of the surface of template accounts for 30–40 per cent of the whole area. Therefore, the fact of a small transmission may only be interpreted as follows: most of the channels of the AAO membrane cross each other, and few channels are absolutely hollow so that the x-rays are blocked off, thus leading to a very small transmission. It can be expected that if all of the channels are parallel to each other and remain hollow from one end to the other, the transmission will enhance remarkably.

In conclusion, we have prepared well-aligned, catalyst-free nanoscale carbon tubule array and carried out the soft x-ray channelling experiment through such NCT array for the first time, to our best knowledge. Although the as-prepared NCTs are different from the generally referred carbon nanotubes, our results can pave the way for further study of the propagation behaviour of x-rays in carbon nanotubes. In this paper, it is shown that the transmission of the AAO/NCTs composite is comparable to or even higher than that of the bare AAO template when the photon energy is lager than 1300eV. We present a simple qualitative explanation. Though the transmission is small, our results have shown the possibility of such NCTs to serve as x-ray waveguides, which may be important for x-ray imaging, x-ray microscopy and x-ray lithography in future. Further investigations about

the propagation properties of x-ray in nanoscale carbon tubules are under way.

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