

Novel Fabrication of ZnO Film-coated Carbon Nanotube Arrays in Modified AAO Membrane

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The AAO membrane was modified by immersion within $\text{Zn}(\text{NO}_3)_2$ solution. Zinc-containing film would be formed over the inner surfaces of membrane. Using this as template, ZnO film-coated carbon nanotube arrays were fabricated in plasma-enhanced CVD.

Zeolite, porous silica, anodic aluminum oxide, and other porous material have been extensively used in templated preparation of carbon nanotubes.¹⁻⁴ In order to extend their applications in fields of catalysis, optics, sensors, microelectronics, field emission, and others, it is necessary to decorate the nanotubes with nanoparticles or thin films. For preparation of nanoparticle-doped carbon nanotubes, several methods have been proposed. As the inert graphite surface is oxidized by strong acid, some active organic groups can be generated to provide a point to joint foreign nanoparticles. But it is difficult to prepare film-coated nanotubes using this method.

Up to now, reports were seldom released on the preparation of film-coated nanotubes. In Nagatsu's work, a large-area surface-wave plasma device was used both for growth of multiwalled carbon nanotubes on Ni-evaporated Si substrate and then for deposition of thin α -C layer over carbon nanotubes.⁵ Yi and co-worker prepared vertically aligned multiwalled carbon nanotubes by hot filament plasma-enhanced chemical vapor deposition. The nanotubes were then coated with either a SiO_2 or MgO film by a magnetic sputtering method.⁶ In Shi's experiments, ultrathin pyrrole films were deposited on disordered carbon nanotubes using plasma polymerization treatment.⁷ Unfortunately, the above methods were not suitable for template-preparation of nanotubes owing to the short distance between nanotubes.

In our previous work, several nanoparticle-doped carbon nanotube arrays have been fabricated by modifying the inside structure of AAO membrane, i.e., preloading nanoparticles within membrane.⁸⁻¹⁰ It is obvious that the modified membrane can determine the morphology of nanotubes. If thin solid film is made over the inner surfaces of AAO membrane, film-coated nanotube arrays would be conveniently fabricated. In this paper, ZnO film-coated carbon nanotube arrays are fabricated by this novel method.

Nanoporous anodic alumina membrane (Anodisc 47, 200 nm) was commercially obtained and used as received. The preparation process is summarized in Figure 1. Membrane was immersed into aqueous $\text{Zn}(\text{NO}_3)_2$ solution (1 M) for 12 h. It was dried at 50 °C for 8 h and then calcined at 550 °C for 3 h in air (step A). During this process, ZnO film was formed over the inner surfaces of membrane.

Corona-discharge-enhanced CVD technique was used to prepare carbon nanotubes (step B). The experimental setup

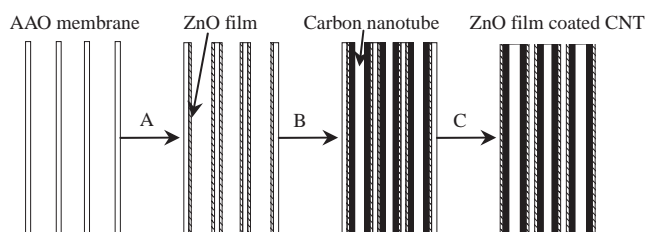


Figure 1. Schematic diagram of templated preparation of ZnO film-coated carbon nanotubes.

and preparation conditions have been introduced in a previous report.¹⁰ After plasma reaction, the as-prepared carbon nanotubes were released from membrane in 1 M aqueous NaOH solution (step C). The microscopic features of the sample were observed with a TECNAI-F20 transmission electron microscope (TEM, 200 kV) and a Philips XL 30 scanning electron microscope (SEM).

Figure 2 shows the SEM image of as-prepared carbon nanotubes. Their diameter is ca. 200 nm, similar to the membrane nanopores. The outer walls of these carbon nanotubes are obviously not smooth, which is much different from previously made carbon nanotube at the same scale. Carbon nanotubes seem to be coated with a thin film on the outer surface.

The TEM images of nanotubes are shown in Figure 3, from which two kinds of nanotubes are clearly found. They both have similar diameter, which is due to the uniform size of AAO nanopores. But they are much different in brightness, i.e., the wall thickness of nanotubes. They are enlarged in Figures 3b and 3c, in which the wall thickness of the dark nanotube (B) is ca. 70 nm, and the wall thickness of the bright nanotubes (A) is ca. 30 nm. After detailed analysis, nanotube (A) is not integrated, and this nanotube is indeed composed of many small flat particles. The gaps among particles are clearly seen. In Figure 3c,

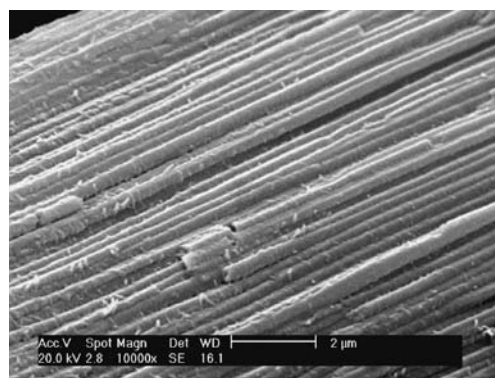


Figure 2. SEM image of ZnO film-coated carbon nanotube arrays.

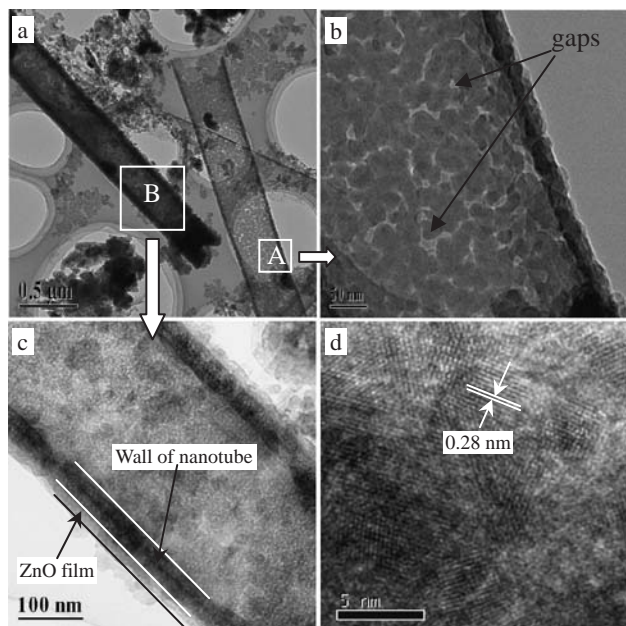


Figure 3. TEM images of ZnO film-coated carbon nanotube.

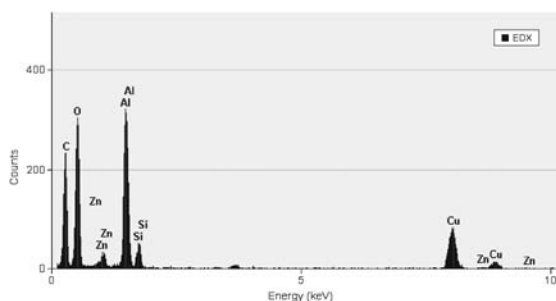


Figure 4. EDX spectrum of ZnO film-coated carbon nanotube.

the wall of nanotube (B) can be divided into two parts. It can be concluded that the inner nanotube is covered with the outer thin film, which is accordant with the SEM analysis. Therefore, nanotube (A) and nanotube (B) are not the same.

The high-resolution transmission electron microscopy (HRTEM) image of the outer thin film of nanotube (B) is shown in Figure 3d. The surface structure of the film is clearly resolved, and the lattice fringes can be clearly seen. Among the possible carbon-containing or zinc-containing compounds, the 0.28-nm lattice fringes of it are indexed to ZnO(100) lattice planes. In addition, the EDX spectrum of the nanotubes (B) is shown in Figure 4, which indicates the existence of C and Zn elements. Therefore, it can be concluded that nanotube (B) is ZnO film-coated carbon nanotubes. The carbon nanotubes are composed of disordered graphene layers, and the layers are not parallel to the tube axis. These template-prepared carbon nanotubes have been extensively researched in previous work.^{4,9}

The HRTEM and EDX characterization of nanotubes (A) also indicate the existence of ZnO and C elements. But this nanotube is different from ZnO film-coated carbon nanotubes in morphology. The authors think nanotube (A) should be ZnO nanotube. The C element in EDX spectrum might be resulting from oil vapor in the sample chamber.

In template preparation, modification of the template can determine the morphology of nanotubes. The modified membrane is the secondary template for preparation of nanotube. The ordinary and simple method to modify AAO membrane is incipient wetness impregnation, which can load nanoparticle or film onto the inner surface. The morphology of metal or metal oxide in membrane is heavily depended on the metal precursor and their interaction with alumina. As to the nitrate salts of Ni, Pt, and La,^{8–10} they are thermally decomposed into metal or metal oxide particles in AAO membrane during calcinations. As to the nitrate salts of Ag and Ce,^{11,12} they are decomposed into thin film. It is thought that strong interaction of AgNO₃ and Ce(NO₃)₃ make them homogeneously adsorbed over the inner surface of AAO membrane.

ZnO/Al₂O₃-based catalysts have been extensively studied for their application to carbon monoxide partial oxidation. The interaction of ZnO with Al₂O₃ support has been extensively investigated. Maezawa and co-workers found zinc ions are highly dispersed in ZnO/Al₂O₃ catalysts, owing to the strong interaction with alumina.¹³ In Zou's work, ZnO is also well dispersed on the surface of 10% ZnO/Al₂O₃ sample.¹⁴ ZnO/Al₂O₃ sample with higher Zn loadings shows the phase of ZnO. In this paper, when AAO membrane is immersed into aqueous Zn(NO₃)₂ solution, zinc ions soon adsorbed over the inner surfaces of membrane, forming thin Zn(NO₃)₂ film. When calcined in air, Zn(NO₃)₂ is thermally decomposed into ZnO, so ZnO nanotube arrays are formed within AAO membrane. During corona-discharge-enhanced CAD process, carbon species are deposited within ZnO nanotube/AAO composite. After removing AAO membrane by alkaline treatment, ZnO film-coated carbon nanotubes are formed. If the entrances of ZnO nanotube/AAO composite are blocked, carbon deposition does not occur in the nanopores, ZnO nanotube will be retained, just as shown in Figure 3.

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