Water-Dispersible and Magnet-Responsible Carbon Nano Test Tubes with Controlled Size

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Abstract

Uniform carbon nano test tubes including magnetic metal particles inside their one-dimensional cavities were synthesized by the template method. The "as synthesized" metal-filled test tubes (35 nm in diameter and 1400 nm in length) were dispersible in ethanol, but not in water. To improve the water-dispersibility of the test tubes, their surface was treated with hydrogen peroxide and, as a result, they became water-dispersible and kept the dispersion state for several months. The tubes dispersed in water are responsive to an external magnetic field. If drugs, proteins or other biomacromolecules are incorporated into the cavities of such metal-filled test tubes, they would be useful for the delivery of biomacromolecules to a target tissue by a magnetic field.

Introduction

Nanocarbon materials are one of the possible candidates as a carrier for drug and gene delivery system (Pantarotto et al.), since carbon has less toxicity and its surface modification is very easy. The delivery by using a magnet has been proposed (Häfeli et al.) as one of the delivery methods. In this technique, a carrier conjugated with a magnetic material is leaded to a target tissue by an external magnetic field. However, nanocarbons useful for such applications have rarely been reported except for a few studies (Utsumi et al.).

Very Recently, we have succeeded in the synthesis of carbon nano test tubes with tunable size both in diameter (10 nm~) and length (~10 μm) by using nanochannels of an anodic aluminum oxide (AAO) film as a template (Orikasa et al.). Since the tubes are water-dispersible and one of their ends is always open, they can be used as a capsule for the delivery system. In the present study, with the future application to the magnetic drug delivery system in mind, we attempted to introduce a magnetic material into the nano test tubes and to synthesize water-dispersible and magneto-responsive carbon tubes.

Experimental

The synthesis processes of the metal-filled carbon nano test tubes are illustrated in Figure 1. First, the AAO layer was formed by the anodization of an electropolished Al substrate, followed by chemical etching for its pore widening. As a result, the diameter of nanocahnnels in the AAO film was controlled to about 35 nm. Second, carbon was deposited uniformly on the inner wall of the nanochannels together with the outer surface of the film by acetylene chemical vapor deposition at 600 °C. To introduce Ni-Fe alloy into the cavities of the nano test tubes, conventional electroplating was conducted using the carbon-coated film as an anode. Its experimental details are described elsewhere (Wang et al.). Usually excess amount of metal was deposited on the outer surface of the coated AAO substrate, but the metal could easily be peeled off. Then the carbon deposited on the outer surface was completely etched by oxygen plasma treatment, and both AAO layer and Al substrate were removed by washing with NaOH aqueous solution. Finally, the metal-filled test tubes were cleaned through the repetition of careful centrifugation and washing, and collected by filtration. The resulting test tubes were immersed in H_2O_2 (30 wt%) at 50 °C for 1h to improve their water-dispersibility.

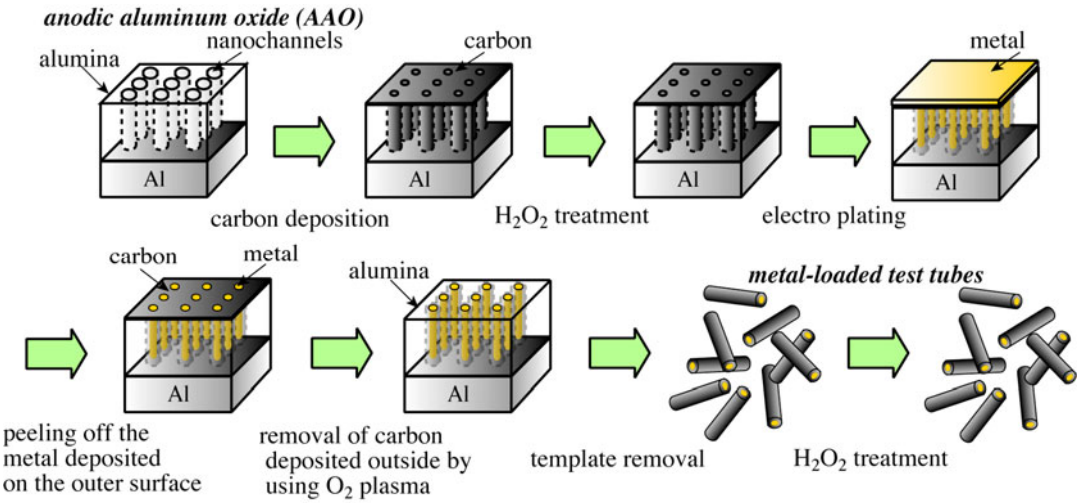

Figure 1. Schematic of synthesis process of metal-filled carbon nano test tubes

Results and discussion

Figure 2 shows transmission electron microscope (TEM) images of the metal-filled nano test tubes after the H_2O_2 treatment. There are many uniform carbon nano test tubes with a diameter of about 35 nm and each of the tubes contains a large number of nano particles. The minimum caliper size of the particles is almost the same as the tube inner diameter (around 25 nm). From the analysis of their TEM images, it is estimated that the particles occupy about 21 vol.% of the tube cavities.

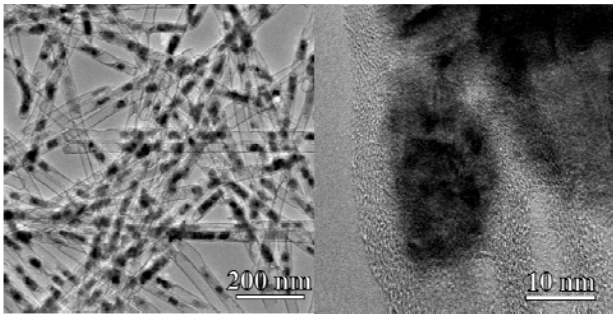

Figure 2. Metal-filled carbon nano test tubes after H_2O_2 treatment

In an X-ray diffraction (XRD) profile of the metal-filled test tubes, a broad peak (around 24 °) and two sharp peaks were observed. The former peak can be attributed to carbon 002 layers stacking and the latter ones are due to the presence of Ni-Fe alloy nano particles in the tube cavities, as observed in Figure 2. It is well known that lattice spacings of Ni-Fe alloy vary with its composition. From the lattice spacing obtained from the XRD peak for 111 diffraction (d = 0.3577 nm), Ni/Fe atomic ratio was estimated to be about 50/50. The measurement of the magnetization curve revealed that the metal-filled tubes show ferromagnetism with high coercivity (1300 Oe). These findings clearly indicate that magnetic metal was successively introduced into the cavities of the test tubes.

As described in Introduction, the empty carbon nano test tubes are water-dispersible, because of the presence of an electric double layer on the outer surface of each tube. However, it was found that the metal-filled nano test tubes without H_2O_2 treatment were not dispersible in water. Upon the H_2O_2 treatment, they became water-dispersible (Figure 3), and this dispersed state could be kept at least for several months. The observed improvement of the water dispersibility by the H_2O_2 treatment should be ascribed to the increase in the amount of oxygen-containing functional groups on the tube surface. In fact, X-ray photoelectron spectroscopic analyses indicated that O/C atomic ratio on the surface was increased by the H_2O_2 treatment from 0.14 to 0.21. As a result, the repulsive force due to the electric double layer became strong enough to overcome the attractive force that works among the ferromagnetic metal-filled tubes.

To investigate the response to a magnetic field, a magnet (neodymium magnet, surface inductive flux = 4500 Oe) was kept near a vial containing water dispersion of the metal-filled test tubes. Figure 4 shows a change of the dispersion state with time. The tubes were attracted by the magnet, and the color of the dispersion liquid was changed from dense black to transparent and colorless over a period of hours. After the removal of the magnet, the tubes were re-dispersed by mild agitation in several seconds and again kept the dispersion state. This peculiar magneto-responsive behavior has never been reported for any carbon materials and is quite favorable as a carrier for the delivery of biomacromolecules by a magnetic field.

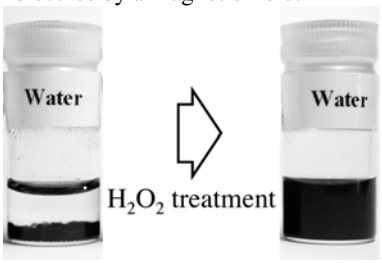

Figure 3. Change in water-dispersibility of metal loaded carbon nano test tubes by H_2O_2 treatment

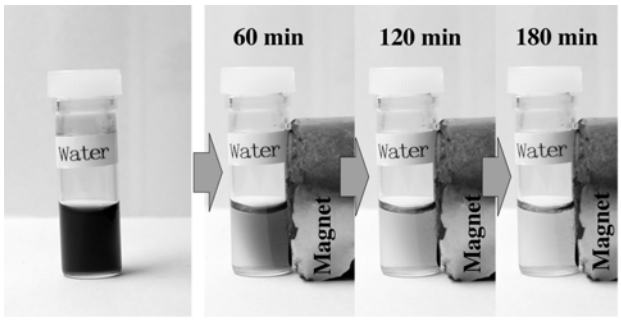

Figure 4. Magneto-responsive behavior of water-dispersible carbon nano test tubes

Conclusion

In conclusion, carbon nano test tubes including Ni-Fe alloy particles were synthesized, and it was demonstrated that they are water-dispersible and responsive to an external magnetic field. If the encapsulation of drugs, proteins and others together with magnetic metals into the cavities of the test tubes is achieved, the tubes could successfully be used as a capsule for the delivery of drugs and biomacromolecules to a target tissue by an external magnetic field.

References

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