Template synthesis of water-dispersible and magnetically responsive carbon nano test tubes†

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Water-dispersible and magneto-responsive carbon nano test tubes with a controlled length (1.3 μm) and diameter (35 nm) were synthesized by using the nanochannels of anodic aluminium oxide as a template.

Very recently, by using the nanochannels of an anodic aluminium oxide (AAO) film as a template, we have succeeded in the synthesis of water-dispersible carbon nano test tubes (CNTTs) with tunable size both in diameter (10 nm ∼) and length (∼ 10 μm).[1] Since one end of each CNTT is always open, it is possible to introduce other materials into the cavities of the CNTTs. If magnetic materials are loaded into the CNTTs and the CNTTs keep their water-dispersibility even after the loading, they are useful in many fields of applications. For example, when drugs or biomacromolecules are introduced into such magneto-responsive CNTTs, they are applicable as carriers for magnetic delivery system, where the carriers are guided to a target tissue by an external applied magnetic field. So far many types of magnetically responsive nanocarbons have been prepared for this purpose,[2–5] but none of them are completely free from serious problems such as the lack of water-dispersibility[2,4,5] and size-controllability.[3,5] Needless to say, both of these properties are indispensable for such biomedical applications. Here we report the synthesis of size-controlled, water-dispersible and magneto-responsive CNTTs. Moreover, we try to estimate the interaction potentials that work among the metal-loaded CNTTs and understand the effect of the magnetic interaction on the water-dispersibility.

A synthesis process of the magneto-responsive CNTTs is illustrated in Fig. S1 in Supporting Information†. Briefly, an AAO layer with a large number of nanochannels was prepared by the anodic oxidation of an aluminium substrate in sulfuric acid. The size of the nanochannels was controlled to 35 nm in diameter and 1.5 μm in length. Then carbon was deposited uniformly on the whole inner walls of the nanochannels together with the outer surface of the resulting AAO layer. For the metal loading into the cavities of the carbon-coated nanochannels, the electro deposition of NiFe alloy was performed by the method employed in our previous research.[2] This electroplating process was followed by oxygen plasma treatment for the removal of the carbon layer deposited on the external AAO layer. Upon the liberation from the AAO template by alkaline treatment, metal-loaded CNTTs were obtained as insoluble matter. They were then subjected to the surface oxidation treatment with H_2O_2 to improve the hydrophilicity of the CNTT outer walls.

TEM images of the CNTTs synthesized are shown in Fig. 1, where CNTTs with a diameter of about 35 nm are observed and they contain many small particles inside the tube cavities. It should be noted that no particles are present outside the cavities (Fig. 1a). The lengths of 36 tubes were measured using two TEM images with different sights and the result was found to be 1280 ± 130 nm (tubes with a length less than 1000 nm were not counted because they were probably cut during the washing process). The length of each tube should correspond to that of the thickness of the original AAO layer (1500 nm), but it is a little shorter and has some small variation. Such non-uniformity can be ascribed to the plasma treatment, which not only removed the external carbon layer but also may slightly etch the carbon inside the AAO nanochannels near the external surface. The higher magnification image (Fig. 1b) reveals that the minor axis of the particle is around 25 nm, which is the same as the inner diameter of the CNTTs, and the thickness of the carbon tube wall is around 5 nm. A selected area electron diffraction (SAD) pattern from several metal-loaded CNTTs is shown in Fig. 1c. Many bright diffraction spots and two evident rings constituted of bright spots were observed, all of which can be assigned to the diffraction from NiFe alloy crystals. In addition, diffused rings that can

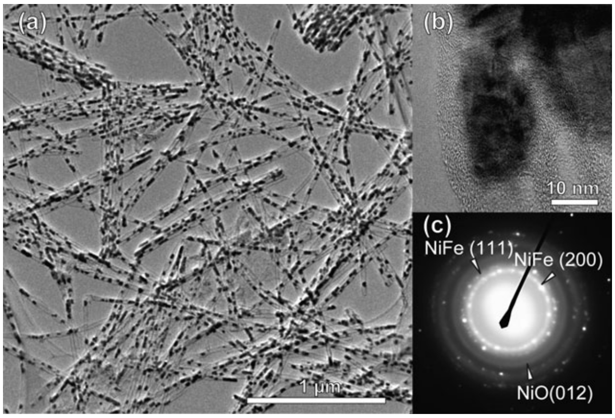

Fig. 1 TEM images and SAD pattern of metal-loaded CNTTs.

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† Electronic supplementary information (ESI) available: Details of the synthesis method for magnetic metal-loaded CNTTs (Fig. S1), their XRD profile (Fig. S2), and the analysis of their water-dispersibility (Fig. S3–5). See DOI: 10.1039/b800475g

be ascribed to NiO are present, indicating that the NiFe is partially oxidized to NiO. Since the diffused rings from NiO were observed even in the sample before the H_2O_2 treatment, NiO may be formed during air exposure and/or the alkaline treatment for the AAO removal.

In an XRD profile of the metal loaded CNTTs (Fig. S2†), two well-defined peaks were observed together with a broad peak (around 24°) derived from carbon layer stacking. The former two peaks are assigned to NiFe alloy, but there was no peak from NiO. Probably the crystalline size and/or the amount of NiO are too small for the XRD analysis. The magnetization curve of the metal-loaded CNTTs (Fig. 2, measured with a vibrating sample magnetometer at room temperature) shows a clear hysteresis loop, proving the sample to be ferromagnetic. In the magnetization curve, the CNTTs hold a significantly large coercivity over 1000 Oe, although the coercivity of NiFe alloy is generally less than 130 Oe despite its composition.[6] Such large coercivity would originate from the exchange anisotropy induced by interfacial exchange coupling between the ferromagnetic NiFe and the antiferromagnetic NiO.

As we have already reported, empty CNTTs are dispersible in both ethanol and water without any post-treatment.[1] However, for the metal-loaded CNTTs, they are dispersible in ethanol but not in water. Surface oxidation by using H_2O_2 is necessary to make the metal-loaded CNTTs water-dispersible (Fig. 3). The achieved dispersed state in water could be kept at least for a month. When a magnet (neodymium magnet, surface inductive flux = 4500 G) was put near a vial of the water dispersion, the CNTTs were slowly attracted by the magnet, and the color of the dispersion liquid changed over a period of hours from dense black to transparent and colorless (Fig. 4). After the removal of the magnet from the vial, the agglomerated CNTTs could be re-dispersed by mild agitation for several seconds. This observed magneto-responsive property shows promise as carriers for the delivery of bio-macromolecules.

The improvement of the water dispersibility upon the H_2O_2 treatment would be attributed to an increase in the amount of acidic oxygen-containing functional groups on the carbon surface. Indeed, X-ray photoelectron spectroscopy analysis indicated that O/C atomic ratio on the surface was increased by the H_2O_2 treatment from 0.14 to 0.21. Furthermore, the ζ-potential measured in neutral water was negatively increased by the treatment (Table 1). Such increase in ζ-potential fostered the repulsive force among the CNTTs due to their electric double layers (EDL) and the dispersibility was improved, as a result. However, the increase in ζ-potential cannot fully explain the change in the water dispersibility.

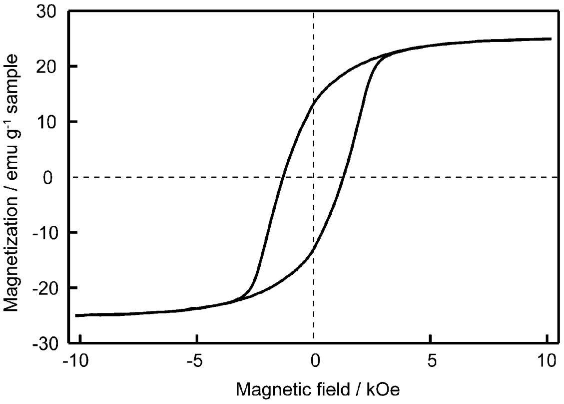

Fig. 2 Magnetization curve of magnetic metal-loaded CNTTs.

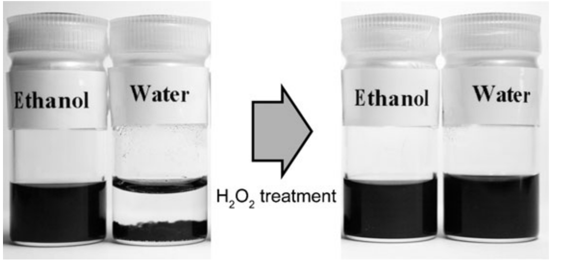

Fig. 3 Change of the dispersion state of magnetic metal-loaded CNTTs upon the H_2O_2 treatment.

To evaluate the water-dispersibility more quantitatively, ‘salting-out’ of the CNTTs was performed by the addition of KCl aqueous solution into the water suspension (0.02 mg metal-loaded CNTTs in 1 mL of water). The results of the salting-out are summarized in the third column of Table 1. For empty CNTTs, irrespective of the H_2O_2 treatment, they are water-dispersible and keep the dispersed state until the KCl concentration reaches 0.040 mol L^{-1} (treated) and 0.015 mol L^{-1} (non-treated).[1] However, for the metal-loaded CNTTs, the non-treated ones are not water-dispersible, and even for the treated ones, they precipitated when the KCl concentration was 0.004 mol L^{-1} or higher. Obviously, the metal-loaded CNTTs are less dispersible than both types of empty CNTTs, suggesting that an attractive force that works among the magnetic metal particles present inside the cavities of the CNTTs affects the water-dispersibility.

To understand the effect of the magnetic interaction on the water-dispersibility, the interaction between two metal-loaded CNTTs was roughly estimated by using a simple model, where the carbon wall of a part of one CNTT is simplified to a flat graphite plate (100 nm in length, 35 nm in width and 5 nm in thickness) and a spherical NiFe particle with a diameter of 25 nm is placed in contact with the graphite plate (see the inset of Fig. 5). The area of the graphite plate (100 nm × 35 nm) corresponds to the projected area of one CNTT with a length of 100 nm. Since we assume in this model that the 25 nm

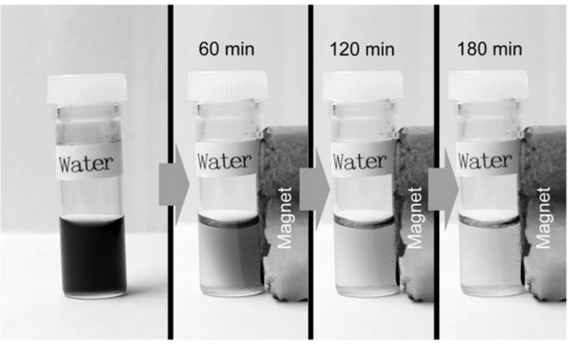

Fig. 4 Magneto-responsive behavior of metal-loaded CNTTs dispersed in water.

Table 1 ζ-Potential and critical aggregation concentration of KCl for various types of CNTTs

Sample	ζ-Potential/ mV	Critical aggregation concentration of KCl/mol L^{-1}
Empty CNTTs without H_2O_2 treatment	−29	0.015[a]
Empty CNTTs with H_2O_2 treatment	−39	0.040
Metal-loaded CNTTs without H_2O_2 treatment	−25	n.a.[b]
Metal-loaded CNTTs with H_2O_2 treatment	−37	0.004

[a] From ref. 1. [b] Not dispersible in water.

diameter particle is present in the 100 nm length CNTT, the metal filling ratio corresponds to about 25% and this value is almost the same as the actual filling ratio determined from the CNTTs in the TEM image (Fig. 1). The repulsive potential due to the presence of EDL, van der Waals potential between the two graphite plates, and the magnetic dipole–dipole interaction between two metal particles were calculated (details of the calculation are available in Supplementary Information†). The resulting three potential curves are plotted in units of kinetic energy (kT) under two different ionic strengths (0.0001 mol L^{-1} and 0.001 mol L^{-1}) at 25 °C in Fig. 5, where the sum of the three curves, *i.e.* an overall potential curve is also drawn. In both ionic strengths, the magnitude of the magnetic interaction is comparable with that of the repulsive interaction of EDL. In other words, the magnetic interaction certainly affects the water-dispersibility.

When the ionic strength is low (0.0001 mol L^{-1}), there is an energy barrier high enough to overcome the energy of Brownian motion (kT) at around the distance of 20 nm. The CNTTs can thus keep their dispersed state. On the other hand, under the higher ionic strength (0.001 mol L^{-1}), a valley of the potential was observed at around the distance of 50 nm. Since the bottom of the valley is deep enough to be metastable, the metal-loaded CNTTs should form agglomerate. Indeed, in the salting-out experiment, the metal-loaded CNTTs precipitated at 0.004 mol L^{-1} (Table 1) and this value is not far from the value estimated based on the present simple model ($\sim$0.001 mol L^{-1}).

When one increases the filling ratio of the metal in the CNTTs, the magnetic interaction is negatively increased, and consequently, the potential barrier is decreased. For the model employed here, the potential barrier becomes comparable with the thermal energy (kT) when the filling ratio is over 50% (Fig. S4†). In other words, the metal-loaded CNTTs with a filling ratio higher than 50% are not water-dispersible even after the H_2O_2 treatment. To improve the water-dispersibility of CNTTs with a higher metal-filling ratio, further surface modification might be effective. Alternatively, to employ CNTTs with thicker carbon wall would be useful. When the carbon wall is thicker, the magnetic interaction is reduced relative to the repulsive interaction. From our rough estimation, even for fully metal filled CNTTs, they would be water-dispersible when the thickness of the carbon wall is over 15 nm (Fig. S5†).

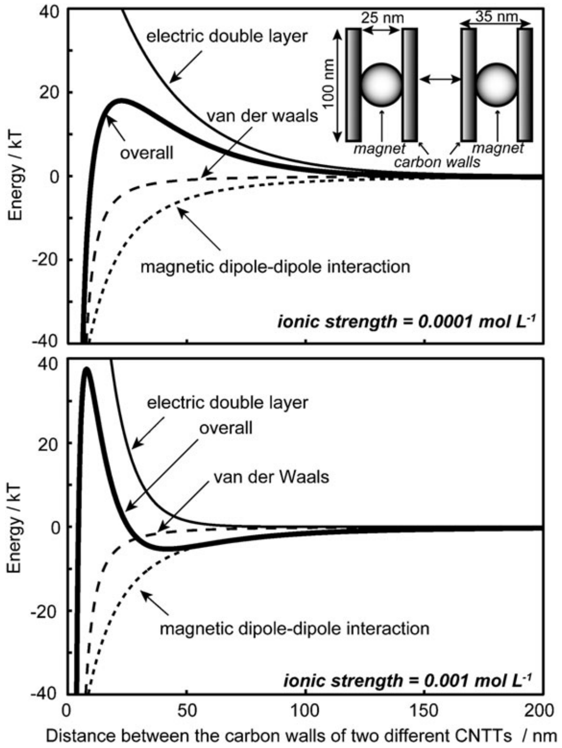

Fig. 5 Potential curves that works between two metal-loaded CNTTs.

In summary, well size-controlled CNTTs including NiFe alloy particles inside the tube cavities were successfully synthesized. They are water-dispersible and responsive to a magnetic field. In addition, their water-dispersibility was analyzed in a semi-quantitative manner, and the analysis revealed that the magnetic interaction substantially affects the water-dispersibility.

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