

Electric Supplementary information for:

Template Synthesis of Water-Dispersible and Magnetically Responsive Carbon Nano Test Tubes

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1. A synthesis process of the magnetic metal loaded CNTTs

A synthesis process of the magnetic metal-loaded CNTTs is illustrated in Fig. S1. The AAO layer with a large number of nanochannels was prepared on an aluminum substrate by its anodic oxidation in 20 wt% sulfuric acid at 20 V, 10 °C, and the size of the nanochannels is controlled to 35 nm in diameter and 1.5 μm in length. Then carbon was deposited uniformly on both the inner walls of the nanochannels and the outer surface of AAO by a chemical vapor deposition using acetylene (20 vol% in N₂) at 600 °C. The resulting carbon-coated substrate was treated by 10 wt% H₂O₂ at 60 °C for 1h to increase the wettability to the plating aqueous solution of Ni-Fe alloy. The electro deposition of Ni-Fe alloy into the cavities of the carbon-coated AAO was performed potentiostatically for 30 min at 20 °C by using a conventional two electrode cell.¹ The metal deposits both on the top surface of the substrate and inside the cavities, but the metal deposited on the top surface can easily be peeled off by tweezers. Then, the external surface of the substrate was exposed to oxygen plasma (100 W, 90 s, Yamato PR301S) and the carbon deposited on the substrate outer surface was removed. Then, the substrate (AAO and Al) was dissolved by 3 M NaOH. After the template removal and careful washing of the liberated CNTTs by using a centrifugal separator, the surface of the metal loaded CNTTs was oxidized by H₂O₂ (30 wt%) at 50 °C for 1 h to improve the surface hydrophilicity.

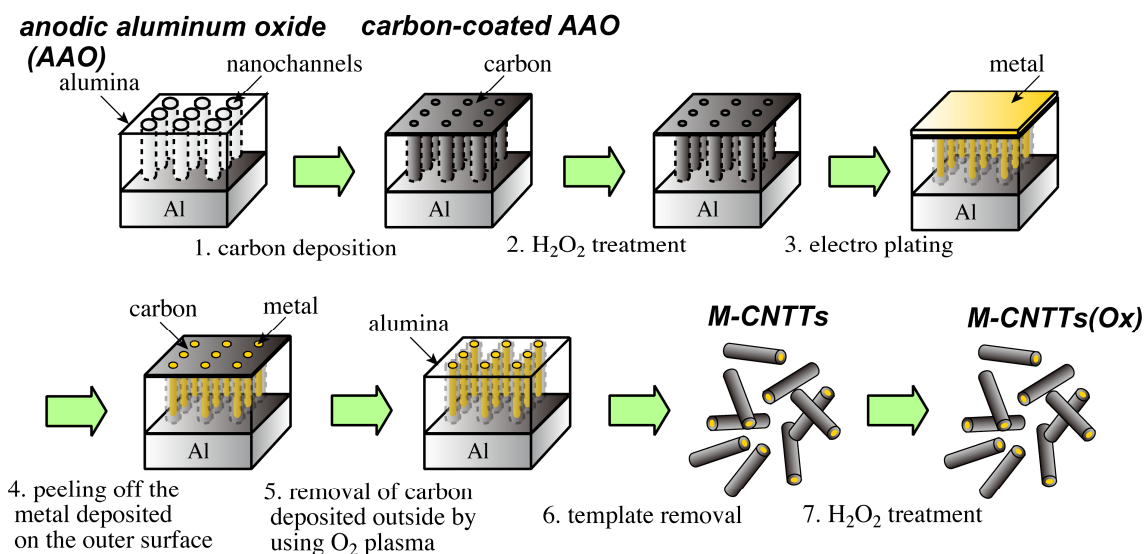


Fig. S1 A synthesis process of the magnetic metal loaded CNTTs

2. XRD profiles of magnetic metal-loaded CNTTs.

In an XRD profile of the metal loaded CNTTs, a broad peak (around 24°) and two well-defined peaks were observed irrespective of the H_2O_2 treatment. The former peak is attributed to carbon 002 layer stacking, and the latter peaks are assigned to Ni-Fe alloy. However, no NiO peak was observed (Fig. S2).

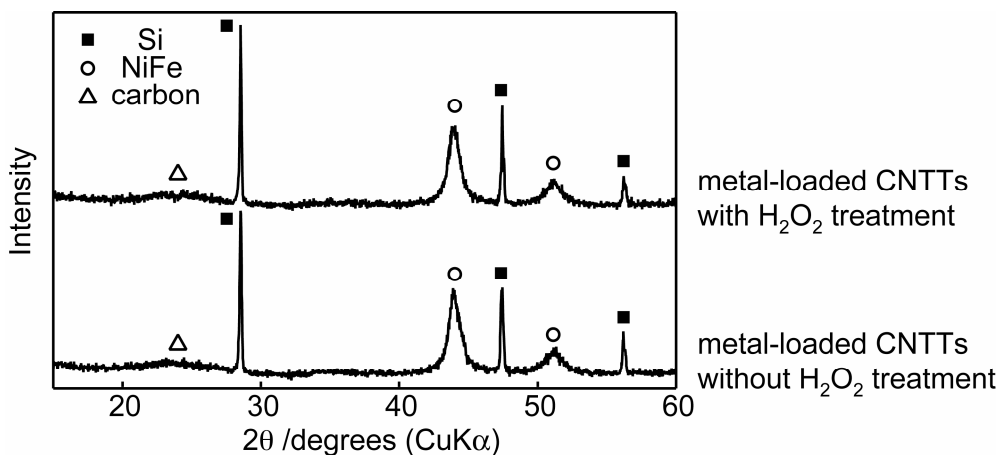


Fig. S2 XRD profiles of metal-loaded CNTTs.

3. Rough estimation of the potential between two metal-loaded CNTTs.

The interaction between the two magnetic metal-loaded CNTTs was roughly estimated by using a simple model (Fig. S3). The overall potential curve (U) is estimated as the sum of the repulsive potential due to the presence of electric double layer (E), the attractive potential from van der Waals (V) and the magnetic dipole-dipole

interaction (*D*).

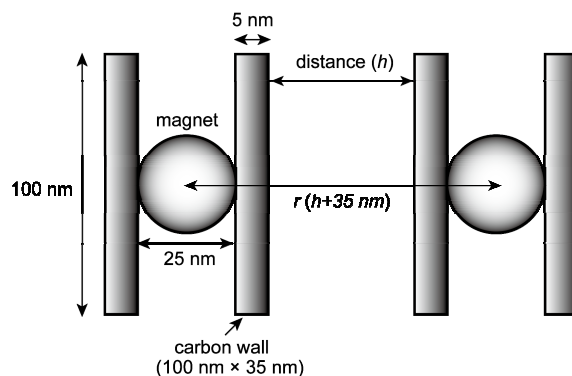


Fig. S3 A model of magnetic metal-loaded CNTTs.

3.1 Repulsive interaction by the electric double layers.

The repulsive interaction by the electric double layer at 25 °C is expressed by the following equations:

$$E = \frac{1.58 \times 10^8 c}{\kappa} \gamma^2 \exp(-\kappa h) \times S$$

$$\kappa = 3.3 \times 10^9 \sqrt{c}$$

$$\gamma = \tanh\left(\frac{e\phi_0}{4kT}\right)$$

where c , k , T (25 °C) and ϕ_0 , is ionic strength, Boltzmann constant, temperature and the surface potential (assumed to be a little lower than the measured ζ -potential: -50 mV), respectively.

3.2 Vander der Waals potential

Van der Waals potential (V) between the facing two flat carbon plates was estimated by the following equation.

$$V = -\frac{A}{12\pi h^2} \times S$$

where A is a Hamaker constant (assumed to be $1 \times 10^{-19} \text{ J}^2$), h is a distance between the two plates and S is a area of the carbon plates ($35 \text{ nm} \times 100 \text{ nm}$ in the model). Since the

carbon plates (wall of CNTTs) have a thickness of 5 nm, 'r' is always larger than 'h' by 35 nm (Fig. S3).

3.3 Magnetic dipole-dipole interaction between two magnetic particles.

The potential of dipole-dipole interaction (D_{ij}) between two magnetic moments (m_i and m_j) with a distance of 'r' is expressed as follows:

$$D_{ij} = \frac{1}{r^3} \left\{ m_i \bullet m_j - \frac{1}{r^2} (m_i \bullet r_{ij})(m_j \bullet r_{ij}) \right\}$$

where r_{ij} is a vector parallel to the line joining the centers of the two dipoles. The D_{ij} become a minimum when m_i and m_j are parallel. Since the magnitude of m_i and m_j is identical for the model, the minimum of D_{ij} (D) is defined as follows:

$$D = -2m^2/r^3$$
$$m = Mv \times \pi d^3/6$$

where m is the magnitude of m_i and m_j , d is a diameter of the particles and Mv is a volumetric magnetization of the magnetic metal (assumed to be 1000 emu/cm³).

4. Effect of the metal filling ratio on the water-dispersibility

The model of Fig. S3 represents CNTTs with a metal filling ratio of 25 % (The 25 nm-diameter particle is present in the 100 nm-length CNTT.). When the filling ratio of the metal is increased, the overall potential curve changes significantly. Fig. S4 shows the potential curves with different filling ratios (25, 33, 50, 70 and 100 vol.%). The ratio are changed by controlling the length of the graphite plate in this model. The 25, 33, 50, 70 and 100 vol.% corresponds to the length of 100, 75, 50, 35 and 25 nm, respectively. Fig. S4 clearly indicates that the potential barrier that hampers the agglomeration of the metal-loaded CNTTs is lowered when the filling ratio is increased, and the barrier becomes almost ignorable when the filling ratio is 70 and 100 %, *i.e.*, in these cases, the metal-loaded CNTTs are not dispersible.

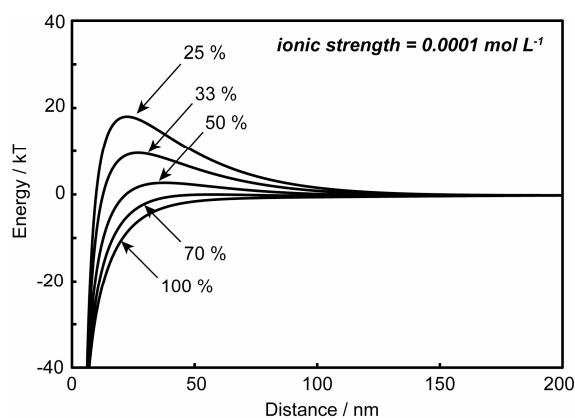


Fig. S4 Overall potential curves when the metal filling ratio of the tube cavities is 25, 33, 50, 70 and 100 vol.%.

5. Effect of the carbon wall thickness on the water-dispersibility of the magnetic metal-loaded CNTTs.

Fig. S5 represents the effect of the thickness of the carbon wall. As it is evident from this figure, the distance between the magnetic particles changes despite that “*h*” is unchanged. Thus, when the carbon wall is thick, the attractive interaction due to magnetic dipole-dipole interaction is decreased in comparison with the repulsive interaction that acts between the carbon walls. Fig. S6 shows the overall potential curves of the completely filled CNTTs when the thickness of the carbon wall was changed. As mentioned above, the CNTTs are not dispersible when the thickness is 5 nm. However, when the carbon wall becomes thicker and thicker, the potential become higher and higher. When the wall reaches more than 15 nm, a clear potential barrier can be observed, indicating that the metal-filled CNTTs are dispersible even though the magnetic metal particles completely fill the cavities of CNTTs.

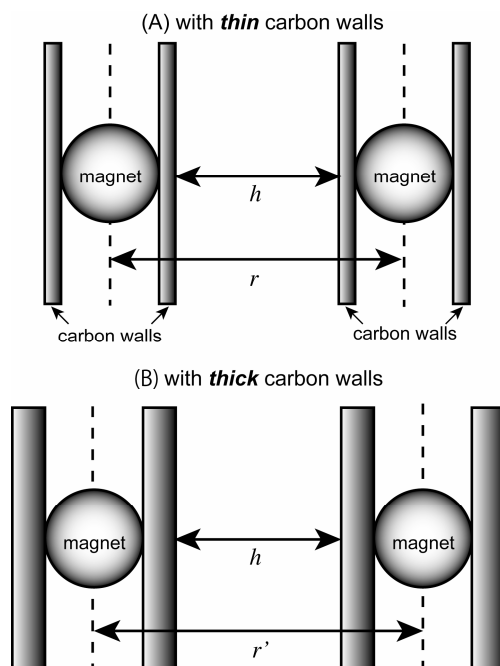


Fig. S5 Models of metal-loaded CNTT (a) with thin carbon walls and (b) the CNTTs with thick carbon walls.

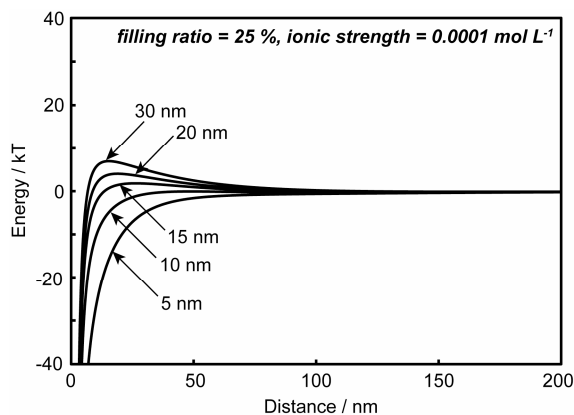


Fig. S6 Overall potential curves when the wall thickness of the CNTTs is 5, 10, 15, 20 and 30 nm (The magnetic metal filling ratio of the tube cavities are fixed at 100 %).

References

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2. R. R. Dagastine, D. C. Prieve, L. R. White *J. Colloid. Interface Sci.* 2002, **249**, 78.; J.-L. Li, J. Chun, N. S. Wingreen, R. Car, I. A. Aksay, D. A. Saville *Phys. Rev. B* 2005, **71**, 235412.