Mineralization of Cholesterol-based Nanotube with Ni and its Magnetic Property

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(Received February 14, 2005; CL-050200)

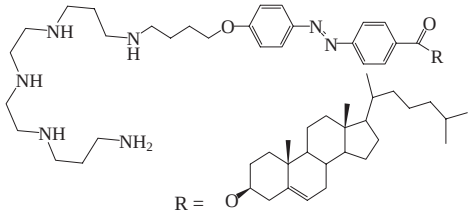
The self-assembled cholesterol-based nanotube **1** was mineralized with Ni nanocrystal, and measured its magnetic property to survery the advanced applications in the nanometre scale.

The design and fabrication of nanometer-sized functional materials have become a widely studied field in nanotechnology because of their potential use as building blocks in nanodevices.[1] Smart nanotubes, which can recognize specific complementary molecules, have become increasingly important to design nanodevices for electronic, magnetic, photonic, and sensor applications.[2,3] Particularly, over the past decade, there has been an immense interest in the fabrication of nanotubes, owing to their potential to serve as building blocks for emerging nanometer-sized wires, particles, and devices.[4] The study in formation of tubular structural amphiphiles has been attracted considerable interest for the development of advanced magnetic devices for medical applications and for magnetic recording media, nowadays known as spintronics.[5–7] Particularly, the lipid nanotubes coated by magnetic nanoparticles would be useful in drug delivery system. It is necessary to functionalize these nanoparticles in order to add the suitable physical properties required for specific device applications. In spite of these lines of importance, there have been reported only a few amphiphiles which possess functional group such as sugar,[8a] peptide,[4b,4c,8b] or amino acid.[8c] Furthermore, the examples on the mineralization of lipid nanotubes with nanoparticles are still very limited.[7a] If these metal-binding nanotubes are incorporated into nanoparticles, we can grow nanocrystals in controlled sizes on the nanoparticles, which may ultimately be used to tune the magnetic and electronic properties of nanoparticles.[7]

With these object in mind, here we report a novel method of growing uniform nanocrystal directly on nanotubes surfaces by reducing of Ni, and address its magnetic property to survey the advanced applications in the nanometre scale. A major advantage of this approach is the simple, efficient and reproducible control of the Ni nanocrystal size on the template nanotube, which adds tunability of the magnetic property to resulting nanotube.

We synthesized the cholesterol-based amphiphile **1** possessing polyamine unit by a similar method reported previously,[8d] designed to immobilize Ni nanocrystal. Generally, the polyamine moiety showed high affinity toward Ni ion,[9] and crystallized Ni efficiently in the presence of reducing agent. The fibrous structures were confirmed by energy-filtration and high resolution transition electron microscopes (EF-TEM and HR-TEM). The formation of self-assembled nanotubes was tested in various organic solvents. The cholesterol-based amphiphile **1** (Scheme 1) formed efficiently the nanostructure in acetonitrile and acetone.

The deposition of Ni nanocrystal on the self-assembled nanotube of **1** was carried out by heating. **1** (ca. 5.7×10^{-3} mmol) in acetonitrile for 30 min. The solution was maintained for 30 min at room temperature to form a stable supramoelcular assembly. Then, 2.0 equivalence of aqueous $NiCl_2$ solution was added to the preorganized nanotubes solution. The reaction mixture was allowed to sit undisturbed overnight under nitrogen to completely mineralize Ni on the nanotube. Then, this was followed by addition of 2.0–3.0 equivalences of $NaBH_4$ as a reducing agent to mineralize the Ni nanocrystal on the nanotube. All process was performed in nitrogen dry box to preserve from any uncontrolled oxidation.



Scheme 1.

Figure 1 shows SEM and TEM pictures of the lipid nanotube **1** obtained in acetonitrile. The self-assembled cholesterol-based **1** formed the efficiently nanosized tubular structure in high diluted acetonitrile solution. The nanotubes have ca. 30-nm outer diameter, ca. 20-nm inner diameter and 50–100-μm length. The tubes are open-ended with uniform shape and internal diameter. The nanotube might be induced with suitable balance between polyamine moiety as a polar head and chiral cholesterol tail groups which give rise to packing anisotropy within lipid bilayer sheets formed in organic solvents.

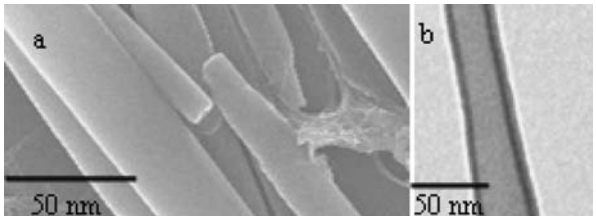


Figure 1. (a) SEM and (b) TEM images of the lipid nanotube **1** obtained from acetonitrile.

TEM images of the cholesterol-based nanotube **1** mineralized with Ni nanocrystal are shown in Figure 2. Interestingly, when Ni ion forms complex with the nanotube of **1**, Ni nanocrystal with 2.5 ± 0.5 nm (Figures 2a and 2b) diameter efficiently decorated the surface of well-defined lipid nanotube. The Ni nanocrystal on the surface of the cholesterol-based nanotube was deposited approximately 30 wt %, according to TGA (thermo gravimetric analyzer) analysis. This observation strongly suggests the specific interactions between the lipid molecules

at the exposed part of the surface and metal ions. Also, this finding is a rare example for the mineralization of the synthetic lipid nanotubes with magnetic nanocrystal. It is not clear that why TEM image of the tube shows almost the same contrast after mineralization. We consider that probably this phenomenon relates to Ni metal particles.

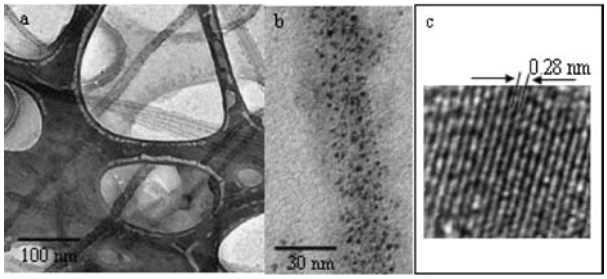


Figure 2. (a and b) EF- and (c) HR-TEM images of the lipid nanotubes mineralized with Ni nanocrystal.

X-ray powder diffraction showed that the nanotube surface is coated with mostly face-centered cubic Ni nanocrystals but that face-centered cubic (fcc) NiO was present approximately 9%. These results imply that the shells of the Ni nanocrsystal exist as NiO by oxidation, respectively. Examination of Ni nanocrystal as shown in Figure 2c gives lattice spacing of 2.8 Å for the (111) plane.

The magnetic property of the Ni-nanocrystal-coated nanotubes was studied by a quantum design superconducting quantum interference device (SQUID) magnetometer. The magnetic susceptibility $\chi(T)$ was measured at 100 Oe. In Figure 3a for the Ni-nanocrystal-coated nanotubes, $\chi(T)$ exhibits a cusp in the zero-field-cooled (ZFC) susceptibility and irreversibility between the ZFC and the field-cooled (FC) susceptibility. Such a glassy behavior is likely related with the random anisotropy and the dipolar interactions.[5,6] Above the cusp temperature, the Ni nanocrystal is free to align with the field during the measuring time. This state is called superparamagnetic and the cusp temperature is the blocking temperature $T_B \sim 15$ K. It should be noted that the magnetic property is strongly dependent not only on intrinsic material parameters such as saturation magnetization, M_s, remanent magnetization, M_r, and coercive field, H_c, but also on the special types of microstructures. Figure 3b shows the magnetic hysteresis loop $M(H)$ for temperatures below and above the cusp, being indicative of a ferromagnetic phase. The hysteresis loop gives a value of $H_c = 80$ Oe. However, there is

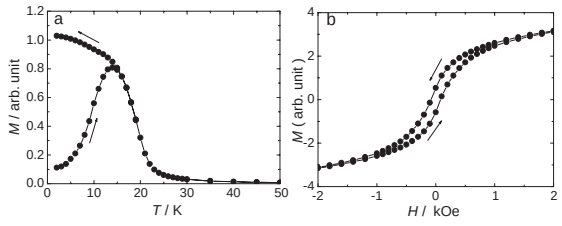


Figure 3. (a) Temperature dependence of magnetic susceptibility $\chi(T)$ measured at 100 Oe in the zero-field-cooled (ZFC) and field-cooled (FC) cases for the Ni-nanocrystal-coated nanotubes. (b) Magnetic hysteresis loop $M(H)$ at 10 K.

no saturation found in fields up to 7 T (not shown here), which may be associated with the magnitude of two different magnetic interactions. The ferromagnetic/superparamagnetic interaction of the Ni nanocrystals contributes to the saturation term of $M(H)$, while the antiferromagnetic interaction of NiO contributes to the H-linear term of $M(H)$.

In summary, we have demonstrated that mineralization of the cholesterol-based nanotube led to efficient Ni nanocrystal growth on the nanotube surface. The lipid nanotube coated by Ni nanocrystal behaves as an assembly of finite-sized ferromagnet with superparamagnetic behavior. We believe that this magnetic nanotube fabrication method can be extended to other magnetic species with nanotubes. This type of smart nanotube with tunable magnetic properties may be useful as a building block for magnetic devices such as medical device, spintronics, and recording media. These magnetic cholesterol-based nanotubes also provide potential for in vivo sensing and advanced applications

This work was supported by Korea Research Foundation Grant (KRF-2004-015-C00242). We also thank J. G. Kim and J. Kim in KBSI for TEM observation.

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Published on the web (Advance View) May 14, 2005; DOI 10.1246/cl.2005.806