A Novel Method for Fabrication of Unique Cobalt Nanostructures

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In this article, a novel method has been developed for extracellular prepared of amorphous ring and chain cobalt nanostructures using *Staphylococcus epidermidis* in combination with PVP as template. The nanostructures consist of cobalt nanoparticles with the average particle size of 50 nm. The morphological difference between chain and ring nanostructures is determined by the interaction between PVP and bacteria. Extracellular prepation of nanostructures using bacteria as template opens up a new possibility to fabricate metal-based nanostructures in biological system.

The nanoscale magnetic materials have a wide variety of applications such as the high density magnetic recording media,[1] catalysts,[2] and biomedicine.[3] Currently, there are considerable interests in synthesis of materials with unique nanostructures. Living microorganisms such as bacteria, fungi and virus have been developed as the biotemplate for preparetion of nanoparticles.[4–6] We considered that whether bacteria can be developed as the reactor for fabrication of metal nanostructures, in which bacterial surface provided the biotemplate for nanostructure formation and the bound metal ions were reduced by the agents like $NaBH_4$. However, it seems that bacteria[6] cannot provide the template for extracellular fabrication of nanostructures, unlike DNA or virus which is well suitable to assemble one-dimensional nanostructure because of their sizes and well-organized structures. An encapsulated *Staphylococcus epidermidis* strain, which bacteria are enclosed within a capsule layer, has been obtained from a clinical specimen when we cultured tumor cell. Herein, we show a novel method for extracellular fabrication of cobalt nanostructures using PVP in combination with encapsulated *S. epidermidis* as template.

The *S. epidermidis* (1×10^6 per mL) for experiment was cultured overnight in the Dulbecco minimum essential medium (DMEM) with supplement of 5% the fetal bovine serum (FBS). The whole process was carried out at room temperature under the nitrogen atmosphere. In a typical reaction, 5 mL of 1×10^6 per mL living-state bacteria was added to the 25 mL of aqueous solution containing 1 g of polyvinylpyrrolidone (PVP, K-30, $M_w = 49000$), then 25 mL of 53.125-g $CoCl_2 \cdot 6H_2O$ solution was added in, and magnetically stirred for 30 min. Following this was the addition of 20 mL of 16 mM $NaBH_4$. The as-prepared products were collected, washed several times with absolute alcohol, and finally dried in a vacuum oven at room temperature. The morphology of as-prepared products was observed by FESEM (JEOL-6700F), TEM (H-800, Hitachi) and AFM (AJ-III). TEM observation was performed at 200 kV. The phase of the as-synthesized products was determined by an X-ray diffractometer with monochromatized Cu Kα radiation ($\lambda = 1.5418$ Å).

The high yield of cobalt chain nanostructures was achieved by the addition of 1 g of PVP to bacterial suspension before reduction. The detailed chain nanostructures are showed in Figures 1a and 1b. The chains are disorderly wrapped together. The chain consists of Co nanoparticles with the average particle size of 50 nm. The X-ray diffraction pattern (see Supporting Information S1)[14] of as-prepared product shows only one broad peak at the 2θ range from 40 to 55°, which indicates that chain nanostructures may be amorphous. The TEM image (Figure 1c) confirms that the cobalt chains are linked by bacteria. The selected area electron diffraction (SAED) pattern (insert of Figure 1c) exhibits a diffuse ring, which further confirms that the chain nanostructures are amorphous.

A sample was made without washing so that PVP chains remained in structures. Then Co nanoparticles were removed off by H_2O_2. The remained PVP chains were bound to bacterial surface (see Supporting Information S2).[14] It confirms that PVP chains can link to the capsular polysaccharide molecules on *S. epidermidis* surface. The control experiments, in which the samples were prepared in the absence of bacteria, have shown that only separate Co nanoparticles were obtained without the existence of chain-like structures. On the contrary, when the samples were prepared by the addition of bacteria and in the absence of PVP, Co nanoparticles deposited on the bacterial surface and formed the disordered flakes with pleated structures (see Supporting Information S3).[14] These results verify our deduction that *S. epidermidis* in combination with PVP chains can provide the template for chain nanostructure formation.

Then, PVP solution was added into a $CoCl_2 \cdot 6H_2O$ solution and ultrasonically dispersed 15 min before exposure to bacteria. Representative AFM images of products prepared by the addition of 212.5 mg of $CoCl_2 \cdot 6H_2O$ and 10 g of PVP are shown in Figure 2. Cobalt nanoparticles encircled the bacteria and formed the ring-like nanostructures. These encircling Co nanoparticles as the magnetic dipoles formed the bistable flux closure

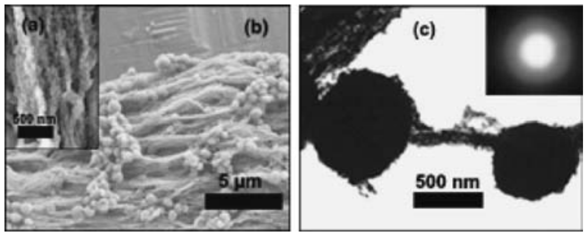

Figure 1. (a), (b) FESEM images of cobalt chain nanostructures. (b) detailed images of cobalt chain nanostructures. (c) TEM images of detailed chain structures; insert in (c): SAED pattern of cobalt chain.

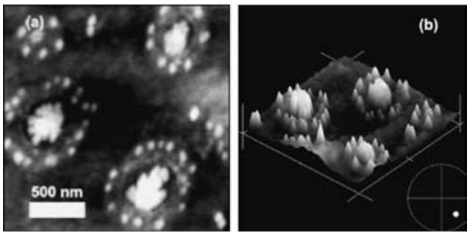

Figure 2. Representative AFM images of cobalt ring nanostructures. (a) top view; (b) surface view.

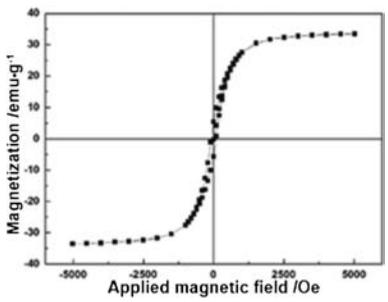

Figure 3. Magnetic hysteresis loops of as-prepared products of cobalt chain nanostructures.

states. These flux closure structures produced a net moment of zero which greatly reduced both the magnetic energy and the field outside the ring.[7] That may be the main reason for cobalt rings remaining stable during the synthesis process and drying process in vacuum oven. These cobalt ring nanostructures probably have great potential application in fabricating spin-polarized electronic devices and in studying magnetic properties of nanomagnets.

The magnetic character of the cobalt chain nanostructures was investigated by SQUID at room temperature (see Figure 3). The hysteresis curve of cobalt chain nanostructures shows a ferromagnetic behavior with a saturation magnetization (Ms) of 33.52 emu/g, coercivity (Hc) of 83 Oe, and remanence ratio (Mr/Ms) of 0.16 which is much lower than the corresponding values of bulk samples ($M\text{s} = 168$ emu/g, $H\text{c} = 1500$ Oe).[8] Normally, amorphous magnetic materials, owing to absence of magnetic anisotropy and domain wall energy, almost have no coercive force and remanence.[9] It seems that strong ferromagnetic coupling exists in the cobalt chain nanostructures. Cobalt nanoparticles can be ferromagnetically coupled together and behave as magnetic nanochains rather than as individual particles.[10] These novel ferromagnetic nanostructures in which cobalt nanochains are linked by the bacteria will provide a new model system for the study of magnetic properties of one-dimensional magnetic nanostructures.

On the basis of the facts mentioned above, a likely mechanism of cobalt nanostructures formation is shown in Figure 4. In general, the PVP chains were wrapped together in solution. Whereas, once the PVP solution was added to the bacteria suspension, the PVP chains were drawn straight by bacteria, which were mediated by the PVP and acetylated capsular polysaccharide molecules of bacteria via nonchemical bond attachment such as hydrogen bond and van der Waals forces.[11,12] Therefore, the cobalt chain nanostructures came into being when Co nanoparticles as the magnetic dipoles deposited along the PVP chains

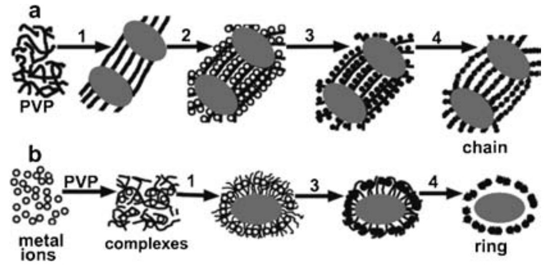

Figure 4. Schematic diagrams of preparation of cobalt nanostructures. a) chain nanostructures; b) ring nanostructures. 1) bacteria; 2) cobalt ions aqueous solution; 3) $NaBH_4$; 4) washing with alcohol. ○: metal ions, ●: cobalt nanoparticles.

and magnetically coupled together. On the other hand, the Co/PVP complexes were prepared firstly, which effectively inhibited the presence of free cobalt ions. The Co/PVP complexes with central cobalt ions surrounded by enormous PVP chains[13] were exposed to bacteria. And the PVP chains probably linked to bacterial surface. Meanwhile, the isolated cobalt ions were prevented from attaching to the capsular polysaccharide molecules of the bacterial surface. So they encircled the bacteria. The encircling Co nanoparticles were assembled into ring nanostructures upon reduction.

In summary, a novel method for extracellular fabrication of amorphous ring and chain cobalt nanostructures has been proposed utilizing *S. Epidermidis* in combination with PVP as template. The amorphous cobalt nanostructures consist of Co nanoparticles with the average particle size of 50 nm. Cobalt chain nanostructures show a ferromagnetic behavior with Ms of 33.52 emu/g and Hc of 83 Oe. This novel method opens up a new possibility to fabricate metal-based nanostructures in biological system.

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14 Supporting Information is also available electronically on the CSJ-Journal Web site, http://www.csj.jp/journals/chem-lett/index.html.

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