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# Synthesis of cobalt nanoparticles in polymeric membrane and their magnetic anisotropy

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## Abstract

We systematically synthesized cobalt nanoparticles in the perfluorinated sulfo-cation membrane (MF-4SK) in aqua solution using ion-exchange method. The average radius of cobalt nanoparticles in the polymer film is determined to be $3.5\pm1.0$ nm by TEM. FMR measurements show that the angle dependence of resonance field ($H_r$) follows the characteristics of flat-plate magnetic film and the easy axis lies along the surface of the polymer film. The experimental results suggest that the magnetic anisotropy comes from magnetized polymer film containing Co nanoparticles.


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*Keywords:* Cobalt nanoparticles; MF-4SK; Ion-exchange; Magnetic anisotropy

In material science, nano-sized magnetic materials have been produced as isolated aggregates, as deposits of aggregates, such as carbon nanotubes and nanocages filled with magnetic material, as well as electrodeposits of magnetic material in nanoporous polycarbonate membranes [1]. Although these methods are pretty powerful to produce the nano-sized magnetic materials, there are still problems in production since many of above methods need high vacuum system. On the other hand, polymeric ion-exchange system [2] is a good candidate for ferromagnetic nanoparticles due to the efficiency in synthesis and size control. The main idea of this new method is as follows. First, cations of ferromagnetic metals are fixed on charge groups. After the recovery process, ferromagnetic particles are obtained according to the electrochemical reaction. It turns out that the size distribution of particles and the distance among them depend on the concentration of transition metal ions in the film and the structure of ion channels of polymer membrane.

In synthesis, perfluorinated sulfo-cation exchange polymeric membrane, MF-4SK (molecular weight: $1100\pm100$, thickness: 0.190 mm) was used. The schematic picture of the physical structure for MF-4SK is shown in Fig. 1. In MF-4SK, sulfogroups, counter-ions and water molecules form ionized channels. It has been shown that the linear fragment of this channel length is less than 10 nm with 4 nm channel width, which is dependent on humidity and counter-ions [3]. We used $Co^{2+}$ as counter-ion from an aqua solution of hydrous cobalt salt ($CoCl_2 \cdot 6H_2O$). In this solution, Co ions ($Co^{2+}$) were diffused and substituted for hydrogen ions ($H^+$) at the sulfonate groups. These Co cations incorporated in MF-4SK were recovered to metal nanoparticles according to the electrochemical reaction where $NaBH_4$ was used as a reducing agent. During the recovery process from $Co^{2+}$ to $Co^0$, self-aggregated metal nanoparticles ($nCo^0$) were formed. In Table 1, theoretically calculated concentration ($Con^{cal}$) and experimentally measured one ($Con^{ex}$) using ICP-AES technique are compared. At low concentration ($<1.6\times10^{20}$), experimental values determined by measuring concentration of Co ions in the solution before and after ion exchange process are well matched with theoretical expectation.

Fig. 2(a) shows FE-TEM image of the cobalt nanoparticles of the sample, which reveals black dots with relatively bright stripes. We believe that circular shaped black dots observed in TEM come from the Co

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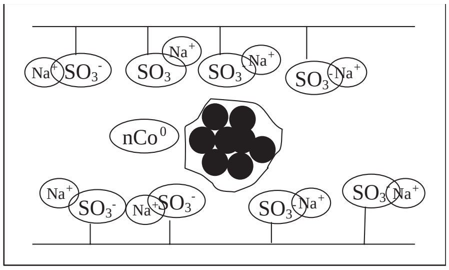
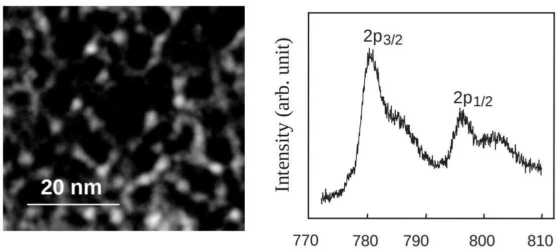



Fig. 1. Schematic representation of perfluorinated membrane channel fragments: recovering from $Co^{2+}$ to $Co^0$.

Table 1
Theoretically calculated concentrations $Con^{cal}$ and experimentally obtained concentration $Con^{ex}$

| | Co-I | Co-II | Co-III | Co-IV | Co-V |
|---|---|---|---|---|---|
| $Con^{cal}$ | $1.9\times10^{19}$ | $3.2\times10^{19}$ | $7.8\times10^{19}$ | $1.6\times10^{20}$ | $3.6\times10^{20}$ |
| $Con^{ex}$ | $1.9\times10^{19}$ | $3.2\times10^{19}$ | $7.8\times10^{19}$ | $1.6\times10^{20}$ | $2.4\times10^{20}$ |




(a) (b)

Fig. 2. Co-III nanoparticles (a) TEM image. and (b) XPS data.

nanoparticles in the polymer since they were not seen before absorption. The average radius of Co nanoparticles in the film was determined to be $3.5\pm1.0$ nm by statistical analysis. This image shows the presence of non-agglomerated small particles homogeneously dispersed in the polymer. High resolution XPS scan shows two binding energy peaks of $2p_{3/2}$ (779 eV) and $2p_{1/2}$ (794 eV) for cobalt as shown in Fig. 2(b).

The dependence of the resonance field ($H_r$) for a Co-embedded MF-4SK at 9.8 GHz (X band) on the applied field angle (polar angle, $\theta$) (See Fig. 3) in the vertical plane is shown in Fig. 4(a). The lowest resonance field of 1.8 kOe occurs for the external magnetic field applied parallel ($\theta=0°$) to the sample. The axis of $\theta=0°$ is determined to be easy axis since $H_r$ is the lowest at $\theta=0°$. Our experimental evidence indicates that the resonance field increases with increasing polar angle, reaching 7.0 kOe at $\theta=90°$. This phenomenon seems to be due to the demagnetisation of the flat-plate-like sample [4]. The angular dependence of the linewidth ($\Delta H$, *the peak to peak in the first derivative*), which gives the information of the distribution of the particle

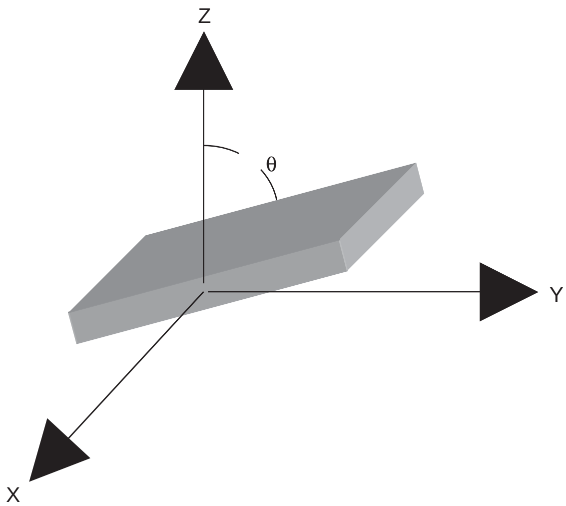
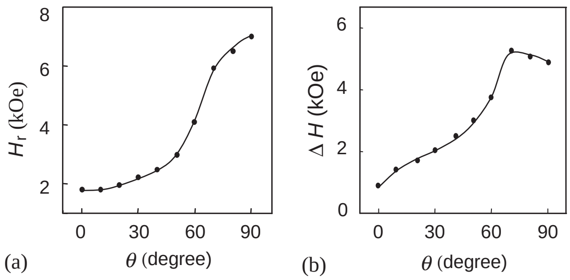



Fig. 3. Geometric coordinates of the FMR.




(a) (b)

Fig. 4. (a) The resonance field ($H_r$). and (b) linewidth ($\Delta H$) for Co-IV at room temperature.

orientations, shows that $\Delta H$ at $\theta=0°$ is the lowest revealing approximately 1.0 kOe and increases with increasing $\theta$, reaching a maximum of 5.2 kOe at $\theta=70°$.

In summary, detailed processes of synthesis for cobalt nanoparticles embedded polymer film using a new method, ion-exchange, were introduced. The average radius of Co nanoparticles in the polymer is determined to be $3.5\pm1.0$ nm. FMR measurements show that the magnetic anisotropy comes from magnetized polymer film revealing the characteristics of the flat-plate-like magnetic polymer. The easy axis is parallel to the surface of polymer sample.

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