Templated Fabrication of Co@Au Core-Shell Nanorods

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Abstract

In this study attention was focused on a templated fabrication of Au nanotubular structures that could carry a highly magnetic entity such as cobalt. In brief, experimentation was performed to create Co@Au core-shell nanorods of different lengths. The preliminary core-shell structures were first characterized using x-ray diffraction (XRD), scanning electron microscopy (SEM), and energy dispersive analysis using x-rays (EDAX). XRD results revealed that electrodeless depositions of gold nanotubes (~50 nm in diameter in polycarbonate track-etch [PCTE] membranes) were having preferred (111) orientation. These Au-filled PCTE membranes were later used as electrodes to potentiostatically deposit cobalt to form Co@Au nanorods. These core-shell structures were found to be highly magnetic in nature and could easily be separated by dissolving the PCTE membranes in 1,2-dicholroethane. These magnetic nanostructures are promising vehicles for new forms of drug delivery systems, hyperthermia, high-density data storage, and many other applications. It is therefore a priority to advance techniques in the fabrication of these nanostructures so that the ones with the most ideal magnetic properties may be realized.

Introduction

Magnetic nanostructures have the ability to make great contributions in the way of microelectronic and biomedical technology. Their size alone brings forth a rich combination of optical, electronic, and magnetic properties distinguished from their bulk counterparts. Such applications include magnetic memory storage, magnetic transport of biochemical complexes, and magnetic resonance imaging (MRI) enhancement.[1,2] Common to most ideal magnetic materials is their affinity to oxidize in ambient conditions. These traits are unacceptable for biomedical applications. Just as well, many of these materials are biohazardous and not suitable for *in vivo* studies unless they can be specially modified. With this reasoning in mind, great efforts have been put forth in the study and development of nanoscale core-shell structures. The idea is simply to coat these structures with compounds that will remain stable in ambient conditions and restrain from interfering with the magnetic properties of their core compound. Researchers in the past have commonly worked with cores such as Fe, Co, and Fe_3O_4. Shells were composed of Au, SiO_2, and Pt. On these outer-core shell surfaces, researchers were able to experiment with the binding of thiolated biomolecules (i.e., DNA, antibodies, genes). Methods in use today fabricate micrometer-sized magnetic core-shell structures that are too large to be functional for *in vivo* applications. Work must be done to render structures with tunable magnetic properties that are highly stable and can be fabricated to a size smaller than 20 nm (proposed size for MRI applications).[3]
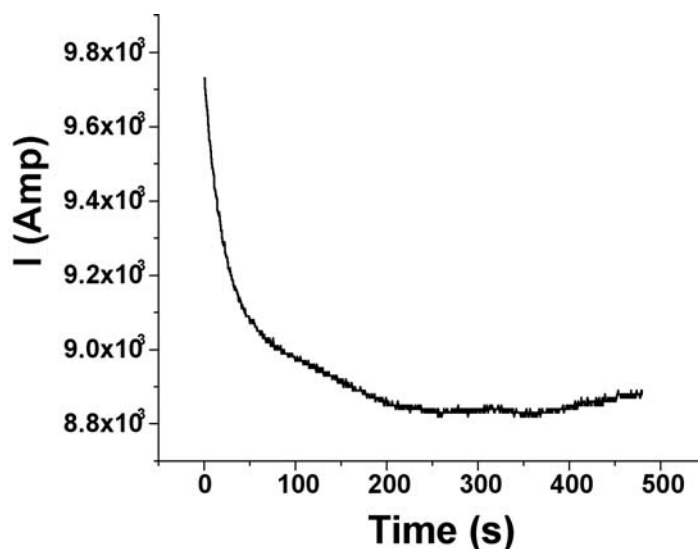

Figure 1: A current-time transient curve for a Co electrodeposition in Au-filled PCTE membranes. Co was electrodeposited for eight minutes in a standard three-electrode electrochemical cell using Co as a counter electrode in a sulphate bath at a potential of -1.1 V vs. SCE.
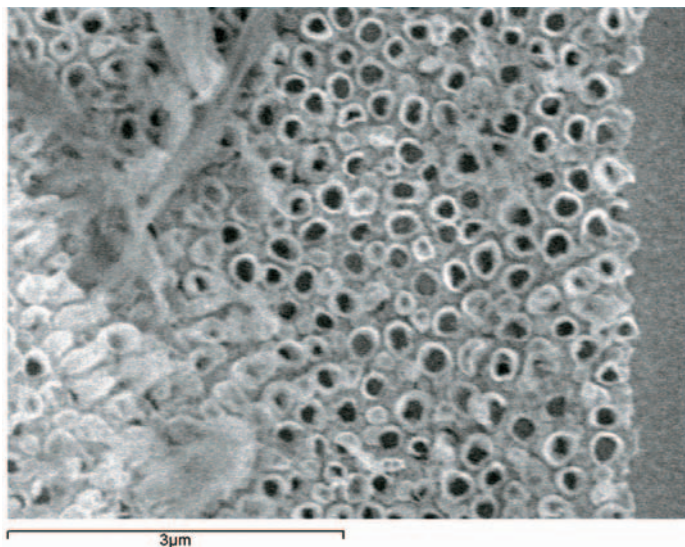
Figure 2: An illustrative SEM image of a top view of Au nanotubes in an AAO membrane. The AAO surface was modified beforehand with a monolayer of glutaric acid.

Background

Past research on magnetic nanostructures has focused significantly on experimentation with iron oxides. These structures were identified as prominent subjects for experimentation because of their ability to produce a dipole moment under the application of a magnetic field. Recent research has placed emphasis on nanostructures composed of the transition metals: Fe, Ni, and Co and their alloys.[4] These metals possess several properties that are more ideal than those of their iron oxide predecessors. Transition metal nanostructures exhibit ferromagnetic behavior, while those of iron exhibit superparamagnetic behavior. Ferromagnetic structures produce a larger magnetic moment than superparamagnetic structures. Also, transition metals retain their magnetic properties in the absence of a magnetic field; iron oxide nanostructures

do not.[2] Through solution chemistry, Fe_3O_4 nanoparticles and their core-shell structures are magnetically poorly defined, and controlling their magnetic properties is difficult. Several complications are encountered in these synthesis procedures: a mixture of several iron oxide phases, poor crystallinity of the core, and a large dispersity in core size. They all muddle with the interpretation of magnetic properties. Furthermore, if a perfect magnetic core is desired, it is necessary to develop a new set of synthesis routes for each magnetic core material.[5]

The magnetic properties of nanostructures are highly sensitive to size and shape. Currently, Quantum dots stand as a center of focus for research performed with magnetic nanostructures. These are spherical nanostructures with diameters smaller than 100 nm. This experimentation has focused on the development of

nanorods. Concerning the interests of this study, the shape of rods are advantageous because, using the same volume of material as a corresponding nanosphere, the nanorod will exhibit a greater dipole moment under the application of the same magnetic field. The idea for this particular study was to capitalize on these magnetic properties to make rod-shaped nanostructures of Co. Co is ideal because it has a high magnetic susceptibility, but it has several properties that are undesirable. It oxidizes easily in ambient conditions, which compromises its use with biomedical applications and data storage as well. Since Co is also toxic to the body, the surface of a Co nanorod would need to be modified with another type of material. For the purpose of coating the surface of a Co nanorod, Au is an ideal substance. Au is highly stable in ambient conditions and can reasonably be used for an *in vivo* study as research progresses. Also, Au is the most exploited nanomaterial that is commonly used for biomolecular anchoring. In this study, a templated approach is utilized for the synthesis of Co/Au core-shell nanorods. This direction proves to be an inexpensive, wet-chemical alternative to more complicated processes that often necessitate the use of a vacuum-controlled atmosphere.

Approach

Experimentation was performed on commercially available polycarbonate track-etch (PCTE) and anodic aluminum oxide (AAO) nanoporous membranes. The size of the pores in both membranes was ~50 nm. Both membranes had monodisperse pores with narrow pore-size distribution and uniform diameters. The pores in AAO membranes form a hexagonal array. They have pore densities of ~10^{11} pore/cm^2. The polycarbonate

membranes have random pore distribution and smaller pore densities than the AAO membranes; these densities are ~10^9 pore/cm^2. With its even pore distribution and greater pore density, the properties of the AAO membrane make it ideal for use in this experimentation.

A few AAO membranes were used in the electroless Au depositions. The methods used in this experiment were originally designed for use with polycarbonate membranes. Attempts were made to make use of the AAO membranes by first modifying the surface of the membranes with glutaric acid self-assembled monolayers and then performing the same electroless deposition. Following the deposition, these membranes exhibited virtually no change in color. After an electroless deposition of gold, membranes will normally change color from white to a light purple. The longer the membranes are immersed in the final solution, the darker the purple will appear to be. Signs of a proper deposition can usually be seen within 12 hours. After imaging one of these AAO membranes with an SEM, Au nanotubes revealed themselves only in small patches at different locations on the tip of the membrane.

The process used for the electroless deposition was a combination of two similar methods reported by C. Martin et al.[6,7] The membranes were first immersed in methanol for five minutes. Next, the membranes were kept in a solution of 0.025 M $SnCl_2$ + 0.07 M trifluoroacetic acid for 45 minutes. The membranes were then washed using methanol two consecutive times for 2.5 minutes. The membranes were reimmersed in an aqueous ammoniacal solution of $AgNO_3$ for 5 minutes. The membranes were then thoroughly rinsed using methanol for

5 minutes. After this, the membranes were kept in water for another 5 minutes. The membranes were then immersed in a gold plating bath that contained 0.127 M Na_2SO_3, 0.0625 M formaldehyde, 0.025 M $NaHCO_3$, and 7.9 x 10^{-3} M of the commercial gold plating solution. The gold plating solution used is called "Oromerse SO Part B" (Technic Inc.). Typically the concentration of the gold solution and the formaldehyde would be doubled in order to obtain a faster deposition rate. Before immersing the membranes in the gold plating bath, the pH would be adjusted to ~10 by adding drops of 0.5 M H_2SO_4 while constantly stirring.

The electrodeposition of cobalt was performed using a constant voltage of -1.1 V. During the deposition, variances in current were monitored (Figure 1). A smooth change in current over time would indicate an even distribution of Co onto a given membrane. In this deposition, our porous membrane stood as the working electrode, with a Co rod as the counter electrode, and a saturated calomel electrode (SCE) as the reference electrode. An acid bath consisting of cobalt sulfate with boric acid was used for the electrodeposition. Following the electrodeposition, a

small piece of the membrane would be removed and placed near a strong magnet to check for magnetic susceptibility. Nearly all the membranes would exhibit movement when the magnet came in the vicinity of the Co membranes. Following the electroless deposition and the electrodeposition, all the membranes were dissolved in dichloroethane at room temperature. Centrifuge was used to separate broken remnants from the rest of the solution. These remaining particles were then washed with chloroform and then suspended in ethanol. These partially etched membranes were readied for SEM imaging by sticking them to copper tape.

Results and Discussion

Electroless Au Deposition

Increasing the concentration of formaldehyde results in a faster deposition of the Au in the PCTE pores. Throughout experimentation, it became evident that the pH level of the gold plating bath must be around 10. Membranes immersed in baths with levels above 11 do not show any signs of Au deposition. In the article illustrating the method used, it states that "lower pH plating bath results in nanotubules with more uniform inside diameters."[6,7] The effectiveness of
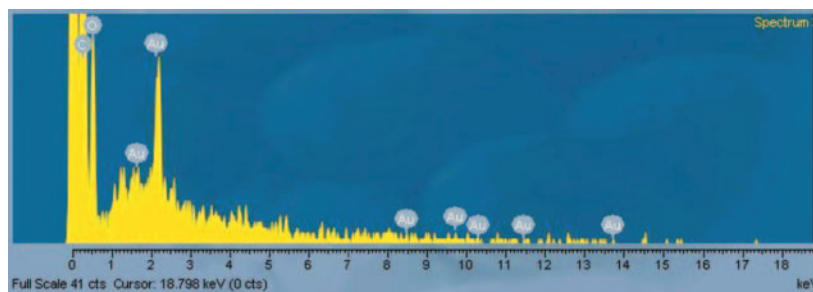

Figure 3: An EDAX spectrum of Au nanotubes partially embedded in a PCTE membrane. The membrane was partially dissolved in dichloroethane.
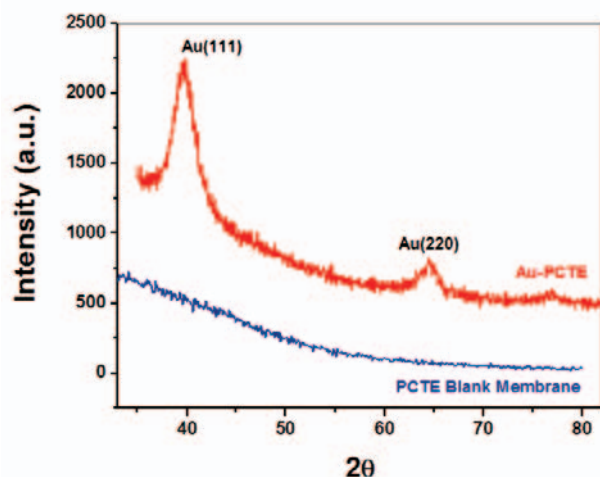
Figure 4: A superimposed x-ray diffraction pattern of a blank PCTE membrane and another following an electroless deposition of Au in the membrane.

the depositions performed is checked to study the homogenous deposition rate in the membranes. Collectively, the effectiveness of each deposition is far from being uniform. In some cases, signs of effective deposition can be seen within 12 hours. In other cases, the signs of deposition may appear after two days. The indicator used for measuring the effectiveness of a deposition is no more than the color of the given membrane. A uniform faint purple seen evenly throughout a membrane indicates an effective deposition. This purple color will gradually darken the longer the membrane stays in the final solution, perhaps turning a dark plum purple before appearing completely black. Some membranes may show purple only in patches on the membrane rather than the model even distribution.

Membranes with deposited Au are imaged using SEM to confirm the presence of Au nanotubes. Au nanotubes can be identified by their shiny appearance in individual pores scattered throughout the surface of the membrane (Figure 2). The black holes surrounded by solid white rings indicate that the pores are uniformly filled. The debris shown in one area is most likely due to overfilling of the pores. A quick confirmation came with an EDAX study revealing Au peaks in a partially etched PCTE membrane (Figure 3). The C peak results from the use of a polymer template. For further analysis, the membrane was subjected to an XRD study (Figure 4). The strong (111) peak illustrates the presence of highly oriented Au nanotubes inside the pores.

Electrodeposition of Cobalt into Pores of PCTE and AAO Membranes
The electrodeposition is carried out at constant DC potential to ensure that the current response could be monitored during the deposition process. Co is deposited during this cathodic reduction. The effect of varying the deposition time should be investigated so as to determine the connection between deposition time and the quantity of cobalt deposited. At any given potential, the electrodeposition amperage is directly proportional to the area of the electrodeposit — hence, the current-time curves recorded during the electrodeposition reveal different stages of the process (Figure 1). Here the PCTE membrane is coated with a thin silver layer to make an electrode. The pore diameter and pore length for this sample are about 50 nm and 6 μm, respectively. As electrodeposition continues in the Au-filled membranes, cobalt fills the pores from the bottom upward. After an initial transient, the current-time curve exhibits a region of very gradual decrease of the current, which corresponds to the electrodeposition of cobalt into the pores of the PCTE membrane.

SEM is further used to image the substrates with deposited solution containing the Co@Au nanorods. Figure 5 shows a prospective-view SEM image of one of these substrates. The rods shown are generally about 50 nm in diameter and 800 nm in length. A decent cross-sectional view of the rods has yet to be imaged. High-resolution images show that the cobalt-filled Au tubes have a grainy surface. This is most likely due to the imperfections in the holes of the pores of the membranes, as well as the Au vertical growth during the process of the electroless deposition. An EDAX study performed during the imaging of the rods confirms the presence of Au, Co, and Ag (Figure 6). A small proportion of Ag is to be expected, as silver is used as back electrode. Although SEM is less sensitive to density variations than TEM, it can be confirmed through EDAX studies that cobalt is electrodeposited at the bottom of Au-filled tubes (Figure 6).
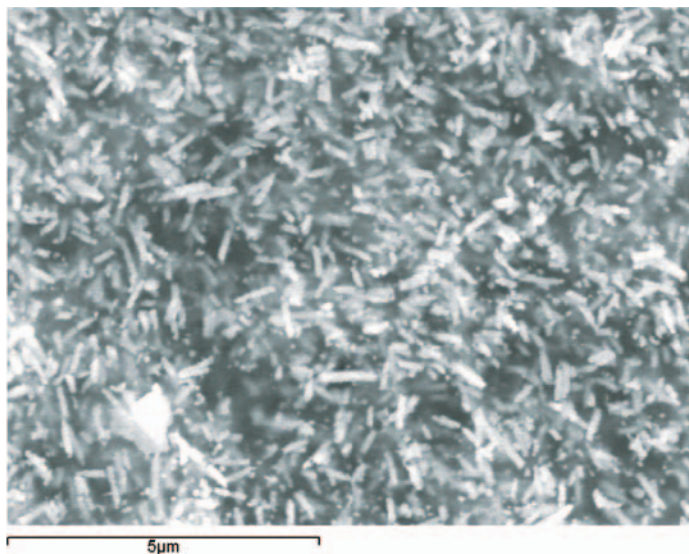
Figure 5: A top-view SEM image of Co@Au nanorods. Co was potentiostatically deposited at -1.1 V vs. SCE.

Conclusions

In summary, SEM/X-ray scattering confirmed the core-shell nature of these nanorods. The templated approach gave crystalline, preferentially textured Au nanotubules. A modified electrodeposition was applied to deposit different aspect ratios of cobalt. Average-sized rods were determined to be 50 nm in diameter and 800 nm in length. Biocompatible Au-covered Co nanorods are potentially important for many technologies, considering the vast amount of research currently in progress with varying types of bio-bar code rods and Quantum dots. The experimentation performed here establishes the feasibility of fabricating such core-shell, rod-shaped nanostructures.

Subsequent research would involve further in-depth imaging of the rods to determine exactly how much of the Au nanotubes' interiors are being filled with Co. Following this would be attempts to optimize the filling of the tubes. If a proper method of fabricating the rods could be established, then perhaps it would be possible to experiment with the attachment of different thiolated molecules. These studies would give insight on whether or not the surface of the rods and their magnetic properties will meet the hopes of the scientific community.
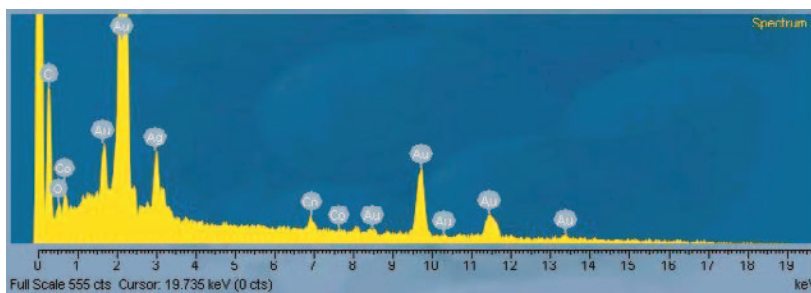
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Figure 6: An EDAX spectrum of Co@Au nanorods partially embedded in PCTE membranes.