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Electrochemical Synthesis of Core-Shell Magnetic Nanowires

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Abstract.- (Fe, Ni, CoFe) @ Au core-shell magnetic nanowires have been synthesized by optimized two-step potentiostatic electrodeposition inside self-assembled nanopores of anodic aluminium templates. The optimal electrochemical parameters (e.g., potential) have been firstly determined for the growth of continuous Au nanotubes at the inner wall of pores. Then, a magnetic core was synthesized inside the Au shells under suitable electrochemical conditions for a wide spectrum of single elements and alloy compositions (e.g., Fe, Ni and CoFe alloys). Novel opportunities offered by such nanowires are discussed particularly the magnetic behavior of (Fe, Ni, CoFe) @ Au core-shell nanowires was tested and compared with that of bare TM nanowires. These core-shell nanowires can be released from the template so, opening novel opportunities for biofunctionalization of individual nanowires.

Key words.- Fe@Au; Core-Shell; Magnetic; Nanowires; Electrodeposition; Biofunctional

1. Introduction

Magnetic nanostripes/nanowires (NS/NW) are attracting much interest in connection with their striking magnetic behavior and their application in advanced technologies. Specific functionalization offers novel opportunities in energy and environmental developments (e.g.,

electrochemical capacitors or magnetocaloric systems)^{1,2} as well as biomedical treatments^{3, 4}.

Currently, template-assisted electrochemical growth has demonstrated to be a very successful method for the production of nanoscaled systems with nearly ideal cylindrical characteristics⁵⁻⁷. Most typically, anodic aluminum oxide (AAO) membranes are employed as templates to grow arrays of columnar nano-objects with an adjustable geometry thanks to its versatility and low cost⁸.

Recent advances have allowed the synthesis of multisegment NW with modulated diameter and composition along their length⁹. Next step is likely related to the challenging growth of NW with radially distributed composition (i.e., bilayer or core-shell cylindrical nanowires). Besides, the use of transition metals compounds, especially Fe oxides, as well as Au allows the use of NW in biological applications thanks to their low toxicity¹⁰. In transition metals-Au core-shell nanowires (TM@Au NW), Au protects the metallic core against oxidation while offers a platform for biological functionalization¹¹. Electroless is the most extended approach to the synthesis of this kind of core-shell NW. Nevertheless, it creates impurities in the synthesized NW due to the template charging or the action of mediator molecules used during the process^{12, 13}. Electrodeposition alternatives avoid this problem, but demands multiple steps^{14, 15}. Thus, the main objective of this study is to introduce a less expensive, relatively simple and reliable, two-step electrodeposition method for the scalable synthesis of TM@Au NW¹⁶. After a controlled electroplating of Au nanotubes along the lateral wall of the pores in AAO membranes, a wide variety of TM (i.e., Fe, Ni, Co and their alloys) core magnetic systems have been grown in a second electrodeposition. A second objective has been the testing of the particular magnetic behavior of such TM@Au NW, together with their release to confirm their possible use in subsequent biofunctionalization.

2. Experimental.

Anodic Aluminum Oxide, AAO, templates were prepared by a two-step anodization under oxalic bath to form an hexagonal lattice of parallel self-assembled cylindrical pores¹⁷. The alumina barrier layer was removed using H₃PO₄ (5 wt%) and the pores widened to 80 ± 5 nm diameter while

the interpore distance remained at 105 ± 5 nm. A thin film of Au (~ 35 nm thickness) was then sputtered at the membrane bottom avoiding the complete covering of the pores.

Controlled two-step potentiostatic electrodeposition was employed to fill the nanopores using a three-electrode system. In the first step the Au shell is grown inside the nanopores, with an electrolyte composed by $0.93 \text{ g}\cdot\text{l}^{-1} \text{ H AuCl}_4 \cdot 3 \text{ H}_2\text{O}$ and $30 \text{ g}\cdot\text{l}^{-1} \text{ H}_3\text{BO}_3$. Different potentials were considered (-0.35 V , -0.8 V , -1 V and -1.25 V) to determine the optimal conditions for the shell growth. The second electrodeposition was performed to fill the shells with a range of different magnetic core. The electrolytes used were: i) for Fe core: Fe ($60 \text{ g}\cdot\text{l}^{-1} \text{ FeSO}_4 \cdot 7 \text{ H}_2\text{O} + 10 \text{ g}\cdot\text{l}^{-1} \text{ H}_3\text{BO}_3 + 10 \text{ g}\cdot\text{l}^{-1} \text{ C}_6\text{H}_8\text{O}_6$); ii) for Ni core: Ni ($30 \text{ g}\cdot\text{l}^{-1} \text{ NiSO}_4 \cdot 7 \text{ H}_2\text{O} + 46 \text{ g}\cdot\text{l}^{-1} \text{ NiCl}_2 + 40 \text{ g}\cdot\text{l}^{-1} \text{ H}_3\text{BO}_3$); and iii) for CoFe core: $\text{Co}_{90}\text{Fe}_{10}$ alloy ($35 \text{ g}\cdot\text{l}^{-1} \text{ CoSO}_4 \cdot 7 \text{ H}_2\text{O} + 5 \text{ g}\cdot\text{l}^{-1} \text{ FeSO}_4 \cdot 7 \text{ H}_2\text{O} + 10 \text{ g}\cdot\text{l}^{-1} \text{ H}_3\text{BO}_3 + 10 \text{ g}\cdot\text{l}^{-1} \text{ C}_6\text{H}_8\text{O}_6$). Electrodeposition voltage was fixed at -1.5 V , -1.0 V and -1.8 V respectively. Fe and CoFe electroplating was kept under N_2 flux to avoid the reactants oxidation.

Shape and dimensions of NW were analyzed using FEI NOVA NANO 230 High Resolution Scanning Electron Microscope (HR-SEM). Compositional distribution of the components in the NW was studied using secondary electrons vCD detector, as well as an Energy Dispersive X-ray Spectrometer (EDX). Local compositional spectra were acquired by a TITAN CT Scanning Transmission Electron Microscope (STEM) using a HAADF detector. The crystal structure was characterized using PANalytical X'pert Pro X-ray diffractometer in Bragg-Bretano geometry. The sample was scanned at $20\text{-}100^\circ$ (2θ) each 0.02° with a $\text{Cu-K}\alpha$ ($\lambda=1.5405 \text{ \AA}$) source. For magnetic response analysis, a Vibrating Sample Magnetometer (VSM), ADE system EV7 KLA-Tencor was employed with a maximum magnetic field of 1.5 T . As control, uncovered magnetic NW were grown in a single step electrodeposition using the electrolytes described.

3. Result and discussion

We have paid particular attention to the continuity of the Au nanotubes obtained and to the adjustment of electrodeposition conditions before their occlusion when growing inside the pores, a less studied aspect in previous reports. Continuity of Au nanotubes is better contrasted when a

different transition metal (TM) is also present so that, **Figure 1(a-d)** shows the secondary electrons Scanning Electron Microscopy, SEM, images of Fe filled Au nanotubes obtained using different potentials during Au growth. Usually, the electrochemical conditions for the growth of Au nanotubes include a low concentration of Au in the electrolyte and a low voltage or current, depending of the method^{19, 20}. In our case, the concentration of Au in the electrolyte was kept constant at a low value (2.75 mM) while the voltage was varied from -0.35 V to -1.25 V. The potential was applied for 30 min for all the cases. The images show that -1.0 V was the most suitable potential to achieve continuous Au walls. Note that the different contrast of Au (brighter) and Fe (darker) elements allows us to identify each element in the images. Darker imaged Fe can be visualized inside non-continuous Au walls (**Figure 1d, inset**). After filling the Au nanotubes, Fe continues growing outside as a nanocolumn fully filling the pores.

Figure 1. SEM cross section image of AAO templates with Au nanotubes grown under different applied potentials: -0.35 (a), -0.80 (b), -1.00 (c) and -1.25V (d) electrodeposited for 30 min and filled with Fe. Fe distribution measured by EDX for samples deposited at -1.00V after 30 min (e) and 60 min (f). SEM image of released Fe@Au NW over a silicon substrate (g).

Regarding the length of Au nanotubes, we observe that during its electrodeposition the thickness of the nanotubes increases as they grow along the pores to finally collapse into a solid NW. In a previous work, for 200 nm pore diameter, the maximum length for open nanotubes was reported to be between 1 and 2 μm ²¹. In our present case, the smaller pore diameter of 80 nm

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produces sooner the occlusion of nanotubes. **Figure 1(e)** and **1(f)** compare SEM images with the Fe distribution profile obtained by Energy Dispersive X-ray spectroscopy, EDX, of samples electrodeposited at -1.00 V potential during 30 and 60 min respectively. The white arrows show the limit of Fe detection over the background signal. For 30 min of electrodeposition, the signal of Fe is observed along all the NW but after 60 min, the presence of Fe inside Au nanotubes region disappears. The longest open shells were obtained for 45 min electrodeposition with a maximum length of 500 nm.

A set of individual Fe@Au NW released from the membrane are shown in **Figure 1 (g)**. To achieve that, the Au thin film at the bottom of the membrane was removed by Ar milling and the alumina membrane etched. The NW were then magnetically precipitated, cleaned and redispersed in ethanol. The image reveals clearly that Fe core and Au shells remain together after releasing. At this point they would be ready for later biological functionalization.

Figure 2. STEM image of a single Fe@Au NW (a). EDX patterns of indicated regions, uncover core in red (b), partially covered core (c) and Fe@Au core shell region in blue (d).

Released Fe@Au NWs were deposited in a STEM grid to analyze their composition locally by EDX and check their core-shell structure. Figure 2 presents a single Fe@Au NW and the EDX spectra obtained at three different regions of the NW circled in green, blue and red. The grey part of the NW corresponds to the Fe continuation of the core (red circle) while the bright one corresponds to the Au shell (blue circle). In the left extreme the green circle considers a partially covered part of the core. Fe peak is observed in all the EDX analysis confirming the continuity of the magnetic core inside the Au shell. When observing the green and the red squared EDX, the peaks of Au come down and certain amount of oxygen is detected in the uncoated or partially coated parts of the NW.

The peak correspondent to Cu is likely caused by the TEM grid. We should note here that the Au shell layer plays a threefold role, it is a very suitable element to facilitate organic surface functionalization¹¹, it can be used itself in medical imaging and treatments²²⁻²³, and it also protects the metallic core against oxidation preserving their magnetic properties.

Alternative transition metals (i.e., Ni) and their alloys (i.e., $\text{Co}_{90}\text{Fe}_{10}$), have been also considered as magnetic core in the TM@Au NW instead of Fe. The length of those cores scale with the corresponding electroplating time. Therefore, the length of the magnetic core can be adjusted to fit with the length of the Au shell to obtain a completely surrounded core (Figure 1 SI).

Figure 3. XRD pattern of Au nanotubes filled with and Fe, $\text{Co}_{90}\text{Fe}_{10}$ and Ni.

Figure 3 shows the X-ray diffraction pattern, XRD, for Fe, Ni, and $\text{Co}_{90}\text{Fe}_{10}$ TM@Au NW. Note that owing to the large amount of Au in the sample (remaining top layer + nanowires shell), the predominant peaks belong to cubic *fcc* Au phase. In the case of Fe@Au and Ni@Au NW, typical cubic (110) *bcc* Fe peaks, and (200) and (220) *fcc* Ni peaks are detected, respectively. For the CoFe@Au NW, the (111) peak of the cubic *fcc* phase which occurs in $\text{Co}_{90}\text{Fe}_{10}$ probably overlaps with the Au (200) peak²⁴. It is important to underline that no peak ascribed to any transition metal oxide has been observed for NW with core and shell of the same length (Figure 1 SI), what confirms the effective protective role of Au coating in the NW.

In addition to the above mentioned biomedical applications, Au shell can play a role to modify in a tailored way the magnetic response of uncovered TM NW. The magnetic behavior of arrays has been analyzed in a vibrating sample magnetometer, VSM, along the out-of-plane (parallel to NW axes) direction. Their behavior is compared with that of completely bare control TM NW. We should note that the diameter, 60 nm, and length, 400 nm, of uncovered NW were adjusted to be similar to magnetic core of Au-covered NW.

Figure 4 shows the hysteresis loops of selected arrays of core-shell NW and their corresponding bare NW. The measurements were carried out over TM@Au NW with fitted core and shell length (**Figure 1 SI**). We should firstly mention that the overall inclined shape of the loops (i.e., relatively reduced susceptibility) can mostly ascribed to the the magnetostatic interactions among NW in the arrays²⁵. The magnetic response of Fe and Ni NW arrays are not deeply affected by the presence of Au shells, and just a slightly decrease of magnetic susceptibility is observed. Such reduction is equivalent to a moderate enhancement of an effective transverse magnetic anisotropy. We should note that both, Fe and Ni NW, exhibit a weak crystalline anisotropy (i.e., *bcc* cubic phase). Nevertheless, in the case of Co₉₀Fe₁₀, a significant decrease of coercivity (from 0.12 to 0.06 T) together with an increase of the initial susceptibility is observed, what produces a drop in the energy loss during the cycle. Interpretation of the origin of such changes is not straightforward, and it requires deeper magnetic analysis. The increase of susceptibility is ascribed to the enhanced axial magnetic anisotropy seemingly induced by the conical-like shape of NW close to their end.

Fig. 4. Hysteresis loops of Fe and Fe@Au (a), CoFe and CoFe@Au (b), and Ni and Ni@Au (c) single core and core-shell NW. Insets show the corresponding low-field regions.

In conclusion, the present work studies the optimum parameters to grow continuous Au nanotubes by potentiostatic electrodeposition and confirms the possibility of fabricating arrays of a wide spectrum of transition metal magnetic NW coated by a shell of Au. Notably, the developed two-step electroplating technique is a less-expensive method to synthesize NW with high homogeneity. Core-shell NW can be prepared inside a hexagonally ordered template, or alternatively, they can be released from the membrane by chemical procedure for subsequent functionalization to specific biomedical applications. The magnetic behavior can be employed in directional functionalization of individual NW. In addition, the magnetic properties can easily be tailored by suitable choosing the composition of the metallic core due to the simplicity of the method.

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HIGHLIGHTS:

- Synthesis of transition metal-Au core-shell nanowires in a simple and scalable method.
- Release of synthesized nanowires for their use in biomedical applications.
- Evaluation of oxidation and magnetic properties of these nanostructures.