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FABRICATION AND CHARACTERIZATION OF SINGLE SEGMENT CoNiP AND MULTISEGMENT CoNiP/Au NANOWIRES

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Abstract. *This paper presents the fabrication of CoNiP single segment and CoNiP/Au multisegment nanowires. We have fabricated these nanowires by electrodeposition method into polycarbonate templates with a nominal pore diameter about 100 nm. The hystersis loops were measured with the applied magnetic field parallel and perpendicular to the wire axis using a vibrating sample magnetometer (VSM). The structure morphology was observed by Scanning Electron Miroscopy (SEM) and the element composition of CoNiP/Au multisegment nanowires were analyzed by EDS. The results show that these nanowires are very uniform with the diameter of 100 nm. The observed coercivity (H_C) and squareness (Mr/Ms) of CoNiP single segment nanowires are larger than the CoNiP/Au multisegment nanowires.*

Keywords: nanowires, single segment, multisegment, electrodeposition, magnetic properties.

I. INTRODUCTION

In recent years, nanoscale materials have attracted a large number of the worldwide scientists. As an inevitable part of these materials, nanowires possess unique electrical, electronic, thermoelectrical, optical, magnetic and chemical properties [1]. Nanowires therefore hold lot of promises for various applications. Up to now, nanowires including metallic nanowires, semiconductor nanowires, oxide nanowires, multisegment nanowires and semiconductor quantum nanowires have been fabricated and applied. Basic electronic devices like junction diodes, transistors, FETs and logic gates can be fabricated by using semiconductor and superlattice nanowires. Thermoelectric cooling system can be fabricated by using metallic nanowires. Semiconductor nanowire junctions can be used for different opto-electronic applications. Moreover, periodic arrays of magnetic nanowires hold high potential for recording media application. Nanowires are also potential candidates for sensor and biomedical applications [2].

Among these types of nanowires, multisegment nanowires play the most important role in the significant application in multiplexed bioanalysis, biosensors, magnetic cell separation and gene delivery with multiple functionalities [3]. The strength of multisegment nanowires is a wonderful combination of magnetic and nonmagnetic segments in only wire. These different segments can be chemically functionalized with multiple molecules on the same nanowires, with different ligands directed to different segments [4]. In most of multisegment nanowires, gold (Au) is used popularly as the nonmagnetic segment because of its particular properties. Gold nanowires are high conductive, more transparent, non-corrosive and are resistant to corrosion or oxidation. The individual gold nanowires are widely used for electrodes and interconnections in the semiconductor industry and nanoelectronics research [5]. In biomedicine field, gold nanowires are also for living cell study, gene delivery [6] and in biosensor [7]. In previous reports, the syntheses, characterization and growth of multisegment soft magnetic nanowires like NiFe/Cu, Au/Fe, Co/Pt and Au/Co have been described [4]. However, hard magnetic materials have a larger coercivity than soft magnetic materials, which affords nonvolatile memory characteristics in magnetic label or barcode function. The multisegment nanowires including Au segment have been applied successfully in many areas especially nanomedicine. For example, Au/Ni/Au multisegment nanowires are used to separating of His-tagged proteins; the gene delivery using Ni/Au multisegment magnetic nanowires exhibits obvious advantages [1].

The properties including length, diameter, and surface of nanowires depend mainly on the synthesis technique. The templating method is the most attractive, as it can be used for synthesizing nanowire with desired composition, size and aspect ratio. Using this technique, different segments can be introduced along the axis of a nanowire, and it is particularly attractive for the realization of multi-functionality. Therefore, the template assisted electrochemical deposition method has been used extensively for synthesizing multisegment nanowires.

In this study, we demonstrate the electrodeposition synthesis and characterization of the CoNiP/Au multisegment nanowires. Our efforts were focused on looking at the structural morphology and magnetic properties of the multisegment nanowires. The CoNiP alloy exhibits a relatively high perpendicular coercivity (Hc) of around 700-1200 Oe and a high saturation magnetization (M_s) of 0.41- 0.52 kG [8] and Au is well known biocompatibility with interesting surface behavior [4, 9]. Hence the combination of these two materials into combined multisegment nanowires maintains both characteristic properties with enhanced functionality.

II. EXPERIMENTAL

Both single segment nanowires CoNiP and CoNiP/Au multisegment nanowires were fabricated through electrodeposition process. At first, we have used porous polycarbonate template with pore diameter of 100 nm and thickness about 3 μm. Before electrodeposition, a copper (Cu) layer of thickness about 200 nm was sputter – deposited onto one side of the polycarbonate template and used as the working electrode to fabricate magnetic nanowires. To synthesize CoNiP/Au multisegment nanowires, two segments CoNiP and Au were deposited alternately into a nanoporous polycarbonate membrane (100 nm in diameter) by changing the corresponding electrolytes in an electrodeposition cell. The experiment was set up at room temperature with a constant applied potential - 0.85 V for CoNiP and -1 V for Au in 82 minutes in total. The electrolyte for the CoNiP contains 0.2M $CoCl_2.6H_2O$; 0.2M $NiCl_2.6H_2O$; 0.25M $NaH_2PO_2$and 0.7M H_3BO_3

with the pH value of the electrolyte bath was 5.5 for single-segment and pH of 6.8 for multisegment nanowires. The electrolyte for the Au consisted of 0.01 M $HAuCl_4$.

The multisegment CoNiP/Au nanowires (and single segment CoNiP nanowires) were separated from the polycarbonate membrane by dissolving the template in dichloromethane. After few minutes, the polycarbonate membrane dissolved in this solution and we obtained the CoNiP/Au multisegment nanowires.

The morphology of these nanowires was observed by scanning electron microscopy (SEM). The vibrating sample magneto meter (VSM) measured the magnetic properties of the nanowires at room temperature along both parallel and perpendicular to the wires. The structure and chemical composition of nanowires was investigated by energy dispersive spectroscopy (EDS).

III. RESULTS AND DISCUSSION

III.1. Morphological structure

The morphology of single segment CoNiP and CoNiP/Au multisegment nanowires was observed by SEM micrographs. The both normal and back scattering SEM images of the nanowires are shown in Fig. 1. Fig. 1(a) shows the single segment CoNiP nanowires spread on the glass substrate after removal of the membrane. The average diameter and the length of the CoNiP nanowires are about 100 nm and 3μm, respectively. The diameter of these single segment CoNiP nanowires are approximately equal to the pore diameter of polycarbonate template. Fig. 1(b) shows back scattering SEM images of multisegment nanowires composed of alternative segment of CoNiP/Au. The electron contrast in back scattered SEM images is the difference in atomic weights. The black and white contrast represents the CoNiP (darker) and Au (lighter) segment.

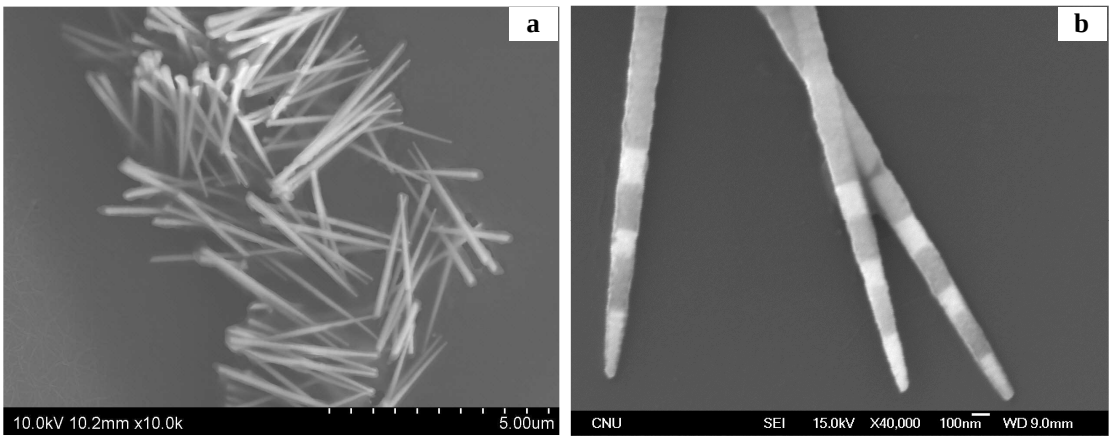

Fig. 1. Structural morphology of nanowire arrays (a) SEM image of CoNiP nanowires and (b) Back scattering image of CoNiP/Au multisegment nanowires

Both single segment CoNiP and CoNiP/Au multisegment nanowires have very uniform length. The average diameter of CoNiP/Au multisegment nanowires is almost equivalent with the diameter of nanopore in polycarbonate membrane with 100 nm. An interest is we can control the

size of nanowire base on measured time with deposition speed. The rate of Au and CoNiP deposition are 1.3 Å/s and 2.9 nm/s, respectively. In our experiment, we had to change the deposition time for each segment to deposit multisegment nanowires.

Particularly, to obtain the CoNiP/Au multisegment nanowire as shown in fig. 1(b), it took 13 minutes to get an Au segment about 100 nm in length and 1.8 minutes to get a CoNiP segment approximately 320 nm in length.

III.2. Chemical composition

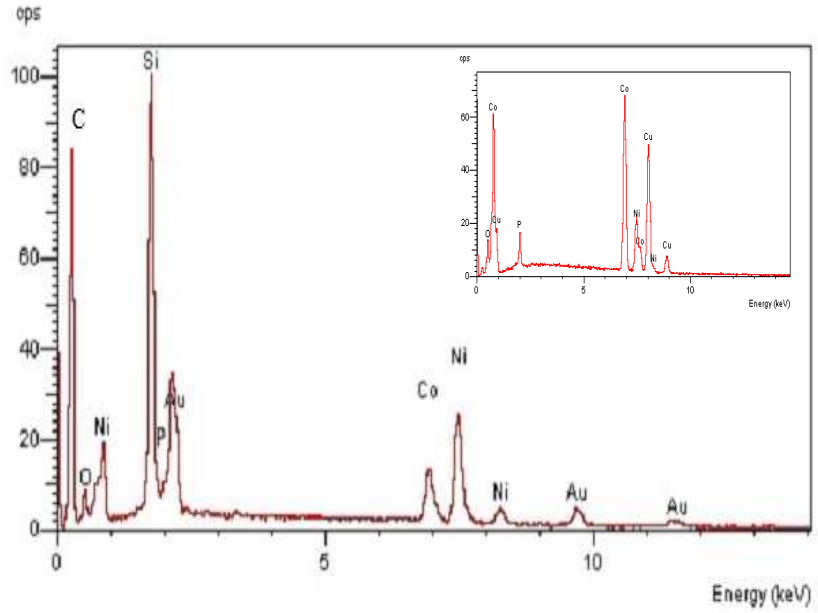

Fig. 2. Energy dispersive spectrum of CoNiP/Au multisegment nanowires (Inset shows EDS image of CoNiP nanowire)

The element composition of single segment CoNiP and CoNiP/Au multisegment were measured by energy dispersive spectra (EDS). Fig. 2 shows the EDS spectrum analysis. For single segment CoNiP nanowires consist only cobalt (Co), nickel (Ni) and phosphorus (P) elements. The copper (Cu) peak is due to the copper film sputtered on the surface of the sample. For CoNiP/Au multisegment nanowires, it indicates the presence of cobalt (Co), nickel (Ni), phosphorus (P) and gold (Au) elements. The C, Si, O peak are due to the substrate and template, which is used to measure the EDS of the disperse nanowire arrays. The EDS results showed that the element contents of Co of single segment is higher than multisegment nanowires.

III.3. Magnetic properties

In order to study the magnetic properties of single segment CoNiP and CoNiP/Au multisegment nanowires, we measured using vibrating sample magnetometer (VSM) with a maximum external magnetic field of 10000 Oe. Fig. 3 shows hysteresis loops for both single segment CoNiP

and CoNiP/Au multisegment nanowires embedded in polycarbonate membrane at room temperature when the magnetic field was applied parallel and perpendicular to the axis of the wires. The coercivity (H_c) and squareness (M_r/M_s) result are shown in Table 1. From Table 1, the coercivity and squareness of single segment CoNiP nanowires are larger than the CoNiP/Au multisegment nanowires for same length.

Table 1. The coercivity and squareness of CoNiP and CoNiP/Au nanowires observed in Fig. 3.

Samples	Applied field	Coercivity H_c(Oe)	Squareness M_r/M_s
CoNiP	$H_{//}$	1980	0.51
	$H_{\perp}$	1220	0.25
CoNiP/Au	$H_{//}$	1310	0.32
	$H_{\perp}$	1390	0.33

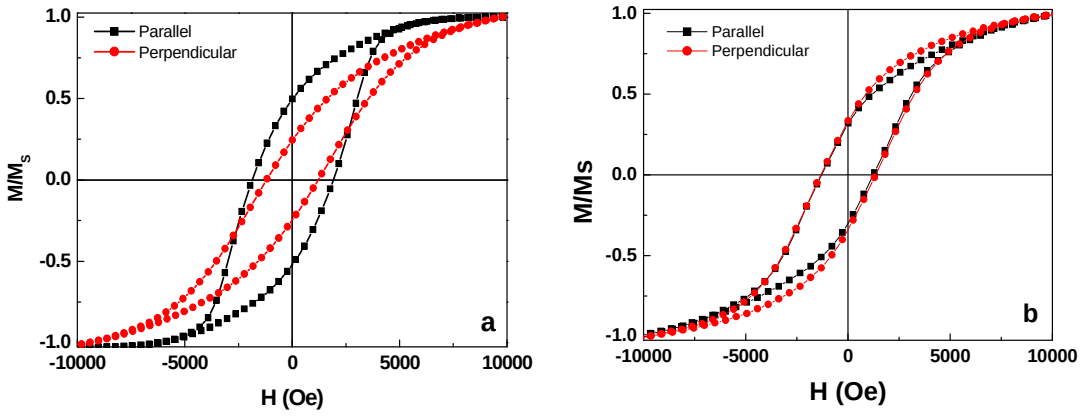

Fig. 3. The hysteresis curves of (a) CoNiP (b) CoNiP/Au nanowire arrays with both applied field parallel and applied field perpendicular to wires.

The highest coercivity value is 1980 Oe and the squareness is as high as 0.51 when the magnetic field is parallel to the axis of the wires as shown in fig. 3 (a). It is obvious that single segment CoNiP nanowires have easy magnetization direction parallel to the wires. Fig. 3 (b) also shows the two loops measured in parallel and perpendicular fields of CoNiP/Au multisegment nanowires are almost overlapping. This indicates that there is no preferential easy magnetization direction. This result is markedly different from that found for single segment CoNiP nanowires. The coercivity as well as the magnetic anisotropy in single segment nanowires are higher than in multisegment nanowires. Because, the higher Co content in single-segment nanowires could produce higher magnetocrystalline anisotropy.

IV. CONCLUSION

In brief, CoNiP and CoNiP/Au nanowires were synthesized successfully through electrodeposition technique in polycarbonate membrane. The multisegment nanowires consisted of segments CoNiP and Au in alternative fashion. The morphology and structure of the single segment CoNiP and CoNiP/Au multisegment nanowires were shown to be very uniform. The hard magnetic property was revealed through the magnitude of H_c. Comparison between the hysteresis loops of both types of nanowires made clearly the role of nonmagnetic segment Au in the hard magnetic multisegment nanowires, CoNiP/Au particularly. These multisegment nanowires will provide extremely promising biosensing applications in future.

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