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Characterization of Iron Nanowires Fabricated by Electrodeposition into Polycarbonate Template

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ABSTRACT

In the present study, commercially available polycarbonate (PC) membranes with different pore diameters were used as a template for electrodeposition of iron nanowires. The iron nanowire forests with average diameters ranging from 125 to 800 nm and several microns in length have been fabricated by reduction of metal ions into the nano-channels of PC templates. The morphology and microstructure of the iron nanowire forests have been characterized by a scanning electron microscope (SEM) and transmission electron microscope (TEM). The SEM results revealed that iron nanowires have a straight and cylindrical shape. TEM studies revealed a polycrystalline nature for the nanowires. These results showed that the iron nanowires prepared by PC templates are long-term promising candidates for the investigation of the size effect dependence of their properties.

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INTRODUCTION

The properties of metallic materials with small dimension have gained increasing attention and have been extensively investigated because of their distinct properties in comparison to bulk counterparts [1]. A number of reports have been published on the compression and tension strength of metallic nanowires/pillars of diameters < 5 μm. In all cases the strength of the wires/pillars increases with decreasing specimen diameter. This is called a size effect or "smaller is stronger" phenomenon. This size effect observation was first introduced by Uchic et al. with experimental studies on Ni nanopillars [2, 3] and followed by researches on a number of face-centred cubic (fcc) and body-centred cubic (bcc) metals. [4-6] Similar size effect behavior is observed for the mechanical behaviors of other specimens with small volumes, e.g. in thin films. The small sample dimension eliminates many of the features that control the strength in bulk metals. Dislocation interactions with free surface or confinement of dislocation strongly affect the mechanical properties. [7]

Metallic nanowires are used in several applications such as optical devices, batteries, semiconductors, or micro-electromechanical systems (MEMS). The metallic nanowires have also been proposed as essential components of flexible, electrically-conductive systems. Therefore, nanostructured materials have been investigated owing to their excellent properties, having usually superior mechanical behavior compared to their bulk counterparts [8, 9]. Understanding of the deformation mechanisms and mechanical properties of miniaturized materials is essential in order to design micro/nanodevices with high reliability. Iron nanostructured materials are relatively inexpensive, they have low to-xicity, and most of them are biocompatible. Therefore, they have been used in biomedical applications such as magnetic resonance imaging and in direct drug delivery systems [10]. In addition to biomedical applications, iron-based nanostructures can also be used in the fields of catalysis, energy and data storage. [11-13]

In the fabrication of nanostructured materials, several manufacturing techniques have been widely used including a template-assisted approach, nanoimprint lithography, and electron and beam processing [14-16]. These techniques enable to achieve and control the final shape of products with high accuracy. However, they are laborious, ineffective and expensive techniques on large-scale fabrication processes. Among these tech-

niques, the most effective method to fabricate nanostructured materials with tailorable dimensions is the template-assisted approach. The anodic aluminum oxide (AAO) and polymer membranes are widely used as commercially available templates [17]. Pore diameters of the AAO templates can be tailored within the range of 10-200 nm, and the thickness of the templates can be controlled from several nanometers to several hundreds of micrometers by changing the anodization conditions such as applied potential, preferred electrolyte, and time [18-20]. The polymer templates are produced by irradiation of heavy ions followed by chemical etching. Although the pores on the membrane are usually non-homogenously distributed across the surface, the polymer templates are chemically more stable such as strong acidic and alkaline solutions as compared to AAO templates [21]. Moreover, they can be readily dissolved in dichloromethane or chloroform.

Kawai et al. examined the magnetic behavior of nanowires of Co and Co-Ni alloys [22] as well as pure Fe [23] electrodeposited using AAO templates. Martin et al. [24] synthesized polymeric and metallic nanotubes into polymer templates with a great number of randomly distributed pores. Whitney et al. [25] studied the fabrication of Ni and Co nanowire arrays into the polymer templates with nanopores. Reports regarding the fabrication of metallic nanowires showed that many metallic nanostructures like Fe, [17, 26-29] Au, [30-32] Co, [27, 33, 34] Ni, [33, 35, 36] Ag [37] and Cu [38] have been successfully prepared using electrochemical deposition method with the help of the template-assisted approach.

The aim of the work reported in this study was to fabricate and characterize iron nanowires with different diameters into randomly distributed porous PC membranes by electrochemical deposition. Here, PC membranes with four different pore diameters, ranging from 125 to 800 nm, were used.. Having a different diameter metallic nanowires will enable the study of the size effect dependence of electrical and mechanical properties and allow a better understanding of the microstructure of metallic nanowires important for deformation mechanisms and mechanical properties.

MATERIALS AND EXPERIMENTAL PROCEDURES

Materials Used

PC templates with randomly distributed nanopores were procured from Millipore UK. The specifications of the PC templates are listed in Table 1. One side of the template was sputter-coated with gold-palladium (Au-Pd) using a Gatan 682 Precision Sputter Coating System for 1 minute to make them electrically conductive for a subsequent electrodeposition process (a few nanometers thick). This coating layer also provided a stable substrate for the growth of the wires. Pieces in sizes of 0.5 cm square were cut from the template sheets and the coated side was placed on a copper metal sheet (3 cm × 5 cm). The area of the PC-templates was measured with a caliper to determine the size of the exposure area. Special care was taken to paint with lacquer around the template to hold it in place and avoid metal deposition onto the copper sheet.

Table 2. Box Behnken test design parameters.

Samples	*Pore Diameter (nm)**	*Porosity (%)**	*Thickness (μm)**	*Average Pore Diameter (nm)***	*Porosity (%)***
Membrane 1	*100*	*4-18*	*25*	*125 ± 12*	*~ 8*
Membrane 2	*220*	*5-20*	*25*	*250 ± 19*	*~ 23*
Membrane 3	*400*	*10-20*	*10*	*430 ± 41*	*~ 14*
Membrane 4	*800*	*5-20*	*25*	*800 ± 48*	*~ 18*

** Information from the manufacturer*
*** Pore diameters measured via ImageJ software*

Electrodeposition of Iron

Electrodeposition of iron was carried out by a conventional electrochemical three-electrode setup, with a platinum counter electrode, a saturated calomel electrode (SCE) as the reference electrode, and the working electrode which was the PC template placed onto a copper sheet. The electrodeposition of iron was performed at a constant voltage of -900 mV and ambient temperature in 1 M iron (II) sulfate heptahydrate ($FeSO_4 \cdot 7H_2O$, Fisher Scientific, UK) solution with a pH value of 2.4 ± 0.2. A potentiostat method was utilized using the Gill AC instrument (ACM instruments). The electrodeposition time was altered between 30 to 90 minutes depending on the area of the PC template placed on the copper sheet, porosity percentage of the templates and template thickness. After electrodeposition, all specimens were rinsed with distilled water and ethanol and then dried using hot air. Then, the PC template was removed from the copper substrate and placed into a small tubular container (2 ml) to liberate the wires from the template. The PC template was dissolved in dichloromethane (CH_2Cl_2, Merck) with repeated changes of fresh solvent to separate the wires completely from the polymer. Then the small container filled with dichloromethane was sonicated in an ultrasonic bath for approximately half an hour to obtain individual nanowires for subsequent TEM characterizations.

Characterization Studies

The microstructure of the iron nanowires and surface of the templates were characterized via high-resolution SEM and TEM. A PHILIPS XL30 SEM (FEI, Eindhoven, The Netherlands) was used for the analysis of the surface morphology and geometry of the templates and the wires.

ImageJ software was used to measure the average pore diameter and dimensions of the nanowires from 25 SEM images with different magnifications. TEM was employed to obtain crystallographic information of the fabricated wires using the 200 kV PHILIPS CM20 analytical TEM (FEI, Eindhoven, Netherlands). For this, individual iron nanowires were prepared by dispersing the suspension containing the wires on a carbon mesh TEM grid using an airbrush. Diffraction data were acquired to identify the crystal structure of the iron nanowires, and bright field (BF) images were collected for obtaining structural information. Only nanowires with a maximum thickness of 115 nm were examined due to the limitation of electron transparency. Post-processing of diffraction pattern data was performed in Gatan microscopy software. The distance between the rings in the diffraction pattern was measured using the line profile method by adjusting the endpoints of a line. While indexing the diffraction pattern, the ratios of the diameters of the first five rings were measured. The ratios of the diameters of the rings enable to identify the crystal structure of the nanowire.

RESULTS AND DISCUSSION

The SEM images in Fig. 1 show the surface of the PC templates. The PC templates had a porosity of less than 25% and the nanopores were randomly distributed in the templates. Apart from the suppliers' data, the average pore diameters of the membranes were calculated as 125 ± 12 nm, 250 ± 19 nm, 430 ± 41 nm, and 800 ± 48 nm for membrane 1, 2, 3 and 4, respectively (shown in Table 1). These pore diameters represent the diameter of the final product. The porosity percentages for the membranes were ranging from 8 to 24%.

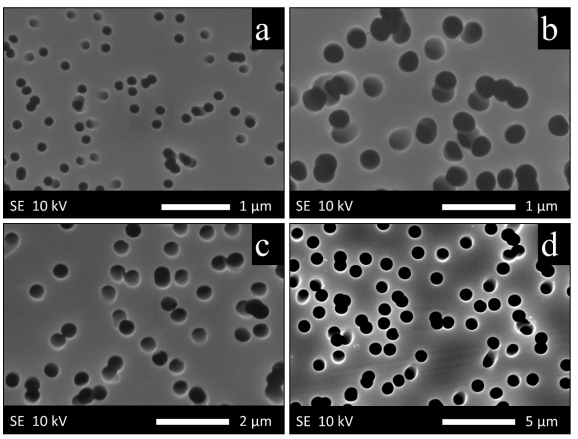

Figure 1. Top-view SEM images of the PC templates with average diameters of: (a) 125 ± 12 nm (b) 250 ±19 nm (c) 430 ± 41 nm (d) 800 ± 48 nm

Fig. 2 (a-d) shows the SEM images of liberated iron nanowire forests with average diameters ranging between 125 and 800 nm. The SEM images of free-standing nanowire forests indicate that the electrodeposition of iron in the pores was homogeneous. The final shape and morphology of the nanowires usually depend on electrodeposition conditions [39, 40]. While the length of the nanowire forest can be controlled by the deposition time, the diameters of the wires cannot be changed because of the inherent nature of the PC template [21, 39-41]. The forest, with a nanowire lengths up to 25 µm, was prepared. The average lengths of the fabricated iron nanowire forests were approximately 25, 8, 5 and 10 µm for the membranes 1, 2, 3 and 4, respectively. The SEM images in Fig. 2 (a-d) show that the nano-channels are not in parallel alignment indicating some variations of the final length of the wires. The PC membranes, as presented in this work, provide suitable templates for basic research and applications where a high degree of parallelism is not of importance, as well as for the size effect studies on magnetic, electrical and mechanical properties.

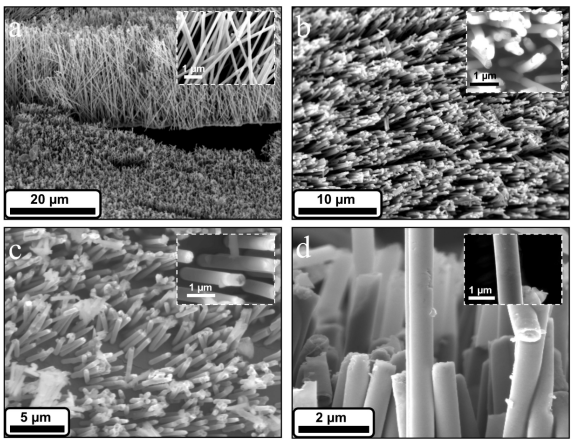

Figure 2. Representative SEM images of liberated iron nanowires with average diameters: (a) 125 ± 12 nm (b) 250 ± 19 nm (c) 430 ± 41 nm (d) 800 ± 48 nm. Insets show the higher magnification of the nanowires.

TEM investigations of an individual iron nanowire with a diameter of approximately 115 nm is summarised in Fig 3 (a). The diffraction pattern in Fig. 3 (b) confirmed the crystal structure as body-centered cubic (bcc) and the wires to be polycrystalline. Single-crystal nanowires are achieved at higher temperatures and lower voltages, which possess homogeneous and smooth surfaces. The voltages used in the experiments are quite high and temperatures low (room temperature) compared to a previously reported study in the literature [38]. Altering the electrodeposition conditions such as temperature and voltage might produce single crystal iron nanowires with smooth surfaces. The diameter of the nanowires could be decreased under 80 nm to obtain a single crystal nanowire by electrodeposition [30]. The results indicated that polycrystalline iron nanowires with four different diameters are promising candidates for the investigation of size effects of their optical, electrical, magnetic and mechanical behaviors and evaluating their potential applications.

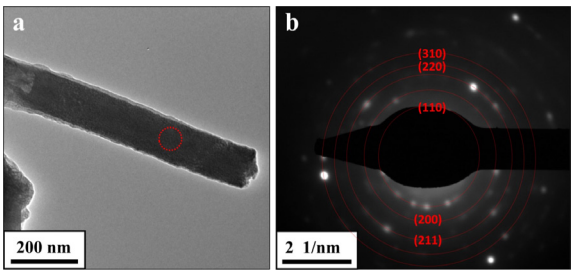

Figure 3. (a) Bright-field TEM image showing an iron nanowire (115 nm in diameter) used for diffraction pattern studies with the area marked with a dashed circle indicating where the diffraction pattern was taken. (b) A typical diffraction pattern of one iron nanowire; the rings are indexed.

CONCLUSION

An effective template-assisted approach has been presented to fabricate polycrystalline iron nanowires with diameters of 125 to 800 nm and length of 25 μm in an iron sulfate ($FeSO_4{\cdot}7H_2O$, at room temperature) solution by electrodeposition into PC templates with randomly distributed pores. The SEM results showed that the forests of iron nanowires ranging from approximately 125 to 800 nm in diameter can be successfully manufactured. The diameters of the fabricated iron nanowires are similar to the nominal diameter of the pores. The nanowires with a length of up to 25 μm could be fabricated by controlling the deposition time. Furthermore, the final shape of the metallic wires directly reflects the shape of the pores in the PC template. Finally, the TEM studies revealed that iron nanowire with a diameter of 115 nm was found to be polycrystalline and the reflection of the diffraction pattern matches with bcc structure type.

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