J Mater Sci (2006) 41:5598–5601
DOI 10.1007/s10853-006-0311-5

Electrochemically and template-synthesized nickel nanorod arrays and nanotubes

Shouhong Xue · Chuanbao Cao · Hesun Zhu

Received: 15 October 2004 / Accepted: 4 October 2005 / Published online: 20 June 2006

Abstract Nickel nanorod arrays and nanotubes have been successfully synthesized by electrochemical deposition using a polycarbonate membrane template. The length and average diameter of nickel nanorod arrays are 5–6 μm and 400 nm, respectively. The hysteresis loops indicate that the easy axis of magnetization of nickel nanorod arrays is perpendicular to the membrane plane. By silanizing the PC membrane and increasing the initial voltage, the nickel nanotubes could also be obtained. This method offers a convenient and efficient path to synthesize metal array nanostructures.

Nickel nanowires or nanorods have received considerable attention for their wide and potential applications in sensors and other electronics [1–4]. There are various methods to prepare nickel nanowires or nanorods including microemulsion in water-in-oil [5], electrochemical deposition in anodic aluminum oxide (AAO) template [6], γ-ray irradiation [7], sonochemistry and thermal decomposition of organic metal complexes [8–11], hydrogen arc plasma [12], borohydride reduction of metal salts [13], rapid expansion of supercritical solution [14, 15]. Among these methods deposition in AAO, polycarbonate (PC) membrane or other template is believed as a simple, less expensive and efficient way to synthesize Ni [6], Au [16, 17], Cu [18, 19], Pd [18, 19], Ag [20], Fe [21], Co [21] and other metallic nanostructures. In this study, the large area, highly uniform nickel nanorod arrays with conic morphology were successfully prepared in polycarbonate template by electrochemical deposition. The magnetic properties of nickel nanorod arrays were also studied. Furthermore, the nickel nanotubes were obtained by controlling initial voltage and polycarbonate membranes treatment process. The tip ends of highly uniform nickel nanorod arrays could potentially be used as probe in atomic force microscopy (AFM). For being hollow structure and instinctive magnetic property, the nickel nanotubes could serve as extremely small containers for encapsulation, as host materials to load pharmaceutical particles or catalysts, and carry them moving directly under outer magnetic field. This magnetic nanotube offers another way in drug releasing which varied from coating treatment of pharmaceutical particles.

In the study, the commercially available polycarbonate membranes (Whatman Inc.,) with cylindrical pore diameter 0.4 μm, 6–10 μm thickness and a pore density of ~10^8 pores/cm^2 were employed as template to prepare nickel nanorod arrays and nanotubes. Before the deposition of nickel nanorods, a thin Cu layer was sputtered on one side of membrane as working electrode, the graphic electrode acted as anode in two-electrode system. To prepare nickel nanotube, the special treatment of silanization for PC membranes was performed. The PC membranes were immersed in a beaker containing methanol for 5 min and silanized by sonicating for 3 min in a 3% (v/v) solution of vinyl triethoxylated silane in a normal hexane. Then the membranes were removed from this solution and heated overnight at 40 °C under Ar atmosphere. Lastly, a thin Cu layer was sputtered on one side of the silanized membrane to act as working electrode. In the experiments, all of the reactants used in electrodeposition system were analytical grade and without any further purification. The electrolyte consisted of 0.05 M $NiSO_4 \cdot 6H_2O$, 0.05 M H_3BO_3, 0.01 g/l

S. Xue · C. Cao (✉) · H. Zhu
Research Center of Materials Science, Beijing Institute of Technology, Beijing 100081, P.R. China
e-mail: cbcao@bit.edu.cn.

sodium laurylsulfonate (SDS), and de-ions water with a resistance higher than 18 MΩ. The electrolyte was stirred by Ar gas flow at room temperature and kept current density at 1.5 mA/cm^2, plating time varied from 20 min to 1 h.

The morphology and structure of the nickel nanostructures were characterized by scanning electron microscopy (SEM, Hitachi S-3500), energy dispersive X-ray spectroscopy (EDS), transmission electron microscopy (TEM, Hitachi H-800). Room temperature magnetic characterization was performed using a DMS vibrating sample magnetometer (VSM).

Figure 1 shows the SEM images of nickel nanorod arrays electrodeposited with 0.4 µm pore diameter polycarbonate membranes for plating time 20 min, plating voltage at 2.2 V. The nickel nanorod arrays have the length of 5–6 µm, the diameter of 400 nm, approximately. The measured diameter of nickel nanorods corresponds closely to the pore diameter that shows the diameter of nickel nanorods is decided by pore diameter in PC membrane. From SEM image we can easily see the conic morphology of nickel nanorods. Figure 2 shows the TEM image of nickel nanotubes.

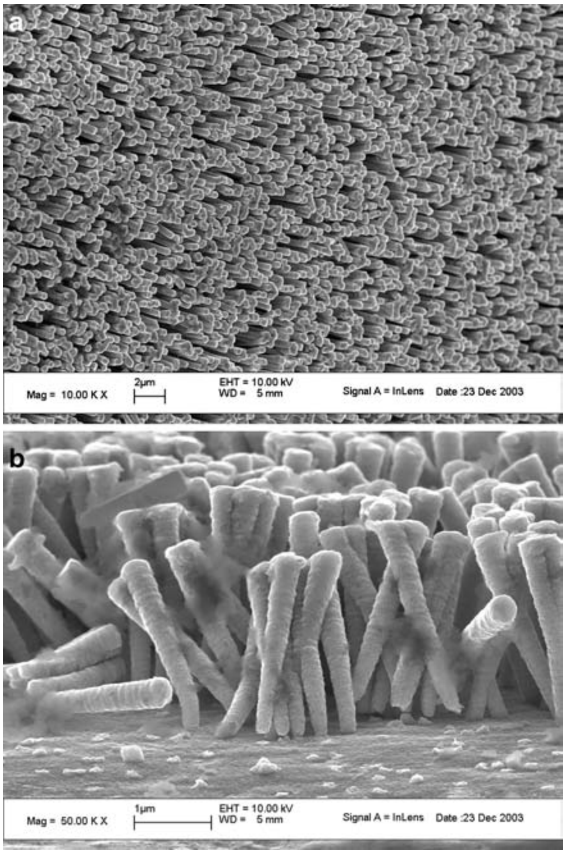


Fig. 1 SEM image of nickel nanorod arrays electrodeposited with 0.4 µm pore diameter polycarbonate membranes for plating time 20 min, plating voltage at 2.2 V

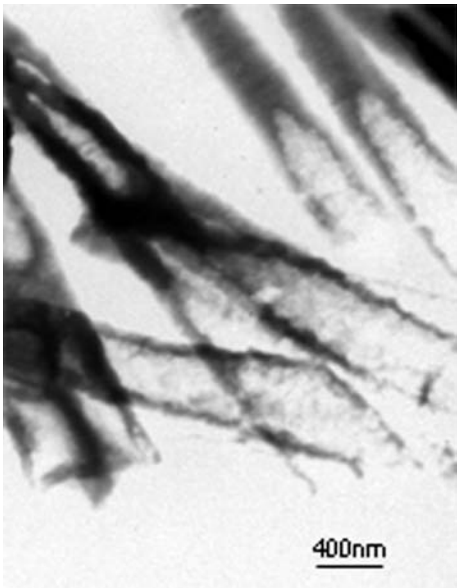


Fig. 2 TEM image of nickel nanotubes with 0.4 µm pore diameter polycarbonate membranes for plating time 10 min, plating voltage at 2.2V

In a two-electrode system, the reduction reaction occurs on the interface between cathode and solution. The process of electrochemical nickel deposition obeys the Nernst equation

$$\varphi = \varphi^{o} - \frac{0.0592}{n} \lg Q$$

where φ^{o} is standard electrode potential, $\varphi^{o} = \varphi^{o}(\mathrm{H}^{+}/\mathrm{H_2O}) - \varphi^{o}(\mathrm{Ni}^{2+}/\mathrm{Ni}) Q = \mathrm{C}^{4}_{[\mathrm{H}^{+}]}/\mathrm{C}^{2}_{[\mathrm{Ni}^{2+}]}$, $n = 4$. In the experiment, pH value was adjusted to 3 by 0.05 M H_3BO_3. Based on the Nernst equation and hydrogen overpotential in the solution, the corresponding equilibrium-reaction potential was calculated at 2.2 V.

During plating, nickel ions were reduced and nickel atoms were filled into template (PC membranes) that contained a large number of cylindrical holes with a narrow size distribution. After the deposition, the templates were dissolved away in dichloromethane, then the desired nanorod arrays or nanotube was obtained. Generally, there are two possible growing mechanisms in membrane pores. Firstly, the metal atoms nucleate on the surface of copper layer and they attach the copper layer to grow from bottom to up and fill up the pore. This bottom-up growing mechanism is easily form nanorod or nanowire. To keep the surface energy minimized during the deposition, the conical morphology of nickel nanorod arrays would be formed. Secondly, the metal atoms nucleate on the surface of PC membrane pore and grown along the pore wall. The nanotube would be formed at earlier stage of deposition. But with the increasing of deposition time, the membrane pore would be filled up and the nanotube would turn into nanorod. The nanotube could be obtained by controlling deposition time.

According to our experiments, we couldn't obtain nanotube through decreasing deposition time, so we thought that the nickel nanorods produced on column growth mechanism. For obtaining nickel nanotube, we tried to use vinyl-triethoxylatedsilane as pore-wall-modifying agent and increased the initial voltage. Through these processes, we did obtain nickel nanotube. We believed that the vinyl triethoxylated silane could form the strong affinity of the ethoxyl-groups of the modifying agent for Ni^{2+}. It resulted in a coating of the inner part of the PC membrane pores with Ni^{2+} ions and caused preferential deposition and growth of Ni on the pore walls when $Ni^{2+}$was electrodeposited with constant current mode. This process contributed to the nickel nanotube formation. On the other hand, we increased the initial voltage at the beginning of plating, and the initial current density increased and reached to 100 mA/cm^2. The increased initial voltage produced the large over-potential similar to the high saturation degree in the solution that profited the more crystal nucleus generating. These crystal nucleus acted as nucleated centers in the later plating. The later reduced metal ions preferentially attached the initial crystal nucleuses to grow along the pore wall. Based on these two steps that were both benefit to nickel nanotube forming, the nickel nanotubes were obtained.

Figure 3 shows the EDS analysis of highly uniform nickel nanorod arrays. It indicates the nickel nanorod arrays were made of pure nickel.

Figure 4 shows the hysteresis loop of nickel nanorod arrays measured with a maximum applied field of 12k Oe at room temperature. The field applied (⊥) represents magnetic field applied perpendicular to PC membrane plane and the field applied (//) represents magnetic field applied parallel to PC membrane plane. The coercivities (H_c) of nickel nanorod arrays for $H\perp$ and $H//$ orientation are about 174 Oe and 183 Oe, respectively. They are superior to that of the bulk nickel (< 10 Oe) [22]. The saturation magnetizations (M_s) of nickel nanorod arrays for the applied field parallel and the applied field perpendicular are about 1.782E–1 emu/cc and 1.713E–1 emu/cc that take place in a field of 6200 Oe. From hysteresis loops, the remanent magnetization for the applied field parallel is larger than that for the applied field perpendicular. This indicates that the easy axis of magnetization of nickel nanorod arrays is parallel to the membrane plane and perpendicular to the axis of nanorods. The further study on the magnetic behavior of nickel nanorod arrays was needed.

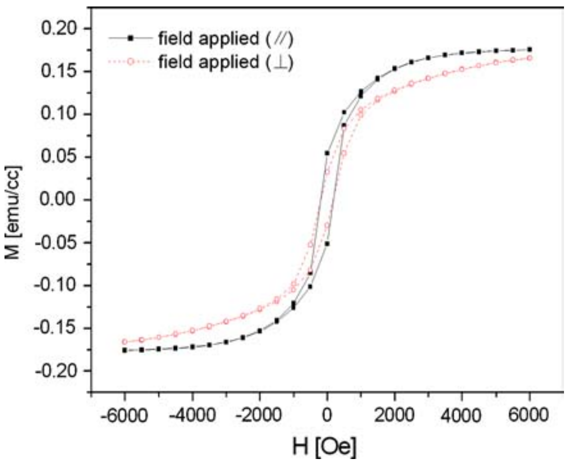
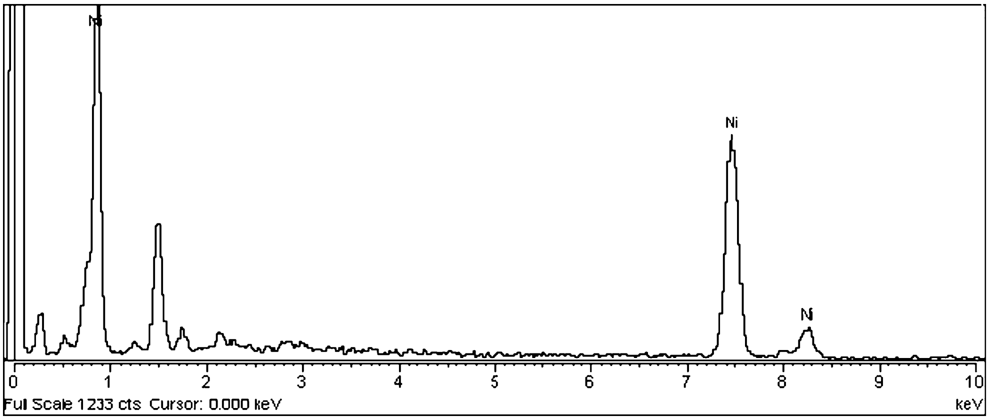


Fig. 4 Hysteresis loops of Ni nanorod arrays embedded in PC membrane at room temperature. The field applied (⊥) represents magnetic field applied perpendicular to membrane plane and the field applied (//) represents magnetic field applied parallel to membrane plane

In summary, the electrochemical deposition method had been described for synthesizing nickel nanorod arrays and nanotubes by using polycarbonate membranes as template. The length and average diameter of nickel nanorod arrays are 5–6 μm and 400 nm, respectively. The tips of nickel nanorods have conical morphology. The coercivities (H_c)

Fig. 3 EDS analysis showing the forming of high purity nickel nanorod arrays



of nickel nanorod arrays for the applied field parallel and the applied field perpendicular are about 183 Oe and 174 Oe, respectively. The saturation magnetizations (M_s) of nickel nanorod arrays for the applied field parallel and the applied field perpendicular are about 1.782E–1 emu/cc and 1.713E–1 emu/cc that take place in a field of 6200 Oe. The hysteresis loops indicate that the easy axis of magnetization of nickel nanorod arrays is perpendicular to the axis of nanorods. By silanizing the PC membrane and increasing the initial voltage, the nickel nanotube could be obtained. This method offers a convenient and efficient path to synthesize metal nanostructures.

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