

# Synthesis and magnetic properties of highly arrayed nickel-phosphate nanotubes

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## Abstract

In this study, nanotube arrays of nickel-phosphate have been developed by electroless deposition into sub-micro to nanometer sized pores of the porous alumina templates by hypophosphite electrolytic solution composed of NiSO<sub>4</sub>, NaH<sub>2</sub>PO<sub>2</sub>, NaC<sub>2</sub>H<sub>3</sub>O<sub>2</sub> and Na<sub>3</sub>C<sub>6</sub>H<sub>5</sub>O<sub>7</sub> at 80–100 °C and pH = 3–6. The dimension of the formed nanotubes has 1 μm in length, 200–300 nm in diameter and 80–150 nm in thickness of tube walls. Transmission electron microscopy examination of the nanotubes clearly show amorphous hallow structure with a average grain size of ~ 5 nm. The hysteresis loops of the nanotube arrays show a coercive field of about 200 Oe under treatment in 95%N<sub>2</sub>/5%H<sub>2</sub> atmosphere at 500 °C as the magnetic field was applied along parallel and perpendicular to tube axis. The nanotube arrays also exhibit an anisotropic magnetic property with easier saturation along the perpendicular direction. However, both coercive field and saturation of remanent magnetization of the nanotube arrays become lower while continually increasing heat treatment temperature up to 900 °C.  
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## 1. Introduction

Magnetic film and nanowires have been the most interesting and intensely investigated fields of material in recent years [1–5]. The fabrication of magnetic metal arrays has not only the fundamental worth in these materials but also their potential utilization in magnetic recording. For high density storage media, one single nanosized pattern, ordered nanodots or nanotubes is a single domain structure and denotes one bit signal. Magnetic period nanostructure arrays as an ultra-high-density magnetic storage can achieve recording densities of more than 100 Gbit/in<sup>2</sup>, which is more than the continuous magnetic film of 40 Gbit/in<sup>2</sup> [6–8]. Arrays of ferromagnetic nanodots, nanowires or nanotubes may be fabricated by several methods such as e-beam lithography, imprint technology or template. The porous template can be considered as one quicker and cheaper method to prepare highly perpendicular magnetic anisotropy structure [9–12]

because AAO (anodic aluminum oxide) has high oriented porous structure with uniform and nearly parallel pores that can be organized the pseudo ordered nanowires or nanotubes array. Such structure also shows high magnetic anisotropy phenomena with the shape axis parallel to the nanowire arrays.

On the other hand, it is well known that transition metals such as Fe, Co, Ni and their alloy have higher saturation magnetization as well as Curie temperature, and lower crystalline anisotropy. Furthermore, magnetic properties are strongly influenced by the dimension and crystal properties, which also depend on the physical structure of templates and growth mechanism of wires or tubes. Recently, magnetic properties of nickel nanowires have been investigated by several groups because nickel nanowires show important applications in magnetic recording [13,14].

Compared with the electrodepositing method, electroless deposition needs neither power nor smooth interface. In this study, it was found that there exist some variation in nucleation rate from heterogeneities process and some defects are also induced in this process. By adjusting deposition,

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we have fabricated uniform size nanotube and nanowire arrays by autocatalytic electroless deposition in AAO. Furthermore, the effect of experimental conditions on the morphology of nanostructure will be discussed. The preliminary results of their magnetic properties are also reported.

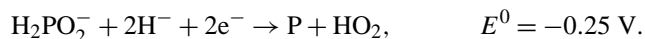
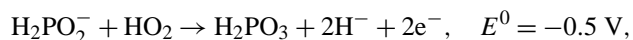
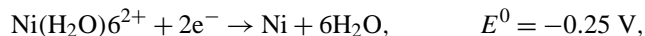
## 2. Experimental procedure

High ordered AAO templates with pore diameter of about 50–200 nm were used from commercial porous alumina templates (Whatman 6809 7013). The electrolyte solution was prepared from NiSO<sub>4</sub> (0.05 M), NaH<sub>2</sub>PO<sub>2</sub> (0.04 M), NaC<sub>2</sub>H<sub>3</sub>O<sub>2</sub> (0.01 M) and Na<sub>3</sub>C<sub>6</sub>H<sub>5</sub>O<sub>7</sub> (0.005 M). One side of AAO templates was sputtered with 200 nm Au film as catalytic layer. The coated template was first immersed in an aqueous solution and kept at low vacuum environment to enhance the solution into the pores. Subsequently, Ni–P nanowire arrays were deposited in the pores from the electrolyte solution at 80–95 °C and pH 3–6 adjusted by sulfuric acid and ammonia. For obtaining the isolated Ni–P nanowire arrays, the Ni–P deposited AAO was dissolved in 5 wt% NaOH solution at 25 °C for 20 min and then slightly washed several time to remove the original AAO template.

The microstructure and morphology were characterized by transmission electron microscopy (TEM) and scanning electron microscopy (SEM). The magnetic properties were measured by magnetometer. X-ray diffraction (XRD) and energy dispersive spectra (EDS) are employed to study the morphology and chemical composition of nanotubes. The magnetic property of Ni–P nanotubes is characterized using a vibrating sample magnetometer (VSM).

## 3. Results and discussion

The redox reactions would take place spontaneously in electroless bath if total electrochemical potential  $\Delta E^0$  value is positive. The autocatalytic redox reactions of Ni–P nanotube arrays in an acid medium are shown in the following equations:



The  $E^0$  represents the single electrode potential. If the  $E^0$  value of a reducing reaction is lower than that of oxide reaction, the Ni–P deposited reaction will possibly take place in electrolytic solution. According to the  $E^0$  value, Ni and P could be reduced by NaH<sub>2</sub>PO<sub>2(aq)</sub>. However, as a rule, these reaction could not proceed without catalyst. Therefore, Au film usually acts as a catalyst in the reaction.

Fig. 1 shows pH-potential of Ni–H<sub>2</sub>O group and P–H<sub>2</sub>O group at room temperature. Three stable regions of Ni<sup>2+</sup>,

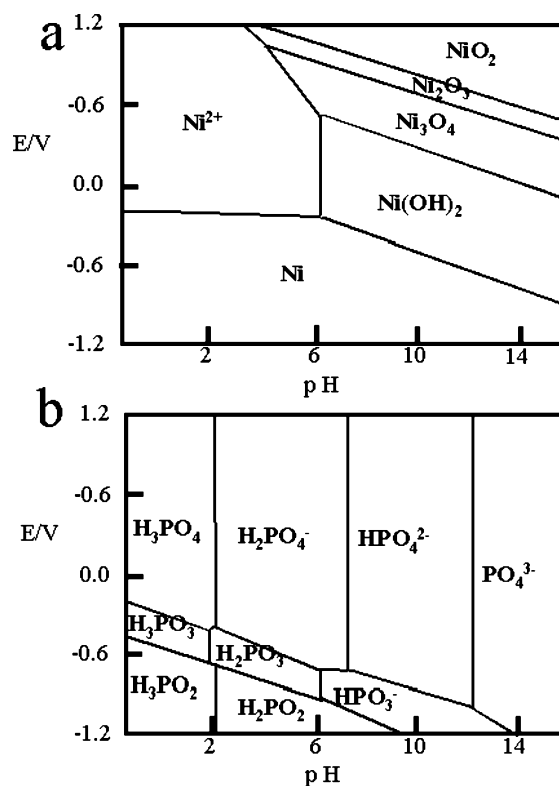


Fig. 1. (a) The diagram of pH-potential of Ni–H<sub>2</sub>O group and (b) P–H<sub>2</sub>O group at room temperature.

Ni and NiO are illustrated in Ni–H<sub>2</sub>O group: Ni keeps stable at low potential for any pH values. If potential increases ( $> -0.25 \text{ V}$ ), Ni will be oxidized as Ni<sup>2+</sup> (at pH  $< 6$ ) or NiO (at pH  $> 6$ ). In pH-potential of P–H<sub>2</sub>O group, it can be found that H<sub>2</sub>PO<sub>2</sub>–H<sub>2</sub>PO<sub>3</sub> group appears at pH  $< 6$  in acid region and H<sub>2</sub>PO<sub>2</sub>–HPO<sub>3</sub> group appear at pH  $> 6$  in alkaline region. It is clear to understand that Ni could be formed regardless of at acid and alkaline electrolytic bath. However, precipitated NiO is much easily formed in alkaline electrolytic bath so that it would be better to control the bath at the pH  $< 6$ . Besides, while changing temperature and complex agent (NaC<sub>2</sub>H<sub>3</sub>O<sub>2</sub> and Na<sub>3</sub>C<sub>6</sub>H<sub>5</sub>O<sub>7</sub>), pH-potential will be shifted but the tendency remains similar.

After removing the AAO in aqueous NaOH, Fig. 2 shows the SEM image of Ni–P nanotube arrays formed in an electrolytic bath at 90 °C and pH = 4.5. The nanotubes were estimated with the average dimension of 200–300 nm and length of about 2  $\mu\text{m}$ . The TEM image of Ni–P nanotubes in Fig. 2c further shows that these nanotubes are uniform with the wall thickness about 40 nm and the corresponding electron diffraction pattern indicates it is an amorphous structure. So far, most of the investigations in the literature have demonstrated the solid nanowires structure can be developed via AAO template. However, in this work, the formation of the tube structure could be explained as follows. As the Au was sputtered into the pores, hollow structure could be formed as show in Fig. 2d. Next, the deposited Ni–P could cause preferring growth on the pore wall to form nanotubes.

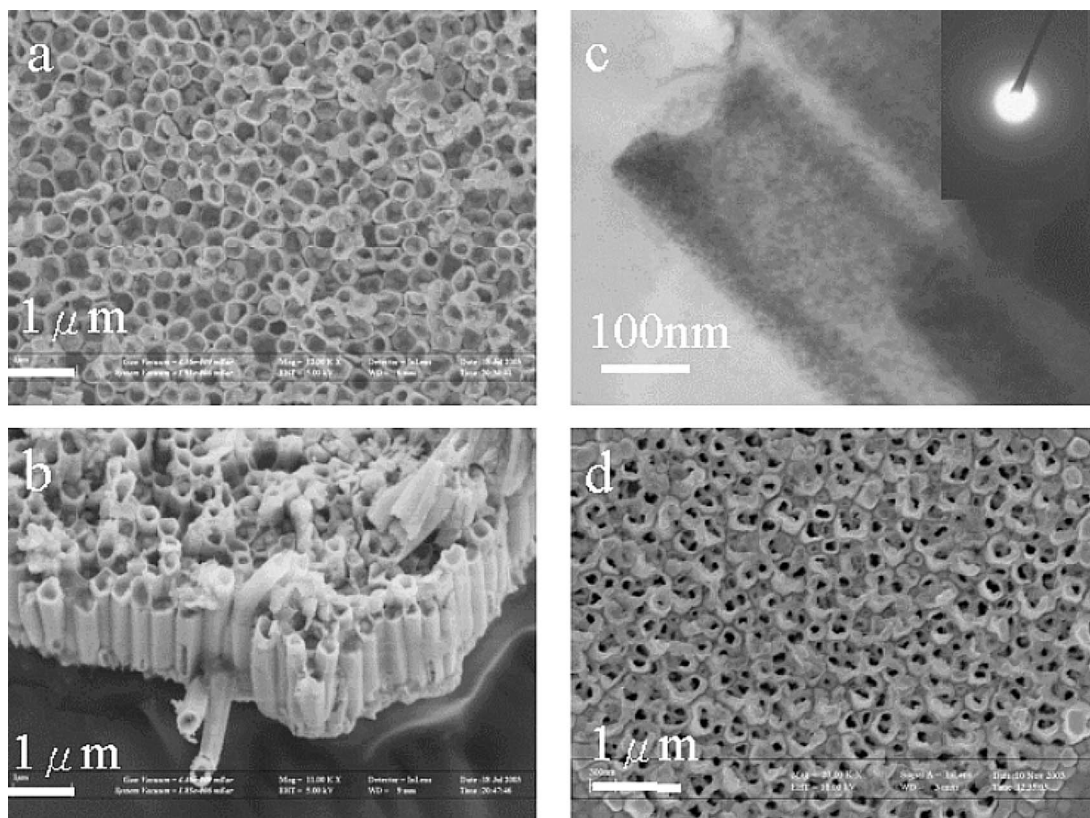


Fig. 2. (a), (b) Up view and side view of the SEM image of Ni–P nanotube arrays controlling electrolytic bath at 90 °C and pH = 4.5. (c) TEM image and diffraction pattern of Ni–P nanotubes. (d) The hollow structure of catalyst Au film after removing the AAO in NaOH(aq).

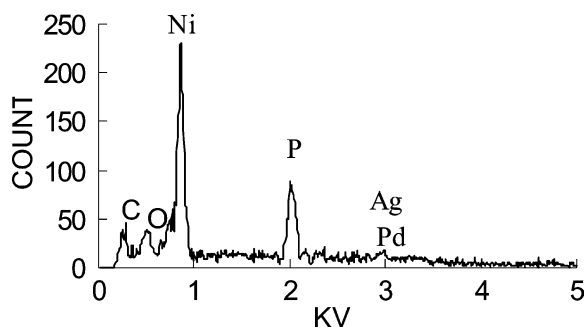


Fig. 3. An energy disperse spectrometry analysis of nanotubes. The conductor film is the composition of Ag and Pd.

The energy disperse spectrometry analysis indicates that the nanotubes are composed of Ni and P (Fig. 3).

The XRD patterns of Fig. 4a further indicate that the Ni–P nanotubes exhibit amorphous structure with  $\sim 5$  nm ultra-fine grains. However, as the nanotubes were heated up to 500 °C in 95% N<sub>2</sub>/5% H<sub>2</sub> atmosphere, Nickel HCP phase was detected as shown in Fig. 4b. The grain size in the Ni–P nanotubes increases with increasing temperature. At 700 °C, the average grain size was estimated as 35 nm.

Moreover, it was found that different solution pH values in electrolytic bath result in the morphology change of the nanostructure. The wall of the nanotubes becomes thinner while increasing pH to 6 because the deposited rate will

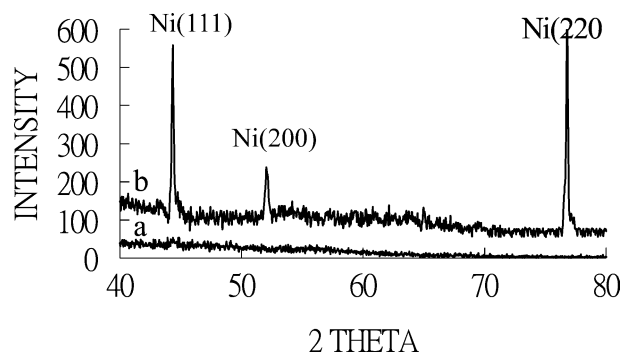


Fig. 4. XRD diagram of Ni–P nanotubes (a) As-deposited sample reveals amorphous structure and (b) heated up to 500 °C sample at 95% N<sub>2</sub> / 5% H<sub>2</sub> atmosphere appears as Nickel HCP phase.

decrease under high pH value. Fig. 5a shows this kind of structure where many sheet residues appear due to the deposition of NiO. On the other hand, at lower pH value, i.e., 3, both reduction and deposition rate of metal ions in the electrolytic bath become faster at the bottom of the pore. Therefore, nanowires instead of nanotubes were grown along the pore channel to form a solid structure (Fig. 5b).

Fig. 6 shows the hysteresis loop of the Ni–P nanotubes array measured at room temperature. The H(pl) and H(pd) represent external magnetic field parallel to Ni–P nanotubes and perpendicular to Ni–P nanotubes, respectively. While the sample was heated less than 300 °C, no clear hystere-

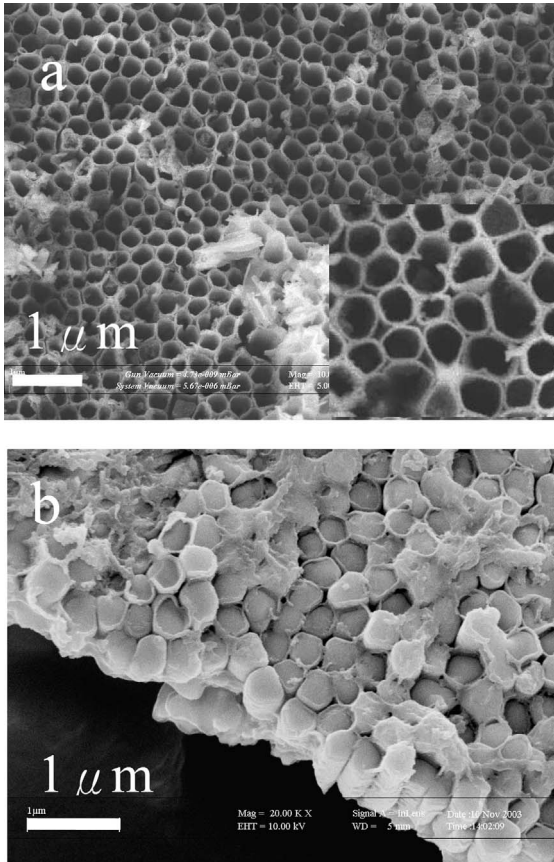


Fig. 5. (a) The SEM image of thinner wall nanotubes are obtained while increasing pH to 6. (b) The solid nanowires structure is generated at pH = 3.

sis loop of Ni–P nanotubes array was detected as shown in Fig. 6a that might be related to the amorphous structure. As

heating the sample up than 500 °C, a distinct hysteresis loop (Fig. 6b) begins to appear and this suggests the formation of crystalline structure. It would be also found that both saturation magnetization ( $B_s$ ) and remanence ( $B_r$ ) of H(pl) are larger than those of H(pd). However, the coercive field ( $H_c$ ) for H(pl) and H(pd) orientation are similar about 200 Oe. As compared with the  $H_c$  of Co–P nanowires (800–1300 Oe), the Ni–P nanotubes array are more suitable for magnetic recording.

The hysteresis loop also shows different magnetic anisotropy and this indicates that the easily magnetized direction is perpendicular to the nanotubes axis. Moreover, the arrays appear very low remanent magnetization less than 20%  $B_s$ . However, while continually increasing heat-treatment temperature up to 900 °C, both coercive field and saturation of remanent magnetization of the nanotube arrays become much lower. This indicates that magnetic anisotropy of the nanotube arrays gradually disappears under overmuch thermal effect.

#### 4. Conclusion

Electroless deposition with Au catalyst can be applied to fabricate Ni–P magnetic nanotube arrays by controlling electrolytic bath at 90 °C and pH = 4.5–6. The studies indicate that the highly ordered array nanotubes are amorphous structure with the average diameter of 200–300 nm and length of 2 μm and form a highly ordered array. The hysteresis loop of the array nanotubes shows magnetic anisotropy with the easily magnetized direction perpendicular to the nanotubes axis.

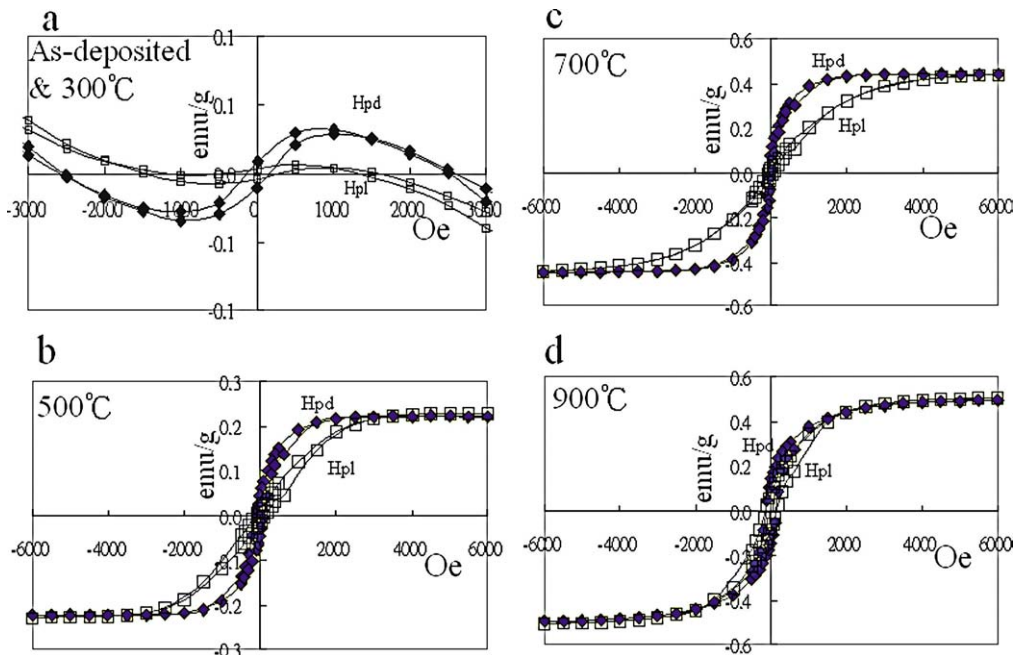


Fig. 6. The hysteresis loop of Ni–P nanotubes array measured at room temperature, 300 °C, 500 °C, 700 °C and 900 °C.

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