FABRICATION OF IRON NICKEL ALLOY PHOTONIC CRYSTALS BY ELECTRODEPOSITION

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SUMMARY

We have demonstrated a promising route to fabricate FeNi photonic crystals by electrodeposition into colloidal crystal templates formed by self-assembly of polystyrene (PS) spheres. The photonic crystals obtained acts as an air-sphere/FeNi nanocomposite with inverse opal structure and tuning pore size, which have high application potentials in photonics.

Keywords: Nanocomposite; Photonic crystals; FeNi alloy; Inverse opal; Electrodeposition

INTRODUCTION

Photonic crystals (PCs), the materials with a periodic modulation of dielectric constant, have attracted a great attention due to their unusual optical properties and promising applications. One of the important classes of PCs is three dimensionally ordered macroporous (3-DOM) materials with inverse opal structure, usually prepared by colloidal crystal templating (CCT) method [1-2]. Ni-based nanomateriasls have important physical properties and potential applications in the fields of catalysts, high-density data storage, electrodes, and sensors [3-5]. The production of 3-DOM magnetic materials is of importance in a range of applications, such as photonic crystals and high density magnetic data storage devices. The properties of 3-DOM materials are critically dependent on their dimensionality and morphology. Moreover these materials often exhibit new and enhanced properties over their bulk counterparts, which have made magnetic nanostructures of a particularly interesting class of materials for both scientific and technological explorations. Therefore ordered macroporous magnetic structures provide a unique model system to study these effects. Preparation of morphology-controlled ordered porous Fe-Ni array should be of importance both in fundamental research and in applications.

According to their applications, the fabrication process must be carefully controlled to obtain sufficient porosity, different pore sizes and microstructure. In the past few years, a new approach using colloidal crystals as self-assembled templates for macropores has been used to prepare macroporous materials with well defined pore sizes and controlled three-dimensional ordering. A typical procedure to prepare 3-DOM materials by CCT method includes three steps, namely, the self-assembly of the template, infiltration of the desired materials and removal of the template. Various methods have been applied to introduce the desired materials into the void spaces between spheres in the colloidal crystal template. These are r.f. magnetron sputtering [6], chemical vapor deposition [7], nano-particle infiltration [8], electro-chemical deposition [9-10], chemical precipitation [11] and sol-gel process [12-13]. Electrodeposition is a feasible method for the production of 3-DOM metal and alloys because it is possible to attain a complete filling of interstitial space from the bottom up to the top layers of the template with good “volume templating” and negligible shrinkage, so that the inverse opal resembles the interstitial space very closely.

Recently, Hao et al have reported the magnetic properties of ordered macroporous nickel structures, which gives us a thorough preview of magnetic property on nickel system [14]. Bartlett et al have reported the researches on the preparation of two- or three-dimensionally ordered macroporous cobalt, iron, nickel, and nickel iron alloy films [15]. In this work, we report the synthesis of 3-DOM FeNi alloy films by CCT method. The relationalship between the parameters of electrodeposion and the morphology and structure of 3-DOM FeNi alloy film were discussed in details.

EXPERIMENTAL

Materials

The starting materials used were styrene (C_8H_8) , potassium persulfate($K_2S_2O_8$), nickel sulfate, ferrous sulfate, boric acid, sodium dodecyl sulfate (SDS) and toluene. All solvents and chemicals were of reagent quality and were used without further purification.

Monodisperse polystyrene (PS) latex spheres with diameters from 200 to 600 nm and relative standard deviation smaller than 4% (on the diameter) were synthesized through an emulsifier-free emulsion polymerization technique [16].

Self-assembly of PS colloidal crystal templates

Polystyrene colloidal crystals were grown on indium-tin oxide (ITO) coated glass. The preparation process was as follows: ITO glass substrate was placed into a cylindrical vessel and an aqueous suspension of PS spheres (0.1 vol%) was added. The vessel was then placed into an incubator at 55 °C until a complete-growth was achieved. As a result a well-ordered multi-layer PS colloidal crystal was obtained on the ITO substrate, which can then be used as the template. The templates appear opalescent with colours from green to red, depending on the angle of observation and the diameters of PS spheres.

Fabrication of 3-DOM iron nickel alloy films

Electrodeposition was carried out in a standard three-electrode cell. The aqueous solution used for FeNi deposition was composed of $NiSO_4$ (0.08mol/L), $FeSO_4$ (0.02mol/L), H_3BO_3 (0.1mol/L) and SDS. The pH value was adjusted to 3.0-3.5. The working electrode was an ITO glass substrate with a PS colloidal crystal film. A platinum plate and a saturated calomel electrode (SCE) were used as the counter and reference electrodes, respectively.

After deposition the deposit was washed immediately with water to remove other ions covered on it. The polystyrene template was then removed by immersing in toluene for

12 h. Air sphere/ iron nickel nanocomposites have been formed and display bright iridescence due to Bragg diffraction indicating the pores arranged in a well ordered structure with pore diameter in the range of the wavelength of visible light.

Characterization

The morphologies of 3-DOM iron nickel films were characterized by using a Hitachi S-4800 scanning electron microscope operating at 20kV and an optical microscope. The crystal structure of the alloy film was investigated by X-ray diffraction (XRD, Phillips X Pert diffractometer system with $Cu_{K\alpha}$ source).

RESULTS AND DISCUSSION

The structures of the final 3-DOM materials obtained are strongly dependent on the electrodeposition time. Fig. 1 shows SEM micrographs of top surface of macroporous iron nickel alloy films electrochemically deposited with different deposition time at a deposition potential of -0.9V *vs*. SCE. In general, the thickness of the film increases with increasing electrodeposition time. When deposited for 1 min, 2 DOM FeNi film was observed with each air hole surrounded by six spherical voids (Fig.1(a)). When electrodeposition time is increased to 2 min (Fig.1(b)), the FeNi film has begun to grow around the spheres in the upper layer and 3-D structure was formed, but the pore walls has not been deposited completely, and the surface of the film is not smooth. After electrodeposition for 5 min, it is apparent that spherical voids are arranged in a well ordered, close packed hexagonal network. The spherical holes are located above three neighboring hollow sites in the crystal. Each cavity formed by the PS particles has three dark spots corresponding to the contact points with the three particles in the layer below (Fig.1(c)). When the thickness of the FeNi alloys exceeds that of the PS template, the growth of FeNi alloy will extend from the spaces among the colloidal spheres toward the colloidal surface. After the removal of the template the 3-DOM structure will be destroyed. The preparation of 3-DOM metal and alloy films with different thickness is a convenient method by which to study the evolution of the surface morphology and shapes of the pore. The measured average center to center distance between the air spheres is the same as the diameter of the original PS spheres used to prepare the colloidal crystal templates. Usually shrinkages around 17%~35% have been reported in the literatures by other infiltration method [17]. This indicates that the 3-DOM iron nickel film does not suffer any shrinkage after the removal of the template by using electrochemical deposition method.

The 3-DOM iron nickel alloy electrodeposited from PS colloidal crystal templates with different diameters of PS spheres were characterized by optical microscope. Fig. 2 shows the optical microscope images. The size of the voids is determined by the size of the PS spheres used. With the increase of the size of the voids, the 3-DOM iron nickel films appear colours from purple to red due to light reflection. The light emission of the surface of 3DOM FeNi can be explained by Bragg's law, $2d\sin\theta = n\lambda$, where λ is the wavelength, θ is the scattering angle, n is integer representing the order of the diffraction peak, and d is the interplanar distance, here d is the center to center distance of air spheres. When the incident angle is fixed, λ will change with the change of the interplanar spacing of the crystal, and the film will display different colours.

The macroporous structure of the materials synthesised using CCT method is the inverse of the original template and therefore the 3-DOM structure of iron nickel film directly reflects the packing of the PS spheres in the colloidal crystal template. By using PS templates with different packed arrays of spheres, 3-DOM iron-nickel films with different arrays of interconnected spherical voids can be obtained. Fig.3 (a) and (b) show SEM images of 3-DOM iron nickel films with different air sphere arrangements. In Fig.3 (a) the spherical pores are arranged in a well ordered hexagonal array, while in Fig. 3(b) they are arranged in a square array. Fig. 3(c) and (d) show SEM images of the PS colloidal crystal template with corresponding sphere arrays used for electrodeposition.

The electrodeposition temperature has been found to be another parameter that affects the morphology of 3-DOM iron nickel alloy thin films, as indicated in Fig.4 (a)-(c). The effect observed is an increase of roughness of pore walls with increasing temperature. Fig. 4(a) shows the SEM image of 3-DOM FeNi film deposited at 40℃. The architecture is of high quality with smooth pore walls and uniform pore diameter. Three pore windows can be observed through the pore mouth of the first layer. When the deposit temperature was raised to 50 ℃, the network keeps the 3-D structure while the pore walls lose their smoothness, as shown in Fig. 4(b). When deposited at 60 ℃, the thickness and roughness of the pore walls increase, while the ordered arrangement of the airspheres decreases (Fig. 4(b)).

Metal ions in the solution migrate toward the working electrode with the colloidal crystal template in the electrodeposition process. Subsequently, metals reduce and deposit into the interstitial spaces of the templates. The migration speed of ions is higher at higher deposition temperature, which will lead to a higher deposition rate and the formation of larger FeNi grains. The larger grains deposited in the voids between PS spheres will lower the smoothness of the films. In our experiment, we also found that PS colloidal crystal templates were easy to delaminate in the electrolyte with a higher temperature (>60℃) and the ordering of the spheres cannot be preserved.

Fig. 5 shows the X-ray diffraction pattern of the 3-DOM iron nickel alloy thin film deposited on the ITO substrate after the PS template has been removed. The X-ray diffraction pattern shows a characteristic reflection of cubic iron nickel alloy phase which displays a (111) growth orientation. The peaks at 2θ=44.5°, 64.9° and 82.3° are identified to (111), (200) and (211) facets of the alloy, respectively. The other peaks marked in the figure are the characteristic diffraction peaks of ITO coater on the substrate, the peaks at 2θ=30.1°, 50.2°, 60.2° and 82.3° can be identified to (222), (400), (441) and (622) facets.

CONCLUSIONS

We have presented results of templated assisted electrochemical deposition of iron nickel magnetic alloys in the interstitial spaces of self-assembled templates. The resulting magnetic nanostructures have three dimensionally ordered macroporous network. The template growth technique offers the potential of a low-cost preparation method for submicron patterned magnetic media. The factors chosen for investigation in this study were electrodeposition time, temperature and colloidal crystal template used. The deposition time is a key parameter affects the thickness of the film. Packing arrays and diameters of the PS colloidal spheres affect directly the arrangement and the sizes of the void in 3-DOM structures. By controlling the deposition temperature, 3-DOM FeNi alloy with well ordered macroporous structure can be obtained.

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References

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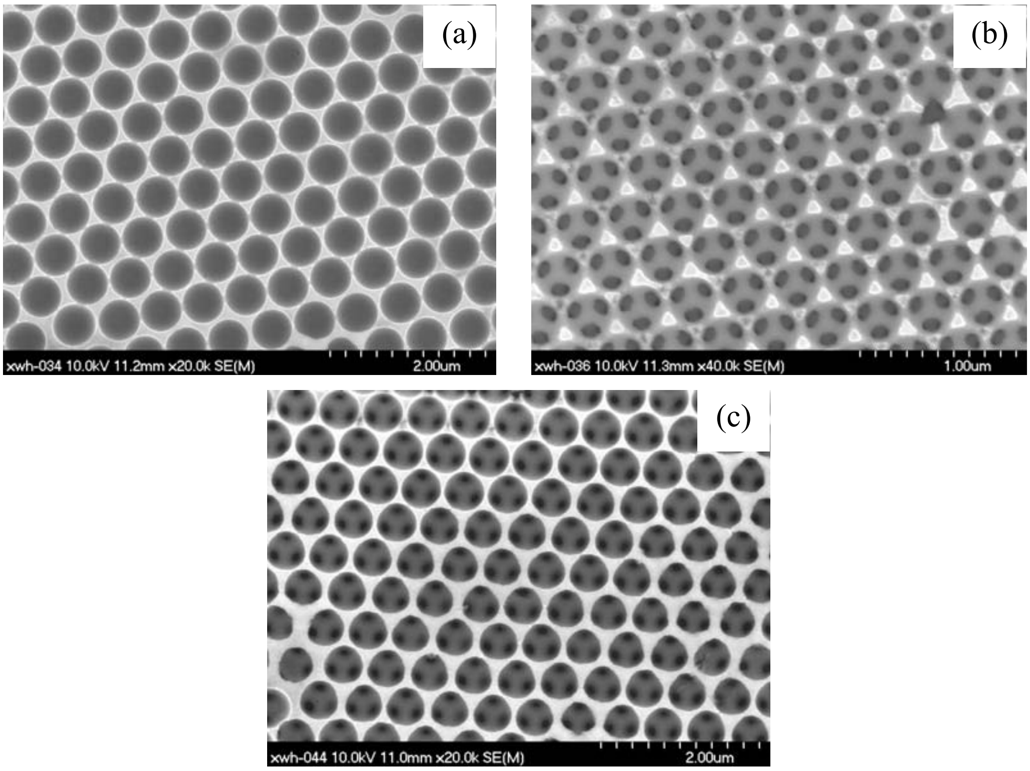

Fig. 1 SEM images of 3-DOM iron nickel alloy thin films electrodeposited for different times. (a) 3 min; (b)4 min; (c)5 min

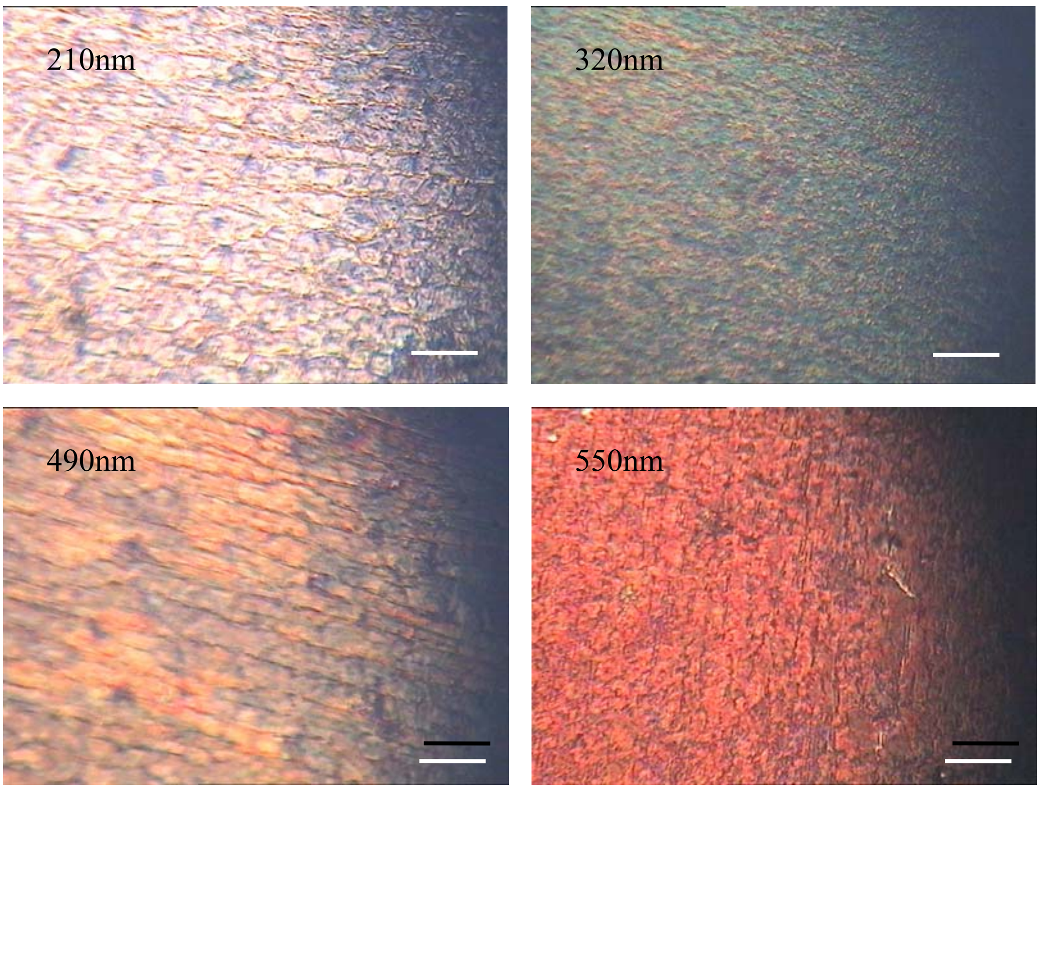

Fig. 2 Optical microscope images of 3-DOM iron nickel alloy films deposited from PS template of the diameters indicated, scale markers 50 μm .

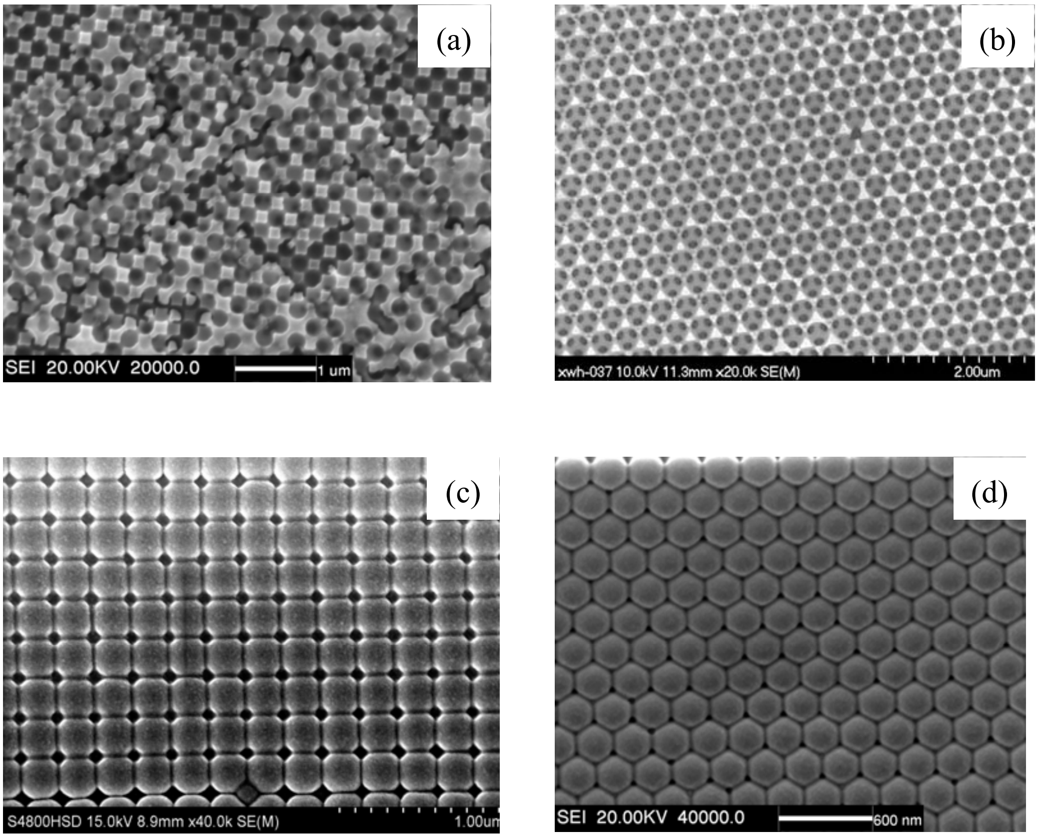

Fig. 3 SEM images of 3-DOM FeNi alloy film with air spheres arranged in (a) square array and (b) hexagonal array ; Polystyrene colloidal crystal templates with corresponding (c)square array and (d) hexagonal array.

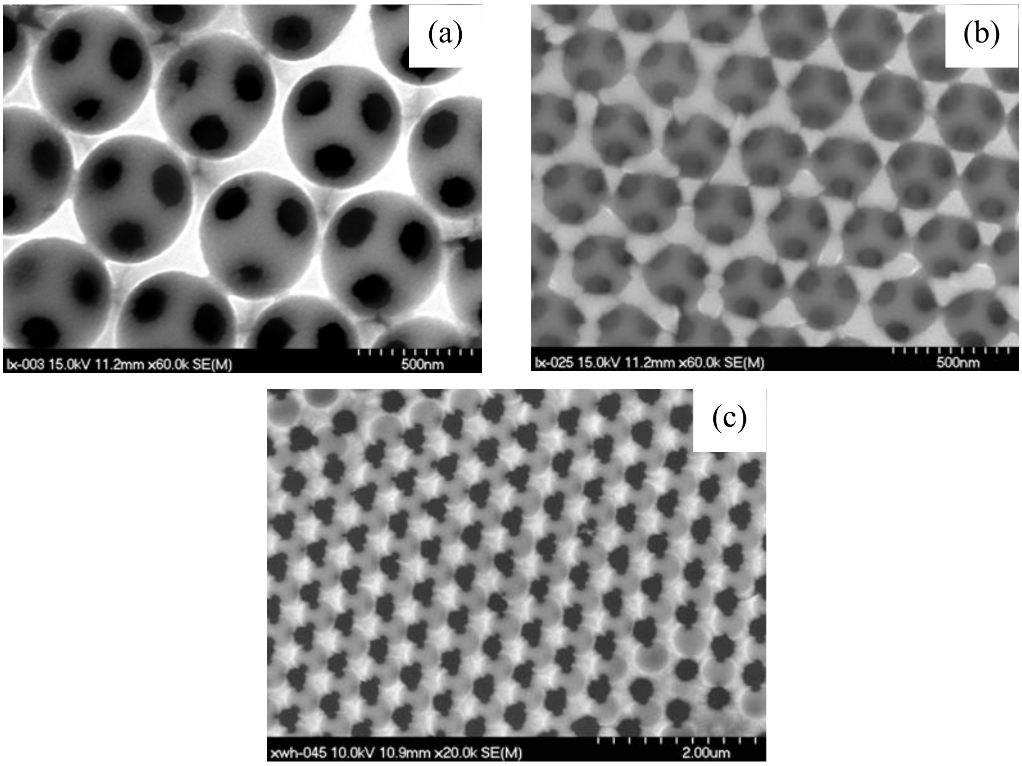

Fig. 4 SEM images of 3-DOM iron nickel alloy films electrodeposited at different temperatures. (a) 40 ℃, (b) 50 ℃ and (c) 60 ℃.

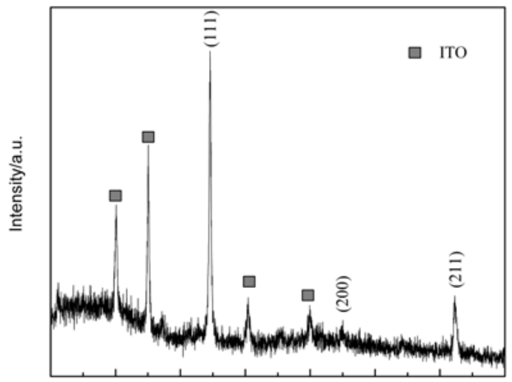

Fig. 5 X-ray diffraction pattern of the 3-DOM iron nickel alloy deposited on the ITO substrate after the PS template has been removed.