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Characterization of electrodeposited nanostructured macroporous cobalt films using polystyrene sphere templates

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The electrodeposition of highly ordered macroporous films of cobalt with regular arrays of spherical pores of the diameters 200, 550, 600, 750 and 1000 nm was carried out into the interstitial spaces of a template formed by polystyrene latex spheres. The spheres were self-assembled on flat gold electrodes of 1 cm^2 surface area to produce a highly periodic, hexagonal close packed, interconnected network of monodisperse spherical pores within the metal film. The size of pores was determined by the diameter of the polystyrene latex particles used to prepare the template. The nanostructure of the films was studied by the scanning electron microscopy. Magnetic studies of the films were carried out with an Aerosonic 3001 vibrating sample magnetometer. The nucleation and the growth mode of cobalt were investigated via a chronoamperometry study.

Keywords: *electrochemical deposition; macroporous films; chronoamperometry; magnetic properties; polystyrene latex*

1. Introduction

Metal electrodeposition is of great importance, both for the basic science involving the process and for its major technological applications in electroplating, metal electrofining and electrowinning. Porous metals are important for many engineering applications such as filters, catalysts, supports, heat exchangers, fuel cells, electrolytic cells, thermal screens, and vibration dampers [1–4]. In many applications, a high specific surface area is required. The production of materials with micron and submicron scale structures in two and three dimensions is of importance in the range of applications such as photonic materials, high density magnetic data storage devices, microchip reactors and biosensors [5–9].

The electrochemical deposition of nanoscale Ni and Au meshes through templates made from a closely-packed silica sphere array have been described by Xu et al [10].

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Several important differences were found between the method described in this work over that of Xu et al. These differences can be summarized as follows: (i) the polystyrene latex particles used are commercially available in a range of sizes; (ii) the closely-packed templates can be prepared by evaporation rather than by sedimentation over a period of several months; (iii) there is no need to sinter the template; (iv) the metal deposition is achieved in a few minutes rather than over 36 h; (v) the template can be removed by dissolving the polystyrene in toluene rather than requiring the use of HF.

In the paper, we report on the preparation of highly ordered macroporous metal films. The preparation of the structured macroporous films was carried out via the electrochemical reduction of $CoSO_4$ in aqueous solution within the interstitial spaces of a closely packed polystyrene latex sphere template, self assembled on a gold surface. The influence of the pore diameter of polystyrene latex spheres on the magnetic properties of the electrodeposited Co films is reported. The nucleation and the growth mode of Co onto gold substrates were investigated via current–time transient curves during potentiostatic deposition. The morphologies of the Co films were investigated by the scanning electron microscopy (SEM). Magnetic hysteresis curves were recorded with an Oxford Instruments Aerosonic 3001 vibrating sample magnetometer at room temperature.

2. Experimental

Materials. All solvents and chemicals were of reagent quality and were used without further purification. The monodisperse polystyrene latex spheres, with diameters of 200, 550, 600, 750 and 1000 nm were obtained from an Alfa Asear a 2.5 wt. % solution in water. Propanol and toluene were obtained from Aldrich. The gold electrodes used as substrates were prepared by evaporating 10 nm of a chromium adhesion layer, followed by evaporating 200 nm of gold, onto 1 mm thick glass microscope slides. The gold electrodes were cleaned by sonication in propanol for 1 h followed by rinsing with deionized water. All solutions were freshly prepared using reagent-grade water (18 MΩ·cm) from a Whatman RO 80 system coupled to a Whatman Still Plus system. The deposition solution was 0.1 mol·dm^{-3} $Co(Ac)_2$ with 0.1 mol·dm^{-3} KAc and 0.1 mol·dm^{-3} H_3BO_3 to produce pH 3.7. The deposition was carried out potentiostatically at the potential of –0.95 V vs. SCE.

Instrumentation. An analytical scanning electron microscope (JEOL 6400) was used to study the morphology and thickness of the electrodeposited cobalt films. Magnetic hysteresis loops were measured using an Oxford Instruments Aerosonic 3001 vibrating sample magnetometer. Electrochemical deposition was carried out in a conventional three electrode configuration using an EG G 273. A large area platinum gauze was used as the counter electrode, saturated calomel (SCE) as the reference electrode and the template coated gold substrate as the working electrode.

Assembly of the colloidal templates. The polystyrene sphere templates were assembled by sticking a 1.0 cm internal diameter Teflon ring onto the gold substrate using double-sided tape. Approximately 0.3 cm^3 of an aqueous suspension of the monodisperse polystyrene spheres of 200, 550, 600, 750 and 1000 nm in diameter diluted with water to 0.5 wt. % was spread over the area of the gold electrode surrounded by the Teflon ring (0.785 cm^2); this corresponds to a template layer about 2.0×10^4 nm thick. The sample was then kept in a controlled humidity chamber and allowed to dry slowly over a period of 3–4 days. After all the water had evaporated, the Teflon was removed to leave a circular area covered by the template. The templates are robust and adhere well to the gold substrate. There is no evidence for the resuspension of the latex particles when these are placed in contact with the deposition solutions.

Synthesis of highly ordered macroporous cobalt films. The electrochemical deposition was performed at fixed potentials of –0.95 V vs. SCE. The cobalt films were grown with a constant and gradient thickness. The gradient ranged from 0.0 to 1500 nm across the sample 1 cm in diameter. This was done in order to allow a systematic study, by SEM measurements, of the properties of the films, as a function of the film thickness. When the electrochemical deposition was complete (25–30 min), the cobalt films were soaked in toluene for 24 h to dissolve away the polystyrene template. All experiments were performed at room temperature (20–23 °C).

3. Results and discussion

3.1. Characterization by chronoamperometry

Chronoamperometry is a widely used technique for the deposition and observation of the growth process during the film formation. The chronoamperometric curve in Fig. 1a shows three different regions, in which *A* region corresponds to a rapid increase under an applied potential of –0.95 V vs. SCE. A slow current decay is observed in the B region which is followed by a constant current in C region. A rapid surge and exponential decay of the current observed in region A is due to double layer charging, which takes 6 s to reach the peak current of 4.7 μA. A continuous decay current observed in region B corresponds to the formation of cobalt films [11]. The current in region C is characteristic of diffusion controlled growth. In this region, the diffusion rate of Co^{2+} is equal to the reduction rate of Co^{2+} at the electrode surface, current keeps steady. This means that at longer time gradual increase of the diffusion zone increases the volume the depleted region. The diffusion zone between the electrode surface and the electroactive species in the bulk solution increase which leads to extension of the diffusion zone into the bulk solution (high population region of the electroactive species) causing linear diffusion of species to the electrode surface [1, 12, 13]. Thus, (i) cobalt deposition after double layer charging, (ii) critical nuclei

formation, and (iii) further diffusive controlled growth of the cobalt films, are the responsible steps for the nuclei formation and subsequent growth of cobalt thin films.

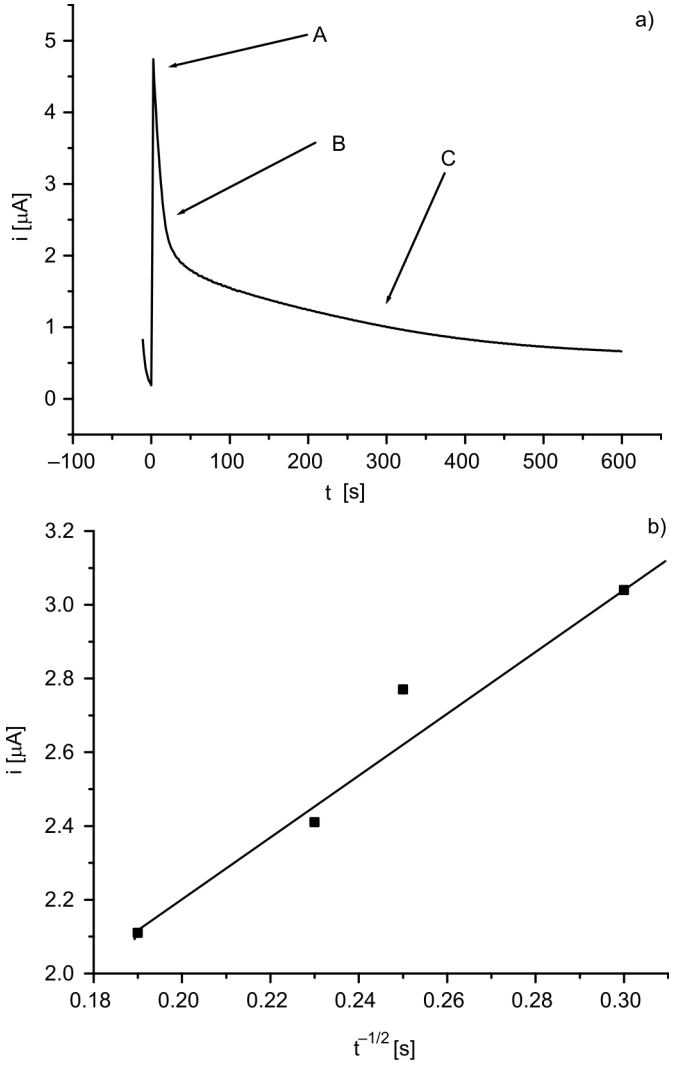

Fig. 1. Time dependences of current during deposition of cobalt at an applied potential of –0.95 V vs. SCE (a) and the Cottrel plot at E_f = –0.950 V (b)

By choosing the data for a short time from the experimental points selected in Fig. 1a, a Cottrel plot was obtained as a dependence of current on the reciprocal square root of time (Fig. 1b). The slope of the Cottrel plot yields the diffusion coefficient $D = 5.2\times10^{-10}$ $m^2 \cdot s^{-1}$. Cobalt thin films were deposited from an optimized bath composition by applying the –0.95 V vs. SCE deposition potential for various time durations. Figure 2 shows the plot of film thickness against the amount of charge re-

quired for the deposition of films. It was observed that the film thickness increases as the quantity of change increases.

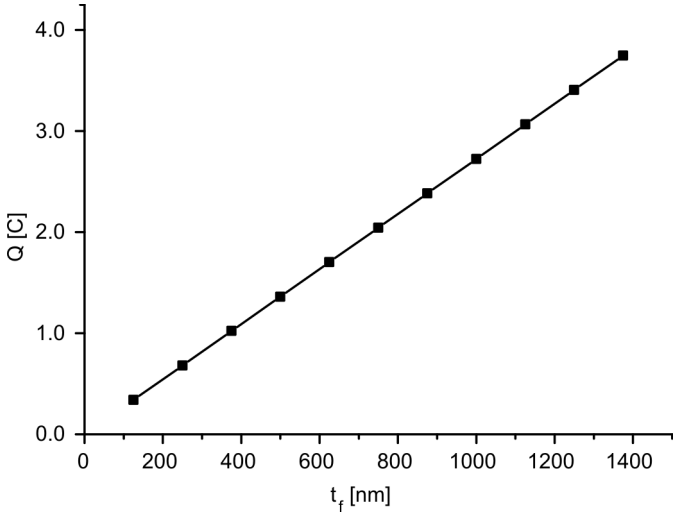

Fig. 2. Dependence of the charge required
for deposition of cobalt films on the film thickness

3.2. Characterization by SEM

Figure 3a shows an exemplary SEM image of the surface of a macroporous cobalt film on a gold substrate covered with templates made of 550 ± 20 nm diameter polystyrene spheres. The electrochemical deposition was carried out at potentials of –0.95 V vs. SCE (total charge passed 2 $C \cdot cm^{-2}$).

The SEM images show that the spherical voids left in the gold films after the removal of the polystyrene sphere are arranged in a well ordered, single domain, closely packed structure. Measurements of the centre-to-centre distances for the pores in Fig. 3a, and for similar images of other films, confirms that the spherical voids within the cobalt films have the same diameter as the polystyrene spheres used to fabricate the template. Figure 3b shows an image for a macroporous cobalt film prepared with a template of spheres 750 nm in diameter. Figure 3c shows a cross section of a cobalt film fabricated using templates formed from 750 nm polystyrene latex spheres. These micrographs also reveal the formation of three-dimensional macroporous films. The spherical voids have diameters determined by the diameter of the polystyrene latex spheres used for the template and are arranged as a part of an hexagonal lattice, again indicating that the polystyrene latex particles were arranged in a three-dimensional, hexagonal, closely packed structure. This was also confirmed by scanning electron micrographs of the template themselves before the deposition of the metal.

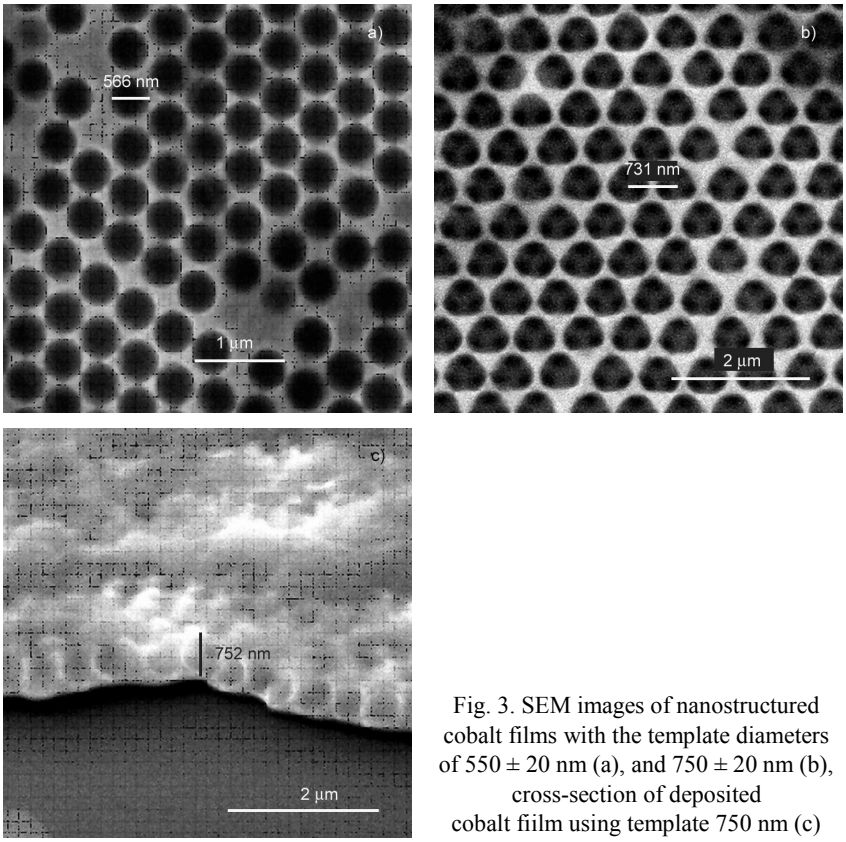

Fig. 3. SEM images of nanostructured cobalt films with the template diameters of 550 ± 20 nm (a), and 750 ± 20 nm (b), cross-section of deposited cobalt fiilm using template 750 nm (c)

It was noted that self-assembled layers of polystyrene latex particles formed on gold surfaces by slow evaporation of water from the latex suspension can be used as templates through electrochemical deposition of metal films. In the resulting metal/polystyrene composite, the polystyrene spheres are in contact and can be dissolved out of the metal to leave a regular array of interconnected spherical voids. The size of each of these voids is determined by the size of the polystyrene latex particles used. Polystyrene latex particles of tightly controlled size distribution are readily commercially available controlled. The final film thickness can be controlled by appropriately regulating the quantity of charge employed in the electrochemical deposition. Thus this method provides a simple route for the fabrication of ordered macroporous films of metals with potentially interesting and useful photonic, catalytic, magnetic, or other properties.

3.3. Magnetic properties of cobalt films

The film thicknesses were controlled by changing the diameter, *d*, of the polystyrene latex spheres, used to form the template, and the amount of charge passed during

the electrodeposition process [14]. Consequently, the grain structure and morphology of the electroplated cobalt films obtained from water and from the template mixture may be significantly different.

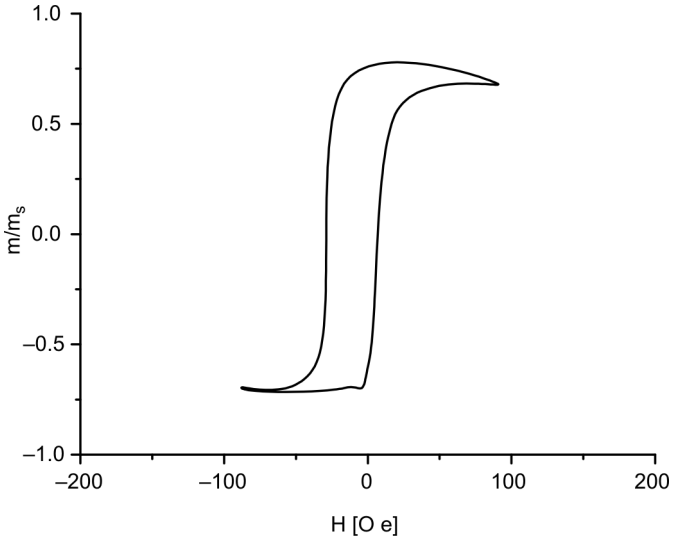

Fig. 4. Normalized in plane magnetic hysteresis loop at 550 nm

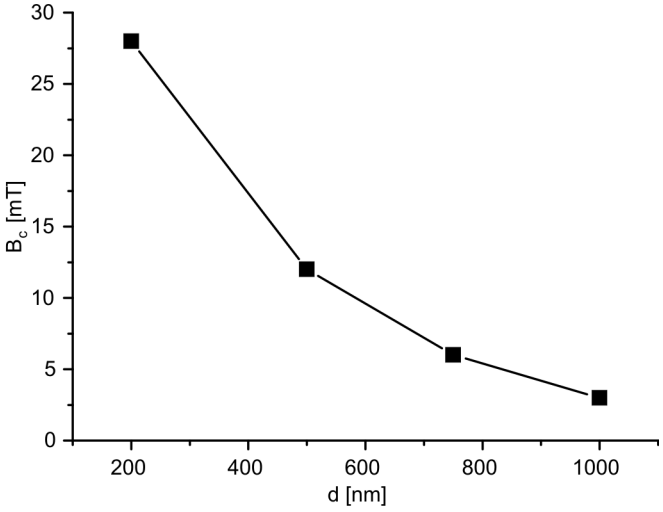

Fig. 5. Dependence of the measured coercivity on the diameter of the polystyrene sphere

Figure 4 shows an example of a normalized in plane magnetic hysteresis loop recorded at room temperature for cobalt film electrochemically deposited on a gold substrate using a polystyrene sphere of 550 nm in diameter. It was found that the hystere-

sis decreases as the the diameter of the polystyrene sphere increases. Figure 5 shows the dependence of the coercivity on the diameter of the polystyrene sphere. It is clear that the coercivity is proportional to the inverse of the diameter of polystyrene sphere. The nanostructuring significantly affects the shape of magnetization loops and drastically changes the coercive field β_c which found to show a maximum with variation of sphere diameter [15]. Measurements of the dependence of β_c on the thickness of the magnetic film, t_f, revealed that the coercive force changes periodically as a function of film thickness.

4. Conclusions

Using a simple method, we have successfully produced nanostructured films of cobalt via electrochemical deposition using templates prepared by assembling close packed arrays on monodisperse polystyrene spheres of various diameters (200, 550, 600, 750, and 1000 nm). The resulting electrochemical deposition is highly ordered. Three dimensional macroporous thin films of cobalt are robust and stable when the the template is removed. The diameter of the spherical voids is determined by the diameter of the polystyrene latex spheres employed to form the template. Scanning electron microscopy confirms the presence of a highly regular macroporous structure. The thickness of the films is controlled by varying the charge passed in their deposition. It was noted that the synthesis exhibits the Cotterellian behaviour at short time. This means that the diffusion controlled limiting current is proportional to $t^{-1/2}$.

Magnetic measurements show that the magnetic properties of cobalt films were strongly influenced by the diameter of the polystyrene sphere and the film thickness. It was found that the hysteresis loops and coercivity decrease with increasing the diameter of polystyrene sphere.

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