



The key factors in fabrication of high-quality ordered macroporous copper film

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ABSTRACT

The template-directed fabrication of highly-ordered porous film is of significant importance in implementation of the photonic band gap structure. The paper reports a simple and effective method to improve the electrodeposition of metal porous film by utilizing highly-ordered polystyrene spheres (PSs) template. By surface-modification method, the hydrophobic property of the PSs template surfaces was changed into hydrophilic one. It was demonstrated that the surface modification process enhanced the permeability of the electrolyte solution in the nanometer-sized voids of the colloidal template. The homogeneously deposited copper film with the highly-ordered voids in size of less than 500 nm was successfully obtained. In addition, it was found that large defects, such as microcracks in the template, strongly influenced the macroporous films quality. An obvious preferential growth in the cracked area was observed.

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1. Introduction

The fabrication of photonic band gap (PBG) materials based on ordered arrays of colloidal spheres has attracted great interest of researchers because of their unique applications in optical devices [1], high-density magnetic data storage device [2], chemical and biochemical sensors [3], and other applications booming from new physics brought about by PBG structures [4]. The highly-ordered macroporous materials are good candidates for the realization of PBG. The colloid template (CT)-directed synthesis of the macroporous material attracted much interest of many researchers due to its convenience and low cost. The ordered macroporous metals are considered to have excellent PBG effect due to their high optical refraction index [5]. Four main techniques are reported to be able to fabricate a metal film with 3-D macroporous structure [6–9]. In particular, electrochemical deposition has the advantage in fabrication of the dense and robust metal film due to the little shrinkage and the perfect interconnection of the porous structure.

A big issue, however, was encountered in this plating process due to the overlay of the colloid template on the working electrode. Since the interstitial channels among polystyrene spheres (PSs) are of only several tens nanometer size, it is very difficult for the electrolyte solute to infiltrate into the template film. This induced seriously inhomogeneous growth of macroporous metal film on the working electrode. Several factors can dominate the infiltrating

process, including surface tension, channel size, wettability and surface charge.

In this paper, we studied the fabrication of the macroporous copper film to solve the problem and clarify the mechanism of the electrochemical deposition in the CT. In order to increase the permeability of the electrolyte ions in the CT, the surface property of the PSs was modified from hydrophobic to hydrophilic.

2. Experimental

The PSs with the averaged diameters of 486 nm and 340 nm were synthesized by the conventional laboratory route [10]. TEM examination showed that the synthesized PS has a narrow size distribution of less than 5%.

The CT was produced by the vertical self-assembly method [11]. In concise words, a clean ITO/glass slide was put vertically in a glass vial containing the PSs suspension of 0.1% volume fraction. The template film could be obtained with evaporation of water and sedimentation of PSs on the ITO/glass slide. The growth temperature and humidity were kept at 50 °C and 35%, respectively. The growth process lasted 3 days.

ITO/glass slide covered with the CT was used as the working electrode. The surface-modification was made by putting the template into the sodium dodecyl sulfate (SDS) solution (0.1 M) for about 24 h. Subsequently, it was washed by deionized water and dried naturally. It should be noted that SDS cannot be directly put into the electrolyte solution since sedimentation may occur due to the chemical reaction between SDS and the electrolyte solution. To keep a relatively fixed area for electrodeposition, the surface of

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working electrode was partially covered by nail varnish and an exposed area of about 0.5 cm^2 was kept.

All of electrochemical experiments were carried out by using an electrochemistry working station CHI660B and a three electrode cell (40 ml capacity). Chronopotentiometry technique was used in experiment. The electrolyte solution was composed of 60 g $\text{Cu}_2\text{P}_2\text{O}_7$, 280 g $\text{K}_4\text{P}_2\text{O}_7 \cdot 3\text{H}_2\text{O}$ and 20 g $(\text{NH}_4)_2\text{HC}_6\text{H}_5\text{O}_7$ per liter of purified H_2O . A large area ($1.5 \times 4 \text{ cm}^2$) platinum sheet was used as the counter electrode. During the deposition process, the pH value and the temperature in the electroplating bath were kept at 8.2 and 40°C , respectively.

After the deposition of copper, we put the sample in toluene for about 24 h to remove the polystyrene spheres completely.

3. Results and discussion

The adsorption of SDS molecules to polystyrene surfaces has been studied by light scattering and neutron reflection techniques [12]. It was indicated that a monolayer of SDS molecules with the thickness of 15 \AA could be adsorbed on the polystyrene surface. An SDS molecule consists of a carbon chain of 12 atoms along with a hydrophilic sulfate headgroup. It is well known that the surface of the polystyrene sphere is hydrophobic. The hydrophobic end of SDS molecule stuck on the surface of the PS when the templates were immersed in SDS solution, while the hydrophilic headgroup was put towards the aqueous solution. Therefore, a hydrophobic PS surface changed into a hydrophilic surface. The comparison between the copper films with and without surface-modification

indicated that the immersing process is very important for the synthesis of high-quality porous copper films, as shown in Fig. 1a. The CT of the sample I did not undergo any surface-processing, while the sample II was modified by SDS solution. It can be seen that a homogeneous macroporous copper film could be successfully obtained on a large area of the sample II. In contrast, the copper film cannot be deposited on the most part of the glass substrate.

A schematic illustration of the electrodeposition process was shown in Fig. 1b and c. The apertures of the channels confined by the PSs are of only tens of nanometer size, and the surfaces of the PSs form the inner walls of these channels. The hydrophobic property of the PSs induced the walls to repulse the aqueous solution due to the existence of the large surface tension. Therefore, it is difficult for the aqueous electrolyte to enter the space among the PSs. For this reason, the copper ions are scarcely to be reduced on the substrate. On the contrary, if the inner wall was modified to be hydrophilic, the electrolyte can easily penetrate into the nano-channels induced by the capillary force. As a consequence, the electrolyte will fulfill the voids among the PSs shown in Fig. 1c, and the copper ions can be well reduced on the substrate even with the overlay of the template.

One of the key factors for the synthesis of high-quality macroporous films is that the homogeneous nucleation on the substrate should be realized in the electrodeposition process. This could be realized by the enhancement of the permeability of electrolyte in the nano-channels through the previously reported SDS modification technique. The experimental results on the

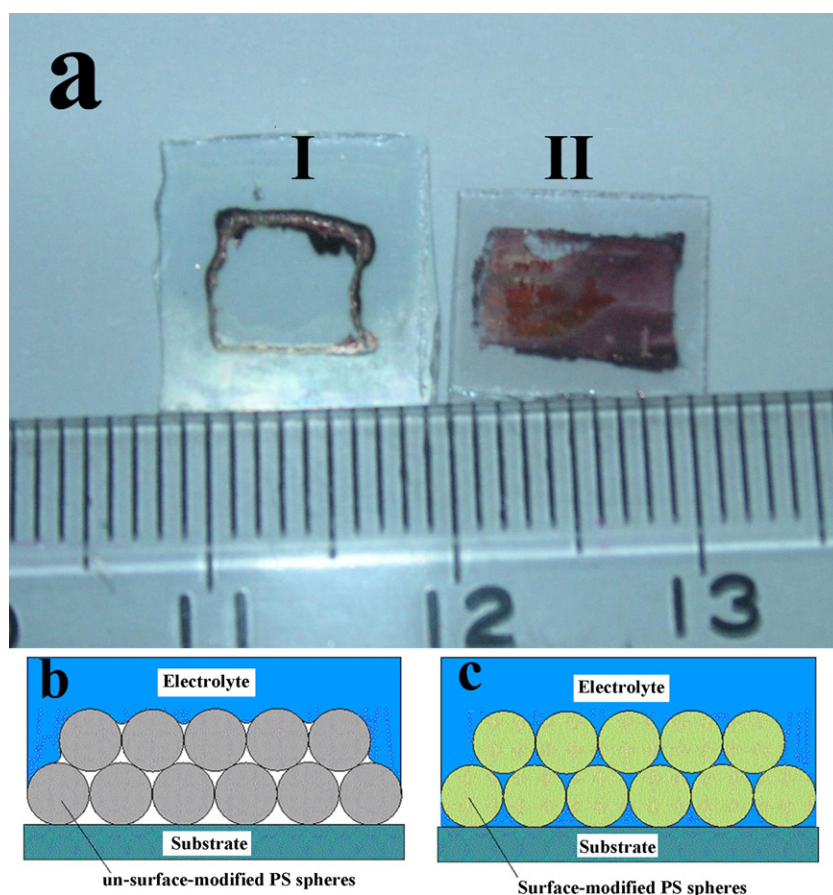


Fig. 1. A photograph on the electrodeposited samples and the contrast of permeability of the electrolyte in the voids enclosed by the PSs: (a) the templates of sample I and II was un-modified and modified with SDS respectively, (b, c) the permeability of the electrolyte with and without surface-modification, respectively.

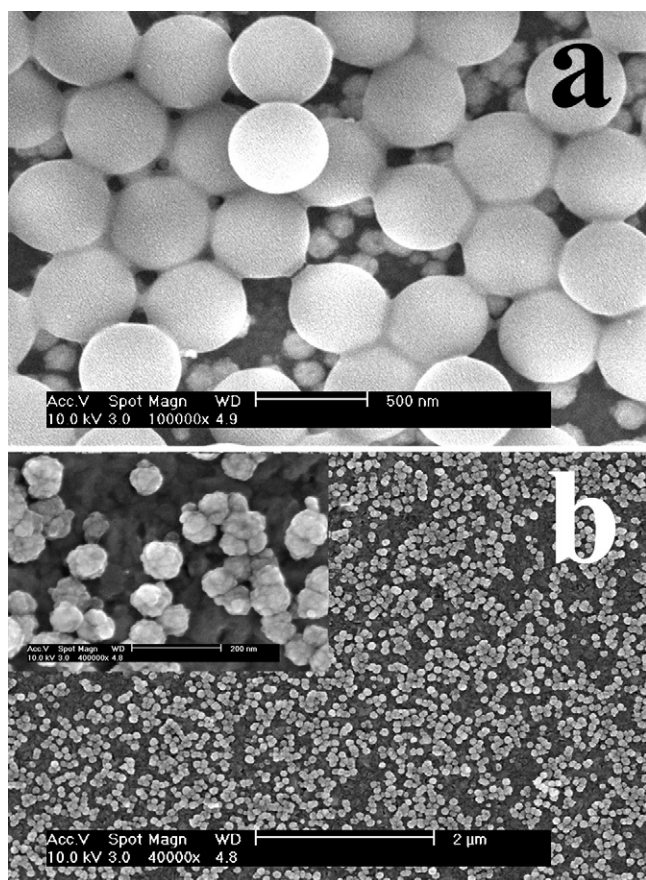


Fig. 2. The SEM images of the nucleation on the conducting substrates: (a, b) before and after removal of the colloidal templates, respectively.

nucleation process in the electrodeposition were shown in Fig. 2. We stopped the deposition process after a very short deposition time (the cathodic time = 10 s, cathodic current = 3 mA). It was found that the copper nucleation initiated from the area enclosed by the PSSs, as shown in Fig. 2a. When PSSs were eliminated from the substrate, a good nuclei distribution was clearly shown in the Fig. 2b. The inset of the Fig. 2b shows that the nucleus has spherical shape.

Protracting the cathodic time to 300 s, we could get the 3-D ordered macroporous copper. Fig. 3a shows the section of the CT after electrodeposition, which indicates the copper was filled in the voids very well. The surface morphology of the 3-D ordered macroporous copper films was shown in Fig. 3b and c. The pore sizes are about 490 nm (see Fig. 3b) and 345 nm (see Fig. 3c), respectively. Each top air sphere was connected with other three bottom air spheres through three tunnels. This structure can be seen more clearly from the inset of Fig. 3b. All the air spheres are packed in an fcc structure, which reveals that the surface-modification method of the CT is very effective in the fabrication of perfect ordered macroporous copper films with electrodeposition method.

The large defect embedded in the template is another important factor that influences the growth of high-quality macroporous film. Fig. 4a–c shows the surface images of the films with different cathodic time (the cathodic currents are same), and the cathodic times are 50 s, 250 s and 300 s, respectively. We found that the cracks of colloidal template could influence the 3-D macroporous copper film strongly. Because there are more spaces in the cracks than that of the nano-channels, the copper ions

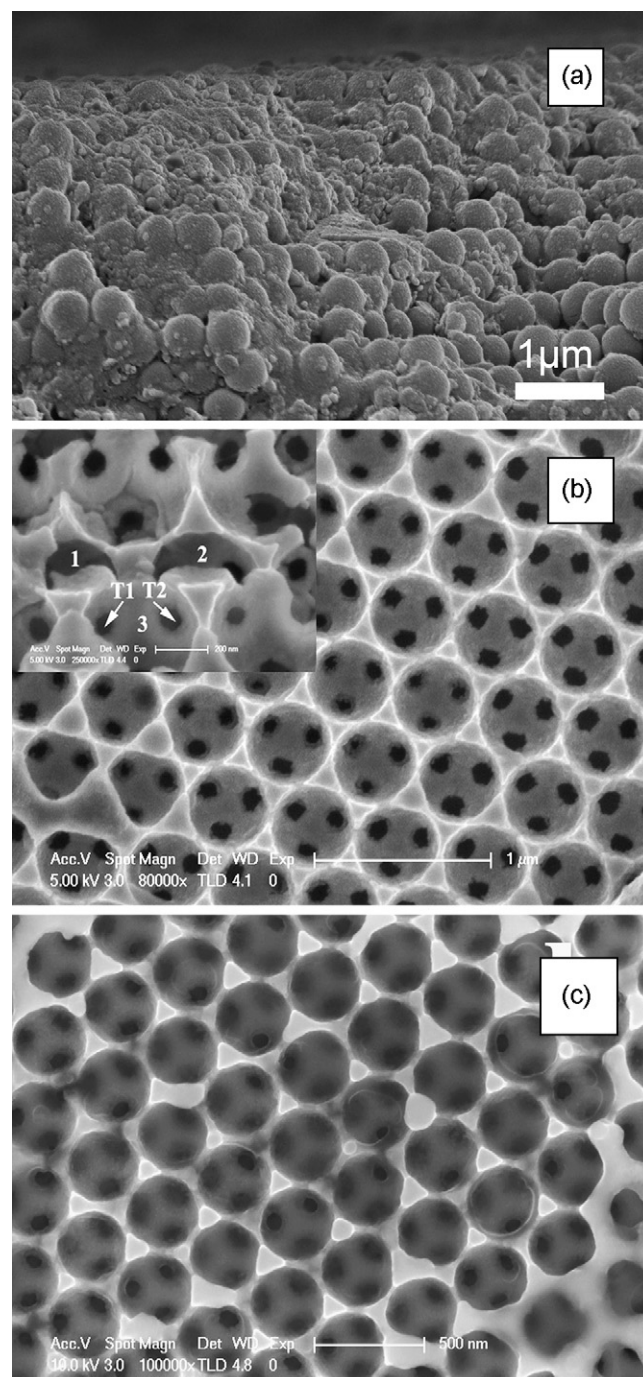


Fig. 3. the typical SEM images of 3D macroporous copper films: (a) the section of copper film before removal of the colloid template, (b, c) the pore sizes of 490 nm and 345 nm, respectively.

diffuse faster in the cracked region, which is helpful for the copper deposition. The fast growing areas of the copper films became the ridges, and the multilayer structure of the ridge is shown in the inset of Fig. 4b. The protruding growth from the ridges destroyed the integrality of the whole macroporous copper film, which was clearly illustrated in Fig. 4c. Therefore, a colloidal template with scarce cracks is very important for the preparation of the highly-integrated macroporous copper films. However, up to now, the crack elimination in the colloidal templates is still an open problem.

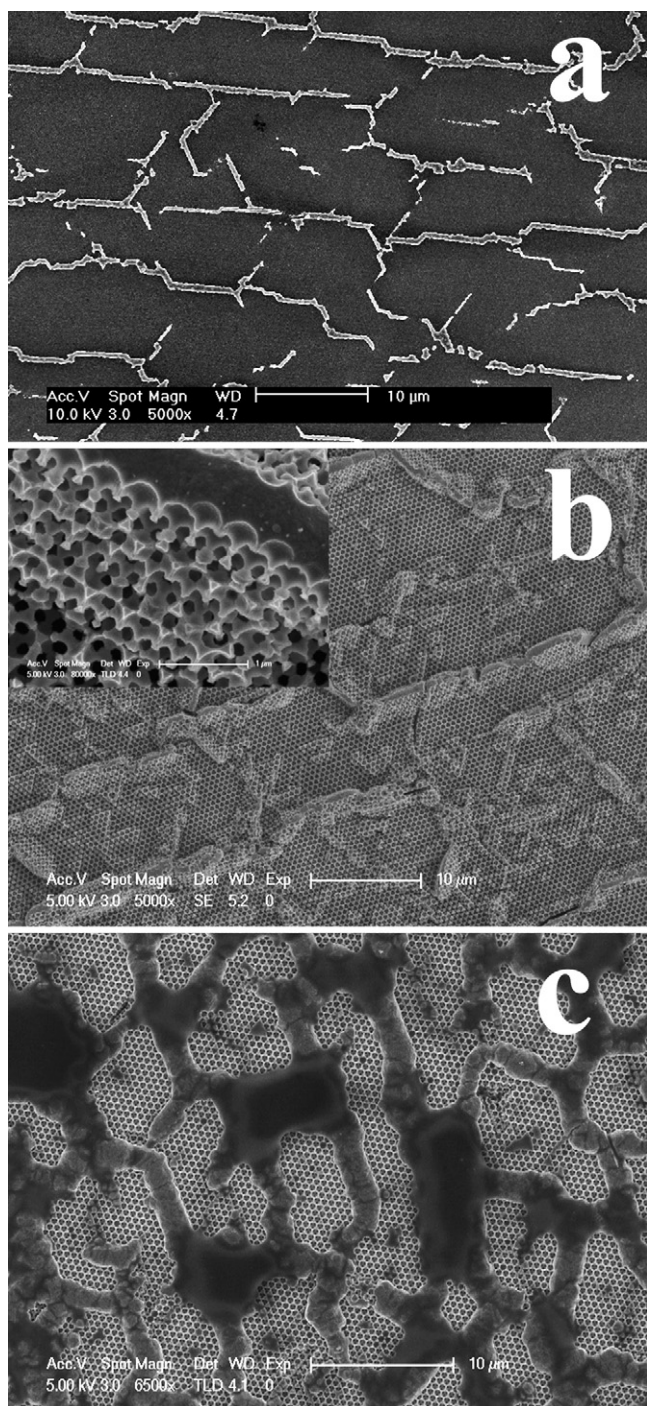


Fig. 4. the SEM images of the films made in the same cathodic currents, and the cathodic times are 50 s (a), 250 s (b) and 300 s (c), respectively.

4. Summary and conclusions

We used a simple and effective method to get highly-ordered 3-D macroporous copper films with large area. The wetting property

of the colloidal sphere surfaces is the most important factor that influences the nucleation of metal on the conducting substrate, and the homogeneous nucleation will determine the growth of the porous metal film subsequently. Another important factor is the preferential growth of the metal in the inherent cracks of the CT, which influences the integrality of the macroporous copper film. Most researchers use PSs of size above 600 nm and the electrolyte contained SDS [13], or mono-layer colloidal films [14,15], or SiO₂ spheres colloidal films as templates [6] to avoid the limitation of the wetting property of the nano-channels enclosed by the latex spheres. However our method reduces size limitation of the PSs for the fabrication of the copper 3-D porous structure, and this method can be conveniently employed for other porous metal preparation.

It should be noticed that the experimental mode (potentastatic or constant-current mode) does not change the conclusions presented in this paper, although the current densities are different for the two modes. In our experiments, the areas of the samples for the electrodeposition are nearly same (about 0.5 cm²). During electrodeposition, the current density kept in about 6 mA/cm². In this paper, the wetting property of the colloidal sphere surfaces was the most important factor, which would determine the permeability of electrolyte in the voids. The difference of current densities had little influence on this result. We mainly studied the copper deposition process in the cracks on the condition of constant current. To change the electrodeposition time, we could study the growth process of the copper in the cracks. In our experiments, the current densities of different samples were nearly the same, and the differences of the growth process could be shown by the morphologies of the copper that deposited in the cracks within different time.

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References

- [1] K. Takano, K. Nakagawa, *Leice T Commun.* E84B 5 (2001) 1295–1303.
- [2] P. Tran, *J. Opt. Soc. Am. B* 16 (1999) 70–73.
- [3] B.H. Cumpston, et al. *Nature* 398 (1999) 51–54.
- [4] H. Kosaka, T. Kawashima, A. Tomita, M. Notomi, T. Tamamura, T. Sato, S. Kawakami, *Appl. Phys. Lett.* 74 (1999) 1370–1372.
- [5] A. Moroz, *Europhys. Lett.* 50 (2000) 466–472.
- [6] J.E.G.J. Wijnhoven, S.J.M. Zevenhuizen, M.A. Hendriks, D. Vanmaekelbergh, J.J. Kelly, W.L. Vos, *Adv. Mater.* 12 (2000) 888–890.
- [7] H.W. Yan, C.F. Blanford, B.T. Holland, M. Parent, W.H. Smyrl, A. Stein, *Adv. Mater.* 11 (1999) 1003–1006.
- [8] O.D. Velev, P.M. Tessier, A.M. Lenhoff, E.W. Kaler, *Nature* 401 (1999) 548.
- [9] P. Jiang, J. Cizeron, J.F. Bertone, V.L. Colvin, *J. Am. Chem. Soc.* 121 (1999) 7957–7958.
- [10] G. Tuin, A.C.I.A. Peters, A.J.G. Vandiemmen, H.N. Stein, *J. Coll. Inter. Sci.* 158 (1993) 508–510.
- [11] P. Jiang, J.F. Bertone, K.S. Hwang, V.L. Colvin, *Chem. Mater.* 11 (1999) 2132–2140.
- [12] S.F. Turner, S.M. Clarke, A.R. Rennie, P.N. Thirtle, D.J. Cooke, Z.X. Li, R.K. Thomas, *Langmuir* 15 (1999) 1017–1023.
- [13] P.N. Bartlett, M.A. Ghanem, I.S. El Hallag, P. de Groot, A. Zhukov, *J. Mater. Chem.* 13 (2003) 2596–2602.
- [14] B.Q. Cao, W.P. Cai, F.Q. Sun, Y. Li, Y. Lei, L.D. Zhang, *Chem. Commun.* 14 (2004) 1604–1605.
- [15] F.Q. Sun, W.P. Cai, Y. Li, B.Q. Cao, F. Lu, G.T. Duan, L.D. Zhang, *Adv. Mater.* 16 (2004) 1116–1121.