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Improving nucleation in the fabrication of high-quality 3D macro-porous copper film through the surface-modification of a polystyrene colloid-assembled template*

Lan Ding(蓝　鼎), Wang Yu-Ren(王育人)†, Yu Yong(于　泳),
Ma Wen-Jie(马文杰), and Li Cheng(李　程)

National Microgravity Laboratory, Institute of Mechanics, Chinese Academy of Sciences, Beijing 100080, *China.*

A new approach is developed to the fabrication of high-quality three-dimensional macro-porous copper films. A highly-ordered macroporous copper film is successfully produced on a polystyrene sphere (PS) template that has been modified by sodium dodecyl sulfate (SDS). It is shown that this procedure can change a hydrophobic surface of PS template into a hydrophilic surface. The present study is devoted to the influence of the electrolyte solution transport on the nucleation process. It is demonstrated that the permeability of the electrolyte solution in the nanochannels of the PS template plays an important role in the chemical electrodeposition of high-quality macroporous copper film. The permeability is drastically enhanced in our experiment through the surface modification of the PS templates. The method could be used to homogeneously produce a large number of nucleations on a substrate, which is a key factor for the fabrication of the high-quality macroporous copper film.

Keywords: photonic band-gap materials, macroporous, electrodeposition, colloidal self-assembly.

PACC: 4270Q, 6460Q, 8270D, 8280F

1. Introduction

3D macroporous materials are of importance in a wide range of applications such as photonic crystal, catalytic surface, electrochemical sensors and microelectronic devices.[1] In recent years, colloid assembling technique has attracted many researchers' attention due to its convenience and low cost in fabricating the 3D macroporous materials. Colloidal particles with a diameter of several hundred nanometres could be assembled along the air–water interface to form regularly arranged particle arrays.[2] The template film containing well-arranged colloid spheres can be obtained through the evaporation of water. The PSs or silica spheres[3,4] are usually used for fabricating the template films. Subsequently, the interstices among the colloid spheres are infiltrated by the high refractive index materials. The highly ordered macroporous materials can be produced by removing the colloid spheres after infiltration.

Many kinds of materials have been employed to produce the macroporous materials such as oxides, semiconductors and metals. In order to realize the full photonic band-gaps, materials with a high refraction index should be used to produce the macroporous structures. Metals have high refraction indices and thus are good candidates for this purpose.[5] There are four main methods that could be used to construct a metal film with the macroporous structure. The first method is utilizing metal salts. In this procedure, the metal ions are changed into the metallic oxide. The macroporous metal film could be obtained through reducing the metal oxide.[6] The second method is using electroless deposition method[7] of fabricating the macroporous metal films, including nickel, cobalt, copper, silver, gold and platinum films. The key point in the third method is to use the colloidal gold particles (usually under 10 nm in size) to infiltrate the interstices of the colloidal particles.[8]

In addition to the above methods, Wijnhoven *et al*[9] synthesized the ordered porous gold film by using the electrochemical deposition method. The electrochemical deposition technique has the advantage in the fabrication of dense and robust macrop-

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orous structures because the porous metal film has little shrinkage, and can preserve well-interconnected nanochannels in the plating process. However, a big issue is encountered in this plating process due to the existence of the colloid template on a working electrode. Considering that the interstitial channels among PS spheres are only several tens of nanometres in size, it is easy to understand that the infiltrating the electrolyte ions into the template film is very difficult. This induces seriously inhomogeneous growth of macroporous metal film on the working electrode. Several factors dominate the infiltrating process, including surface tension, channel size, wettability and surface charge. To solve the problem and clarify the mechanism in the electrochemical deposition of metals on the PS templates, we study the fabricating of the macroporous copper material on a polystyrene colloid template in the present paper. A new approach is put forward to increasing the permeability of the electrolyte ions in the colloid template. More significantly, our research can provide a new clue to solving the problem of the electrochemical deposition in macroporous media.

2. Experiment and analysis

The PS colloid spheres with an averaged diameter of 486 nm are synthesized by the conventional laboratory scheme.[10] The diameter deviation of the synthesized PS spheres is less than 5%, which is determined by the SEM examination. The PS colloid template is produced by the vertical self-assembly method.[11] The glass slide covered with indium–tin oxide (ITO) conducting film is used as a substrate. Before the growing process, the ITO glass slides are placed in chromic acid and ultrasonically washed for 30 min. The glass cells are immersed in chromic acid for over 24 h. Then the slides and cells are washed by an amount of deionized water. Then, they are immersed in purified water for 24 h. Afterwards all slides and cells are dried naturally. The ITO glass slide is located vertically in the growth cell containing the colloid suspension of PSs in a volume fraction of 0.08%. The template film is grown at 50 °C in a humidity of 35% for 3 days. Figure 1(a) shows the SEM image of the PS colloid template. It can be seen that the template film contains highly ordered PS sphere arrays.
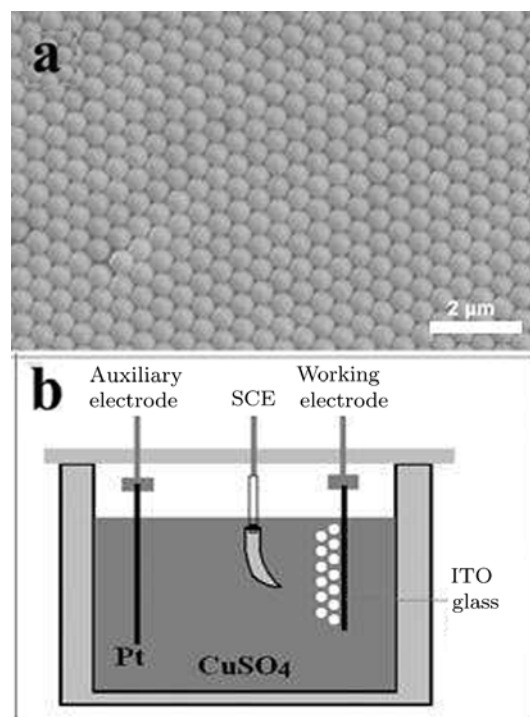

Fig.1. (a) The SEM image of the PS colloid template. The diameter of PS sphere is 486 nm. (b) A schematic of the electrodeposition working cell.

To enhance the diffusion of the metal ions in the template film, a small amount of sodium dodecyl sulfate (SDS) is dripped into the template film. It is expected that this procedure could change the hydrophobic PS surface into the hydrophilic surface. It should be addressed that the SDS cannot be directly put into the electrolyte solution because the SDS may react with the electrolyte solution. The electrochemical deposition of copper is carried out in an electrochemistry working station CHI660B as shown schematically in Fig.1(b). Constant-current deposition is used in the experiment. The ITO glass slide with the template film is used as a working electrode, while the counter electrode is Pt in material and electric potential is measured relative to that of a saturated calomel reference electrode (SEC). The electrolyte solution is composed of 60 g $Cu_2P_2O_7$, 280 g $K_4P_2O_7 \cdot 3H_2O$ and 20 g $(NH_4)_2HC_6H_5O_7$ per litre of deionized Milli-Q water. During the deposition, the pH and the temperature are kept at 8.0–8.2 and 40 °C, respectively. The copper-deposited sample is placed in the tetrahydrofuran solution for removing the PSs embedded in the deposited film.

Figure 2 shows the SEM images of macroporous copper films with different porous sizes. The deposited film contains a large perfect region with highly ordered spherical voids. The structures of individual

voids could be well recognized in the inset of Fig.2. It should be pointed out that the high-quality template containing small voids could be successfully obtained by using our method as shown in Fig.2(b). Generally speaking, it is very difficult for the electrolyte ions to move freely in PS template with void size being under 500 nm. In the previous study,[12] it was reported that the presence of the template film blocked the growth of metal from the substrate and hindered the supply of metal ions from the solution through diffusion to the surface of the growing metal film. This viewpoint could be confirmed in our experiment as shown in Fig.3. Sample A is fabricated without the SDS used. The copper film cannot be well deposited on the most part of the glass substrate due to the serious blocking effect even though a long-time deposition is performed. On the contrary, a homogeneous copper film could be easily obtained on the substrate of sample B that has been treated with the SDS. We have studied the effect of SDS addition on the nucleation process of the deposited copper on the ITO substrate.
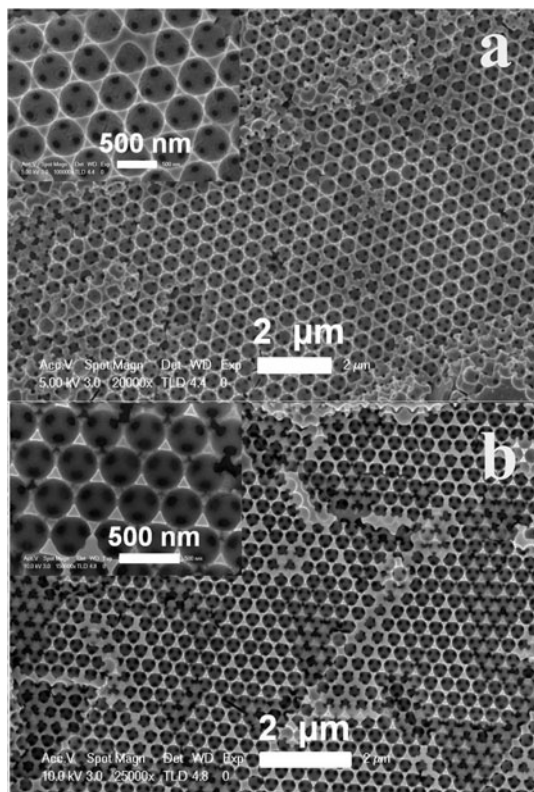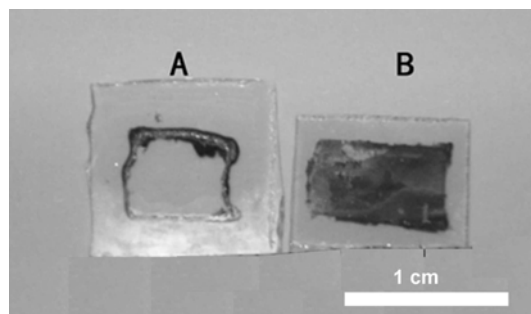
Fig.3. A photograph of the electrodeposited samples. The template of sample A is unmodified with the SDS, while the template of sample B is modified with the SDS. The deposition time and the applied electric current for the two samples remain at a cathodic current of 3 mA and the cathodic time of 80 s.

Figure 4 shows the SEM images of the initial stage of the electrodeposition process on the substrates with and without SDS modification. To reveal the nucleation process, the deposition process stops in a very short deposition time so that the discrete nucleus could be well distinguished after removing the template film. Therefore, the dense and homogeneous nucleation is obtained for the sample with SDS addition that could be well clarified through a comparison between Fig.4(a) and Fig.4(b). It is demonstrated that the blocking effect of the template can be drastically reduced by the SDS addition. The adsorption of SDS molecules to polystyrene surface has been studied by light scattering and neutron reflection techniques.[13,14] It is indicated that a monolayer of SDS molecules with a thickness of 15Å is adsorbed on the polystyrene surface. An SDS molecule consists of a 12-atom-long carbon chain with a hydrophilic sulfate headgroup. It is well known that the polystyrene surface is hydrophobic. The hydrophobic end of SDS molecule sticks on the surface of the PS sphere in the template film in the dripping process of SDS, while the hydrophilic headgroup is positioned towards the aqueous solution. Therefore, the PS template surface changes into a hydrophilic surface through the dripping process. It should be noted that this surface modification process plays an important role in enhancing the electrolyte permeability in the nanoporous media. As mentioned before, the channel size is only tens of nanometres. Kuo *et al*[15] has studied the molecular transport through nanoporous membranes by controlling the electrokinetic flow. It is shown that the permeability of electrolyte ions in a nanochannel strongly depends on the wettability of the channel wall and the surface charge density. For a hydrophobic wall, the permeability of electrolyte ions is very small, which


Fig.2. The SEM images of copper macroporous films electrochemically deposited on the ITO glass substrates covered with PS templates in the case of the PS diameter 486 nm at a cathodic current of 3 mA and cathodic time of 300 s (a); in the case of the PS diameter 339 nm (b). The porous structure details could be well distinguished in the insets.

means that it is difficult for electrolyte ions to move in a hydrophibic nanochannel. On the contrary, the permeation greatly increases for a hydrophilic nanochannel. Therefore, the obvious increase in nucleus number and the homogeneous distribution of the nuclei shown in Fig.4(b) are due to the enhancement of the ion permeation in the intra-connected nanochannels of the template film.
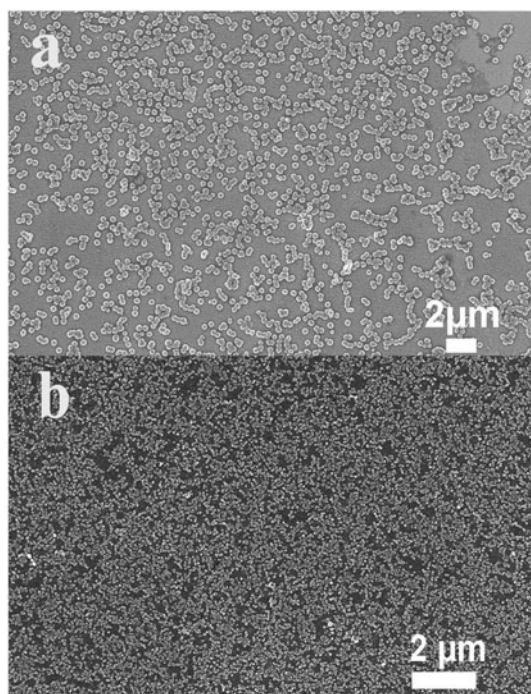
Fig.5. The SEM images in the initial stages in the electrodeposition process for the PS template with the SDS modification at a cathodic current of 0.2 mA and cathodic time of 7200 s (a) and without the SDS modification at a cathodic current of 3 mA and a cathodic time of 10 s (b).

Several researchers have also studied the influence of organic additives on the nucleation and growth in the electrodeposition process. It is shown that the influence of organic additives is complicated by the absorbance of the organic additives on the substrate and the growth kinetics of the deposited film.[16] In particular, surfactant usually acts as an inhibitor of nucleus formation. However, it should be noted that the SDS is directly put into the electrolyte solution and the deposition is performed on a planar electrode without overlay of the PS template film in these studies. The SDS is applied directly to the working electrode, while the SDS in our experiment is absorbed on the template film. Therefore, the influence of SDS addition on the electrodeposition process in our experiments is different from that in these studies.

3. Summary

In summary, a new approach has been put forward to the fabricating of the high-quality 3D macro-porous copper films. A highly-ordered macroporous copper film is successfully produced by electrochemical deposition on a polystyrene template. It is demonstrated that the permeability of the electrolyte solution in the nanochannels of the PS template plays an important role in synthesizing high-quality macroporous films. The permeability can be drastically enhanced through the surface modification of the PS template. It is shown that this procedure changes the hydrophobic surface of the PS template into the hydrophilic surface. The dense and homogeneous nucleation is obtained on the glass slide substrate through the SDS modification of the template film.

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