Preparation of 3D Colloidal Crystal Film and Gold-Infiltrated Silica Artificial Opals*

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Abstract: A free-standing 3D colloidal crystal film (opal) was fabricated at a water-air interface using purified monodispersed SiO_2 colloids. The gold/silica opal was obtained through the infiltration of gold nanoparticles by electroplating. The transmission and reflection spectra of the gold/silica composite opal show a red shift with increasing electroplating time. SEM images show that gold nanoparticles can be directly deposited on the surface of silica spheres in the opaline structure. Gold/silica composite opal film could provide a simple way to tune opal properties through controlling the amount of gold in the silica opal.

Key words: 3D; silica opal; spectra; gold; electroplating
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1 Introduction

Synthetic opals could be exploited as photonic bandgap (PBG) materials to control the propagation of electromagnetic waves in all three directions of space, and their photonic properties have attracted much attention in various applications[1]. PBG properties of 3D metallo-dielectric PhCs made of gold-coated dielectric spheres[2] and chrome spheres[3] have been experimentally studied only in the GHz spectral range. Several strategies have been reported to prepare metallodielctric inverse opals, including layer-by-layer (LBL) self-assembly of nanoparticles on suitable colloid particles[4], precipitation/chemical conversion[5], direct penetration of metal nanocrystals[6], electroless deposition[7], and electrochemical reduction methods[8]. It is well known that metallodielectric inverse opals prepared to date, especially pure gold and gold, are rather fragile, lacking mechanical and thermal stability[9~11]. On the other hand, even though the opals cannot exhibit a full PBG, the infiltration with materials may turn them into interesting structures and there are many interesting applications that do not require a complete PBG, such as sensors, super-refractive devices catalysis, and templates for other materials[12].

Here, we demonstrate a simple method to directly fabricate silica free-standing colloidal crystal (opal) film at a water-air interface by raising the temperature of silica suspension in a half-close environment. And an electroplating process to directly infiltrate gold nanoparticles into the order periodic opal structure was studied in detail. The transmission and reflection spectra of the gold/silica composite opal were presented after each treatment of electroplating-washing-drying circle. Our main idea is to use a regular 3D silica opal film as a template to prepare a metallodielectric 3D silica/gold array, and investigated the relationship of the measured optical property and the system microstructures by optical microscope and SEM.

2 Experiment

2.1 Fabrication of 3D colloidal crystal film at water-air interface

Monodispersed SiO_2 nanoparticles (ca.

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210nm) were prepared at our laboratory using Stöber's method[13]. The 3D colloidal crystal film at the water-air interface is similar to that in our previous report[14]. The detailed procedures are as follows: The white silica sphere solution obtained underwent self-sedimentation for one or two days, after which a whiter higher concentration suspension of particles was formed at the bottom of the beaker. Then, the clear solution at the top part was carefully removed, and the small beaker containing the remaining white suspension was put on a heater and covered with a big beaker (diameter: 5cm) to form a half-closed environment. Since the interior space of big beaker was in a half-closed environment, the reacting suspension solution in the small beaker could not be evaporated very fast, even at 80℃. Thus, the humidity was enough in the interior of that half-closed environment, facilitating an excellent self-assembling procedure of silica spheres and the formation on a large scale of the 3D colloidal crystal film on the water surface.

2.2 Infiltration of gold nanoparticles in the 3D periodic structure

The opal film was carefully transferred onto an ITO glass substrate, dried, and calcined at 550℃ for 4h in air. It was then cooled down to room temperature, and the sample for the infiltration of gold was obtained. Electro deposition was carried out by a constant current method in $KAu(CN)_2$ solution (0.5mg/ml). A metal wire attached to the ITO backing with gold paste served as the cathode, and a small Pt strip touching the gold solution served as the anode. The deposition proceeded as follows: the opal film on the ITO glass was put into the gold solution. Then, a constant current with a low density was applied for a different time. The sample was taken out, washed with water, dried at room temperature, and sintered at 80℃ for 4h. The transmission and reflection spectra were measured, and optical microscope images were obtained. The above treatment was repeated several times to get the final composite opal sample. The current was controlled with an EG & G 273 A potentiostat-galvanostat.

2.3 Characterization

Measurements of the transmission and reflection spectra of our Au/SiO_2 opal were made using a microregion reflection/transmission spectrophotometer system. Scanning electron microscopy (SEM) and optical diffraction measurements were carried out on JEOL JSM-6500F microscope.

3 Results and discussion

The optical properties were tested to identify the effect of the infiltration of gold by measuring the transmission and reflection spectra from 450 to 650nm at room temperature. The spectra were measured at normal incidence ($\theta = 0$) to the (111) plane of the sample. The optical spectra of the pure silica and the corresponding gold/silica composite opal films are shown in Fig. 1. The Bragg diffraction peak of the pure silica opal structure is initially located at 556nm, corresponding to the diameter of silica spheres (curve *a* in Fig. 1(a) and Fig. 1(b)). Obviously, the peak of transmission and the reflection spectrum of the sample both shifted to longer wavelengths after electro-

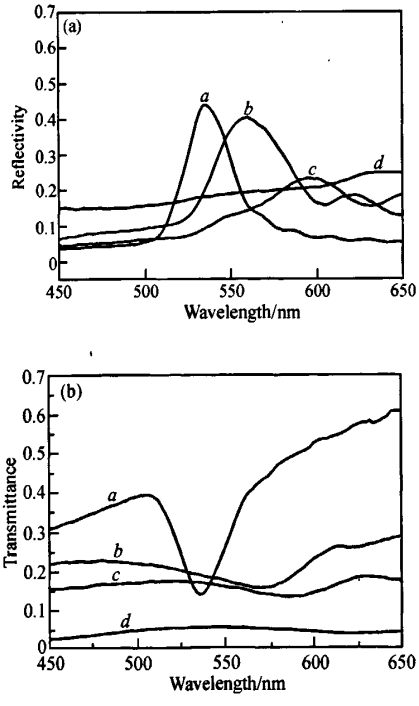

Fig. 1 Normalized optical spectra of the sample at different plating stages at normal incidence (a) Reflection; (b) Transmittance The electrodepositing times (second) are 0 (*a*), 20 (*b*), 40 (*c*) and over 200s (*d*), respectively.

plating 20s (curve *b* in Fig. 1(a) and Fig. 1(b)) and 40s (curve *c* in Fig. 1(a) and Fig. 1(b)). However, from curve *d* in Fig. 1(a) and Fig. 1(b), we can clearly see that the peaks of both the transmission and the reflection spectra of the sample disappeared because of the longer deposition time. Here, we propose that the infiltration of gold resulted in the red shift. After adding an applied constant current, Au^+ adsorbed in the voids of the 3D silica opal due to the capillary force was reduced to Au nuclei and deposited around the surface of the spheres, forming Au/silica composite opal. As a result, the effective refractive index increased, and the average reflection and transmittance peaks shifted toward to a longer wavelength. On the other hand, it is worth pointing out that the intensities of both reflection and transmittance decreased (even disappeared) because the deposition time was too long. These results show the relationship between the structure and composition, which could control the optical properties of the colloid array.

Figure 2 (a) shows a typical top-view scanning electron microscopy (SEM) picture of a silica opal after the first electroplating cycle. The spheres form well-ordered crystal domains with dimensions of several tens of micrometers. As shown in Fig. 2(a), some cracks and point defects are observed on the surface of the colloidal opal. Despite these defects, the opals still exhibited a strong reflection peak, showing that they had a larger tolerance to the geometric disorder (as compared with dielectric inverse opals)[15]. The magnified SEM images in Fig. 2(a) further confirm that the silica spheres were crystallized into a hexagonally close-packed ordered structure, and that gold particles have been coated on the silica spheres (Fig. 2(b)). Figure 2(c) shows the SEM images of opal sample after a longer deposition (over 200s). Compared to Fig. 3(a), Figure 2(c) shows that more gold was assembled into the 3D ordered structure, and the voids of the silica spheres seem to have been filled. Combining this with curve *c* in Fig. 1, we might propose that the intensities of both reflectance and transmittance decreased (even disappeared; see curve *c* in Fig. 1) since there were many more gold particles after the long deposition time. Judging from the SEM images, this is because too many gold particles assembled on the surface of the silica spheres might cause a loss of strong diffraction within the colloid crystal due to the scattering of light (in directions other than the normal reflection and transmission). These results give evidence of the relationship between the structure and composition, which could control the optical properties of the 3D colloid crystals.

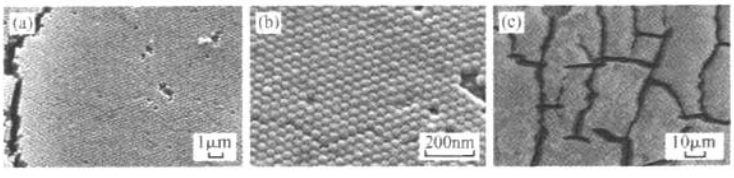

Fig. 2 SEM images of the sample at different plating stages (a) Plating 20s; (b) Magnified pictures of (a); (c) Plating over 200s

4 Conclusion

We have proposed a method to fabricate gold/silica complex opal by an electroplating method in an ITO glass cell. A red shift of the reflection and transmittance spectra was clearly observed with the increasing of electroplating time. This crystal structure has potential for use in nano-photonic circuits, white-light LEDs, and photocatalysts.

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3D胶状晶体膜及其渗透金的氧化硅人工蛋白石的制备*

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摘要：用纯的单分散氧化硅胶体微球作为基质，在水-空气界面构筑无载体三维有序胶质晶体膜. 该高度有序三维周期性结构具有明显的光学衍射现象. 利用电沉积的方法将纳米金渗透到这种人工蛋白石的空隙中，构成 gold/silica 复合蛋白石材料. 详细研究了该复合蛋白石的透射光谱和反射光谱，用扫描电镜观察了复合蛋白石结构的形貌特征，并对渗透金后蛋白石的光谱移动进行了分析.

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