Cu_2O particles with ordered pores via electrochemical deposition method

Ailun Zhao (赵爱伦), Ming Fu (富　鸣)*, Yinglei Tao (陶颖镭), Lier Deng (邓立儿),
Dawei He (何大伟), and Yongsheng Wang (王永生)**

Institute of Optoelectronic Technology, Beijing Jiaotong University, Beijing 100044, China
**E-mail: mfu@bjtu.edu.cn; ***e-mail: yshwang@bjtu.edu.cn*

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Cu_2O particles cube with ordered pores are electrodeposited by using colloidal crystal template method. The shape of Cu_2O cube particle is partly determined by its growing habit. Therefore, Cu_2O cube particles with ordered pores are fabricated instead of three dimensional inverse opal structures.

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Materials with porous structures have various technologically important applications and special properties due to their distinctive structures. Conventional applications include sound-absorbing[1] materials, supports in catalysis[2], ion exchanger, filters in separation[3], and so on. Over the past several decades, inverse opal structural material, which possesses highly ordered porous structure, exhibits a novel optical property of photonic bandgap (PBG)[4,5]. The unique optical properties of PBG and photonic crystals (PhCs) provide the basis for numerous applications, such as low-threshold lasers, low-loss waveguides, on-chip optical circuitry, and fiber optics. As a result, a number of technologies and methods were developed to fabricate the high quality inverse opal[6−8]. Most of the research focuses on the large scale size and fewer unwanted defects. In this letter, we introduce a non-traditional inverse opal structure material that is the cubic particles with ordered pores structure of Cu_2O crystal.

The fabrication process of Cu_2O particles with ordered pores is divided into three major steps: polystyrene colloidal crystals template fabrication, electrodeposition of Cu_2O particles inside the template, and polystyrene colloidal crystals template removal. Figure 1 shows the flow chart of the fabrication process.

The three dimensional polystyrene templates have been fabricated by vertical deposition[9] from a colloidal solution onto a 1×5 (cm) glass substrate. In order to carry out the electrodeposition, a conductive layer is needed. For this reason, the substrate is covered with indium-tin oxide (ITO). The fabrication of artificial opal uses the colloidal solution of monodisperse sphere with 529- and 240-nm diameter polystyrene spheres and 0.5% in weight. The substrates are placed into the 15-ml weighing bottle filled with suspensions of polystyrene and kept an inclination of 80°. The vessel containing the substrates is then placed into an oven and the temperature is set at 53 °C lasting for 5 days. In the whole process, any quiver should be avoided.

Cu_2O crystal particles are then deposited inside the colloidal crystal templates by electrochemical method using a conventional three-electrode setup. The aqueous solution is 0.02-mol/L $Cu(NO_3)_2$. The electrodeposition of Cu_2O has been carried out under the condition of a constant current density of 0.15 mA/cm^2, holding for 480 s every time. After the deposition, the samples are dried at the room temperature for several hours before the next steps.

At last, colloidal crystal template is removed in order to obtain the Cu_2O particles with ordered porous structure. In this process of removal, two different methods are applied, one physical and the other chemical. The physical method is calcination where the samples are placed into muffle furnace keeping the temperature at 400 °C for 2.5 hours. When the chemical method is used, the samples are soaked in the toluene which can dissolve the polystyrene spheres for 24 hours.

A series researches have been widely developed on the ability of tuning the shapes of crystal materials[10,11]. Through accurately adjusting the various parameters of electrodeposition of Cu_2O crystal, such as concentration of solution, temperature, current density, electric potential, etc., Cu_2O crystal with some certain shapes can be obtained. The cubic shape Cu_2O crystal particles are deposited after a number of deposition conditions are investigated and the proper parameters are chosen. The cubic shape is proved to be the optimum one for our final purpose because its deposition can be easily controlled and its porous structure has sufficient mechanical intensity. Figure 2 shows the scanning electron microscopy (SEM) images of Cu_2O crystal particles deposited on the substrate without colloidal crystal template. Figures 2(a)-(c) show that Cu_2O crystal cube can grow along different direction and all of the Cu_2O particles have the extremely regular form which is favorable for generating optical property.

Figure 3 shows SEM images of the cross section and top view of a colloidal crystal template that is made from

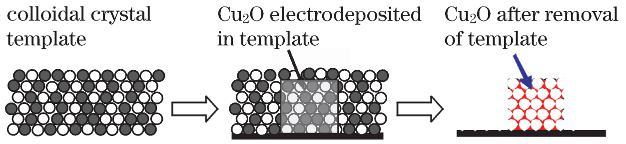

Fig. 1. Flow chart of fabrication process of Cu_2O with ordered pores.

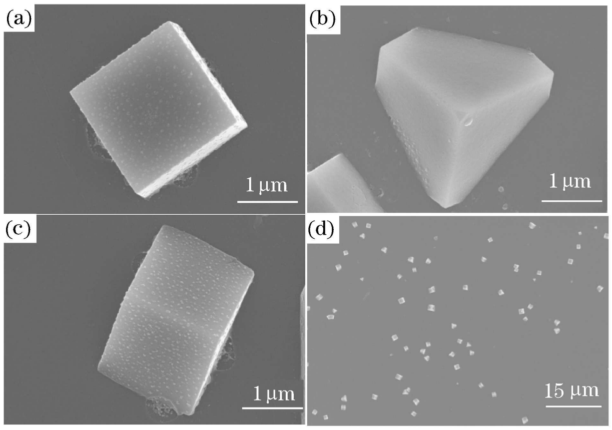

Fig. 2. SEM images of octahedral Cu_2O crystals with different shapes.

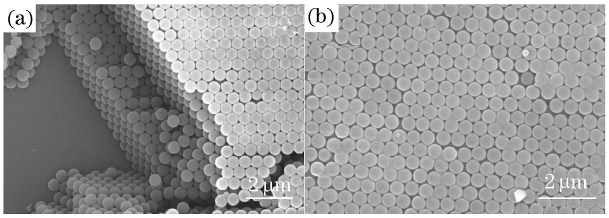

Fig. 3. SEM images of polystyrene colloidal crystal template in microsphere diameter of 529 nm. (a) Cross section, (b) top view.

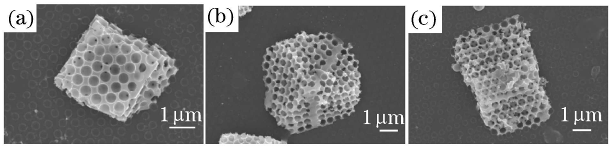

Fig. 4. SEM images of different shapes of Cu_2O crystal particle with pores.

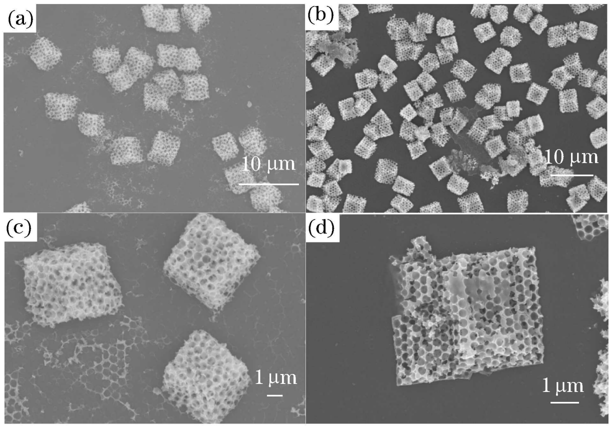

Fig. 5. SEM images of Cu_2O crystal particles with ordered pores. (a), (c) and (d): results of calcination, (b): result of dissolved by toluene.

polystyrene microspheres with a diameter of 529 nm on an ITO substrate. The colloidal crystal template has a high degree of order in all directions on the substrate, which is the precondition for the optical property. The deposition of Cu_2O crystal can still proceed though there is a film of colloidal crystal just because of the existence of interstices among the microspheres. Figure 4 shows the various final shapes of Cu_2O particles with ordered pores after deposition of Cu_2O in colloidal template and removal of template. In order to make Cu_2O have the same shape with original shape of Cu_2O without template, suitable electrodeposition conditions mentioned in the experiment part have been chosen. From comparing Fig. 4 with Fig. 3 respectively, we can find that the Cu_2O can basically maintain its original shape when it grows in the interstices among the microspheres of template. This is the guarantee that the Cu_2O with ordered pores can be deposited successfully. However, the polystyrene template has influence on the distribution of Cu_2O particles on a large scale. As a result most of the Cu_2O particles are more concentrative than the ones on the substrate without template. Though each Cu_2O particle with ordered pores has the same structure with the inverse opal structure, possessing single particle and regular shape differentiates it from the traditional inverse opal structure.

In the process of removing polystyrene template, two different methods, physical calcination and chemical dissolution, are tested in order to obtain the optimum porous structure. Figure 5 shows the different results in different dealing ways. The expectable ordered porous structure of Cu_2O crystal can be basically obtained through both of the two methods. As shown in Figs. 5(a) and (b), a considerable of regular and ordered pores have existed inside the Cu_2O crystal particles. The calcination seems to be a convenient and simple process due to the low melting point of polystyrene.

Although a 2.5-hours process at 400 °C has yielded to some good results, it is observed from Figs. 5(c) and (d) that inversion is not achieved regularly. The resulting ordered porous structures after the calcination process present plenty of damage probably originated by the mechanical stress generated in the calcination process which is an inevitable destruction accompanying with the high temperature heating. As a contrast, the chemical removal of the polystyrene using toluene generates near perfect inverse opal in the Cu_2O crystal, such as Figs. 4 and 5(b). So the chemical methods is more preferable than physical one for removing polystyrene.

The Cu_2O crystal particle with ordered pores structure has similar optical property with the inverse opal structure duo to their identical interior structure, such as photonic bandgap. The optical properties of the samples are characterized with optical microscopy and the results of the optical characterization of samples are shown in Fig. 6. Obvious optical phenomenon has been observed on the samples which use the template of microspheres with diameter in 240 nm. By comparing Figs. 6(a) with (b), we can find that the reflection of light from the sample of Cu_2O crystal with ordered pores is remarkably intensified. Unquestionably, it is the photonic bandgap generated by the inverse opal of Cu_2O particles that strengthens the reflection. In further, the frequency of the bandgap basically accords with the theoretic value.

In summary, Cu_2O crystal cube with ordered pores has been firstly successfully fabricated by electrochemically depositing Cu_2O inside polystyrene template. The most important steps include the fabrication of

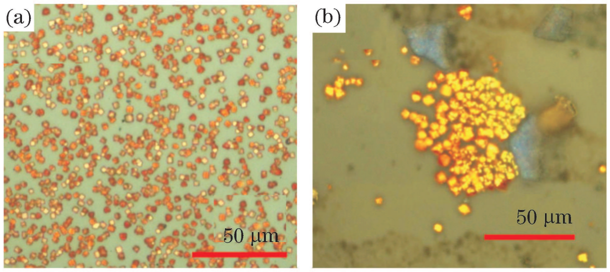

Fig. 6. Optical microcopy images of (a) Cu_2O crystal particles on the substrate and (b) Cu_2O crystal particles with ordered pores.

high ordered polystyrene template and the removal of polystyrene microspheres which are the premise for the ordered and regular porous structure. The characterization of samples' optical property proves that Cu_2O crystal particle with ordered pores also has the photonic bandgap, which indicates that Cu_2O crystal particle with ordered pores may have potential applications on the photonic device.

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