FABRICATION AND OPTICAL PROPERTIES OF AIR SPHERE/SILICON NANOCOMPOSITE

X.Liu, Y.Zhang, Y. Li*, D.T.Ge
Center for Composite Materials and Structure, Harbin Institute of Technology, Harbin, China
* Corresponding author (liyao@hit.edu.cn)

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1 General Introduction
Photonic crystals (PCs) or photonic band gap (PBG) materials have attracted rapidly growing interest because of their potential applications in photonics and other devices. Silicon has a very high refractive index ( $\lambda$ =1.1μm, n=3.53), making it a very promising candidate for photonic applications. The Si photonic crystal obtained as an air-sphere/ Si nanocomposite with periodical ordered pores in three dimensions has high application potentials in photonics, ultra fast optical switching, low-loss optical waveguides and solar cell[1-3]. Electrodeposition is a feasible method for the production of this sort of materials because it offers the opportunity of a complete infilling of the vacancies from the bottom up to the top layers of the template. Unfortunately, silicon can hardly be obtained in aqueous solutions as its deposition in water is always accompanied by hydrogen evolution. However, silicon can be quite easily electrodeposited in ionic liquids. Here we report for the first time on the synthesis of air-sphere/Si nanocomposite by template-assisted electrodeposition into colloidal crystal templates formed by self-assembly of polystyrene (PS) particles in ionic liquid.

2 Experimental section
Monodisperse PS spheres with an average diameter of 235nm and 587nm were self-assembled on ITO glasses by using a controlled vertical drying method to form highly ordered colloidal crystal templates, as the reference has mentioned[4]. The electrochemical experiments were performed in a Nitrogen-filled glove box. The electrochemical cell was made of Teflon and clamped over a Viton O-ring onto the ITO. During the electrochemical deposition, [Py$_{1,4}$]Tf$_2$N was used as the electrolyte. PS templates on ITO glasses were used as a working electrode (WE). A copper wire was in contact with the ITO substrate to provide a better connection to the potentiostat. Ag wires and Pt ring were used as a quasi-reference and counter electrodes, respectively. The electrochemical measurements were performed using a CHI660C electrochemical station. The deposit was then removed from the glove box and rinsed quickly with isopropanol to avoid redundant ionic liquid left on deposited Si. The polystyrene template was removed by tetrahydrofuran and to obtain the air sphere/silicon composite structure.

The morphologies and pore size of the air sphere/silicon composites were characterized by scanning electron microscope (SEM). Elemental analysis was characterized by X-Ray photoelectron spectroscopy (XPS). Optical reflectance measurements were performed to measure the photonic stop band behavior.

3. Results
Fig.1 shows the comparison of three cyclic voltammetry curves, in the pure ionic liquid [Py$_{1,4}$]Tf$_2$N on ITO substrate (the thinnest line), [Py$_{1,4}$]Tf$_2$N containing 0.1mol/L SiCl$_4$ system on the ITO substrate (the thicker line) and with 0.1mol/L SiCl$_4$ in [Py$_{1,4}$]Tf$_2$N on the ITO substrate with PS (diameter 587 nm). In the pure ionic liquid system the ionic liquid [Py$_{1,4}$]Tf$_2$N has large electrochemical window and enough stability, which make it suitable for silicon electrodeposition. In the
thicker curve there are two main reduction peak of silicon, at potential of -2.65V with peak current of \( I_p = -2.01 \times 10^{-4} \text{A} \) and at potential of -1.93V with peak current \( I_p = -7.89 \times 10^{-5} \text{A} \), respectively. The lower potential is corresponding to the nucleation of silicon, and the larger potential is corresponding to the bulk electrodeposition of silicon on the ITO conductive substrate. The larger reduction peak of -2.65V on the ITO is corresponding to the silicon reduction. However, on the ITO covered with PS, the conductivity becomes lower, and the reduction peak is about -2.5V with current of -6.88 \times 10^{-5} \text{A}, which corresponding to the bulk silicon electrodeposition on the pores between the colloidal crystal templates.

Fig.2 shows SEM images of air sphere/Si nano composite. The deposit has a well ordered macroporous nanoarchitecture consisting of close packed spherical uniform pores. The holes connecting the pores are clearly visible, indicating the three dimensional ordering of the structure. The EDX analysis of the deposit shows, besides silicon, indium, tin, sodium, calcium and oxygen from ITO substrate can be observed.

The XPS measurement is employed to further determine the composition of the surface of the deposit. XPS analysis shows the silicon film is rapidly oxidized as soon as exposed to the air. XPS gives the information that the silicon films exist SiO\(_2\) bond. After Ar\(^+\) etching, 2p peak of pure silicon is shown.

The optical properties of the air sphere/Si nanocomposite are also studied. Our results show that by using template-assisted electrodeposition, 3D ordered macroporous silicon can be fabricated successfully. The results might be of considerable interest to improve the efficiency of solar cells.

References


