Electrochemical Synthesis of Silver Hollow Microsphere Arrays†

CHENGLIANG HAN[*], CHANGAN TIAN, CHONGHAI DENG and DING MING

Department of Chemistry and Materials Engineering, Hefei University, Hefei 230022, P.R. China

*Corresponding author: E-mail: hfuuhan@163.com

Silver hollow microsphere arrays were fabricated by electrophoresis deposition (EPD) approach based on monolayer polystyrene (PS) colloidal crystal template technique. Every silver hollow microsphere is made of many silver nanoplates which are standing on the surface of micro-sphere and cross-linking each other. The formation of nanoplates is attributed to oriented-attachment-growth of small silver nanoparticles. This prepared method is reproducibility, inexpensive and easy to make.

Key Words: Hollow microsphere, Polystyrene, Ag nanoplates, Electrophoresis deposition.

INTRODUCTION

The self-assembly and high-order organization of micro- and nanostructured units into complex architectures with hierarchy across extended length scales is a key challenge in current materials synthesis and application[1-3]. Over the past decade, silver nanostructures have received considerable attention owing to one of their remarkable properties known as localized surface plasmon resonance (LSPR), which has enabled a rich variety of applications, including their use as optical probes, contrast agents, sensors, plasmonic waveguides and substrates for surface enhanced Raman scattering (SERS)[4,5]. Until recently, there were only limited methods for the synthesis of silver metal films and silver nanoparticles have gained favour as surface enhanced Raman scattering substrates[6-8].

Herein we report an electrophoresis deposition approach to fabricate hollow-spherical micro-nanostructured ordered silver hollow microsphere array based on monolayer polystyrene colloidal crystal template technique.

EXPERIMENTAL

First, the monolayer polystyrene colloidal crystals were uniformly prepared on well cleaned glass substrate with 3 cm × 3 cm in size by spin coating the polystyrene colloidal suspension. The formed monolayer polystyrene colloidal crystals were then transferred onto cleaned silicon substrate. A gold layer of 20 nm in thickness was then coated on the surface of the colloidal crystal by plasma sputtering deposition by controlling the deposition current and time.

Secondly, 0.2 g $AgNO_3$, 0.5 g PVP and 0.2 g $Na_3C_6H_5O_7\cdot 2H_2O$ were added to 200 mL of water followed by stirring till complete dissolution. Such aqueous solution was used as electrolyte for electrophoresis-deposition-growth. A graphite flake was used as anode and Au coated polystyrene colloidal crystals arrays as cathode. The electrophoresis deposition was carried out under current density 5 µA/cm^2 for about 10 h at room temperature. After that, the substrate with products were taken out were immersed methylene chloride (CH_2Cl_2) for 10 min to dissolve the polystyrene colloidal crystals and cleaned with distilled water for several times and dried with high-purity flowing nitrogen and characterized by X-ray diffraction (XRD) (Philips X'pert-PRO, CuK$_\alpha$ (0.15418 nm) radiation) and field emission scanning electronic microscope (FESEM, sirion 200 FEG), respectively.

RESULTS AND DISCUSSION

Fig. 1 shows the XRD corresponding to the products shown in Fig. 2b. Four diffraction peaks (2θ) 38.2, 44.3, 64.4 and 77.3º, corresponding to the (111), (200), (220) and (311) planes, respectively, for the face-centered cubic (fcc) structure of Ag with space group Fm3m (JCPDS89-3722) were observed.

Fig. 2a shows the FESEM of the monolayer polystyrene colloidal crystals template with size of 2000 nm in diameter. It can be seen a hexagonal-close-packed arrangement of this template. After electrophoresis deposition about 10 h, the structure and the morphology of our products were shown in Fig. 2b. It can be clearly seen that an ordered micro-sphere
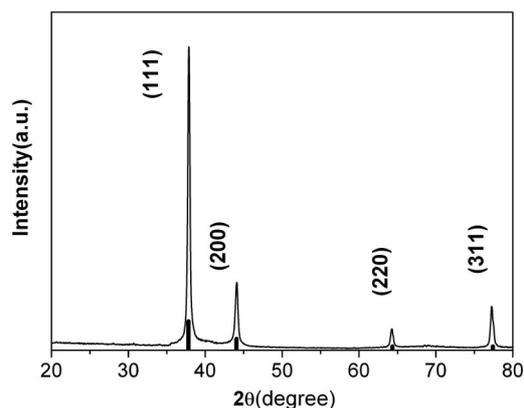
Fig. 1. XRD pattern of Ag hollow microsphere array
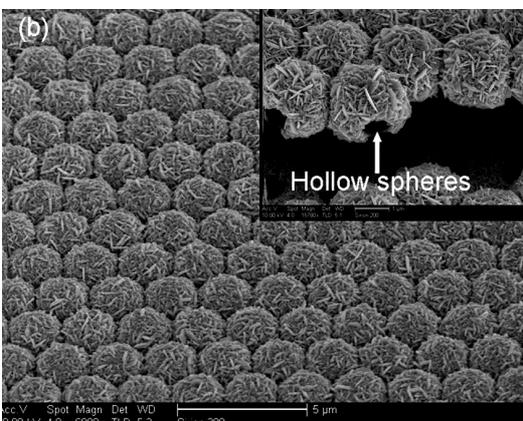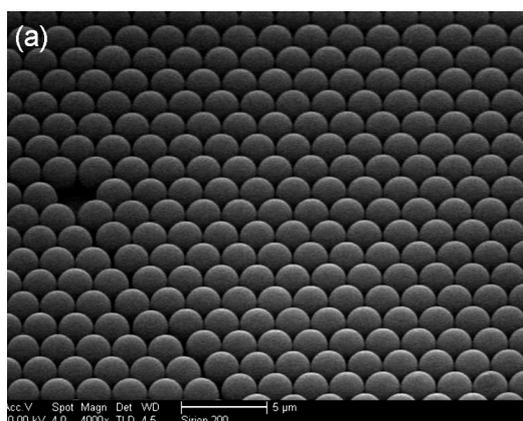
Fig. 2. SEM images of monolayer polystyrene array (a) and Ag hollow sphere array (b)

arrays kept with a hexagonal-close-packed arrangement were synthesized. Every hollow Ag micro-sphere has a very rough surface (inset).

The formation of Ag hollow sphere arrays is attributed to selectively oriented nucleation of Ag and quasi-equilibrium preferential growth on the Au film-coated substrate and the formed nanoplates are sparsely covered on the substrate. As we all know, trisodium citrate is a weak reducing agent, which can reduce Ag^+ to Ag at a mild rate[9,10]. The reduced Ag atoms will nucleate and grow up to colloidal Ag nanoparticles in solution. At the same time, trisodium citrate is a static agent, which can prevent colloidal Ag nanoparticle to aggregate.

Under the electric field, those charged colloidal Ag nanoparticle will move to surface of the cathode continually, that is, happened electrophoresis deposition at the cathode. Fig. 3 demonstrates the whole producer of the Ag hollow-spherical arrays. The number density of Ag nanoplates can be controlled by the concentration of sodium citrate. The period of this array can be adjusted by selecting different sized polystyrene colloidal crystals. These hollow sphere arrays hoped to be served as highly active surface-enhanced Raman scattering (SERS) substrates for detection of trace amounts of contaminants and pollutant.
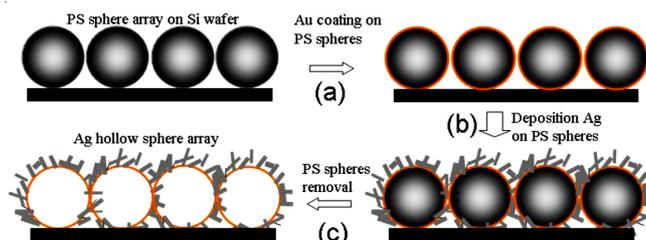
Fig. 3. Schematic formation of Ag hollow sphere array ((a) coating a gold layer on colloidal monolayer by ion-sputtering deponsition; (b) electrophoresis deposition of Ag nanoparticles; (c) removal of PS microspheres)

Conclusion

In summary, Ag hollow spherical arrays were fabricated by EPD, using a monolayer polystyrene colloidal crystal template. The formation of Ag nanoplates can be attributed to oriented-attachment of small Ag nanoparticles. The hollow spherical arrays with higher stablity are good candidates for the highly active surface-enhanced Raman scattering substrates, which can be used for detection of trace amounts of contaminants and pollutant.

REFERENCES

1.   H. Cölfen and S. Mann, *Angew. Chem. Int. Ed.*, **42**, 2350 (2003).
2.   S.C. Glotzer and M.J. Solomon, *Nature Mater.*, **6**, 557 (2007).
3.   Z. Tang, Z.L. Zhang, Y. Wang, S.C. Glotzer and N.A. Kotov, *Science*, **314**, 274 (2006).
4.   V.K. Sharma, R.A. Yngard and Y. Lin, *Adv. Colloid. Interf. Sci.*, **145**, 83 (2009).
5.   K. Aslan, J.R. Lakowicz and C.D. Geddes, *J. Phys. Chem. B*, **109**, 6247 (2005).
6.   S.B. Chaney, S. Shanmukh and R.A. Dluhy, *Appl. Phys. Lett.*, **87**, 031908 (2005).
7.   J.P. Schmidt, S.E. Cross and S.K. Buratto, *J. Chem. Phys.*, **121**, 10657 (2004).
8.   Z.Y. Li, W.M. Tong, W.F. Stickle, D.L. Neiman and R.S. Williams, *Langmuir*, **23**, 5135 (2007).
9.   K.K. Caswell, C.M. Bender and C.J. Murphy, *Nano Lett.*, **3**, 667 (2003).
10. H.Y. Liang, W.Z. Wang, Y.Z. Huang, S.P. Zhang, H. Wei and H.X. Xu, *J. Phys. Chem. C*, **114**, 7427 (2010).