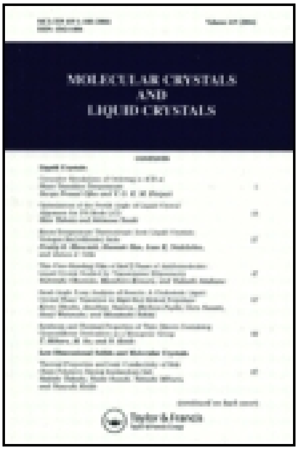

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Evolution of Core-Shell Structure Using Functional Polystyrene and Gold

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A core-shell of a carboxylic functional polystyrene (PS-COOH) with gold was prepared by the combination of surface gold-seeding and subsequent shell growth in a gold solution. The PS-COOH cores were prepared by a dispersion polymerization of styrene for seed formation followed by copolymerization of styrene and methacrylic acid. In the preparation of gold shell, PS-COOH cores were initially immersed into gold nanoparticles containing solution and continuous gold shell was formed by employing a mixed aqueous solution of $Au(OH)_3$ *and* NH_2OH. *The gold nanoparticles impregnated into the PS-COOH cores were used as gold seeds to form continuous gold shells. The characteristics of the PS-COOH/Au core-shells were investigated by SEM, TEM, EDS and XPS.*

Keywords: carboxylic functional polystyrene; core-shell; gold nanoparticles

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INTRODUCTION

The preparation of polymer/inorganic nanoparticles composites has attracted extensive research interest since it provides interesting physical properties. They combine the advantages of polymers (elasticity, transparency, dielectric properties, etc.) and inorganic nanoparticles (electronic and catalytic properties, etc.) In particular, fabrication of metal-coated core-shell particles is currently an attractive area due to their unique optical, biochemistry or potential uses as chemical sensors [1–4].

However, it is very difficult for metallic nanoparticles to disperse onto a pre-shaped polymer matrix. Several routes for such core-shell particles fabrication, chemical reduction [5–8] and self-assembly [9–10] have been investigated. In most cases, the degree of surface coverage is lower than 30% and the metallic coating is non uniform.

In our previous study, a poly (divinylbenzene) (PDVB)/Au core-shell structure was prepared by the chemical reduction of gold-phenanthroline complex [11]. The gold shells were very rough. It was very difficult to tune the thickness and roughness of the metallic shells, and only rough gold shells were obtained. To overcome this drawback, the two step coating technique composed of surface gold-seeding and subsequent gentle growth of gold shell has been proposed in this study, resulting in complete and smooth gold coating on carboxylic functional polystyrene particles (PS-COOH). The presence of polar carboxylic groups on the surface of PS core facilitated the deposition of the gold nanoparticles. The synthesized gold nanoparticles on the PS-COOH cores served as gold seeds for the gentle shell growth which was obtained by employing a solution of $Au(OH)_3$ and NH_2OH to obtain completely uniform and smooth gold shells.

EXPERIMENTAL

Materials

Styrene (St), methacrylic acid (MAA), and divinylbenzene (DVB) (Aldrich Chem. Co, USA) were used after passing them through an inhibitor-remover column. Polyacrylic acid (PAA, Mw: 2000) and polyvinylpyrrolidone (PVP, Mw: 40 000) (Sigma Chem. Co, USA) were used as received. Azobisisobutyronitrile (AIBN) and benzoyl peroxide (BPO) (Sigma Chem. Co, USA) were used as received. $HAuCl_4$ (99.5%, Kojima) was used as received. Sodium dodecyl sulfate (SDS), dibutyl phthalate (DBP), ethanol, methoxyethanol, toluene, NH_2OH, and K_2CO_3 were used as received (Sigma Chem. Co, USA). 4-dimethylaminopyridine (Merck Co, USA) were used as received.

Preparation of the PS-COOH Cores

The PS-COOH cores were prepared by two-step polymerization following the procedure described by Tuncel *et al.* [12]. In the synthesis of carboxyl carrying-particles, the seed latices were first swollen by an organic agent (dibutylphthalate, DBP), then by styrene (S)–methacrylic acid (MAA)–divinylbenzene (DVB) mixture including an oil-soluble initiator (benzoyl peroxide, BPO). The final particles were obtained by the polymerization of monomer mixture in the swollen seed particles by keeping the particle uniformity.

Preparation of Aqueous Gold Nanoparticle Solution

The gold nanoparticle solution was prepared by using a phase transfer method [13], which resulted in a highly concentrated gold solution ($2\,g\,L^{-1}$). The phase transfer of nanoparticles from organic to aqueous solutions has involved irreversible covalent capping of the nanoparticles: gold nanoparticle in toluene across the phase boundary by use of 4-dimethylaminopyridene (DMAP).

Impregnation of Gold Nanoparticles into the PS-COOH Cores

0.1 g of the PS-COOH cores was soaked in 5 ml of the aqueous gold nanoparticle solution for 4 days at room temperature. Subsequently, the excess gold material was removed by filtration.

Gold Shell Growth

The gold nanoparticles impregnated into the PS-COOH cores were used as gold seeds to form continuous gold shells. To grow the gold over layer, we first prepared a solution of gold hydroxide [14–15]. We calculated that 500 ml of gold hydroxide solution and 250 ml of 1.87 mM NH_2OH solution were needed for 0.1 g of the PS-COOH cores ($d = 3\,\mu m$), in order to obtain gold shells with a thickness of 35 nm [16].

Characterization

The morphologies of the PS-COOH cores and (PS-COOH)/Au core-shells were observed using a scanning electron microscope (SEM, Phillips XL30 ESEM-FEG) and a transmittance electron microscopy (TEM, JEOL-3010). An EDS USL 30 analyzer attached to the SEM was used to determine the chemical composition of the samples using an energy dispersive X-ray spectrometer (EDS). The infrared spectra of the PS-COOH cores were obtained by means of an FT-IR spectrophotometer (Bruker IFS-66/S).

RESULTS AND DISCUSSION

The reaction conditions were carefully optimized to obtain PS seed particles having a diameter of 1.3 μm by a dispersion polymerization. The subsequent copolymerization of metharylic acid, styrene and divinyl benzene on PS seeds produced the PS-COOH cores with a diameter of 3 μm, which is an appropriate size for the fabrication of flip chips. The PS-COOH cores were also characterized by FT-IR spectroscopy. Figure 1 shows a comparison of the spectra between the original PS seed particles and the PS-COOH cores. Spectrum 1 shows a strong characteristic C=O stretching band at 1720 cm^{-1} confirming the presence of the carboxylic functional groups in the PS-COOH cores.

The morphology of PS-COOH cores is shown in Figure 2(a). The PS-COOH cores with very smooth surfaces were immersed into the gold nanoparticles containing solution. While soaking the carboxylic acid modified polymer cores in the aqueous gold nanoparticle solution, the gold nanoparticles easily enter the pores of the cores, resulting in the deposition of a gold seed [17].

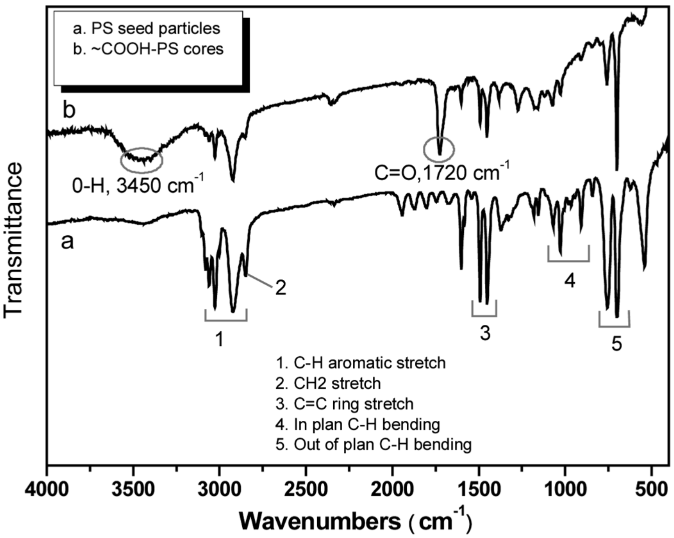
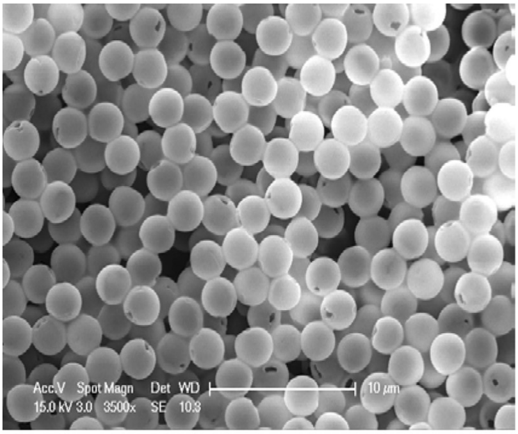
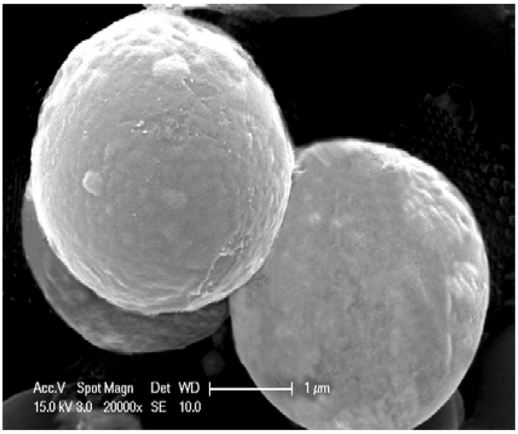


FIGURE 1 FT-IR spectra of (1) PS seed particles and (2) PS-COOH cores.



(a) PS-COOH cores

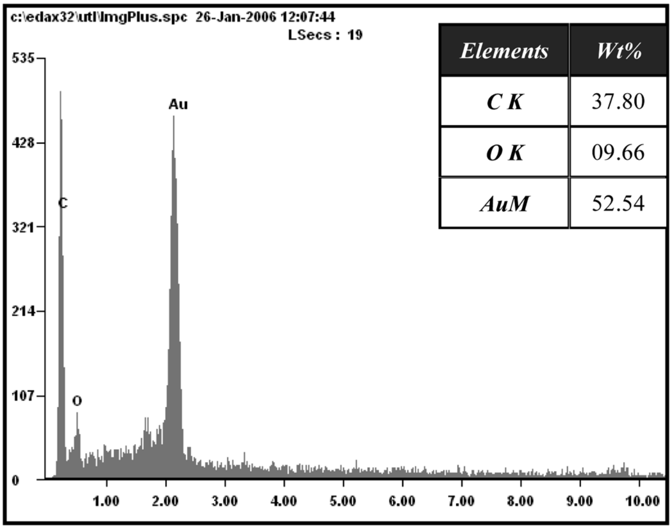


(b) PS-COOH/Au core-shells

FIGURE 2 SEM images of (a) PS-COOH cores and (b) PS-COOH/Au core-shells.

A method of forming gold shells by the reductive growth of small gold nanoclusters on silica spheres was previously developed by Oldenburg *et al.* [18]. In their study, the strong reduction agent, $NaBH_4$, was used to reduce $HAuCl_4$. This resulted in the further growth of most of the small gold particles attached to the spheres, but also caused a significant degree of new nucleation of the many new gold particles present in the solution, which tend to coalesce into clumps that are difficult to remove from the gold shells. Ji also developed a method of forming gold shells by using $HAuCl_4$ and NH_2OH [19]. In this study, it was demonstrated that the growth of the gold nuclei already present could be enhanced by gentle reduction, while suppressing the formation of new nuclei. However, according to our findings, these gold nuclei formed rough shells. We therefore combined the methods of Oldenburg and Ji and used $Au(OH)_3$ prepared from $HAuCl_4/K_2CO_3$ and NH_2OH for the formation of the gold shells by the gentle reductive growth of small gold seed nanoparticles on the PS-COOH cores. As the SEM images in Figure 2(b) show, the gold clusters distributed over the entire surface of the cores led to the formation of completely uniform and smooth shells. The foundation for the formation of the gold shells described herein is the growth of the small gold nanoclusters attached to the PS-COOH cores. These nanoclusters are then enlarged by the gentle reductive action of $Au(OH)_3$. After their initial period of growth, these gold nanoparticles begin to coalesce, and finally form continuous gold shells. These shells can then be grown further to produce thicker shells in Figure 2(b).

In order to verify that the reduction to zero-valent gold did indeed occur, EDS analysis was carried out on the (PS-COOH)/Au core-shells, as shown in Figure 3. Figure 4 gives the TEM image of the cross-section of the (PS-COOH)/Au core-shells. The big circles shown



Elements	*Wt%*
C K	37.80
O K	09.66
AuM	52.54

FIGURE 3 EDS analysis of (PS-COOH)/Au core-shells.

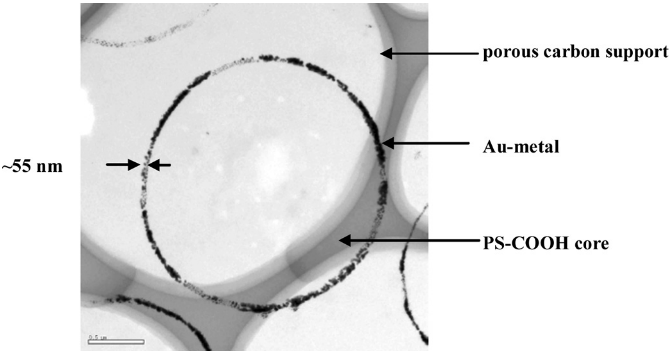


FIGURE 4 TEM image of (PS-COOH)/Au core-shells: cross section.

in the figure is due to porous carbon support. The PS-COOH/Au core-shells structures are clearly shown in the Figure 4. It was observed that Au layer of the core-shells was even deposited on the PS-COOH core and its depth was ca. 50–60 nm.

CONCLUSION

A novel (PS-COOH)/Au core-shell structure was successfully prepared by the electroless deposition of a gold solution onto PS-COOH cores, which was obtained by the copolymerization of MAA and DVB on the PS seed particles. The impregnation of the gold seeds on the PS-COOH cores was carried out using a gold solution. Uniform and smooth gold shells were successfully formed on the surface of the PS-COOH cores, by employing an electroless gold plating solution of Au $(OH)_3$ and NH_2OH. The morphology of the PS-COOH cores and gold shells was confirmed by the SEM-image. The formation of metallic gold was also confirmed by EDS. By TEM-images, it was observed that Au layer of the core-shells was even deposited on the PS-COOH core and its depth was ca. 50–60 nm.

REFERENCES

[1] Briegel, R., Ashauer, M., Ashauer, H., Sandmaier, H., & Lang, W. (2002). *Sensors and Actuators A*, *323*, 97–98.
[2] Kang, E. T., Ting, Y. P., Neoh, K. G., & Tan, K. L. (1993). *Polymer*, *34*, 4994.
[3] Ting, Y. P., Neoh, K. G., Kang, E. T., & Tan, K. L. (1994). *J. Chem. Technol. Biotechnol.*, *59*, 31.
[4] Kang, E. T., Ting, Y. P., Neoh, K. G., & Tan, K. L. (1995). *Synth. Met.*, *69*, 477.
[5] Siiman, O. & Burshteyn, A. (2000). *J. Phys. Chem. B*, *104*, 9795.

[6] Mayer, A. B. R., Grebner, W., & Wannemacher, R. (2000). *J. Phys. Chem. B*, *104*, 7278.

[7] Kobayashi, Y., Salgueirrino-Maceira, V., & Liz-Marzan, L. M. (2001). *Chem. Mater.*, *13*, 1630.

[8] Khan, M. A., Perruchot, C., Armes, S. P., & Randall, D. P. (2001). *J. Mater. Chem.*, *13*, 1630.

[9] Wescott, S. L., Oldenburg, S. J., Lee, T. R., & Halas, N. J. (2000). *Langmuir*, *16*, 6921.

[10] Dokoutshaev, A., James, J. T., Koene, S. C., Pathak, S., Prakash, G. K. S., & Thompson, M. E. (1999). *Chem. Mater.*, *13*, 2389.

[11] Phan, K. X., Cho, M. S., Nam, J. D., & Lee, Y. (2006). *Synth. Met.*, *156*, 872.

[12] Tuncel, I. A., Tuncel, M., Ergun, B., Alagöz, C., & Bahar, T. (2002). *Colloids and Surfaces: A*, *197*, 79.

[13] Gittins, D. I. & Caruso, F. (2001). *Angew. Chem. Int. Ed.*, *40*, 3001.

[14] Xu, H., Tseng, C. H., Vickers, T. J., Mann, C. K., & Schlenoff, J. B. (1994). *Surf. Sci.*, *311*, 707.

[15] Duff, C.G., Baiker, A., Gameson, I., & Edwards, P. P. (1993). *Langmuir*, *9*, 2310.

[16] Graf, D. & Van Blaaderen, A. (2002). *Langmuir*, *18*, 524.

[17] Shchukin, D. G. & Caruso, R. A. (2003). *Chem. Commun.*, 1478.

[18] Oldenburg, S. J., Averitt, R. D., Westcott, S. L., & Halas, N. J. (1998). *Chem. Phys. Lett.*, *288*, 243.

[19] Ji, T., Lirtsman, V. G., Avny, Y., & Davidov, D. (2001). *Adv. Mater.*, *13*, 1253.