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Deposition of Gold Shell on Polypyrrole Coated Poly(divinylbenzene) Core

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Poly(divinylbenzene) (PDVB) beads ($2 \sim 4\,\mu m$) were synthesized by precipitation polymerization and their surface was modified by introducing sulfonic acid groups to yield sulfonated PDVB (sPDVB). The sPDVB cores were initially coated with a polypyrrole (PPy) layer by chemical oxidative polymerization. In the process of formation of the gold shells, gold particles were deposited onto the previously prepared PPy-sPDVB cores as a seed material by in-situ redox reaction between Au(III) and neutral PPy and, then, uniform and smooth gold shells were gently grown on the cores by employing a electroless gold plating solution. The structure of the PPy-Au/PDVB core-shells was investigated by scanning electron microscopy (SEM). The presence of zero-valent gold was confirmed by X-ray photoelectron spectroscopy (XPS).

Keywords: core-shell; gold; poly(divinylbenzene); polypyrrole

INTRODUCTION

Flip chip technologies such as solder bump flip chips, stud bumping using isotropic conductive adhesives (ICAs) and alloy bonding have been developed to accommodate the trends of microelectronics. Recently, a new flip chip technology was developed based on

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anisotropic conductive films (ACFs) [1,2]. ACFs consist of an insulating adhesive polymer matrix with dispersed conductive particles. The conducting particles are normally composed of metallic materials such as Ni, Au, or Ag coated on the surface of spherical polymer bead. For this purpose, several routes have been investigated for the fabrication of metal shells on polymer particles. Shi and his coworkers [3] synthesized gold nanoshells on polystyrene (PS) spheres and demonstrated the tuning of the surface plasma resonance (SPR) absorption of these shells by varying the amount of gold deposited. Conducting polymers are organic conductor having greater reliability, lower resistance and stable adhesive strength to guarantee a better flip interconnection on an organic substrate. Kang *et al*. [4] examined the morphology of metallic gold overlayers deposited onto conducting polymer-coated PS using an electroless deposition method. Their results showed that the gold nanoparticles were randomly dispersed over the surfaces of the PS particles. Schueler *et al*. [5] reported the deposition of silver onto poly(methylmethacrylate) (PMMA) latex particles via thermal evaporation techniques. However, most of the metal particles were randomly dispersed over the surfaces of the polymer particles.

In an attempt to overcome this drawback, we previously fabricated poly (divinylbenzene) (PDVB) beads using the precipitation polymerization of DVB [6]. In this system, the highly crosslinked PDVB beads exhibit a combination of good mechanical strength and thermal resistance, along with excellent chemical stability, and can be prepared with a wide variety of diameters [6,7]. Using these PDVB beads, we designed core/shell structures consisting of modified PDVB/gold [6]. In this way, uniform and smooth gold shells were successfully formed on the surface of the PDVB cores. However, the gold shell was so thin that it was very brittle.

In this study, in order to obtain uniform gold shells on the PDVB cores and to improve the adhesion between them, a layer of conducting polymer, polypyrrole, was inserted between the gold shell and PDVB core. The PDVB cores (2–4 μm) were initially synthesized by precipitation polymerization to yield a fully crosslinked structure. The surface of the cores was then modified by introducing sulfonic acid groups. The presence of $-SO_3H$ groups on the surface of the PDVB cores facilitated the coating of PPy by chemical oxidative polymerization by acting as polymeric dopants. The deposition of gold particles was carried out by employing an electroless gold plating solution of $HAuCl_4$. The resulting gold particles, which served as gold seeds for the growth of the shells, was obtained using a mixed solution of $HAuCl_4$ and NH_2OH to obtain completely uniform gold shells.

EXPERIMENTAL SECTION

Materials

Divinylbenzene (DVB, Aldrich) was used after passing it through an inhibitor remover column. Iron (III) chloride, sodium borohydride, hydroxylamine hydrochloride, acetonitrile, chlorosulfonic acid, 1,2-dichloroethane, and pyrrole were obtained from Aldrich. 2,2-azobis (isobutyronitrile) (AIBN) was obtained from Junsei and $HAuCl_4$ was supplied by Kojima Chemicals. All of the above reagents were used as received.

Preparation of PDVB Beads and Sulfonation of the PDVB Cores (sPDVB)

Mono-dispersed and cross-linked PDVB beads were prepared according to the method reported in the literature [8–12]. The PDVB beads were sulfonated to produce sPDVB according to the literature method [6,13].

Oxidative Polymerization of Pyrrole on the sPDVB Cores: PPy-sPDVB [14]

The sPDVB cores were well dispersed in a 0.5 M $FeCl_3$ solution in methanol and then immersed in pyrrole monomer. The reaction mixture was kept stirring for 12 h. The resulting composite cores were separated by centrifugation and washed with water four times to yield uniform PPy-sPDVB cores.

Deposition of Gold on PPy-sPDVB Cores [15–19]

The PPy-sPDVB cores were reduced in sodium borohydride solution for 1 h and then immersed into a gold-solution of $HAuCl_4$ for the formation of the Au seeded PPy-sPDVB cores. The cores were dipped in the gold solution before they were reduced in the $NH_2OH \cdot HCl$ solution. An outline of the synthesis of the PPy-Au/sPDVB core-shells is shown schematically in Figure 1.

CHARACTERIZATION

The morphology of the PPy-Au/sPDVB core-shells was observed using scanning electron microscopy (SEM, Phillips XL30 ESEM-FEG) and a transmittance electron microscopy (TEM, JEOL-3010). The X-ray

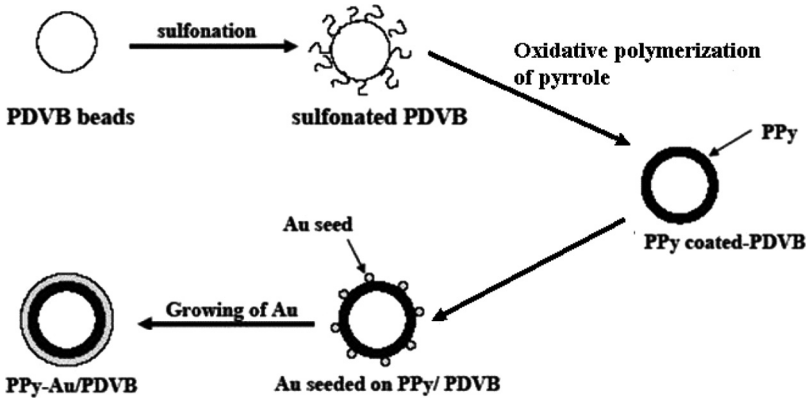


FIGURE 1 Schematic representation of the procedure used for the preparation of the PPy-Au/PDVB core shells.

photoelectron spectroscopy (XPS) measurements were carried out using a VG Scientific ESCA 2000 spectrometer and an Mg-Kα X-ray source operating at a power of 170 W (13 mA and 13 kV) to confirm the presence of zero-valent gold.

RESULTS AND DISCUSSION

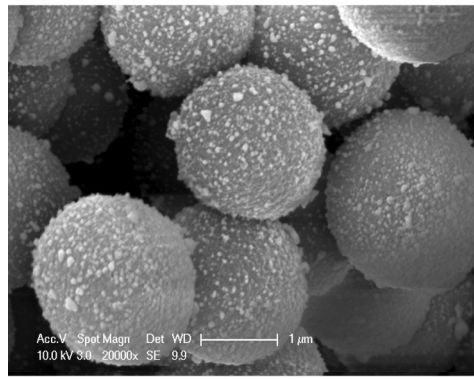
In this study, the reaction conditions were carefully optimized to yield mono-disperse PDVB cores by precipitation polymerization without a stabilizer. The PDVB beads were sulfonated by introducing sulfonic acid groups.

Figures 2(a–c) show the morphology and size of the resulting cores and core shells. All of the cores in the SEM images have a spherical shape with a smooth surface without any coagulation. Figure 2(a) shows the SEM image of the PPy coated sPDVB cores. The PPy layer was well coated on the sPDVB beads by chemical oxidative polymerization in the presence of $FeCl_3$ for 12 h.

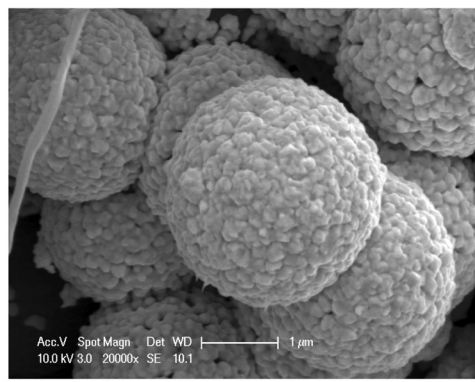
Figure 2(b) shows a typical SEM image of the Au seeded PPy-sPDVB cores obtained using a gold deposition process. The gold particles appeared bright white. There was a considerable difference in the shape and size of the gold particles produced in the shell. Obviously, shells with a low gold coverage are unsuitable for use as conducting particles.

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,

(a)



(b)



(c)

FIGURE 2 SEM images of the PPy coated sPDVB cores (a), Au seeded PPy-sPDVB cores (b), and Au-PPy/sPDVB core shells (c).

$NaBH_4$, 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 amount of newly formed gold particles present in the solution, which tended to coalesce into clumps that were difficult to remove from the gold shells. Ji *et al*. [19] also developed a method of forming gold shells using $HAuCl_4$ and NH_2OH. In their study, it was demonstrated that the additional growth of the gold

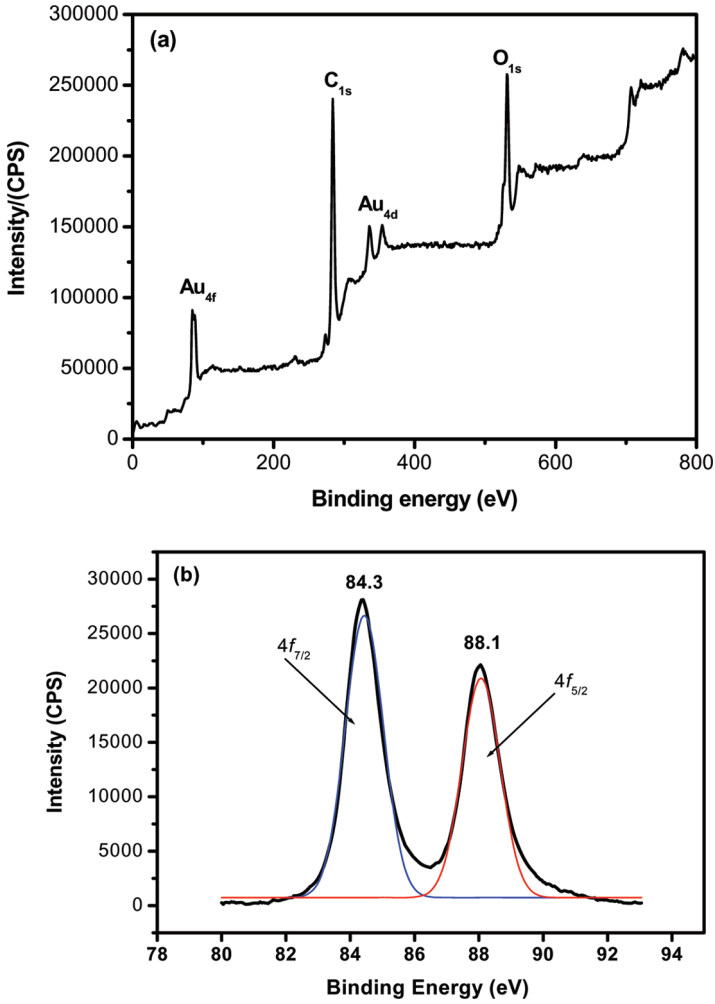


FIGURE 3 XPS spectra: (a) survey and (b) Au 4f XPS core-line spectrum of the (PPy-Au/sPDVB core-shells.

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 particles on the PPy-sPDVB cores. As the SEM images in Figure 2(c) show, the presence of 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 particles attached to the PPy-sPDVB cores. These gold particles are then enlarged by the gentle reductive action of Au $(OH)_3$. After their initial period of growth, these gold particles begin to coalesce and finally form continuous gold shells. These shells can then be grown further to produce thicker shells.

In order to verify that the reduction to zero-valent gold did indeed occur, an XPS study was carried out on the PPy-Au/sPDVB core-shells, as shown in Figure 3. Figure 3(a) clearly shows the detection of a strong pair of doublets at ca. 86 and 340 eV, which are assigned to the photoelectrons originating from the Au 4f and Au 4d energy levels, respectively. Close inspection of the peak-fitted Au core-line spectrum (see Fig. 3(b)) reveals two strong signals due to electrons from the 4f 5/2 and 4f 7/2 energy levels. The 4f 7/2 peak was centered at ca. 84.3 eV and the accompanying 4f 5/2 peak at ca. 88.1 eV. This doublet is characteristic of zero-valent gold [20].

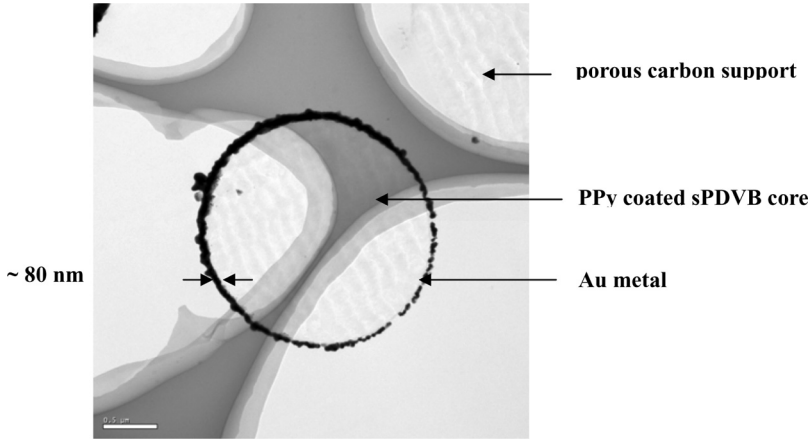


FIGURE 4 TEM image Au-PPy/sPDVB core shells: cross section.

Figure 4 gives the TEM image of the cross-section of the PPy-Au/sPDVB core-shell. It was observed that Au layer of the core-shells was even deposited on the PPy coated sPDVB core and its depth was ca. 60–100 nm. In our work, 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 [15]. The core-shell structure was consisted of polymer and Au-metal without any conducting polymer. The TEM – image of the PS-COOH/Au core-shells indicated that the thickness of Au-layer [15] was thinner than that of the PPy-Au/sPDVB core-shell. In the case of the PPy-Au/sPDVB core-shell the Au seedlings were implanted close together. The conducting polymer, PPy is found to be useful for the adhesion between PDVB core and Au shell.

CONCLUSION

Novel PPy-Au/sPDVB core-shell structures were successfully prepared by the electroless deposition of a gold solution onto PPy-sPDVB cores. These sPDVB core structures were obtained by precipitation polymerization and sulfonation, and then, PPy was coated on the sPDVB cores by the chemical oxidative polymerization of pyrrole. The PPy-sPDVB cores were immersed into a solution of gold particles to allow the impregnation of the gold seeds on the PPy-sPDVB cores. In this way, uniform and smooth gold shells were successfully formed on the surface of the PPy-sPDVB cores by employing an electroless gold plating solution of $Au(OH)_3$ and NH_2OH. The morphology of the PPy-sPDVB cores and gold shells was confirmed by the SEM-images. The formation of metallic gold was also confirmed by XPS. By TEM-images, it was observed that Au layer of the core-shells was even deposited on the PPy coated sPDVB core and its depth was ca. 60–100 nm.

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