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Communications

Preparation of Silver/PMMA Beads via the in Sito Reduction of a Silver Alkylcarbamate Complex

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Introduction

The deposition of metal on non-conducting substrates by electroless deposition is being increasingly used to fabricate electronic circuits.[1,2] In a typical electroless operation, a target surface is immersed in a plating solution, which consists of metal ions and a mild reducing agent.[3-8] Often, a metal catalyst is required to facilitate auto-catalytic deposition of the metal.[9] An important prerequisite for electroless deposition is the slow transfer of electrons from the reducing agent to metal ions to prevent metal ions being reduced other than on the target substrate.[10] Recently, polyelectrolytes,[11,12] sugar,[13] sulfonation[14] and amine derivatives[15,16] have been used to deposit silver and gold on substrates.

Silver organic salts have used to produce silver nanoparticles and conductive silver tracks. In these processes silver carboxylate[17] or silver alkylcarbamate complexes[18-21] were reduced to silver metal by heating or by using different reducing agents.[22] However, only a limited number of reports have described the deposition of silver onto substrates via the one-pot reduction of silver alkylcarbamate complex in solution using hydrazine as reducing agent.

The present communication concerns the deposition of metallic silver coatings on PMMA beads by electroless silver plating in organic solvent, using palladium as a catalyst, silver 2-ethylhexylcarbamate complex as a metal source, and hydrazine as the reducing agent. The PMMA-cored silver composite beads so obtained had a conductivity similar to that of metallic silver.

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Results and Discussion

Siiman and Burshteyn prepared silver-coated polystyrene beads for flow cytometry study by reduction of aqueous silver ions in the presence of sugar-coated polystyrene latex beads.[13] But catalytic nucleation sites, usually of palladium, should be created on surfaces prior to electroless plating on nonmetallic substrates. Crosslinked PMMA beads have no catalytic effect, and thus, appropriate surface-activation is required before electroless plating. PMMA beads are mainly composed of esters, and have no hydrophilic or active groups on their surfaces. In the present study, bead surfaces were hydrolyzed to introduce carboxylic groups. The hydrolyzed PMMA surfaces produced were first sensitized with aqueous $SnCl_2$ and then activated with $PdCl_2$ solution. During this process, $SnCl_2$ acts as a reducing agent and supplies the electrons required to reduce Pd^{2+} to Pd metal. Beads with surface bound Pd nuclei were treated with aqueous hydrochloric acid as accelerator.

The morphologies of the silver-coated surfaces produced were examined by scanning electron microscopy (SEM). SEM photographs of silver-coated surfaces produced using different plating conditions are shown in Figure 1.

Figure 1(a) shows that the pretreated MMA beads ranged in size from 3-10 μm.[23] In order to obtain best images of undamaged beads, we coat beads with gold for SEM examinations. Thus, SEM micrographs obtained were vivid, because beads were charged under the voltages applied during SEM.

Electroless plating composition and conditions are summarized in Table I.[24] Figures 1(b)-(f) show SEM images of PMMA beads produced using silver at different concentrations of PVP and Ag-EHCB.[25] The silver-coated beads obtained were similar to the original PMMA beads in terms of shape. Enlarged images of beads obtained from Entry No.1 showed that silver coatings were composed of silver shell and extraneous silver particles as shown in Figure 1(b).

Jun *et al.* prepared SERS-encoded polystyrene beads composed of silver nanoparticles, Raman labels, and a silica shell by dispersing sulfonated polystyrene beads in a mixture of ethylene glycol, silver nitrate and PVP.[14]

Without PVP as a nano-silver colloid stabilizing agent, much larger Ag nano particles were formed in solution, and these particles abruptly attached themselves into silver shell. When a dilute PVP solution was used, Ag nanoparticles of size 10-30 nm were formed evenly over bead surfaces. Electroless plating with PVP produced more compact Ag shell composed of smaller Ag grains than that of electroless plating without PVP, as shown in Figure 1(c). However, silver colloid produced silver shells with larger Ag particles.

As the Ag-EHCB concentration was increased, more silver was deposited on the bead surfaces, as shown in Figure 1(d). However, excess silver colloid produced irregular and

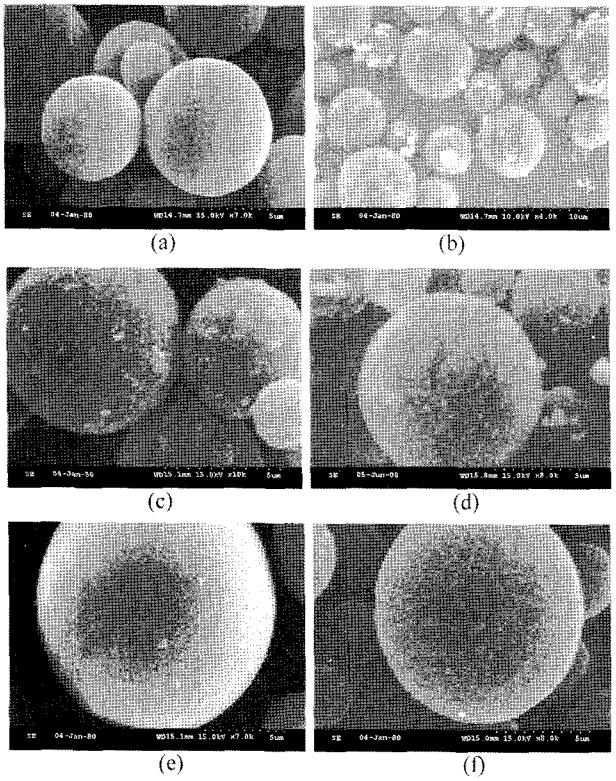

Figure 1. The SEM photographs of the electroless Ag plated PMMA beads. (a) PMMA bead, (b) Entry No 1, (c) Entry No 2, (d) Entry No 3, (e) Entry No 4 and (f) Entry No 5 at 20 °C for 30 min.

Table I. Composition and Conditions for Electroless Plating of PMMA Beads

Entry No.	PVP[a]	Ag-EHCB/DMA (g/g)	Time (min)	Hydrazine (g)
1	0	0.3/5		
2	0.1	0.3/5		
3	0.1	0.5/5	30	0.2
4	0.2	0.3/5		
5	0.4	0.3/5		

[a]Polyvinylpyrrolidone.

heterogeneous silver shells.

As shown in Figures 1(e) and (f), on increasing amount of PVP from 0.1 to 0.2 and 0.4 g to stabilize silver nanoparticles, Ag coatings increased in thickness and compactness. SEM photographs revealed that compact deposition could be obtained on PMMA beads with excellent grain size control without any extraneous silver cluster. In particular Figure 1(f) shows neat silver surface without any extraneous silver fragments.

The formation of silver may be explained as follows. As is known, the silver electroless plating reaction may be represented by $2Ag_2(OCONHC_8H_{17})\cdot 2C_8H_{17}NH_2 + NH_2NH_2 \rightarrow 2Ag + 4C_8H_{17}NH_2 + 2CO_2 + N_2$. This reaction indicates that

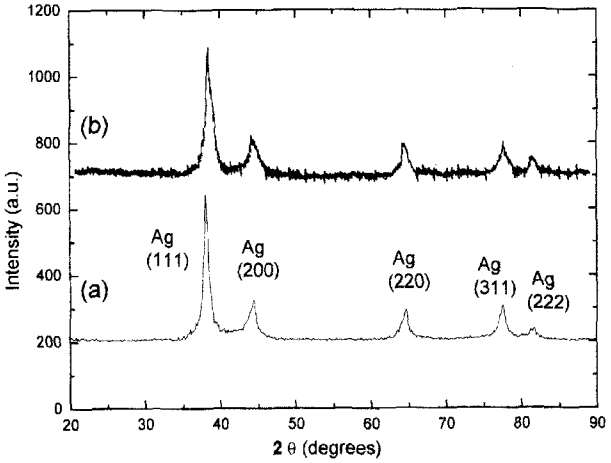

Figure 2. X-ray diffraction patterns of polystyrene beads taken after deposition of silver using Ag-EHCB.

Ag-EHCB is reduced to metallic silver by hydrazine in alcohol solution, and that the reaction is accompanied by organic amine and carbon dioxide release. The nano-sized spherical silver particles, which are originally produced at the PMMA bead/solution interface, possess high surface energy and have a strong tendency to aggregate while depositing on the surface. Without the evolution of carbon dioxide, some neighboring silver particles do not tend to form a surface film and instead grow in lines. Thus, the formations of Ag cluster and particles are suppressed.

The XRD analysis shown in Figure 2 indicates that the silver beads crystallized well and produced sharp peaks at 2θ values of 38.00°, 44.38°, 64.54°, 77.54° and 81.56°, which agree well with literature values for silver nanoparticles. These peaks can be indexed to (111), (200), (220), (311) and (222) planes, respectively, and indicate a face-centered cubic structure. The XRD peaks in Figure 2(b), which are of an Ag film on PMMA beads produced using a mixture of Ag 2-ethylhexylcarbamate and hydrazine, are quite broad, which indicates that the deposited silver consists of nano-sized particles.

In conclusion, we successfully prepared silver/polymer nanocomposites in a straightforward manner by electroless plating using a silver alkylcarbamate complex in the presence of hydrazine at 25 °C. The amounts of Ag-EHCB and PVP were found to play an important role in stabilizing the metal nanoparticles during the preparation of these nanocomposite films. The described method offers a convenient route to the electroless plating of silver on PMMA beads. The mechanical properties, thickness of silver, adhesion between silver and PMMA, and conductivity of the coated beads produced are being comprehensively evaluated. These results will be presented elsewhere in the near future.

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(23) Poly(methylmethacrylate-*co*-ethyleneglycol dimethacrylate) (3-10 μm. 5% cross-linked) beads were purchased from Aldrich Chem. Co.
(24) Electroless plating was carried out using a multi-step processes which included: etching, rinsing, conditioning, sensitization, activation, acceleration and electroless silver plating. MMA (5 g) beads were etched in NaOH (1 M, 500 mL) at 70 °C for 4 h prior to use, rinsed in distilled water, and conditioned in a solution of PEG-1000 (1 g) and water (500 mL) for 5 min. Surface sensitization was performed by immersing these beads on an aqueous solution containing $SnCl_2$ (2 g) and water (100 mL) for 3 min. Beads were then rinsed in a solution of $PdCl_2$ (1 g) and distilled water (1000 mL) for 3 min, and treated with 10% HCl (the accelerator). They were then rinsed with distilled water and completely dried at 40 °C. These pretreated MMA beads (0.5 g) were then dispersed in a solution of PVP (0.1 g)/methanol (40 mL) in a polypropylene container (to avoid silvering of the reaction vessel). To this dispersion was added a solution of silver 2-ethylhexylcarbamate (0.3 g, silver content 10%) in methanol (10 mL) and a solution of hydrazine (0.2 g) in methanol (10 mL) with stirring to increase the density and thickness of the silver coating for 30 min. Finally, the PMMA-Ag composites were filtered and washed with methanol by centrifugation.
(25) The silver 2-ethylhexylcarbamate complex solution (Ag-EHCB, silver content, 10%) was supplied from Inktec Co. Ltd. (Korea).