A Simple Route for Formation of Continuous Ni Nanoshells on Polymer Microspheres

Dong-Hwang Chen,* Jia-Peng Lin, Szu-Han Wu, and Chun-Ting Wang†
Department of Chemical Engineering, National Cheng Kung University, Tainan, Taiwan 701, ROC

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Continuous Ni nanoshells of 1.2 nm-thick were successfully fabricated on polymer microspheres via a simple one-step process. The preferential coating of Ni on the surface of polymer microspheres was attributed to the use of ethylene glycol as a solvent and appropriate reaction temperature.

Recently, the fabrication of a metallic layer on a dielectric core received considerable attention because of wide applications in optics, catalysis and biochemistry. Several approaches have been proposed, including the in situ chemical reduction, surface reaction, seeding and/or electroless plating, self-assembly of metal nanoparticles on the functionalized core surface, and infiltration of metal nanoparticles into polyelectrolyte-coated core.[1–3] Due to the interparticle Coulomb repulsion and/or the passivation of metal nanoparticles caused by capping agents, the degree of surface coverage was low and repeated fabrication was necessary to obtain a higher metal coverage.[1–3] To our knowledge, the fabrication of continuous metal nanoshells on a dielectric core via a simple one-step process has not been reported.

Polyol process has been successfully used for the deposition of nanocrystalline metal films on planar non-conductive substrates.[4] In this work, the fabrication of continuous nickel nanoshells on poly(styrene-*co*-methacrylic acid) (Poly(St-*co*-MAA)) microspheres was attempted using a modified polyol process because of their potential applications in the fields of magnetically controlled photonic crystals,[1,5] electromagnetic interference shielding,[6] and anisotropic conducting adhesive.[7] Poly(St-co-MAA) instead of polystyrene was used because carboxylic groups might favor the adsorption and reduction of Ni ions on polymer surface. Since the high temperature of 120–180 °C usually used in polyol process was not appropriate for poly(St-co-MAA) microspheres, the fabrication of Ni nanoshells was carried out by the hydrazine reduction of nickel chloride in ethylene glycol using NaOH as a catalyst.[8]

Monodisperse poly(St-co-MAA) microspheres were prepared by seeded emulsifier-free emulsion copolymerization of St and MAA.[9] The reaction was performed at 70 °C in a N_2 atmosphere with stirring at 350 rpm. First, 2.4 g St and 170 mL water were put into the reaction system and purged with N_2 gas for 1 h. Then, 0.015 g ammonium persulfate (dissolved in 8 mL water) was added to prepare polystyrene seed particles. After 3 h, 4.0 g MAA, 17.6 g St, and 0.085 g ammonium persulfate (dissolved in 20 mL water) were added in sequence. The reaction was continued for 3 h. The mean diameter of polymer microspheres was 250 ± 16 nm. After being centrifuged and washed with water, they were dispersed in ethylene glycol to yield a latex dispersion of 4.44%wt. For the coating of Ni on polymer microspheres, 1.5 mL latex dispersion, 0.6 mL NaOH (1.0 M), and 0.6 mL hydrazine (20 M) were added to 8.5 mL ethylene glycol solution of nickel chloride (0.015 M) in sequence, and the mixture was stirred at 60 °C for about 30 min to complete the reaction. It was noted that the reaction was not completed at 25 °C even after two weeks. Also, the coating of Ni was incomplete and Ni nanoparticles were formed in bulk phase above 70 °C. So, 60 °C was suggested. By the similar method, Ni nanoparticles could be synthesized in the absence of polymer microspheres.

Figure 1 shows the typical transmission electron microscope (TEM) and high-resolution TEM (HRTEM) imagines for Ni-coated polymer microspheres. The TEM image indicated that continuous Ni nanoshells were formed on polymer microspheres and no significant Ni nanoparticles were formed in bulk phase. Since it was found that the coating of Ni was incomplete and many Ni nanoparticles were formed in bulk phase when the fabrication was performed in aqueous phase, the solvent ethylene glycol might play an important role for the preferential coating of Ni on the surface of polymer microspheres. It was suggested that ethylene glycol might act as a surfactant to surround the carboxylated polymer microspheres via its hydroxyl groups, leading to the preferential growth of Ni films on polymer microspheres. Furthermore, the HRTEM image showed that the continuous Ni nanoshells on polymer microspheres were quite homogeneous, and dense films instead of the nanoparticle-aggregated films as those obtained by repeated seeding/electroless plating and layer-by-layer self-assembly.[1–3]

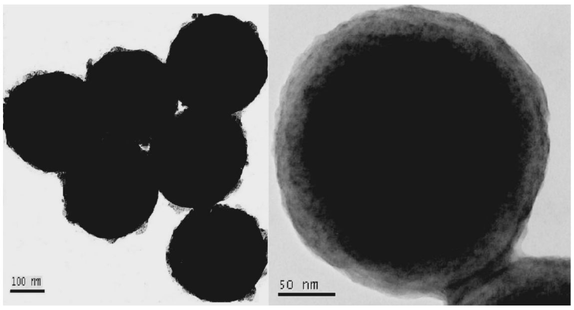

Figure 1. TEM (left) and HRTEM (right) images of Ni-coated polymer microspheres.

To further demonstrate the complete coating of Ni on polymer microspheres, the Fourier transform infrared (FTIR) spectrum of uncoated and Ni-coated polymer microspheres were studied. Figure 2(a) is the spectrum for poly(St-co-MAA) microspheres as evidenced by the characteristic C–H bond for benzene ring (**1**–**2**,**4**,**6**), O–H bend for carboxylic group (**3**,**5**), C–O stretch for carboxylic group (**7**,**8**), C–C stretch for benzene ring (**9**–**11**), C=O stretch for carboxylic group (**12**), C–H bond for mono-substituted benzene (**13**–**15**), O–H stretch for carboxylic group (**16**), the C–H stretch of benzene ring, the O–H stretch of carboxylic group, and the saturated C–H stretch on the main chain of copolymer (**17**,**18**). The numbers in the brackets denote the absorption bands in Figure 2. The spectrum for Ni-coated polymer microspheres as shown in Figure 2(b) is obviously different from that for uncoated one. Except the absorption band **24**, all other absorption bands were attributed to ethylene glycol as the characteristic O–H bend (**19**,**23**), C–O stretch (**20**–**22**), C–H stretch (**25**–**26**), and O–H stretch (**27**). This might be resulted from the adsorbed ethylene glycol on Ni nanoshells.[10] In addition, it is known that aldehydes and ketones were produced in the dehydrogenation of alcohols on Ni(111),[11] and ethylene glycol might dehydrate to acetaldehyde and produce diacetyl by duplicative oxidation in poly process.[12] Therefore, it was suggested that the adsorbed ethylene glycol might be dehydrated and/or oxidized to acetaldehyde and/or diacetyl on Ni nanoshells, and the absorption band **24** could be resulted by the C=O stretch for aldehyde or ketone groups.

For comparison, the spectrum for Ni nanoparticles synthesized in the absence of polymer microspheres was also measured as indicated in Figure 2(c). It was almost the same as Figure 2(b), revealing the absorption bands for polymer microspheres have been completely shielded in Figure 2(b). This demonstrates that polymer microspheres were indeed covered fully by homogeneous and dense Ni nanoshells.

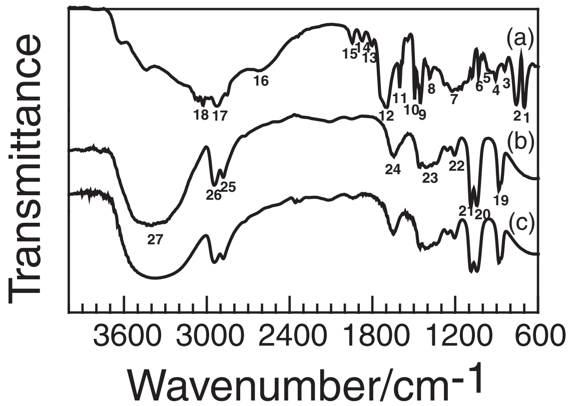

Figure 2. FTIR spectra of uncoated (a) and Ni-coated (b) polymer microspheres and Ni nanoparticles (c). Absorption bands: 700 (**1**), 750 (**2**), 850 (**3**), 900 (**4**), 950 (**5**), 1040 (**6**), 1200 (**7**), 1380 (**8**), 1450 (**9**), 1490 (**10**), 1600 (**11**), 1700 (**12**), 1800 (**13**), 1850 (**14**), 1930 (**15**), 2600 (**16**), 2900 (**17**), 3030 (**18**), 875 (**19**), 1050 (**20**), 1080 (**21**), 1200 (**22**), 1400 (**23**), 1650 (**24**), 2875 (**25**), 2925 (**26**), 3375 (**27**) cm^{-1}.

From the mean diameter of polymer microspheres and the amounts and densities of Ni (8.9 g/cm^3) and polymer microspheres (1.14 g/cm^3), the average thickness of Ni nanoshells was estimated to be 1.0 nm. In order to confirm this value, the thermal decomposition of Ni-coated polymer microspheres was studied. As indicated in Figure 3, the thermogravimetric analysis (TGA) revealed two weight loss steps. The first weight loss step from 100 to 300 °C might be due to the loss of the adsorbed ethylene glycol and acetaldehyde and/or diacetyl. The significant weight loss from 300 to 470 °C should be due to the burning of polymer cores. No significant weight change above 470 °C, revealing polymer cores were removed and Ni was completely oxidized to nickel oxide at this temperature. Thus, polymer microspheres and nickel oxide had a relative weight percentage of 7:2, and the average thickness of Ni nanoshells could be estimated as 1.2 nm. This was consistent with the value estimated above.

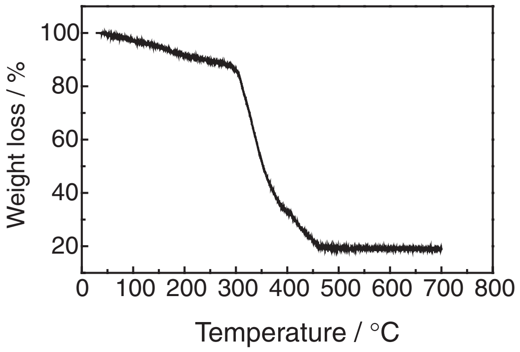

Figure 3. TGA curve of Ni-coated polymer microspheres.

In conclusion, this work proposed a simple one-step method for the fabrication of continuous Ni nanoshells on polymer microspheres. The use of ethylene glycol as a solvent and appropriate reaction temperature were important. The resultant Ni-coated polymer microsphers are of interest in the photonic, magnetic, and electronic applications.

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