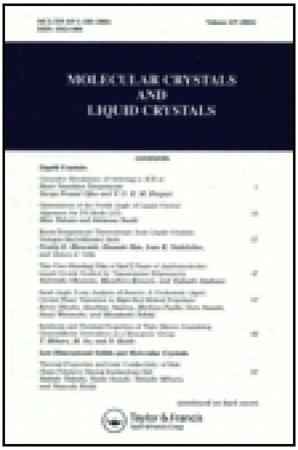

Molecular Crystals and Liquid Crystals
Publication details, including instructions for authors and subscription information:
http://www.tandfonline.com/loi/gmcl20

A Novel Method of Gold-Coating on Modified Poly(divinylbenzene) Cores Using Gold Complex

M. S. Cho [a] , K. X. Phan [b] , Y. Lee [b] & Y. K. Son [c]
[a] Polymer Technology Institute,Sungkyunkwan University, Suwon, Korea
[b] School of Applied Chemistry and Chemical Engineering,Sungkyunkwan University, Suwon, Korea
[c] Department of Chemistry,Sungkyunkwan University, Suwon, Korea

Version of record first published: 22 Sep 2010

To cite this article: M. S. Cho, K. X. Phan, Y. Lee & Y. K. Son (2007): A Novel Method of Gold-Coating on Modified Poly(divinylbenzene) Cores Using Gold Complex, Molecular Crystals and Liquid Crystals, 464:1, 9/[591]-14/[596]

To link to this article: http://dx.doi.org/10.1080/15421400601028443

Mol. Cryst. Liq. Cryst., Vol. 464, pp. 9/[591]–14/[596], 2007
Copyright © Taylor & Francis Group, LLC
ISSN: 1542-1406 print/1563-5287 online
DOI: 10.1080/15421400601028443

A Novel Method of Gold-Coating on Modified Poly(divinylbenzene) Cores Using Gold Complex

M. S. Cho
Polymer Technology Institute, Sungkyunkwan University,
Suwon, Korea

K. X. Phan
Y. Lee
School of Applied Chemistry and Chemical Engineering,
Sungkyunkwan University, Suwon, Korea

Y. K. Son
Department of Chemistry, Sungkyunkwan University, Suwon, Korea

A novel Au/PDVB core-shell was prepared by the chemical reduction of a gold-phenanthroline complex on the poly(divinylbenzene) (PDVB) cores (2–5 μm). The PDVB cores were synthesized by precipitation polymerization, and the surface was modified by introducing thiol and sulfonic acid groups. The degree of sulfonation was measured according to its ion exchange capacity (IEC, 5.72 meq/g), and the surface concentration of thiol group was examined by FT-IR spectroscopy. The modified PDVB cores was immersed in a solution of a gold-phenanthroline complex and subsequently reduced to form gold seeds. The effects of the functional groups on the PDVB cores on fabrication of the gold core shell structure were examined.

Keywords: core-shell; gold-phenanthroline complex; polydivinylbenzene

INTRODUCTION

Applications of electronic package technology exist in the recently rapidly growing electronic industries, for example in the computer,

---

This work was supported by the ‘Local Government Initiated R & D Program (Project No. 2004-0693-200)’ of the Korea Ministry of Commerce, Industry and Energy accompanying with the Gyeonggi Province.

Address correspondence to Y. Lee, Department of Chemical Engineering, Sungkyunkwan University, Suwon, 440-746, Korea. yklee@skku.edu

information communication, mobile communication, and high-tech electronic appliance industries [1–3]. In particular, flip chip technology finds numerous applications in the smart card, liquid crystal display, and communication system industries [4,5]. Such flip chip technology has been developed from a connection process using solders to a connection process using conductive adhesives. Commercially available anisotropic conductive adhesives are composed normally of conductive particles, such as Ni, Au/polymer, and Ag, and insulating resins [6,7]. A conductive adhesive which is of more reliability, lower resistance and higher adhesives strength guarantees a better flip interconnection on an organic substrate. For this, several routes for the fabrication of gold shells on polystyrene (PS) cores have been investigated [8–10]. M. A. Khan and co-workers [11] carried out a systematic study to examine the morphology of metallic gold over layers deposited onto conducting polymer-coated PS via the electroless method. As a result, the surfaces of latexes were randomly decorated with gold nanoparticles and it is believed that these gold-decorated, conducting polymer-coated latexes may be useful as novel supported catalysts.

However, the gold decoration on the linear or partly crosslinking PS is difficult to control because PS cores hardly gains high sulfonation level without deformation in particle shape. Moreover, in most cases as described above, the physical attraction of employed polyeletrolytes on the cores suffers from drawback tuning the thickness and uniformity of the metal shells. Besides, properties of such cores are also concerned with open applicability, especially in flip-chip fabrication.

In our experiments, to overcome the problem of polystyrene beads, poly(divinylbenzene) (PDVB) beads (2–5 μm) were synthesized by precipitation polymerization [12,13]. The PDVB-beads as a fully crosslinked polymer with good physical and chemical properties as well as high thermal resistance are adequate for the input of pressure and heat so that the beads can create electrical contact between the two bond pads of the chip and the substrate in the anisotropic conductive adhesive [14]. Also, the PDVB beads obtained high negative charge on the particle surface by the sulfonation using chlorosulfonic acid, maintaining perfectly spherical shape. The route is facile, versatile, and suitable for the coating of other metal complexes whose complex cation can be reduced in the solution. The surface of the PDVB cores was modified by the sulfonation in order to make complex formation with gold precursor ion. And the PDVB core was further modified by the chloromethylation and then the conversion of $-$Cl group into $-$SH group in order to introduce interaction between gold and $-$SH modified PDVB. The presence of $-SO_3H$ and $-SH$ groups on the surface of the PDVB cores facilitated the deposition of gold nanoparticles using a gold-phenanthroline complex. The gold layer was further grown in the solution of $HAuCl_4$ and NH_2OH. Here, we report the novel preparation methods of PDVB-Au core-shell and the effect of the surface functional groups on the fabrication of gold nanoshell.

EXPERIMENTAL SECTION

Materials

Divinylbenzene (DVB) (80% mixture of isomers), phenanthroline, hydroxylamine solution (50 wt.%), thiourea, trioxane, tin tetrachloride, chlorotrimethylsilane and azobisisobutyronitrile (AIBN) were commercially obtained from Aldrich Chemicals Co. $HAuCl_4$ from Kojima Chemicals and chlorosulfonic acid from Junsei Chemicals were purchased. All the above reagents were used as received.

Preparation of Au/Modified PDVB Cores

The monodispersed and cross-linked PDVB beads were prepared according to the literature [12,13]. The PDVB beads were chloromethylated in the solution of chlorotrimethylsilane and trioxane [15,16]. The chloromethyl group of PDVB cores was successfully converted into the SH-groups by the known procedure [18]. PDVB cores were further modified to introduce sulfonation groups by using chlorosulfonic acid in 1,2-dichloroethane medium for 20 hrs. After the sulfonation, the PDVB cores were post-treated by washing it in a solution of 0.1 M NaOH and 0.1 M HCl and then were kept in de-ionized water [17]. Finally, gold layer was coated on the modified PDVB cores using chemical reduction method of gold-phenanthroline complex, $[AuCl_2(phen)]Cl$. The gold complex was synthesized according to the literature [19].

Characterization

The morphologies of the Au/modified PDVB cores were observed by a scanning electron microscope (ESEM, Phillips XL30 ESEM-FEG). The infrared spectra were obtained by a FT-IR spectrophotometer (Bruker IFS-66/S). XPS measurements were carried out using a VG Scientific ESCA 2000 spectrometer with Mg-Kα X-ray source operating at a power of 170 W (13 mA and 13 kV).

RESULTS AND DISCUSSION

A novel Au/modified PDVB core-shell was prepared successfully using the chemical reduction of gold phenanthroline complex. In this research, we carefully optimized the reaction conditions yielding mono-disperse PDVB cores by the precipitation polymerization without any stabilizer. The monodispersed PDVB-beads were modified by sulfonation, chloromethylation, and then the conversion of chloromethyl group into SH-group. The modified PDVB cores were characterized by FTIR spectroscopy. The sulfonic acid and thiol group were confirmed by FT-IR spectroscopy by observing the bands at $1100\,\mathrm{cm}^{-1}$ and $2500\,\mathrm{cm}^{-1}$ which were attributed to the S=O and S–H symmetric stretching vibration, respectively. In addition, the degree of the sulfonation was determined by the ion-exchange capacity (IEC) measured using the back titration method. The value of IEC is 5.72 meq/g.

The morphology and size of the resulting cores are shown in Figure 1. In the SEM-image of PDVB cores have spherical shape and smooth surface without any coagulation. The SEM-image of Au/modified PDVB cores are also shown in Figure 1. There is a considerable difference in the shape and the size of gold particles reduced in the shell. As a result, the SEM-image indicates clear that the modified-PDVB cores were successfully coated with completely continuous gold shells by this coating route. Besides the ion exchange of H^+ in sulfonic group by gold complex, the thiol group acts as an active functional group which have a good affinity with gold. Gold was well coated on the sulfonated PDVB-cores. In order to verify the metallic gold, XPS studies were carried out the gold/modified-PDVB cores as shown in Figure 2. The figure clearly shows that a strong pair of doublets can be detected at ca. 86 and

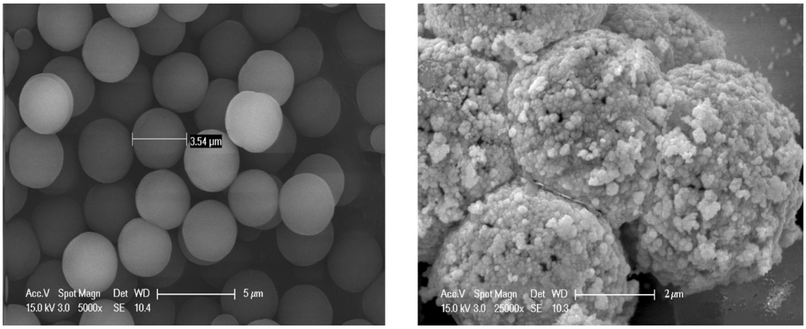

FIGURE 1 SEM-images of PDVB cores and Au/modified PDVB cores.

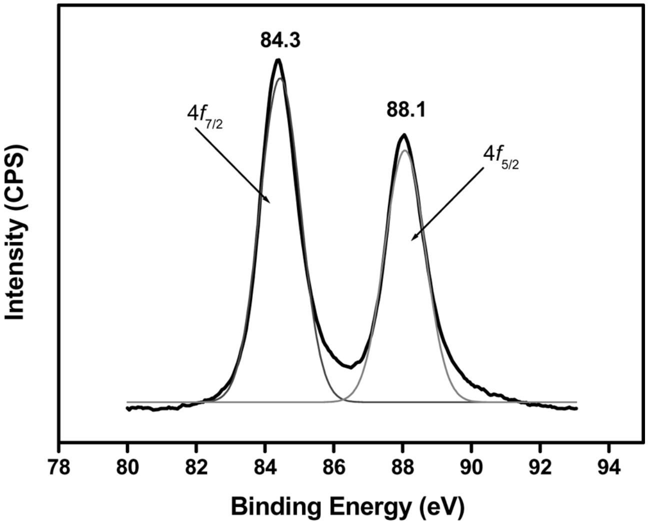

FIGURE 2 XPS spectrum of Au/modified PDVB cores.

340 eV, which are assigned to photoelectrons originating from Au 4f and Au 4d energy levels, respectively. Close inspection of the peak-fitted Au core-line spectrum reveals two strong signals due to electrons from $4f_{5/2}$ 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].

CONCLUSION

A novel PDVB-Au core-shell was prepared by reducing gold phenanthroline complex on the surface modified PDVB. In this research, we carefully optimized the reaction conditions yielding mono-disperse PDVB cores by the precipitation polymerization without any stabilizer. The formation of PDVB-beads and gold shells was monitored by SEM-images. Gold was successfully coated on the modified-PDVB cores having SO_3- and $SH-$ groups. The formation of metallic gold was confirmed by XPS.

REFERENCES

[1] Ji, T., Lirtsman, V. G., Avny, Y., & Davidov, D. (2001). *Adv. Mater.*, *13*, 1254.
[2] Chen, C. W., Serizawa, T., & Akashi, M. (1999). *Chem. Mater.*, *11*, 1381.
[3] Graf, C. & Van Blaaderen, A. (2002). *Langmuir*, *18*, 524.

[4] Velikov, K. P. & Van Blaaderen, A. (2001). *Langmuir*, *17*, 4779.
[5] Yim, M. J. & Paik, Y. W. US Pat. 6, 238, 597.
[6] Zhang, J., Coombs, N., & Sargent, E. H. (2002). *Adv. Mater.*, *14*, 1756.
[7] Phadtare, S., Kumar, A., Vinod, V. P., Dash, C., Palaskar, D. V., Rao, M., Shukla, P. G., Sivaram, S., & Sastry, M. (2003). *Chem. Mater.*, *15*, 1944.
[8] Briegel, R., Ashauer, M., Ashauer, H., Sandmaier, H., & Lang, W. (2002). *Sensors and Actuators A*, *97–98*, 323.
[9] Kang, E. T., Ting, Y. P., Neoh, K. G., & Tan, K. L. (1993). *Polymer*, *34*, 4994.
[10] Ting, Y. P., Neoh, K. G., Kang, E. T., & Tan, K. L. (1994). *J. Chem. Technol. Biotechnol.*, *59*, 31.
[11] Kang, E. T., Ting, Y. P., Neoh, K. G., & Tan, K. L. (1995). *Synth. Met.*, *69*, 477.
[12] Li, K. A. & Stöver, H. D. H. (1993). *J. Polym. Sci., Part A: Polym. Chem.*, *31*, 2473.
[13] Li, K. A. & Stöver, H. D. H. (1993). *J. Polym. Sci., Part A: Polym. Chem.*, *31*, 3257.
[14] Li, K. A. & Stöver, H. D. H. (1998). *J. Polym. Sci., Part A: Polym. Chem.*, *36*, 1543.
[15] Min, K., Hu, J., Wang, C., & Elaissari, A. (2002). *J. Polym. Sci., Part A: Polym. Chem.*, *40*, 892.
[16] Tamaki, R. & Chujo, Y. (1999). *Chem. Mater.*, *11*, 1719.
[17] Dumont, P. J. & Fritz, J. S. (1995). *Chromatogr.: A*, *691*, 123.
[18] Garamszegi, L., Donzel, C., Carrot, G., Nguyen, T. Q., & Hilborn, J. (2003). *React. & Funct. Polym.*, *55*, 179.
[19] Harris, C. M. (1959). *J. Chem. Soc.*, 682.
[20] Briggs, D. & Seah, M. P. (1990). *Practical Surface Analysis*, Wilely: Chichester, UK.,vol. 1.