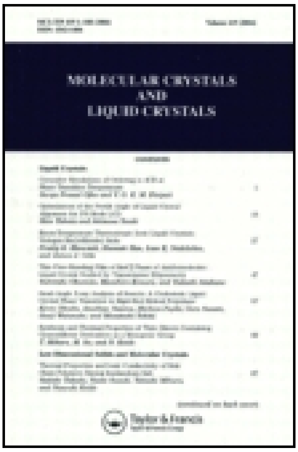

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Facile In-Situ Preparation of Poly(Acrylic Acid)-Silver Nanocomposite Thin Films with Highly Dispersed Silver Nanoparticles

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Facile *In-Situ* Preparation of Poly(Acrylic Acid)-Silver Nanocomposite Thin Films with Highly Dispersed Silver Nanoparticles

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Here we present a facile and simple in-situ method for the preparation of poly(acrylic acid)-silver nanocomposite thin films with highly dispersed silver nanoparticles. From the various available methods to reduce Ag^+ *silver ions, the chemical method was chosen to generate silver nanoparticles in a poly(acrylic acid) matrix. The reducing reagent used in this study was the primary diamine, polyoxypropylenediamine, which reduced the silver ions and simultaneously hardened the poly(acrylic acid) via a cross-linking reaction. TEM images showed that the silver nanoparticles were well dispersed in the poly(acrylic acid) matrix condensed with polyoxypropylenediamine.*

Introduction

Polymer-metal nanocomposites are attractive due to their chemical and physical properties, which combine the attributes of metallic and polymeric materials with the unique characteristics of nanocomposite materials. Among the various polymer-metal nanocomposites, polymer-silver nanocomposites are of significant interest in many fields because silver shows specific optical, magnetic, catalytic, antimicrobial, electrical properties [1–4].

Two methods have been used in the past to obtain polymer-metal nanocomposites. The first is the *ex-situ* approach, in which metal nanoparticles are synthesized and then dispersed into a polymer matrix [5–9]. However, it is difficult to disperse silver nanoparticles homogeneously into a polymer matrix by this *ex-situ* method, since they agglomerate easily in the absence of specific protecting materials. The second method is the *in-situ* approach, which involves the simultaneous synthesis of the polymer and the metal nanoparticles in a composite material. In the *in-situ* method, a monomer can be polymerized around preformed nanoparticles [10], or the metal nanoparticles can be reduced from suitable precursors within the polymer matrix. The latter method is useful to obtain a homogeneous silver-polymer nanocomposite, due to its ability in preventing the agglomeration of silver particles, which is more likely to occur with the *ex-situ* method, as mentioned above.

A number of different routes for the reduction of the silver precursors within the polymer matrix have been reported. Most frequently the silver nanoparticles are generated in

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the polymer matrix by chemical [11–16] or electrochemical [17] reduction, photoirradiation [18–20] or thermal treatment [21–24]. In the chemical method, the silver nanoparticles are reduced by strong reducing reagents such as sodium borohydride [11] and hydrazine [12] added into the silver precursors and polymer mixture, or by functional groups on the polymer matrix (such as hydroxy groups on polyvinyl alcohol (PVA)) under mild thermal annealing [23,24].

In this study, we present a facile and novel *in-situ* method to fabricate polymer-silver nanocomposite thin films with highly dispersed silver nanoparticles, using primary diamines such as polyoxypropylenediamine (D230). The primary diamine polyoxypropylenediamine (D230) is needed to harden the poly(acrylic acid) via a cross linking reaction. We used this hardening agent for an additional purpose, namely to reduce the silver ions in the poly(acrylic acid) matrix without the need for an additional chemical reducing reagent. The poly(acrylic acid)-silver nanocomposite thin films were characterized by transmission electron microscopy (TEM), Fourier transform infrared spectroscopy (FT-IR), X-ray diffraction (XRD), and thermogravimetric analysis (TGA).

Experimentals

Materials

Poly(acrylic acid)-sodium salt (PAA-Na salt) and silver nitrate ($AgNO_3$) were purchased from Sigma-Aldrich Co.. D230 (polyoxypropylenediamine, with a molecular weight of about 230) was supplied by Kukdo Chemical. These chemicals were used without further purification.

Synthesis of Poly(Acrylic Acid)-Silver Nanocomposite Thin Films

The poly(acrylic acid)-silver nanocomposite thin films with highly dispersed silver nanoparticles were prepared by the simultaneous reduction of silver ions (Ag^+) and condensation reaction of poly(acrylic acids) with D230. The preparative scheme for poly(acrylic acid)-silver nanocomposite thin films is shown in Fig. 1. PAA-Na salts (1 mmol) were dissolved in deionized water, and reacted with an aqueous solution of $AgNO_3$ (1 mmol) to produce PAA-Ag salts. PAA-Ag salts were collected by filtration, and washed with deionized water three times [25–27]. The final form of the PAA-Ag salts had 70 wt% water.

The PAA-Ag salts (1 mmol) were then placed in a 100 ml round-bottomed flask equipped with a magnetic stirrer. After adding D230 (0.5 mmol) to this solution, the mixture was placed in an ice bath at 0°C and was vigorously stirred for 10 minutes. The mixture was then placed in a vacuum oven at 0°C for 2 h to increase the viscosity of the mixture for film casting.

The resulting mixture was cast on copper-foil using a scalpel blade, and the film was then slowly dried in a vacuum oven at 50°C for 1 h. To simultaneously reduce the silver precursors and condense the polymer matrix the films were baked at different temperatures (100°C, 130°C and 160°C) for 2 h.

Characterization Methods

Transmission electron microscopy (TEM, PHILIPS, CM30) was used to study the morphology of the silver nanoparticles in the nanocomposite films. TEM samples were prepared by dissolving PAA-Ag salts with D230 in deionized water and then placing one drop

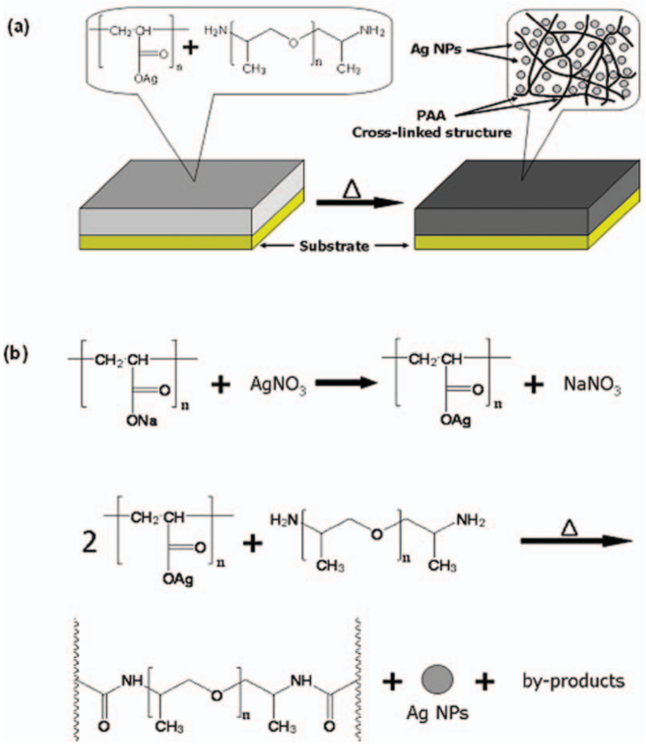

Figure 1. Reaction scheme for the preparation of PAA-Ag nanocomposite thin films with highly dispersed Ag nanoparticles: (a) schematic cartoon and (b) stepwise reaction mechanism.

of the mixture onto a carbon-coated copper grid. The samples were characterized after heating at different temperatures (100°C, 130°C and 160°C) for 2 h. The X-ray diffraction (XRD, Rigaku International Corp. D/MAX-2500) pattern was recorded at a scanning rate of 4 °/min in the 2Θ range 10 to 80 using Cu-Kα radiation ($\lambda = 1.540$Å). Samples for measurement were prepared by film casting on glass slides. Thermal gravimetric analysis (TGA, TA Instruments, 4100 Thermal Analyzer) was used to investigate the thermal stabilities and silver contents for the PAA-Ag nanocomposite films. A nitrogen atmosphere was used with a heating rate of 10°C/min within the temperature range of 50°C to 800°C. Fourier transform infrared (FT-IR, Thermo Electron Corp. Nicolet 380) spectra were collected in the wave range 450 cm^{-1} to 4000 cm^{-1} at a resolution of 4 cm^{-1}. The samples were prepared in the form of pellets together with KBr.

Results and Discussions

Synthesis of Poly(Acrylic Acid)-Silver Nanocomposite Thin Films

The poly(acrylic acid)-silver nanocomposite thin films with highly dispersed Ag nanoparticles were easily fabricated using the in-situ preparation shown in Fig. 1. These nanocomposite thin films were prepared by simultaneous reduction of Ag ions (Ag$^+$) and condensation of poly(acrylic acids) with D230 under mild thermal treatment. Polyoxypropylenediamine (D230) was used as a reductant and hardener. It is well known that

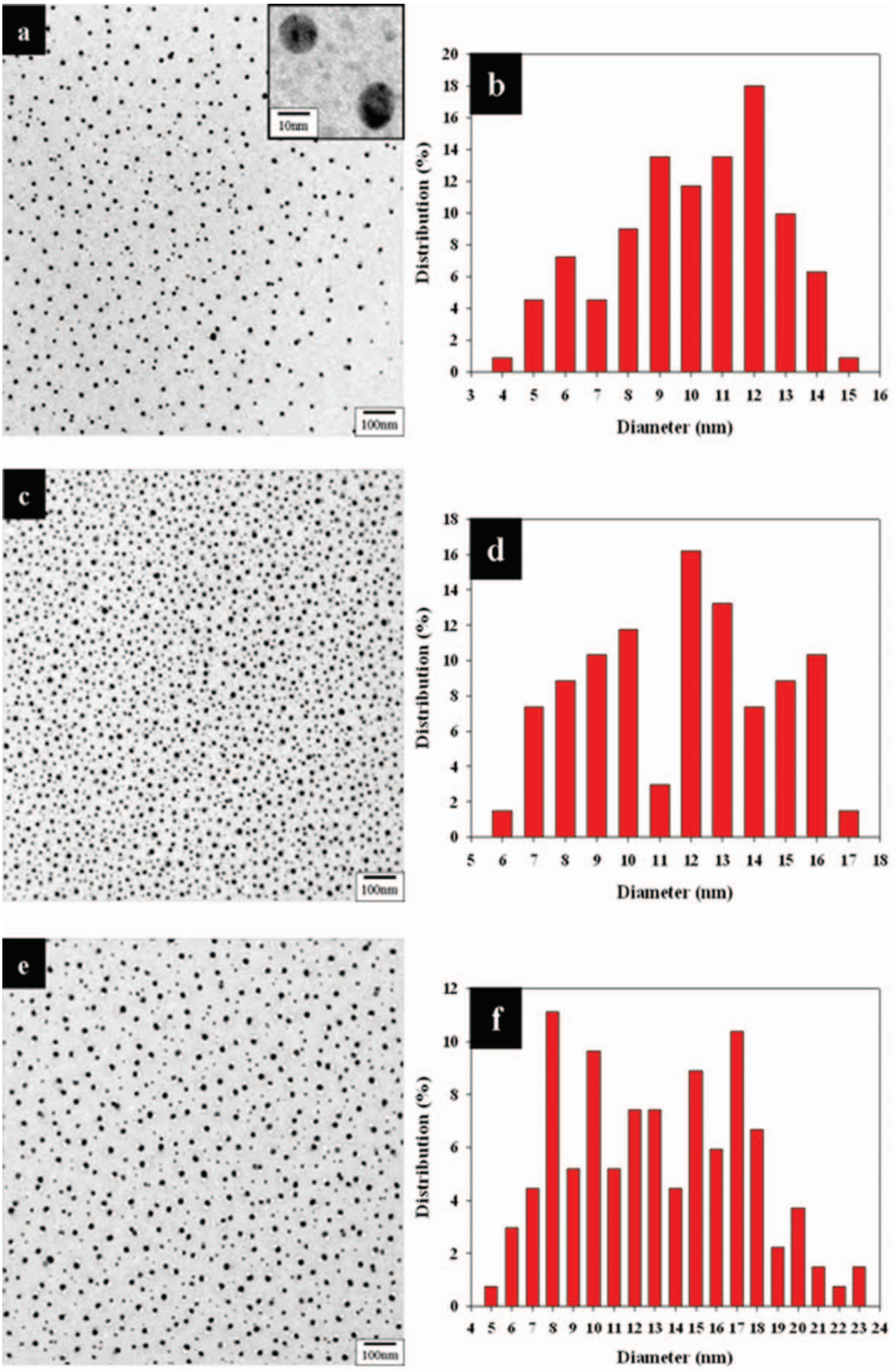

Figure 2. TEM images and size distributions of Ag nanoparticles formed in PAA-Ag nanocomposite thin films: (a, b) 100°C for 2 h, (c, d) 130°C for 2 h and (e, f) 160°C for 2 h.

the primary amines of the D230 molecule reduce silver precursors to silver metals [28] and take part in a condensation reaction with the carboxylic acids of PAA.

Particle Size and Morphology

To investigate the dependence of reduction and condensation on temperature, we prepared three samples baked at 100°C, 130°C and 160°C for 2 h, respectively.

Figure 2 shows TEM images and corresponding particle size distributions for the Ag nanoparticles formed in the PAA-Ag nanocomposite thin films. All Ag nanoparticles formed in the PAA matrix at 100°C, 130°C and 160°C are spherical. As shown in Fig. 2, the average diameters are 10.0 nm (100°C), 11.3 nm (130°C) and 13.0 nm (160°C), respectively, thereby indicating that the diameter of the Ag nanoparticles shows no difference depending on the temperature. However, the number density of Ag nanoparticles at 160°C is lower than those at other two temperatures. It is because Ag crystals with less than 1 nm size can easily form due to too fast formation of Ag crystals and condensation reaction of nanocomposite at 160°C.

X-Ray Diffraction Analysis

Figure 3 shows XRD patterns for Ag nanoparticles formed in PAA-Ag nanocomposite films at 100°C, 130°C and 160°C for 2 h. Peaks typical for a metallic silver phase were observed for the PAA-Ag nanocomposite films obtained at 130°C and 160°C. The prominent peaks at 2θ values of about 38.5°, 45°, 65°, and 78° correspond to the (111), (200), (220), and (311) Bragg's reflections for the fcc structure of a metallic silver [27]. On the other hand, the sample obtained at 100°C did not show the silver crystalline peaks (Fig. 3(a)). This indicates that the spherical nanoparticles of silver shown in Fig. 2(a) are mostly amorphous silver [29].

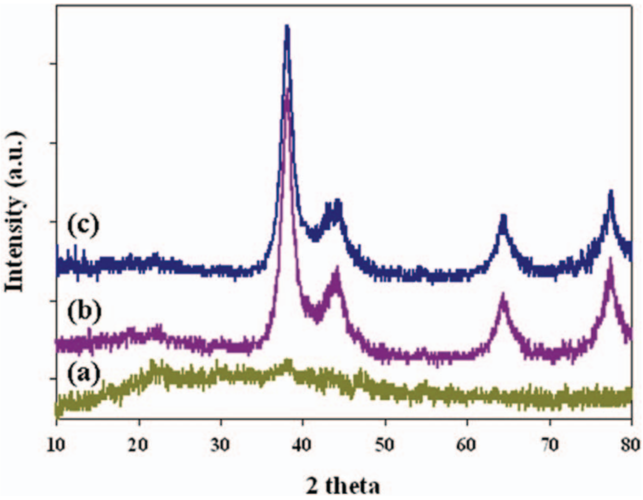

Figure 3. XRD patterns for Ag nanoparticles formed in PAA-Ag nanocomposite thin films: (a) 100°C for 2 h, (b) 130°C for 2 h and (c) 160°C for 2 h.

FT-IR Analysis

FT-IR spectroscopy was used to characterize the condensation of PAA with D230. Figures 4(a) and 4(b) show the FT-IR spectra of pristine PAA and PAA-Ag salts before mixing with D230. The strong peaks at 1710 cm^{-1} (Fig. 4(a)) and 1560 cm^{-1} (Fig. 4(b)) can be attributed to the C=O stretching band of carboxylic acid (-COOH) and carboxylate (-COO^{-}) from PAA and PAA-Ag salts, respectively [30]. Figures 4(c) to 4(f) show the FT-IR spectra of PAA-Ag salts mixed with D230 before heating (c), and after heating at 100°C (d), 130°C (e) and 160°C (f) for 2 h. While the peaks at 1560 cm^{-1} from the carboxylate groups of PAA-Ag salts decrease in magnitude with increasing reaction temperature, the C=O stretching band of the amide groups (-CONH-) at 1640 cm^{-1} becomes more prominent with increasing reaction temperature, indicating the condensation of PAA with D230 [31].

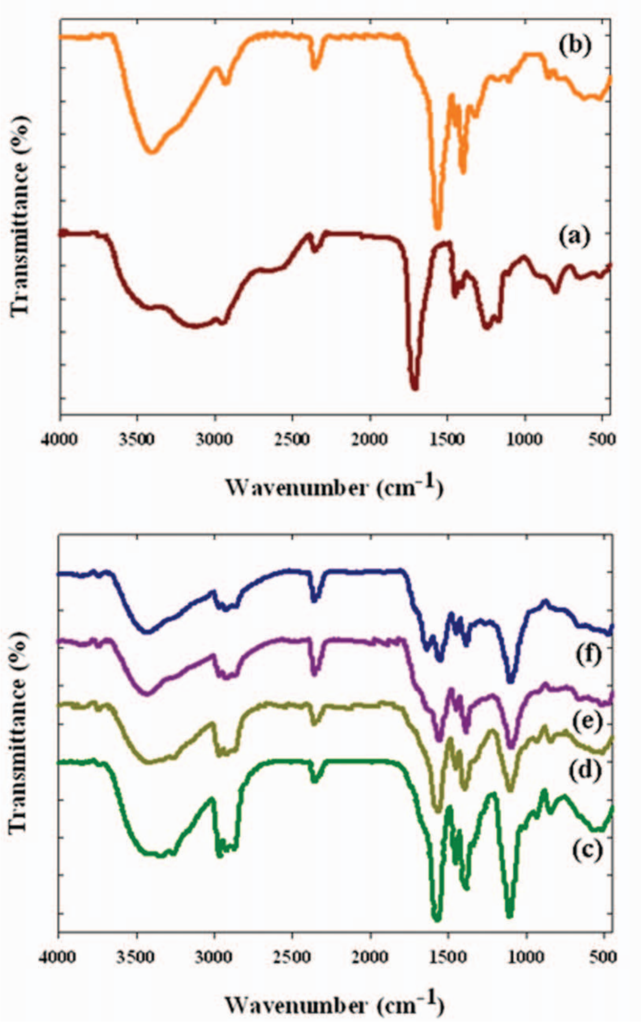

Figure 4. FT-IR spectra of PAA-Ag nanocomposite thin films: (a) pristine PAA, (b) PAA-Ag salts, (c) PAA-Ag salts mixed with D230 before heating, (d) after heating at 100°C, (e) 130°C and (f) 160°C for 2 h.

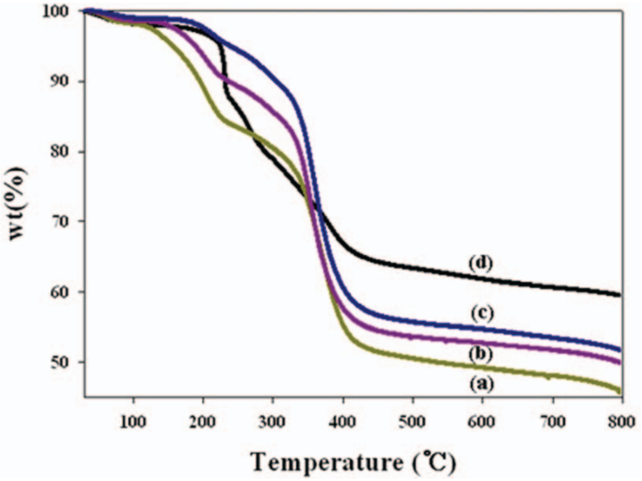

Figure 5. TGA data for PAA-Ag nanocomposite thin films and PAA-Ag salts: (a) 100°C for 2 h, (b) 130°C for 2 h, (c) 160°C for 2 h and (d) PAA-Ag salts.

Thermal Analysis of PAA-Ag Nanocomposite Thin Films

The TGA data show the relative silver contents and thermal stabilities of PAA-Ag nanocomposites and PAA-Ag salts in a nitrogen atmosphere. As shown in Fig. 5(d), the PAA-Ag salts degrade thermally at 230°C and contain 60 wt% silver, which means that the 60% of PAA-Ag salts in weight is silver. The silver contents of the PAA-Ag nanocomposites are 46 wt%, 50 wt% and 52 wt% at 100°C, 130°C and 160°C (heated for 2 h), respectively, which indicate that the silver content increases slightly with increasing heating temperature. Because the cross-linking density of the PAA with diamine increases with increasing heating temperature, the by-products, H_2O molecules, also increase and then make the nanocomposite lose weight due to their evaporation during condensation reaction. Therefore, the relative amount of silver in nanocomposite prepared at higher heating temperature increases. Also, the reason why PAA-Ag nanocomposite thin films have relatively lower amounts of silver than PAA-Ag salts is due to the primary amine (D230) used as a hardener and reductant in addition to PAA-Ag salts in nanocomposites. The primary amine reduces the relative amount of silver in weight by increasing the total weight of nanocomposite.

The thermal degradation of the PAA-Ag nanocomposites (heated at 100°C, 130°C and 160°C) occurred at similar temperatures in all the samples (in the range 350°C to 370°C). These thermal degradation temperatures were higher than that of the PAA-Ag salts, indicating the higher thermal stability of the nanocomposites due to cross-linking by condensation.

Conclusions

In conclusion, PAA-Ag nanocomposite thin films with highly dispersed Ag nanoparticles were successfully fabricated by a facile and simple *in-situ* preparation. The primary amines (in the D230) played an important role in the simultaneous reduction of Ag ions and the condensation of poly(acrylic acid). TEM and XRD data indicated that while silver nanoparticles formed during thermal treatment at 130°C or 160°C were spherical and crystalline, silver nanoparticles formed at 100°C were amorphous. TEM data also showed uniform size distributions for silver nanoparticles with a diameter of around 10 nm. The condensation reaction of carboxylic acids on the polymer backbone with primary amines in D230 was clearly verified by FT-IR analysis.

Acknowledgments

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References

[1] Melaiye, A., Sun, Z., Hindi, K., Milsted, A., Ely, D., Reneker, D. H., Tessier, C. A., & Youngs, W. J. (2009). *JACS*, *127*, 2285.
[2] Clemenson, S., Leonard, D., Sage, D., David, L., & Espuche, E. J. (2008). *Polym. Sci. A*, *46*, 2062.
[3] Temgire, M. K., & Joshi, S. S. Radiat. (2003). *Phys. Chem.*, *71*, 1039.
[4] Zheng, M., Gu, M., & Jin, G. (2000). *Mater. Res. Bull.*, *36*, 853.
[5] Radheshkumar, C., & Münstedt, H. (2005). *Mater. Lett.*, *59*, 1949.
[6] Dirix, Y., Bastiaansen, C., & Caseri, W. J. (1999). *Mater. Sci.*, *34*, 3859.
[7] Akamatsu, K., Takei, S., Mizuhata, M., Kajinami, A., Deki, S., Takeoka, S., Fuji, M., Hayashi, S., & Yamamoto, K. (2000). *Thin Solid Films*, *359*, 55.
[8] Zeng, R., Rong, M. Z., Zhang, M. Q., Liang, H. C., & Zeng, H. M. (2002), *Appl. Surf. Sci.*, *187*, 239.
[9] Zhang, Z., & Han, M. (2003). *J. Mater. Chem.*, *13*, 641.
[10] Sih, B. C., & Wolf, M. O.(2005). *Chem. Commun.*, 3375.
[11] Shon, Y. S., & Cutler, E. (2004). *Langmuir*, *20*, 6626.
[12] Jana, N. R., & Peng, X. G. (2003). *JACS*, *125*, 14280.
[13] Raveendran, P., Fu, J., & Wallen, S. L. (2003). *JACS*, *125*, 13940.
[14] Xiong, Y. J., Xie, Y., Wu, C. Z., Yang, J., Li, Z. Q., & Xu, F. (2003). *Adv. Mater.*, *15*, 405.
[15] Pastoriza-Santos, I., & Liz-Marzan, L. M. (1999). *Langmuir*, *15*, 948.
[16] Lee, G. J., Shin, S. I., Kim, Y. C., & Oh, S. G. (2004). *Mater. Chem. Phys.*, *84*, 197.
[17] Shang, L., Wang, Y., Huang, L., & Dong, S. (2007). *Langmuir*, *23*, 7738.
[18] Yang, Q., Wang, F., Tang, K. B., Wang, C. R., Chen, Z. W., & Qian, Y. T. (2002). *Mater. Chem. Phys.*, *78*, 495.
[19] Huang, H. H., Ni, X. P., Loy, G. L., Chew, C. H., Tan, K. L., Loh, F. C., Deng, J. F., & Xu, G. Q. (1996). *Langmuir*, *12*, 909.
[20] Zhu, Y. J., & Hu, X. L. (2004). *Mater. Lett.*, *58*, 1517.
[21] Zhang, J., Gao, Y., Alvarez-Puebla, R. A., Buriak, J. M., & Fenniri, H. (2006). *Adv. Mater.*, *18*, 3233.
[22] Deshmukh, R. D., & Composto, R. (2007). *J. Chem. Mater.*, *19*, 745.
[23] Fritzsche, W., Porwol, H., Wiegand, A., Bornmann, S., & Köhler, J. M. (1998). *Nanostruct. Mater.*, *10*, 89.
[24] Porel, S., Singh, S., Harsha, S. S., Rao, D. N., & Radhakrishnan, T. P. (2005). *Chem. Mater.*, *17*, 9.
[25] Abe, K., Hanada, T., Yoshida, Y., Tanigaki, N., Takiguchi, H., Nagasawa, H., Nakamoto, M., Yamaguchi, T., & Yase, K. (1998). *Thin Solid Films*, *327*, 524.
[26] Yamamoto, M., & Nakamoto, M. (2003). *J. Mater. Chem.*, *13*, 2064.
[27] Yamamoto, M., Kashiwagi, Y., & Nakamoto, M. (2006). *Langmuir*, *22*, 8581.

[28] Chen, M., Feng, Y. G., Wang, X., Li, T. C., Zhang, J. Y., & Qian, D. J. (2007). *Langmuir*, *23*, 5296.

[29] Salkar, R. A., Jeevanandam, P., Aruna, S. T., Koltypin, Y., & Gedanken, A. (1999). *J. Mater. Chem.*, *9*, 1333.

[30] Wang, Y. J., Yu, A. M., & Caruso, F. (2005). *Angewandte Chemie-International Edition*, *44*, 2888.

[31] Nakata, S., & Brisson, J. (2000). *European Polymer Journal*, *36*, 831.