Preparation and Characterization of Conductive SiO₂-Polyaniline Core-Shell Nanoparticles

Bo-Tau Liu, Jhan-Rong Syu, and De-Hua Wang

Abstract—Recently, polymer-inorganic nanocomposites have attracted great attention as new materials because of their novel mechanical, electrical, and optical properties. In particular, inorganic-polymer core-shell nanoparticles are more promising in such new applications as surface-enhanced Raman scattering, photonic crystals, catalysis, nano-electronic devices, and biochemical sensor. In this study used we 1.2-Aminopropyltriethoxysilane as a coupling agent to synthesize silica-polyaniline core-shell nanoparticles. Preparation and characterization of the core-shell nanoparticles were analyzed and discussed. To evaluate the core-shell effect, the core-shell nanoparticles were incorporated into polyurethane. The nanocomposites containing the core-shellstructure nanoparticle show significant enhancement on electrical and mechanical properties compared to those containing silica nanoparticles.

Index Terms—Conductive, core-shell, polyaniline, silica.

I. INTRODUCTION

Recently, great attention has been paid in the fabrication of core-shell nanoparticles with unique and tailored properties for various applications. Due to diverse structures and properties, the core-shell nanoparticles have wide applications in various fields such as surface-enhanced photonic Raman scattering, crystals, catalysis, nano-electronic devices. and biochemical sensor [1]-[7]. Among the various core-shell nanoparticles, the fabrication of inorganic nanoparticles coated with the shell of polymers has attracted increasing attention as new materials because of their novel mechanical, electrical, and optical properties [8]-[9]. Characteristics of the hybrid colloids can be adjusted through the functionality of polymer moieties.

Polyaniline (PANI), which has been extensively studied in the literature, is a great potential conducting polymer to be used in electronic products due to its low cost, easy preparation, oxidative stability, and excellent conductivity [10]. However, like many other conducting polymers, PANI has poor mechanical properties and insolubility in common organic solvents because of its stiff backbone and strong hydrogen bonding interaction. In order to overcome the insolubility issue, functional organic acids such as dodecylbenzenesulfonic acid (DBSA) and camphorsulfonic acid [11]-[13] are usually doped/bound into PANI to increase compatibility with solvents or other polymers. Recently, it was found that silica is helpful to increase the stability of PANI in solution [14]-[15]. PANI-coated silca nanoparticles also exhibit specially electrorheological behavior [16]. In addition, the polyurethane (PU)-PANI-silica nanocomposites was found to show better mechanical properties if PANI were linked with silica through isocynataes [17].

Although some studies have successfully deposited a thin PANI layer on monodisperse silica micro-particles [18]-[19], PANI-coated nano-silica is still challenging. Jang et al. reported a simple adsorption method for the fabrication of silica-PANI nanoparticles [20]. Because the surfaces of silica nanoparticles and the amino groups of aniline monomers possess opposite charges under pH=3, the silica-PANI-core-shell nanoparticles were synthesized by in-situ polymerization of aniline monomers adsorbed on the silica surface through electrostatic interactions at the pH value. In the study, we used 1.2-Aminopropyltriethoxysilane (APTS) as a coupling agent to synthesize silica-polyaniline (PANI) core-shell nanoparticles. The structure of core-shell nanoparticles was characterized and investigated. The core-shell nanoparticles were incorporated into polyurethane (PU) to evaluate the mechanical and electric properties. The effects of PANI shell on mechanical and electrical properties of the conductive hybrid materials were investigated.

II. EXPERIMENTAL

A. Materials

Polytetramethylene ether glycol (PTMG, MW=2000, Aldrich) and 1, 4-butanediol (Acros) were degassed at 80°C under vacuum for 3 h. Aniline (Alfa Aesar) were purified by pressure. distillation under reduced N-methyl-2-pyrrolidinone (NMP, Tedia) was distilled under vacuum over calcium hydride to remove absorbed water. Tetraethyl orthosilicate (TEOS), 4,4'-methylenebis(phenyl isocyanate) (MDI), dodecylbenzenesulfonic acid (DBSA), dibutyltin dilaurate (DBTDL) were purchased from Sigma-Aldrich. 1.2-Aminopropyltriethoxysilane (APTS, Alfa Aesar), ammonium persulfate (APS, J.T.Baker), and hydrochloric acid (HCl) were used as received. Deionized water (DI water, >18 M Ω ·cm) was used throughout the experiments.

B. Silica-PANI Core-Shell Nanoparticles

Silica nanoparticles (SiO_2) were prepared from TEOS by a sol-gel method as described in the previous reports [21]. The as-prepared silica nanoparticles were redispersed into toluene by ultrasonication. After addition of APTS and a few drops of HCl, the suspension solution was heated at 60°C for 8 h.

Manuscript received April 16, 2013; revised June 13, 2013. This study was supported financially by the National Science Council of the Republic of China (NSC 101-2221-E-224-083).

The authors are with the Department of Chemical and Materials Engineering, National Yunlin University of Science and Technology, Yunlin 64002, Taiwan (e-mail: liubo@yuntech.edu.tw, g9815721@yuntech.edu.tw, m10015020@yuntech.edu.tw).

The modified silica nanoparticles were washed with NMP by centrifugation: centrifuging the suspension, decanting the supernatant, and then redispersing the nanoparticles. The process was repeated several times to remove the residual APTS, resulting in silica nanoparticles featuring amino groups on their surfaces.

APS (0.029 g) was dissolved into 1 N HCl solution (30 ml) with 30 min stirring. DBSA (0.067 g), aniline (0.012 g), APTS-modified silica and 1 N HCl (100 g) were mixed in a four-neck reaction vessel immersed in an ice-water bath. The APS solution was added through peristaltic pump into the reaction vessel. After reacting at ca. 0 °C for 12 h, the suspension solution was filtered to remove the large aggregates or PANI precipitates. The filtered solution was washed with NMP by centrifugation, resulting in the core-shell nanoparticles with 1-wt% PANI (PANI-SiO₂)

C. PU Nanocomposites

The mixture of PTMG and DBTDL in a molar ratio of 1:2 were reacted with MDI in NMP solution at 70 $^{\circ}$ C under nitrogen purge. After 3 h, PANI-SiO₂ was added to the solution. After 2-h reaction, 1,4-butanediol was added into the solution as a chain extender. Finally, DBSA was added into the solution with 3-h ultrasonication. The procedure for the sample preparation is illustrated in Fig. 1. The resulting solution was poured into a Petri dish and dried under reduced pressure at 85 $^{\circ}$ C for 12 h.



Fig. 1. Schematic presentation for the preparation of PU-PANI-SiO₂ nanocomposites

D. Characterization

The morphologies of the as-prepared nanoparticles were examined using a high resolution transmission electron microscope (JEM-2010, JEOL). Surface modification of SiO₂ by APTS and PANI was studied by Fourier transform infrared (FTIR) spectroscopy (Spectrum One, PerkinElmer). The sheet resistance was determined using a four-pin probe meter(Loresta-GP, Mitsubishi Chemical) with a probe (MCP-T610). The mechanical properties of the samples were measured by a universal testing machine using an extension rate of 120 mm/min at room temperature.

III. RESULTS AND DISCUSSION

Fig. 1 shows the TEM image of the as-prepared PANI-SiO₂, which is spherical shapes and ca. 240 nm in diameter. No large particles or aggregates were found under TEM observation. In addition, the core-shell structure can be roughly observed in the TEM image.



Fig. 1. TEM image of PANI-SiO2



Fig. 2. FTIR spectra of the pristine and PANI-coated silica nanoparticles

The FTIR spectra of the pristine and PANI-coated silica nanoparticles were recorded in Fig. 1. Some typical characteristics of silica are observed in the IR spectrum of the unmodified silica nanoparticles: the broad absorption band in the range of 3000-3600 cm⁻¹ corresponds to O-H stretching vibrations from Si-OH; the strong absorption band at1103 cm⁻¹ and the mild absorption peak at 801 cm⁻¹ represents Si-O-Si stretching vibrations and bending vibrations, respectively; the absorption peak at 1625 cm⁻¹ indicates H-O-H bending vibrations due to water absorption [22]. The spectrum of PANI-SiO₂ is similar to that of SiO₂, except the absorption peaks at 2800-3000 cm⁻¹ for C-H stretching vibrations and 1302 cm⁻¹ for C-N stretching absorption. The spectrum of PANI-SiO₂ also features a weaker signal at 3000-3600 cm⁻¹ for O-H stretching vibrations, and the benzenoid and quinoid absorption peaks in pairs at 1501 and 1595 cm⁻¹[23]. These features reveal that PANI was coated on silica nanoparticles.

In order to show the effect of APTS on preparation of the silica-PANI core-shell structure, the PANI-coated nano-silica particles were also prepared by the adsorption method. The silica-PANI-core-shell nanoparticles were synthesized by in-situ polymerization of aniline monomers adsorbed on the silica surface without APTS modification. After washed with NMP by centrifugation and then redispersed several times, the color of the silica-PANI core-shell particles prepared by the electrostatic adsorption gradually became whitish from blue (Fig. 3a), whereas PANI-SiO₂ still showed the characteristic of PANI (Fig. 3b). The result implies that the modification of SiO₂ with APTS is helpful to remain the silica-PANI core-shell structure in PU nanocomposites after the further preparation.



Fig. 3. Photograph images of the core-shell nanoparticles prepared from SiO₂ (a) and SiO₂ with APTS modification (b) after NMP rinses.

In addition, we also found the APTS-modified SiO_2 showed different reactivity compared with the pristine SiO_2 . Both kinds of SiO_2 were reacted with MDI and then dispersed into water. As shown in Fig. 4, the pristine SiO_2 shows dispersible, whereas the APTS-modified SiO_2 presentes lump, indicating that the amino groups have higher reactivity with isocyanates than hydroxyl group and confirming that the APTS has indeed been coated on the surface of silica nanoparticles.



Fig. 4. Photograph images of the results that core-shell nanoparticles reacted with MDI and were then redispersed. Left: SiO₂, Right: APTS-modified SiO₂.

The effect of core-shell structure on the surface resistance of PU-PANI-silica hybrid films are shown in Table I. Without PANI content, PU of PU-SiO₂ does not reveal any electrical conductivity, whereas the resistance of the PU-PANI-SiO₂ with only a 1-wt%-PANI coating shell on silica nanoparticles (PANI is 0.05 wt% of the total nanocomposite) reduces to $1.06 \times 10^{10} \Omega/sq$. In addition, due to the effect of organic-inorganic hybrid, it is not surprising that PU-SiO₂ has higher tensile strength and larger ultimate elongation than PU, shown in Table I. However, the enhancement of mechanical properties increases while silica nanoparticles were modified with APTS. The result may be explained from the fact as mentioned before that amino groups have higher reactivity with isocyanate groups than hydroxyl groups, and thereby more chemical bonding between resin and particles form, resulting in the enhancement of mechanical properties, as shown in Fig. 4. The core-shell structure enhances not only the electrical conductivity but also mechanical properties.

TABLE I: PROPERTIES OF	PU-PANI-SI	O2 NANOCOMPOSITES
------------------------	------------	-------------------

Samples	Surface resistance (Ω/sq)	Tensile strength (MPa)	Ultimate
			Elongation
			(%)
PU	$> 10^{12}$	4.38	192.0
PU -SiO ₂	$> 10^{12}$	5.77	400.7
PU-PANI-SiO ₂	1.06×10^{10}	6.94	594.1

IV. CONCLUSION

Silica-PANI core-shell nanoparticles were fabricated

using APTS as a coupling agent. The PANI shell prepared by the present method revealed a better solvent resistance compared with that by the adsorption method. When the silica-PANI core-shell nanoparticles were incorporated into PU matrix, the PU-PANI-silica nanocomposites showed superior electrical conductivity and mechanical properties compared with the PU- silica nanocomposites.

References

- N. Zhou, L. Polavarapu, N. Gao, Y. Pan, P. Yuan, Q. Wang, and Q. H. Xu, "TiO₂ coated Au/Ag nanorods with enhanced photocatalytic activity under visible light irradiation," *Nanoscale*, 2013.
- [2] W. Li, J. Yang, Z. Wu, J. Wang, B. Li, S. Feng, Y. Deng, F. Zhang, and D. Zhao, "A versatile kinetics-controlled coating method to construct uniform porous TiO₂ shells for multifunctional core-shell structures," *J. Am. Chem. Soc*, vol. 134, pp. 11864-11867, 2012.
- [3] A. Schmid, J. Tonnar, and S. P. Armes, "A new highly efficient route to polymer-silica colloidal nanocomposite particles," *Adv. Mater.*, vol. 20, no. 17, pp. 3331-3336, 2008.
- [4] Q. Fu, D. G. Zhang, M. F. Yi, X. X. Wang, Y. K. Chen, P. Wang, and H. Ming, "Effect of shell thickness on a Au-Ag core-shell nanorods-based plasmonic nano-sensor," J. Opt., vol. 14, pp. 085001, 2012.
- [5] S. Wu, A. W. Shell, M. Lublow, J. Kaiser, T. Aichelle, S. Schietinger, F. Polzer, S. Kuhn, X. Guo, O. Benson, M. Ballauff, and Y. Liu, "Silica-coated Au/Ag nanorods with tunable surface plasmon bands for nanoplasmonics with single particles," *Colloid Polym. Sci.*, vol. 291, pp. 585-594, 2013.
- [6] Z. F. Liu, T. Ding, G. Zhang, K. Song, K. Clays, and G. H. Tung, "Ternary inverse opal system for convenient and reversible photonic bandgap tuning," *Langmuir*, vol. 24, pp. 10519-10523, 2008.
- [7] H. T. Zhang, J. Ding, G. M. Chow, M. Ran, and J. B. Yi, "Engineering magnetic properties of Ni nanoparticles by non-magnetic cores," *Chem. Mater.*, vol. 21, pp. 5222-5228, 2009.
- [8] R. Y. Hong, H. P. Fu, Y. J. Zhang, L. Liu, J. Wang, H. Z. Li, and Y. Zheng, "Surface-modified silica nanoparticles for reinforcement of PMMA," *J. Appl. Polym. Sci.*, vol. 105, no. 4, pp. 2176-2184, 2007.
- [9] B. T. Liu, S. J. Tang, Y. Y. Yu, and S. H. Lin, "High-refractive-index polymer/inorganic hybrid films containing high TiO₂ contents," *Colloids Surf. A*, vol. 377, no. 1-3, pp. 138-143, 2011.
- [10] E. M. Genies, A. Boyle, M. Lapkowski, and C. Tsintavis, "Polyaniline - a historical survey," *Synth. Met.*, vol. 36, no. 2, pp. 139-182, 1990.
- [11] Y. Cao, P. Smith, and A. J. Heeger, "Conterion induced processibility of conducting polyaniline and of conducting polyblends of polyaniline in bulk polymers," *Synth. Met.*, vol. 48, no. 1, pp. 91-97, 1992.
- [12] Y. Cao, P. Smith, and A. J. Heeger, "Couterion induced processibility of conducting polyaniline," *Synth. Met.*, vol. 57, no. 1, pp. 3514-3519, 1993.
- [13] A. J. Heeger, "Polyaniline with surfactant counterions conducting polymer materials which are processible in the conducting form," *Synth. Met.*, vol. 57, no. 1, pp. 3471-3482, 1993.
- [14] J. Stejskal, O. Quadrat, I. Sapurina, J. Zemek, A. Drelinkiewicz, M. Hasik, I. Krivka, and J. Prokes, "Polyaniline-coated silica gel," *Eur. Polym. J.*, vol. 38, no. 4, pp. 631-637, 2002.
- [15] X. W. Li, N. Dai, G. C. Wang, and X. M. Song, "Water-dispersible conducting polyaniline/nano-SiO2 composites without any stabilizer," *J. Appl. Polym. Sci.*, vol. 107, no. 1, pp. 403-408, 2008.
- [16] N. Kuramoto, Y. Takahashi, K. Nagai, and K. Koyama, "Electrorheological properties of poly (o-anisidine) and poly (o-anisidine)-coated silica suspensions," *React. Funct. Polym.*, vol. 30, no. 1-3, pp. 367-373, 1996.
- [17] T. L. Wang, C. H. Yang, Y. T. Shieh, and A. C. Yeh, "Synthesis and properties of conducting organic/inorganic polyurethane hybrids," *Eur. Polym. J.*, vol. 45, no. 2, pp. 387-397, 2009.
- [18] S. P. Armes, S. Gottesfeld, J. G. Beery, F. Garzon, and S. F. Agnew, "Conducting polymer-colloidal silica composites," *Polymer*, vol. 32, no. 13, pp. 2325-2330, 1991.
- [19] N. Kuramoto, M. Yamazaki, K. Nagai, K. Koyama, K. Tanaka, K. Yatsuzuka *et al.*, "Electrorheological property of a polyaniline-coated silica suspension," *Thin Solid Film*, vol. 239, no. 2, pp. 169-171, 1994.
- [20] J. S. Jang, J. Ha, and B. Lim, "Synthesis and characterization of monodisperse silica-polyaniline core-shell nanoparticles," *Chem. Comm.*, no. 15, pp. 1622-1624, 2006.
- [21] B. T. Liu and W. D. Yeh, "An innovative approach to preparation of particles with optimal size distribution: an example of SiO₂," *J. Taiwan Inst. Chem. Eng.*, vol. 42, no. 3, pp. 509-512, 2011.

- [22] B. T. Liu, S. J. Tang, Y. Y. Yu, and S. H. Lin, "High-refractive-index polymer/inorganic hybrid films containing high TiO₂ contents," *Colloids Surf. A*, vol. 377, no. 1-3, pp. 138-143, 2011.
- [23] D. L. Pavia, G. M. Lampman, G. S. Kriz, and J. R. Vyvyan, *Introduction to spectroscopy: a guide for students of organic chemistry*, 4th ed., Brooks/Cole, United States, 2001.



Bo-Tau Liu was born in Hualien, Taipei. He received his Ph.D. degree in chemical engineering with the theoretical and practical combination of colloid and interface science from National Taiwan University in 1998. During the college life, he was nominated for the honor member of Phi-Tau-Phi scholastic honor society, won an award for excellent student of college, and passed the examination of Taiwan environmental engineering technician. He was devoted to the study of the preparation of nanoparticles, nanofluids, and renewable energy in Industrial Technology Research Institute (ITRI) in 1998-2003. Dr Liu incorporated the technologies in colloid science and nanoparticles into the optical films in LCD such as polarizers, antireflection films, antiglare films, and diffusers during working for Compal Electronics, Inc. in 2004 and Daxon Technology, Inc. in 2005-2007. He joined National Yulin University of Science and Technology (in Taiwan) in 2007. He has over numerous articles published in leading surface science, materials and polymer journals. His research interests include in low/high refractive index materials, optical properties of nanostructure surface, functional nanoparticles, transparent conductive films, and colloid and interface science.