Synthesis and Characterization of Conducting Polyaniline-Activated Carbon Nanocomposites

Mohammad Rezaul Karim, Chul Jae Lee, Mu Sang Lee

Department of Chemistry, Graduate School, Kyungpook National University, Daegu 702-701, Korea

ABSTRACT: Conducting polyaniline (PAni)/activated carbon (AC) nanocomposites were synthesized by the *in situ* chemical polymerization method. The resultant shell–core PAni–AC nanocomposites were characterized by elemental analysis, Fourier transform infrared, scanning electron microscopy, thermal gravimetric analysis, X-ray diffraction, and transmission electron microscopy. We did not observe any significant chemical interaction between the PAni and AC, only core–shell coupling between the AC and the tightly coated polymer chain was revealed. Measurement of the physical properties showed that the incorporation of conducting PAni on to AC particles during chemical synthesis increased electrical conductivity and thermal stability by several orders of magnitude to that of the pristine PAni powders. © 2006 Wiley Periodicals, Inc. J Appl Polym Sci 103: 1973–1977, 2007

Key words: conducting polymers; core-shell polymers; synthesis; morphology; nanocomposites

INTRODUCTION

Porous solid materials with high surface areas and large pore sizes are widely employed in many fields of science and technology, including water and air purification, separation, catalysis, and energy storage.[1,2] A wide variety of porous solids exist including zeolites, pillared clays, polymeric solids and porous carbon.[3] Among these, porous carbon, often called activated carbon, displays exceptional porosity, an extended surface area, high adsorption capability and a high degree of surface reactivity. In other words, activated carbon can be defined as an amorphous carbon-based material with a high degree of porosity and an extended inter-particulate surface area as stacks of flat aromatic sheets in a random crosslinked manner. Currently, activated carbon is the most economic and widely used porous solid.[4]

Conducting polymers, however, have aroused great interest among researchers because of their curious electronic, magnetic, and optical properties. The nanocomposite form of conducting polymers has attracted special attention for its universal applications in drug delivery systems and plastic transistors and in microwave components after coating with metal, electronic, and electro-optical devices. Polyaniline is one of the most studied electrically conducting polymers because of its good processability, environmental stability, and potential in the catalyst field, biosensors, batteries, and electronic technology.[5] It is characterized by high chemical and thermal stability in the conductive form and low production costs, and it can also be easily doped with inorganic and organic acids.[6,7] Polymer composites are attractive because they can be combined with the properties of other compounds such as PAni with graphite,[8] carbon nanotubes,[9] and activated carbon[10] that have been accepted to effectively improve electrical conductivity. Among them, PAni–AC nanocomposites are expected to be used in the detection and discrimination of biogenic compounds (e.g., amines, methines, etc.), novel rubbers, and rechargeable batteries.[11]

In general, the template synthesis method, which involves using pores in a microporous membrane as a template for composite formation, is an effective method for synthesizing conducting polymer nanocomposites. Martin and coworkers pioneered the template synthesis of various polymeric materials such as poly(alkyl thiophene),[12] polypyrrole,[13] polyacetylene,[14] and polyaniline[15] tubular forms. Wan et al. recently developed a simple method of *in situ* doping polymerization in the presence of β-naphthalene sulfonic acid as the dopant.[16] The *in situ* doping polymerization method is much easier than the template synthesis method without the microporous membrane, as the template or the anchoring materials bind the polymer to the wall of the microporous membrane. To the best of our knowledge, conducting polyaniline coated on activated carbon (PAni–AC) composites by the *in situ* chemical polymerization method has not been studied yet. Therefore, we expect that AC composites, with the conducting PAni, will provide very interesting results in the synthesizing of new types of

WILEY
InterScience®
DISCOVER SOMETHING GREAT

nanomaterial composites. Thus, the AC was coated with conducting polyaniline, and a new complex material of activated carbon composites containing polyaniline (PAni–AC) was synthesized by using the *in situ* chemical polymerization method.

In this paper, we report on the shell-core PAni–AC nanocomposites that were chemically synthesized by the *in-situ* polymerization method for the first time. The morphology and microstructure of the resulting specimen were characterized, and the physical properties, including thermal and electrical aspects, are discussed in detail.

EXPERIMENTAL

A coal-based commercial granular activated carbon was used in this investigation. The activated carbon sample was obtained from Daejung Chemicals & Metals Co., Ltd. (Shiheung City, Gyeonggi-do, South Korea) and was used directly without further treatment. Aniline monomer (99.5%+), hydrochloric acid, ammonium persulfate [$(NH_4)_2 S_2O_8$, oxidant], and other organic solvents were obtained from Aldrich as reagent grade and were used as received.

A typical *in situ* chemical polymerization method for the PAni–AC composites was carried out by the routine synthesis as follows: 150 mL of a $0.1M$ HCl solution containing AC (0.2 g) was added to a 500-mL double-necked round-bottomed flask equipped with a magnetic Teflon-coated stirrer. The mixture was sonicated for 30 min at room temperature in order to disperse the as-received activated carbon. Aniline monomer (0.7 g/0.685 mL) in 100 mL of $0.1M$ HCl solution was added to the above solution. Then 50 mL of $0.1M$ HCl solution containing ammonium persulfate (0.8 g) was added dropwise in small portions to the suspension in a two-necked flask, with constant sonication. It was kept in an ice-water bath in order to control the reaction temperature between 0°C and 5°C. The reaction mixture was stirred for an additional 4 h under the same conditions. The resultant PAni–AC powder was precipitated in methanol, filtered with a Buchner funnel, and then carefully washed with methanol, hydrochloric acid ($0.1M$), distilled water, and acetone until the filtrate was colorless. The obtained black powder was dried under a vacuum dryer at room temperature for 24 h. The bulk PAni powders were synthesized using a similar method, and the same mole ratios of monomer to dopant were incorporated into the polymerization.

The instruments used for this work included an elemental analyzer (CE Instruments model FISON EA-1110), a scanning electron microscope (Hitachi model S-4300), a transmission electron microscope (Hitachi model H-7100) with an Acc. voltage of 100 kv, a Fourier transform infrared spectroscopy instrument (Bruker

IFS 120HR), an X-ray diffraction (XRD) instrument (Philips model X'Pert APD), and a thermogravimetric analyzer (Dupont model 9900/2100) in a nitrogen atmosphere with a heating rate of 10 K/min in the temperature range of 0°C–800°C. The room-temperature conductivity of the pressed pellets was measured by the four-point probe method using a Jandel Engineering instrument (model CMT-SR1060N).
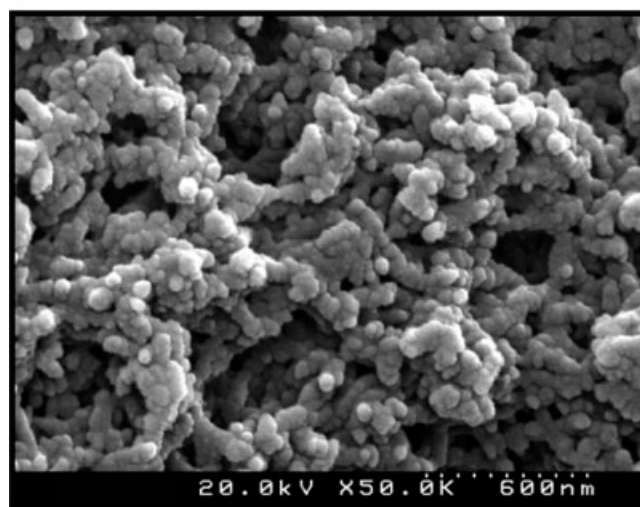
RESULTS AND DISCUSSION

Structural characterization

We used continual stirring throughout the whole polymerization process with a much diluted reaction solution in order to prepare the uniform PAni–AC composites. Figure 1(b) shows the scanning electron microscopy (SEM) image of a uniform view of the
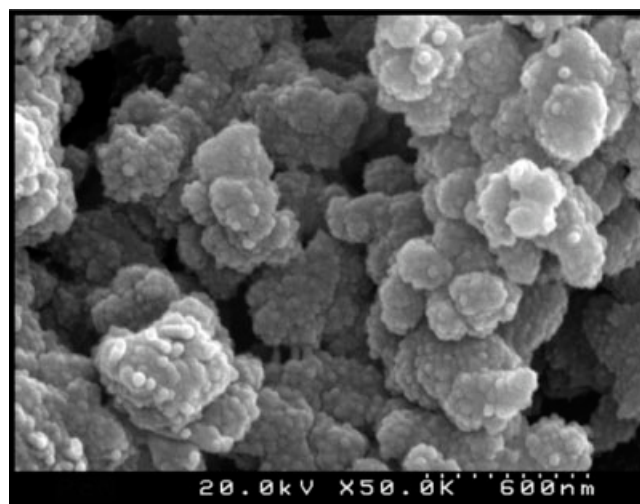
(a)

(b)

Figure 1 SEM images of (a) bulk PAni powders and (b) PAni–AC composites.

PAni–AC composites. From Figure 1(a), it can be seen that the pristine PAni, synthesized without AC, showed typical morphology.

The morphology of the PAni–AC composites was also imaged by transmission electron microscopy (TEM) as shown in Figure 2. Structural characterization showed that there was no significant interaction observed between the PAni and AC; only the PAni was coated on the surface of the granular activated carbon. In Figure 2 the dark inner part (core) is mainly a compound of AC, and the outer coated surface (shell) is conducting polyaniline with variable thickness.

Elemental analysis data showed that the composition of AC and PAni in the PAni–AC composites was about 1 : 1 (wt %): C 61.35, H 0.86, N 0.46, and S 0.83 for AC; C 54.25, H 5.03, N 10.45, and S 3.82 for PAni; C 59.62, H 3.48, N 7.12, and S 1.84 for PAni–AC.

The FTIR spectra of the PAni, AC, and PAni–AC composites are shown in Figure 3. In the PAni spectrum [Fig. 3(c)], it is in correlation with previously reported results.[5,17–19] The bands at 1565 and 1478 cm^{-1} showed the characteristic C=C stretching of the quinoid and benzenoid rings. The peaks at 1301 and 796 cm^{-1} can be assigned to the C—N stretching of the secondary aromatic amine and an aromatic C—H out-of-plane bending vibration, respectively. The relatively small peak at 3445 cm^{-1} can be attributed to the N—H stretching vibration mode. In the region of 1010–1170 cm^{-1} aromatic C—H in-plane bending modes were usually observed. In addition, we found a higher peak at 2930 cm^{-1}, which resulted from crosslinking moieties. These observations indicated that polyaniline was formed in our products. For the as-received AC, a broad envelope band over 900–1300 cm^{-1} and a small band at 1573 cm^{-1} were observed, shown in Figure 3(a). A strong absorption
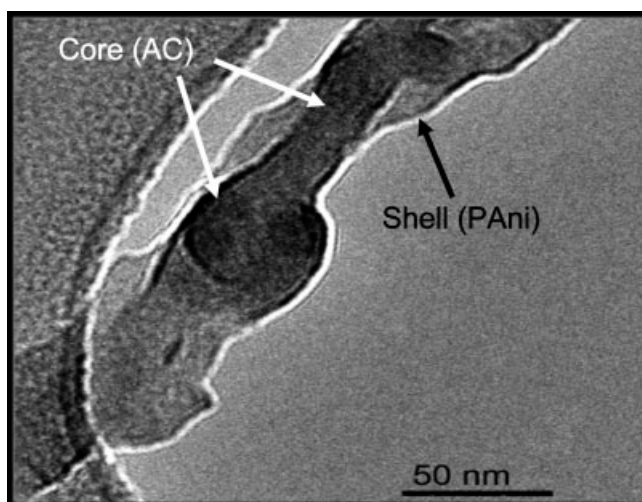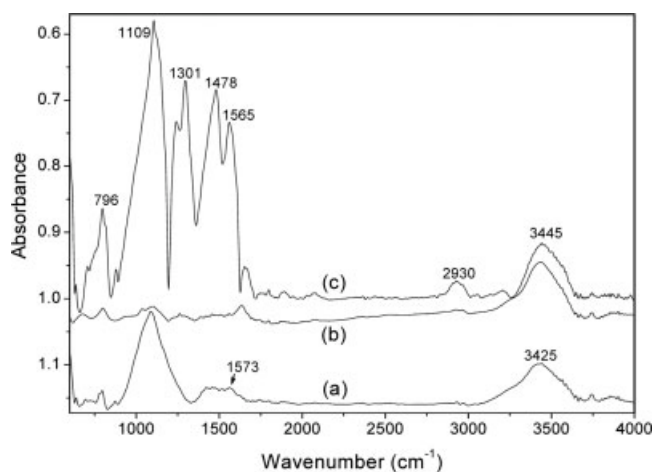

Figure 3 FTIR spectra of (a) as-received activated carbon, (b) PAni–AC composites, and (c) bulk PAni powders.

band was observed at around 3425 cm^{-1} and can be assigned to carboxylic group O—H stretching.[20] No additional peaks, however, were observed in the FTIR spectrum of the PAni–AC composites, except for the characteristic peaks of PAni and AC.

Figure 4 represents the XRD patterns of the as-received AC powders, the *in situ* chemically synthesized PAni, and the PAni–AC nanocomposites. In the pattern of the synthesized PAni, there were three main peaks, at about $2\theta = 25°$, $44°$ and $51°$ [Fig. 4(a)], which were consistent with the third, fourth, and fifth peaks, respectively, in the XRD patterns of polyaniline in previous reports.[5,21,22] The peak, which was centered at $2\theta = 25°$, may be ascribed to the periodicity parallel to the polymer chain, whereas the weak peaks at higher angles could have been caused by the periodicity perpendicular to the polymer chain. For the bulk PAni powders, the XRD pattern exhibited a broad amorphous diffraction peak at $20°$ and two
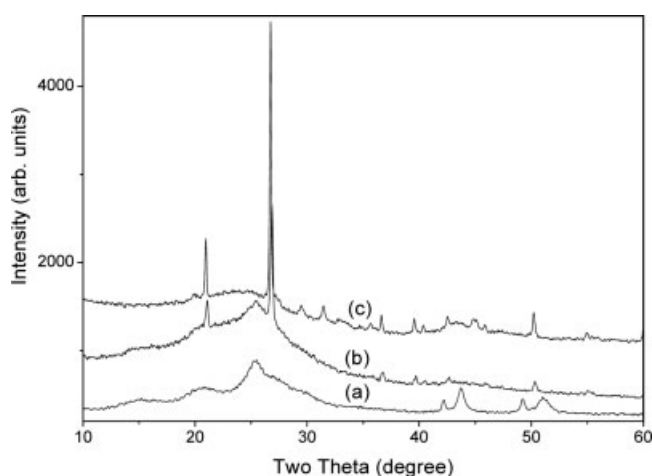

Figure 2 TEM image of PAni–AC composites.

Figure 4 XRD analysis data of (a) bulk PAni powders, (b) PAni–AC composites, and (c) as-received activated carbon.

crystalline peaks at 42.2° and 49.2°. The as-received AC powders, which had two characteristic broad peaks centered at 24.5° and 45°, and that commonly observed in nanosized carbons were in agreement with previously reported results.[23–25] The sharp lines superimposed on the broad carbon peaks were defined as unavoidable impurities (e.g., silica) in the as-received activated carbon.[24] For the PAni–AC composites, the XRD data showed characteristic broad PAni peaks and strong AC peaks. From Figure 4(b), it is clear that the small-angle oscillations were a result of the PAni data.[26] However, no new peaks appeared.

Electrical conductivity

In general, electrical conductivity may be taken as a function of the conjugation length of the polymer and of the amount of active dopant in the polymer, as the number of charge carriers depends on the extent of the dopant concentration, provided that other factors remain unchanged. A powder sample of 0.02 g was loaded and pressed into a pellet 1.2 cm in diameter and a pressure of 170 atm by a manual hydraulic press for 10 min. Then the electrical conductivity of the pellets was measured by a standard four-point probe method, connected to a Keithley voltmeter-constant current source system. The conductivity of the resultant PAni–AC composites at room temperature was 1.53 S/cm, which was higher than that of the pristine PAni ($\sim$ 0.34 S/cm), which was synthesized without activated carbon under the same conditions. The combination of PAni, with activated carbon, had effectively increased the conductivity almost to 350% for the PAni–AC composites. Each reported conductivity value is an average of five measurements.

Thermal analysis

Thermal stability testing was conducted using a thermogravimetric analyzer (TGA). Figure 5 shows a comparison of mass loss in PAni, PAni–AC, and AC upon heating in a nitrogen atmosphere. The as-received AC powders were comparatively more stable in the range between 0°C and 800°C. A very stable and small degradation took place in the range between 100°C and 800°C. Below 100°C, the speedy degradation was a result of a small amount of water or dedoping in the sample. After 100°C, subsequent mass loss was observed because of the impurities in the as-received AC powders. At higher temperatures (above 720°C), some partial degradation took place because of the desorption of surface carbon complexes. An unsteady mass decrease was found for PAni in the temperature range between 100°C and 210°C. A rapid change in mass, however, occurred in the range of 220°C–800°C and below 100°C. Below 100°C, degradation resulted
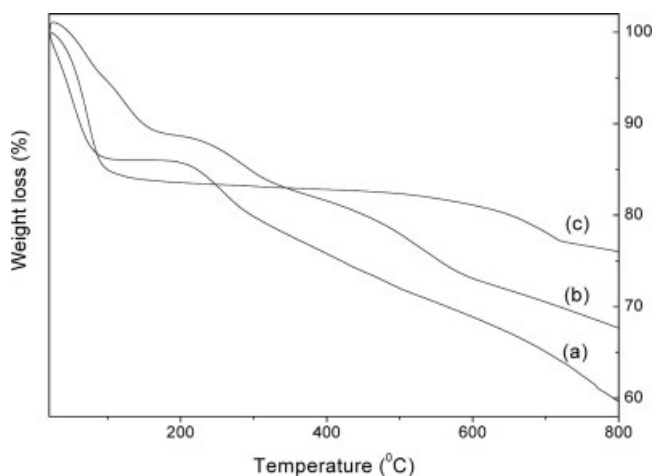

Figure 5 TGA data of (a) bulk PAni powders, (b) PAni–AC composites, and (c) as-received activated carbon measured under a nitrogen atmosphere at room temperature.

from a small amount of water or dedoping in the sample. The total mass loss up to 800°C was estimated to be about 24%, 32.5%, and 40.5% for AC, PAni–AC, and PAni, respectively. The trend in the degradation curve of the PAni–AC nanocomposites was similar to that of PAni; the degradation of PAni–AC was mainly controlled by PAni.

CONCLUSIONS

We have described a widely applicable route for the synthesis of nanometer composites of conducting polyaniline with activated carbon by the *in situ* chemical polymerization method. The characterization of the molecular structure of the PAni–AC composites indicated that no chemical reaction occurred between the AC and PAni and that the activated carbon was encapsulated in the cores of the growing polymer chains, resulting in the formation of a shell–core PAni–AC hybrid material. The conductivity through the PAni–AC was as large as 1.53 S/cm. This was much larger than the usual value of bulk PAni powders ($\sim$ 0.34 S/cm). The PAni–AC nanocomposites showed improved thermogravimetric stability compared to the PAni homopolymer. Finally, the improvements made in the various physical properties of the present PAni–AC composites are expected to enhance the potential applications of conducting PAni in molecular electronics and other fields. Moreover, the cost of the bulk amount of activated carbon is reasonable, which makes the route also economically viable in industrial mass production.

References
1. Foley, H. C. Microporous Mater 1995, 4, 407.
2. Kyotani, T. Carbon 2000, 38, 269.

3. Joo, S. H.; Choi, S. J.; Oh, L.; Kwak, J.; Liu, Z.; Terasaki, O.; Ryoo, R. Nature 2001, 412, 169.
4. Bansal, R. C.; Donnet, J. B.; Stoeckli, H. F. In Active Carbon; Marcel Dekker: New York, 1988.
5. Karim, M. R.; Lee, C. J.; Park, Y.-T.; Lee, M. S. Synth Met 2005, 151, 131.
6. Heeger, A. J. J Phys Chem B 2001, 105, 8475.
7. Hong, K. H.; Kang, T. J. J Appl Polym Sci 2006, 99, 1277.
8. Du, X. S.; Xiao, M.; Meng, Y. Z. Eur Polym J 2004, 40, 1489.
9. Lefrant, S.; Baibarac, M.; Baltog, I.; Mevellec, J. Y.; Godon, C.; Chauvet, O. Diam Relat Mater 2005, 14, 867.
10. Ko, J. M.; Song, R. Y.; Yu, H. J.; Yoon, J. W.; Min, B. G.; Kim, D. W. Electrochim Acta 2004, 50, 873.
11. Luo, K.; Guo, X.; Shi, N.; Sun, C. Synth Met 2005, 151, 293.
12. Cai, Z.; Martin, C. R. J Am Chem Soc 1989, 111, 4138.
13. Cai, Z.; Lei, J.; Liang, W.; Menon, V.; Martin, C. R. Chem Mater 1990, 3, 960.
14. Liang, W.; Martin, C. R. J Am Chem Soc 1991, 112, 9666.
15. Martin, C. R.; Parthasarathy, R.; Menon, V. Synth Met 1993, 55, 1165.
16. Shen, Y.; Wan, M. J Polym Sci Part A: Polym Chem 1997, 35, 3689.
17. Chaudhari, H. K.; Kelkar, D. S. Polym Int 1997, 42, 380.
18. Liu, H.; Hu, X. B.; Wang, J. Y.; Boughton, R. I. Macromolecules 2002, 35, 9414.
19. Gök, A.; Sari, B.; Talu, M. Synth Met 2004, 142, 41.
20. Chingombe, P.; Saha, B.; Wakeman, R. J. Carbon 2005, 43, 3132.
21. Luzny, W.; Banka, E. Macromolecules 2000, 33, 425.
22. Kan, J.; Zhang, H.; Jing, G. J Appl Polym Sci 2006, 99, 1848.
23. Punnoose, A.; Seehra, M. S.; Dunn, B. C.; Eyring, E. M. Energy Fuels 2002, 16, 182.
24. Park, E. D.; Lee, J. S. J Catal 2000, 193, 5.
25. Manivannan, A.; Chirila, M.; Giles, N. C.; Seehra, M. S. Carbon 1999, 37, 1741.
26. Maser, W. K.; Benito, A. M.; Callejas, M. A.; Seeger, T.; Martínez, M. T.; Schreiber, J.; Muszynski, J.; Chauvet, O.; Osváth, Z.; Koós, A. A.; Biró, L. P. Mater Sci Eng C 2003, 23, 87.