ВЫСОКОМОЛЕКУЛЯРНЫЕ СОЕДИНЕНИЯ, Серия Б, 2011, том 53, № 1, с. 126–129

УДК 541.64:537.3

CONDUCTIVE COMPOSITE OF POLYANILINE AND TUNGSTEN CARBIDE[1]

© 2011 г. Hui Huang, Zhongcheng Guo

Faculty of Metallurgical and Energy Engineering, Kunming University of Science
and Technology, Kunming 650093, P.R. China
e-mail: zhongcheng.guo@163.com

Received October 18, 2009
Revised Manuscript Received December 16, 2009

Abstract—Conductive polyaniline/tungsten carbide (PANI/TC) composite was synthesized via polymerization of the aniline monomer by $(NH_4)_2S_2O_8/H_2SO_4$ oxidant system in the presence of an aqueous suspension of TC. The structure, thermal stability and conductivity of PANI/TC composite were studied and the results were also compared with the pure PANI. The results showed that there was a strong interaction between the TC particles and PANI molecular chains. The crystalline structure of TC remained undisturbed upon with interaction with PANI chains. The thermal stability of PANI/TC composite was better than that of pure PANI. The direct current conductivity values of PANI/TC composite decreased slowly as the temperature increased from 25 to 165°C and PANI/TC composite exhibited significantly higher conductivity than the pure PANI.

INTRODUCTION

In recent years, the interest in the development of inorganic/organic composite has grown rapidly due to a wide range of the potential use of these materials [1–4]. Among these materials, one important class is that in which the organic part includes conducting polymers, such as polyaniline [5, 6]. Polyaniline (PANI) has been intensively studied recently due to its high conductivity, ease of preparation, good environment stability, and a large variety of applications especially in light-emitting and electronic devices and chemical sensors [7–9]. Besides, the transition-metal carbides, such as tungsten, have attracted much attention over the past few decades due to the potential for their applications, as gas sensors, photochemical devices, catalysts or catalyst supports [10]. Their catalytic properties have been found to be similar to those of precious metals such as platinum [11]. Tungsten carbide (TC) has been reported to possess a high catalytic activity towards the electro-oxidation of a series of organic molecules such as formaldehyde, formic acid, acetylene and ethylene [12]. Therefore, the synthesis of PANI/TC composite becomes a novel challenge. Moreover, the synthesis of PANI/TC composite has not been reported before. Herein, we look forward to synthesis PANI/TC composite by situ polymerization. The purpose of this paper is to give a preliminary account of our research on the use of PANI /TC composite as suitable anodic materials for hydrometallurgy.

EXPERIMENTAL

Materials

Aniline (Shanghai Chemical Works, China) was distilled under reduced pressure and stored in dark before use. TC (1.5 μm, Shandong, China) was used as such. All other reagents were of AR grade and used as received.

Synthesis of PANI/TC composite

A situ polymerization method for the synthesis of PANI/TC composite was carried out as follows: 4.7 ml aniline was injected into 50 ml of deionized water containing 0.9 g of TC particles under ultrasonic dispersion. After 1 h, 7.2 g $(NH_4)_2S_2O_8$ (dissolved in 25 ml of deionized water) was added to this solution with constant stirring. After 5 min, 60 ml of 1.25 M H_2SO_4 was added to the above solution with constant stirring. Polymerization was allowed to proceed for 6 h at 15°C. A solid product was obtained after filtration and washed with 1.25 M H_2SO_4 and deionized water to remove residual aniline and ammonium sulfate. Finally, it was dried at 60°C for 24 h under vacuum. For the synthesis of the pure PANI, the same procedure was repeated.

Characterization

Fourier Transform Infrared (FTIR) spectra was obtained using a prospect-IR (MIDAC) for which samples were palletized with KBr powder. X-ray diffraction (XRD) pattern was taken with a Shimadzu XD-3A at a 10°C/min scanning speed from 5 to 100°C.

---

[1] Статья печатается в представленном авторами виде.

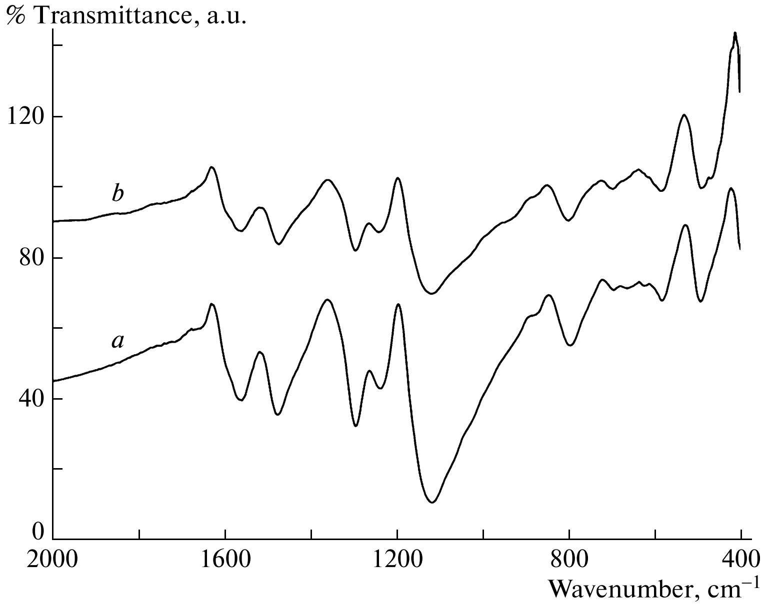

Fig. 1. FTIR spectra of the (*a*) pure PANI and (*b*) PANI/TC composite.

Thermal gravimetric analysis (TGA) was performed with a Shimadzu DT 40 up to 1000°C at a heating rate of 20°C/min in N_2. The direct current (DC) conductivity was measured using a four-probe technique from 25 to 165°C.

RESULTS AND DISCUSSION

The FTIR spectra for the pure PANI and PANI/TC composite are depicted in Fig. 1. The characteristic absorption peaks of the pure PANI at 1561, 1472, 1292, 1239, 1122 and 798 cm^{-1} correspond to C=C stretching mode of quinoid rings, the C=C stretching mode of the benzoid rings, the stretching mode of C–N, the plane bending vibration of C–H (modes of N=Q=N, Q=N$^+$H–B and B–N$^+$H–B) where Q and B represent the quinoid and benzoid rings and C–H bonding mode of aromatic rings [13]. The PANI/TC composite also shows the same characteristic peaks. However, the corresponding peaks of the pure PANI at 1561 cm^{-1} shifted to 1568 cm^{-1}, 1472 cm^{-1} shifted to 1475 cm^{-1}, 1292 cm^{-1} shifted to 1302 cm^{-1}, 1239 cm^{-1} shifted to 1242 cm^{-1}, 1122 cm^{-1} shifted to 1130 cm^{-1} and 798 cm^{-1} shifted to 804 cm^{-1} in PANI/TC composite. This shift may be ascribed to the formation of hydrogen bonding between TC and the N–H group of PANI on the surface of the TC particles. Such kind of interaction between PANI and ZnO particles is also observed by Paul et al. [13]. In addition, there are no characteristic peaks of TC particles in the FTIR spectra of composite, indicating that wrapping the TC particles with PANI in the composite. This result is consistent with the literature reported in [14].

The XRD patterns of the TC powder, PANI/TC composite and pure PANI are presented in Fig. 2. As shown in Fig. 2*a*, the typical XRD pattern of pure PANI shows two broad diffraction peaks centered at $2\theta = 19.5°$ and 25.1°, which can be ascribed to the periodicity parallel and perpendicular to the polymer chains, respectively [15]. The XRD pattern of the TC particles (Fig. 2*c*) presents the hexagonal structure with no extra reflections, and perfectly indexed to (001), (100), (101), (110), (002), (111), (200), (102) and (201) crystal plane of hexagonal TC (JCPDS Card No. 72-0097). Figure 2*b* shows the XRD pattern of PANI/TC composite which contains the characteristic peaks of PANI and TC. In addition, the intensities of broad diffraction peaks corresponding to PANI in the composite become weakened with introducing TC particles, which indicates that TC particles have an effect on the crystallinity of PANI. This indicates that the crystal structure of TC is not modified due to the presence of PANI. This result also shows the interaction between the TC particles and PANI molecular chains due to the adsorption of PANI molecular chains on the surface of the TC particles.

The results of TGA analysis for the TC powder, PANI/TC composite and pure PANI are shown in Fig. 3. It can be observed that the weight losses of the pure PANI and PANI/TC composite occurred in three steps; the range of the first step was from 30 to 120°C, the second from 250 to and around 400°C, and the third started from 550°C. In contrast, the weight loss of TC powder up to 1000°C was nil. The first weight loss was mainly contributed by the elimination of impurities, residual water and non-reacted monomers. The major decrease of mass occurred around 400°C, which is attributed to the degradation of poly-

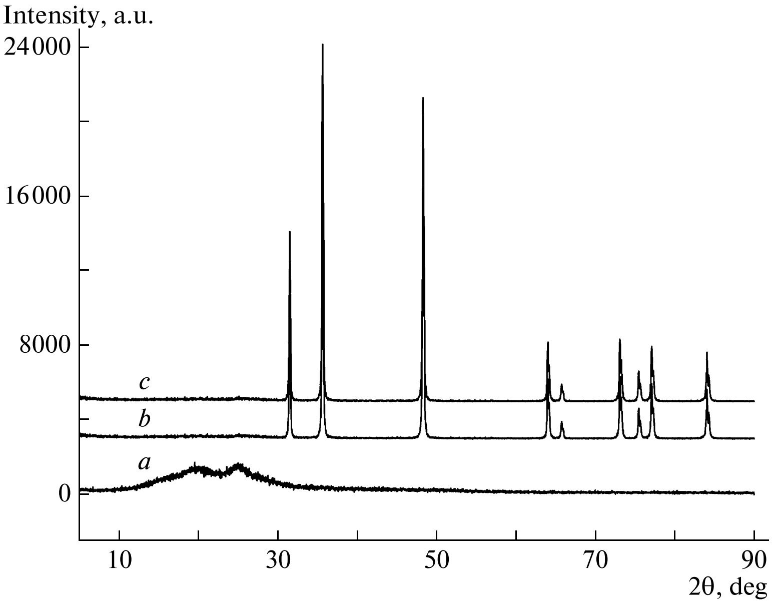

Fig. 2. XRD patterns of the (*a*) pure PANI, (*b*) PANI/TC composite and (*c*) TC powder.

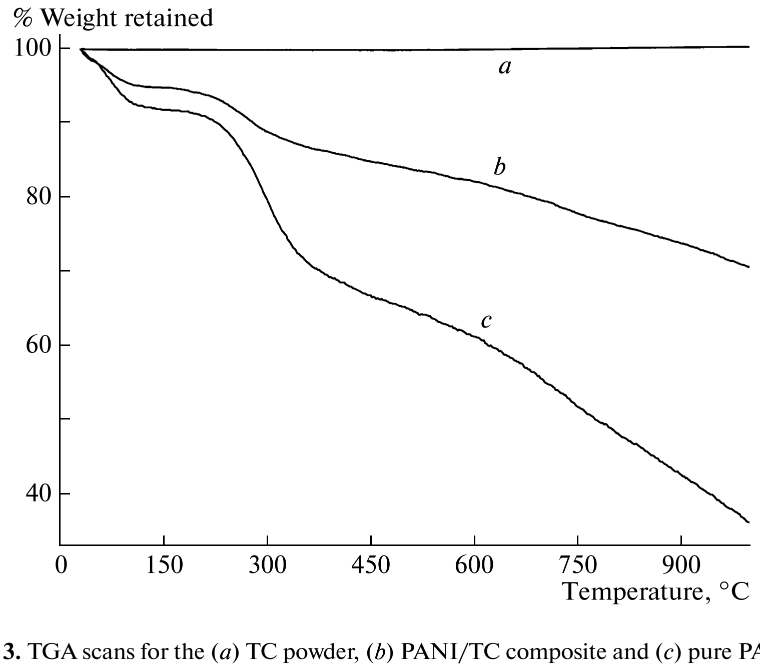

Fig. 3. TGA scans for the (*a*) TC powder, (*b*) PANI/TC composite and (*c*) pure PANI.

mer main chain. The thermal stability for the PANI/TC composite has been improved significantly as higher decomposition temperature (~440°C) is observed for the samples as compared to the pure PANI (~375°C) in the TGA profile. It might be related to the combination of TC crystalline in the polymer matrix, which yielded stronger binding force due to the interaction between TC particles and the lone pair electrons of N atom in the polymer backbone [16]. Thus, PANI/TC composite showed much-improved thermal stability characteristics compared to the PANI. Similar features were also observed in the case of composites of PANI or PPY with other metal oxides such as ZrO_2 [17] and Al_2O_3 [18].

The DC conductivity values of the pure PANI and PANI/TC composite were measured from 25 to 165°C and the results are shown in Fig. 4. The DC conductivity values of PANI/TC decreased slowly as the temperature was increased while that of the pure PANI decreased more rapidly. This behavior is attributed to the effect of TC on the PANI macromolecule. The pres-

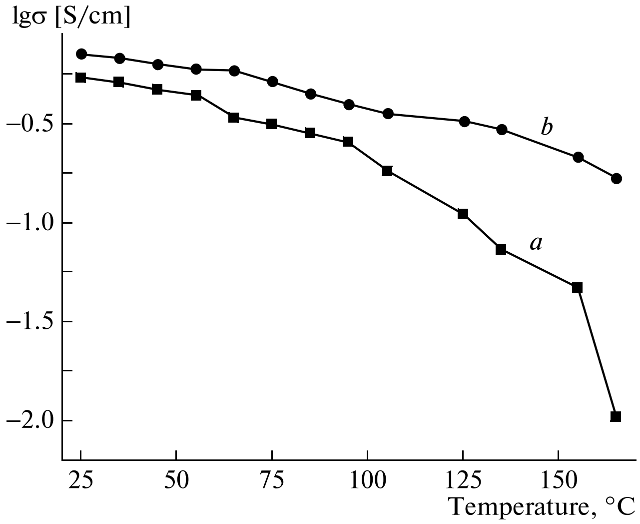

Fig. 4. The DC conductivity values of the (*a*) pure PANI and (*b*) PANI/TC composite.

ence of TC improved the thermal stability and conductivity of PANI/TC composite.

CONCLUSIONS

The PANI/TC composite has been obtained by the polymerization of aniline monomer in presence of suspension of TC in aqueous acidic medium using $(NH_4)_2S_2O_8$ as the oxidant. The analysis indicates that there is a strong interaction between the TC particles and PANI molecular chains. The thermal stability of PANI/TC composite is higher than that of the pure PANI. The DC conductivity value of PANI/TC composite is 7.09×10^{-1} S cm^{-1} at 25°C and this value decreased slowly as the temperature increased from 25 to 165°C. PANI/TC composite exhibited significantly higher conductivity than the pure PANI.

Projects supported by National Nature Science Foundation (50974065) and National Excellent Doctoral Dissertation (20050053) of PR China.

REFERENCES

1. M. Skunik, M. Chojak, I. A. Rutkowska et al., Electrochim. Acta. **53**, 3862 (2008).
2. J. X. Huang, J. A. Moore, J. H. Acquaye et al., Macromolecules **38**, 317 (2005).
3. H. F. Guo, H. Zhu, H. Y. Lin et al., Mater. Lett. **62**, 2196 (2008).
4. H. Sertchook and D. Avnir, Chem. Mater. **15**, 1690 (2003).
5. R. K. Naqarale, G. S. Gohil, S. K.Vinnod et al., J. Colloid Interface Sci. **287**, 198 (2005).
6. T. K. Sarma and A. Chattopadhyay, Langmuir **20**, 4733 (2004).
7. G. Cui, J. S. Lee, and S. J. Kim, Analyst. **123**, 1855 (1998).
8. A. A. Karyakin, L.V. Lukachora, and E. E. Karyakina, Anal. Commun. **36**, 153 (1999).
9. M. M. Ayad, N. Salahuddin, and M. A. Sheneshin, Synth. Met. **132**, 185 (2003).
10. S. J. Thomson and G. Webb, *Heterogeneous Catalysis* (Oliver and Boyd Press, London, 1968).
11. J. B. Joo, J. S. Kim, and P. Kim, Mater. Lett. **62**, 3497 (2008).
12. D. R. McIntyre, G. T. Burstein, and A. Vossen, J. Power Sources **107**, 67 (2002).
13. G. K. Paul, A. Bhaumik, and A. S.Patra, Mater. Chem. Phys. **106**, 360 (2007).
14. J. Jiang, L. H. Ai, D. B. Qin et al., Synth. Met. **159**, 695 (2009).
15. J. P. Pouget, M. E. Jozefowicz, A. J. Epstein et al., Macromolecules **24**, 779 (1991).
16. J. G. Deng, X. B. Ding, and W. C. Zhang, Polymer **43**, 2179 (2002).
17. S. S. Ray and M. Biswas, Synth. Met. **108**, 231 (2000).
18. A. Maity and M. Biswas, J. Appl. Polym. Sci. **94**, 803 (2004).