Preparation of Core–Shell Structured Alumina–Polyaniline Particles and Their Application for Corrosion Protection

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ABSTRACT: Polyaniline (PANI) was synthesized by chemical oxidative polymerization of aniline (ANI) in the presence of alumina (Al_2O_3) particles. The polymerization of ANI occurred preferentially on the surfaces of the particles, resulting core–shell structured alumina–polyaniline (Al_2O_3-PANI) particles. Morphology examination showed that with decreasing of the weight ratio of Al_2O_3/ANI in the reactants, the thickness of the PANI layer increased and changed from an even surface morphology to a particulate morphology. UV–vis and Fourier transformed infrared (FTIR) spectra indicated that there is no chemical interaction between the PANI layer and the Al_2O_3 surfaces. The PANI layer adhered well to the particles and can be used as anticorrosive fillers for polymer coatings. Enhanced corrosion protection performance was achieved for the emeraldine base (EB) form of PANI deposited Al_2O_3 particles (Al_2O_3-EB) filled epoxy coating on carbon steel in 3.0 wt % aqueous NaCl solution. The particles demonstrate both excellent corrosion protection performance and lower cost, which will be of great importance in practical applications. © 2006 Wiley Periodicals, Inc. J Appl Polym Sci 101: 4372–4377, 2006

Key words: polyaniline; alumina; composites; corrosion protection

INTRODUCTION

Polyaniline (PANI) has received considerable attention and become one of the most extensively studied intrinsically conducting polymers because of its easy synthesis, tunable conductivity, controllable chemical/physical properties, good environmental stability, and numerous potential applications, such as sensors,[1] corrosion protection,[2] electromagnetic interference shielding,[3] and so on. The chemical oxidative polymerization of PANI is more feasible for production of PANI on a large scale in comparison with the electrochemical oxidative polymerization.[4] However, the great potential of the as-prepared PANI is masked by its serious disadvantages of intractability, i.e., insolubility and infusibility, as well as poor mechanical property. To address this, many attempts, such as structural modification of PANI by ring or *N*-substitution, doping PANI with functionalized protonic acids, blend of PANI with conventional polymers,[5–7] etc., have been made to improve the processability of PANI. Among these attempts, preparation of PANI composites or blends is considered one of the most promising ways from an industrial point of view in that both the electrical and redox properties of the PANI guest and the mechanical properties of the insulating host matrix is combined in the composites or blends.[8]

Tremendous PANI-based composites or blends have been prepared with various methods and suggested for a variety of applications as reviewed by Anand et al.[8] in 1998. Besides the common polymer/PANI composites, the preparation, as well as applications, of more and more novel PANI-based composites or blends was reported in recent years. For example, PANI/carbon nanotube composites, mostly prepared by in situ polymerization,[9–11] exhibited greatly improved conductivity, thermal stability, and mechanical properties in comparison with the pure PANI, and can be used in electrorheological application,[12] sensors,[13] organic electronics,[14] actuators,[15] and capacitors.[16] Synthesis of PANI composites with inorganic materials like CeO_2,[17] TiO_2,[18] nano SiO_2,[19] V_2O_5,[20] and metals like Pt[21] and Au[22] were also intensively studied, and the composites can be used as high-conducting materials, sensors, catalysts, microwave absorbing materials, and so on.

Corrosion of metals, especially iron-based materials, has long been an important problem, which brings tremendous economic losses in excess of 100 billion dollars annually world wide.[23] Covering the metal surfaces with polymeric or polymers-based coatings were considered one of the most facile and popular

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methods for corrosion protection of metallic materials.[24] Generally, the corrosion protection mechanism can be either a physicochemical one (barrier), or an electrochemical one (inhibition or cathodic protection), or both of them and others,[25] according to the fillers used in the coatings. Among these, the inhibitive metal oxides, such as chromate or molybdate, are deemed as effective corrosion inhibitors. However, their potential environmental and health concerns have necessitated the need to identify environmental friendly candidates with similar effectiveness.[26] PANI is one of the promising candidates and has been extensively studied in both the doped and the dedoped states since the earliest work by DeBerry.[27] Aside from the improving of the protective performance, to low the prices of the materials is also an important issue, especially from an industrial point of view. Therefore, PANI-coated alumina (Al_2O_3) composite particles were prepared by in situ polymerization in this study and suggested for metallic corrosion protection. UV–vis spectroscopy, Fourier transformed infrared (FTIR) spectroscopy, scanning electronic microscopy (SEM), four-probe conductivity measurement, and corrosion protection potential measurement were employed to characterize the structure and properties of the composite particles and their epoxy-based composite coatings.

EXPERIMENTAL

Materials

Aniline (ANI), ammonium persulfate (APS), dimethylformamide (DMF), and methyl isobutyl ketone (MIBK) were analytical grade from Xi'an Chemical Reagent Factory. ANI was doubly distilled in the presence of zinc (Zn) powder and stored in dark. The Al_2O_3 powders were purchased from Nanjing High Technology Nano Co. The bisphenol-A epoxy resin (epoxy value: 0.51 mol/100 g) and the aromatic curing agent (T-31) were from Wuxi Resin Factory. All other reagents were used as received.

In situ preparation of Al_2O_3-PANI composite particles

Typically, 0.93 g of ANI was first dissolved in 100 mL of hydrochloride acid (1 mol/dm^3) and the solution was brought to 20°C. Al_2O_3 powders were then added in the solution and stirred vigorously for 20 min (Table I). 2.28 g of APS in 70 mL hydrochloride acid was added dropwise into the milk white colored dispersion to initiate the polymerization and finished in about 30 min. The reaction was completed 5 h after the dispersion turned green. The product was collected on a Büchner funnel, and the cake was washed several times with deionized water until the filtrate became colorless. Part of the cake was dried at ambient temperature to obtain the conductive PANI-coated Al_2O_3 powder, which is denoted as Al_2O_3-PANI/HCl.The rest of the cake was further treated with 5.0 wt % ammonia water for 0.5 h and then washed to neutrality with deionized water. After dried in vacuum (40°C), the nonconductive emeraldine base (EB) form of PANI-coated Al_2O_3 powders were obtained and is denoted as Al_2O_3-EB.

TABLE I
Ratio of Reactant and Conductivity of the Composite Particles

Samples	Weight ratio of Al_2O_3/ANI	Conductivity (S/cm)
A	5	0.17
B	10	0.05
C	20	0.02
D	40	–
E	60	–
F	80	–

Preparation of the Al_2O_3-EB containing coatings

20 g of the Al_2O_3-EB powders and 10 g of the epoxy resin were added to 30 g of MIBK and mechanically mixed for 30 min. The blue colored dispersion obtained was then thoroughly mixed with 4 g of T-31 and brushed on the surface of prepolished carbon steel plates (100 mm × 20 mm × 1 mm) to form coatings after cured.

Characterization

UV–vis spectra were recorded between 270 and 1000 nm using quartz cuvettes on a U-2001UV/Vis spectrophotometer (Hitachi). Solutions for subsequent spectroscopic studies were prepared by dissolving 0.2 g of Al_2O_3-EB powders in 20 mL DMF, which also served as the reference. FTIR spectra were recorded on a spectrophotometer Spectrum GX (PerkinElmer). Solid specimens were prepared by mixing their powders with KBr and then pressed into round pellets. Electrical conductivity measurements of the Al_2O_3-PANI/HCl powders were performed on pressed pellets employing the standard four-probe technique with a SZ85 digital multimeter (Suzhou Telecommunication Factory, China). SEM images of the composite particles were obtained using a JSM-6460 scanning electron microscope (JEOL). Corrosion potential of the coated carbon steel in 3.0 wt % aqueous NaCl solution was measured using a conventional three-electrode electrochemical cell, which contains a platinum counter electrode and a saturated Ag/AgCl reference electrode on a DJS-292 potentiostat (Leici Instrument Factory, Shanghai, China) at room temperature.

RESULTS AND DISCUSSION

Polymerization

With dropwise addition of the APS solution into the Al_2O_3 powders containing dispersions, the color of all the dispersions changed from the initial milk white to green, then dark green, indicating the formation of PANI. With increasing of the weight ratio of Al_2O_3/ANI from 5 to 80, the time needed for the color change from milk white to green increased from ca. 5 min to ca. 70 min. Even at weight ratio of Al_2O_3/ANI of 80, all the Al_2O_3 powders were coated with PANI, indicating that ANI was preferentially polymerized at the surfaces of the powders [Fig. 1(a)]. This phenomena has been reported previously[28,29] on various substrates. The initially formed oligoaniline cation radicals would be adsorbed on the insulating surfaces, as well as interstices, and the coupling reaction and further polymerization would begin from these nucleation sites, instead of from the bulk system, leading to the preferentially formed adherent PANI layer on the surfaces. If more ANI is presented, the secondary nucleation would occur on the produced PANI layers, resulting then thick layers with particulate appearances (Fig. 1).[25]

Morphology

Morphology examination showed that, at higher weight ratios of Al_2O_3/ANI, the round-shaped Al_2O_3 particles with few PANI adhered are observed [Fig. 1(a)], indicating also the preferentially polymerization of ANI on the surfaces of the Al_2O_3 particles, while at lower weight ratios, Al_2O_3 particles with thicker PANI layer and adhered PANI particles are observed [Fig. 1(d–f)], which is resulted from the secondary nucleation effect of the primary formed PANI layers as mentioned earlier. No peel off the PANI layers was observed for all the samples, indicating the good adhesion of the PANI layer on the Al_2O_3 particles, which is of great importance in applications of the composites particles. The exact thickness of the EB layer was hard to measure due to the distributed diameters of the coated and uncoated particles, and can be only roughly judged by the SEM images (Fig. 1). The formation evolution of the PANI-coated Al_2O_3 particles is, then, schematically shown in Figure 2, with different weight ratios of Al_2O_3/ANI.

Conductivity

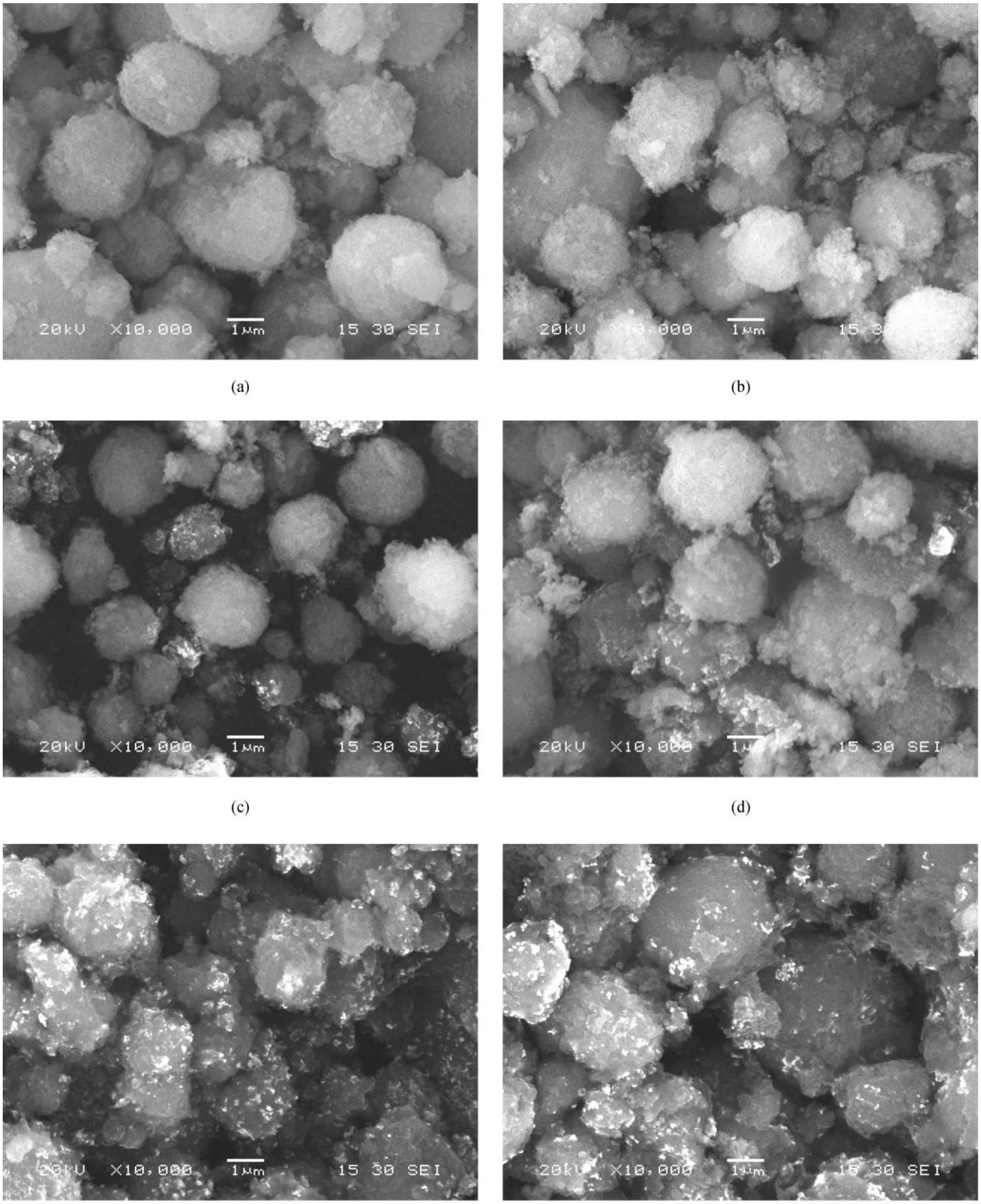
Only the conductivities of the Al_2O_3-PANI/HCl samples prepared with weight ratio of Al_2O_3/ANI less than 20 were determined (Table I). The lower conductivities, as compared with the bulk PANI/HCl sample, were resulted from the few conductive paths formed in the testing pellets. For the samples prepared with higher weight ratios, the pellets used for four-point probe conductivity measurement cannot be obtained owing to the thin PANI layer of the composite particles, which can be roughly judged from the SEM images (Fig. 1), and no conductivity is measured then. All the Al_2O_3-PANI composite particles showed higher yield of ~80% than that of the pure PANI prepared under the similar conditions, which was ~75%, owing to the beneficial effect of the alumina particles, and other insulating particles for initiating the polymerization as mentioned in literature.[24,25]

Spectroscopy

The EB layers on the surfaces of the Al_2O_3 particles would be dissolved by put the composite particles in DMF, and the UV–vis spectra recorded on the solutions were shown in Figure 3. There are two absorption bands appeared in the spectra of the samples. The first absorption band with maximum at ca.320 nm is often assigned to the π–π^* transition in the benzenoid structure and the second band at ca.630 nm is ascribed to exciton formation in the quinonoid rings.[30] The intensities of the bands were associated with the concentration of the EB solutions. The higher the concentration, the higher is the intensity of the bands. Similar results were obtained from the FTIR analysis (Fig. 4). With decreasing of the weight ratio of Al_2O_3/ANI, the intensities of the characteristic bands for EB molecules grow stronger. The bands of 1593 and 1506 cm^{-1} are corresponding to the quinoid and benzenoid ring-stretching modes of EB molecules. The bands at 1510, 1580, and 1608 cm^{-1} are assignable to the aromatic C═C stretch; and an 820 cm^{-1} band to an aromatic C—H out-of-plane bending, while the bands fell in the range of 400–600 cm^{-1} are related with the Al_2O_3 particles. Note that there is no significant interaction between the PANI molecules and the Al_2O_3 particles as revealed from the FTIR results; it is assumed that the good adhesion of the EB layer on the Al_2O_3 particles was of physicochemical nature.

Corrosion protection

For preparing a PANI protective coating or a PANI containing protective coating on metal surfaces, the electrodeposition and the solution cast approaches were widely employed.[31] The shortcoming of the electrodeposition approach is its scalability. For instance, some large objects like bridges components cannot be coated in this approach, while for the solution cast approach, the cost of the as-prepared coating is high owing to the extremely low solubility of PANI in few organic solvents. Thereby, the composite coating prepared by blending the PANI with the polymer matrix was considered one of the feasible ways for metallic corrosion protection, especially from the industrial



(a) (b) (c) (d) (e) (f)

Figure 1 SEM images of the Al_2O_3-PANI composite particles prepared with weight ratios of Al_2O_3/ANI of (a) 80, (b) 60, (c) 40, (d) 20, (e) 10, and (f) 5.

point of view, and excellent performance has been obtained.[32,33] In our case, epoxy coating containing the Al_2O_3-EB particles performed very well in chloride ions containing neutral solution. Corrosion potential of the composite coating coated coupons show no significant decrease during the 3 months of measure-

Figure 2 Schematic representation of the formation of Al_2O_3-PANI particles with decreasing of the weight ratio of Al_2O_3/ANI in the reactants.

ment and remains in the positive potential ranges, which is resulted basically from good barrier effect of the core–shell structured Al_2O_3-EB particles, while for the controlled coupons, which were coated with pure epoxy without use of the composite particles, red/brown corrosion product was observed only after 2 weeks and the coupons were greatly corroded after 2 months, corroborating also the good barrier effect of the composite particles. After 3 month's immersion, the carbon steel surfaces render the sliver-white color after peeling off the composite particles filled coating, indicating the surfaces were greatly passivated[34]; while for the control coupons, the steel was seriously corroded after peeling off the epoxy coating. On the basis of the corrosion protection mechanisms put forward by Fahlman et al.[34] and Schauer et al.[35] for EB, it is considered that the greatly improved corrosion protection performance of the composite coating was derived from both the good barrier effect of the composite coating and the passivation capability of EB. First, the diffusion of the corrosive ions from the immersing solution to the metal surfaces was effectively hindered by the composite particles filled in the epoxy coating, which is evidenced by the remaining positive corrosion potentials of the coupons after 3 months' immersion; Second, the metal surfaces were greatly passivated as suggested by the surface color, which will render more effective corrosion protection performance. The cost of the coating can be greatly lowered owing to the employing of the alumina particles in comparison with the previous studies,[32,33] which will be of great importance in practical applications of the materials.

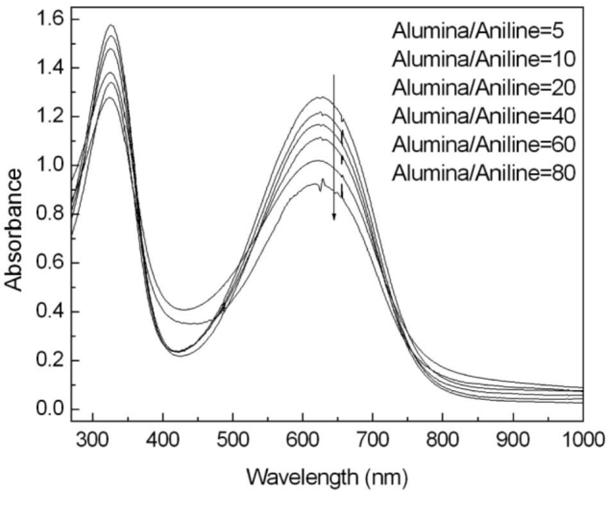


Figure 3 UV–vis spectra of the Al_2O_3-EB particles.

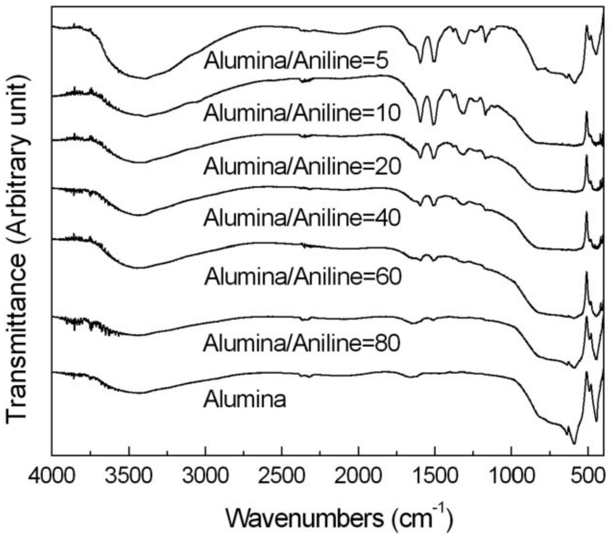


Figure 4 FTIR spectra of the Al_2O_3-EB particles.

CONCLUSIONS

PANI was preferentially formed on the surfaces of the Al_2O_3 particles during chemical oxidative polymerization of ANI in the presence of the particles, resulting core–shell structured composite particles. The thickness of the PANI layer increased with decreasing of the weight ratio of Al_2O_3/ANI in the reactants, and changed from an even surface morphology to a particulate morphology. Although no chemical interaction was observed by spectroscopic analysis, the PANI layer adhered well to the surfaces of the particles. The corrosion protection performance of the epoxy coating was greatly enhanced by use of the Al_2O_3-EB particles as fillers, and the cost was lowered by using of the alumina particles, which is of great importance in practical applications.

References

1. Persaud, K. C. Mater Today 2005, 8, 38.
2. Wessling, B. Synth Met 1998, 93, 143.
3. Koul, S.; Chandra, R.; Dhawan, S. K. Polymer 2000, 41, 9305.
4. Öesterholm, J. E.; Cao, Y.; Klavetter, F.; Smith, P. Polymer 1994, 35, 2902.
5. Namazi, H.; Kabiri, R.; Entezami, A. Eur Polym J 2002, 38, 771.
6. Leyva, M. E.; Barra, G. M. O.; Gorelova, M. M.; Soares, B. G.; Sens, M. J Appl Polym Sci 2001, 80, 626.
7. Angappane, S.; Rajeev Kini, N.; Natarajan, T. S.; Rangarajan, G.; Wessling, B. Thin Solid Films 2002, 417, 202.
8. Anand, J.; Palaniappan, S.; Sathyanarayana, D. N. Prog Polym Sci 1998, 23, 993.

9. Yu, Y.; Che, B.; Si, Z.; Li, L.; Chen, W.; Xue, G. Synth Met 2005, 150, 271.
10. Zhang, X.; Zhang, J.; Liu, Z. Appl Phys A 2005, 80, 1813.
11. Long, Y.; Chen, Z.; Zhang, X.; Zhang, J; Liu, Z. Appl Phys Lett 2004, 85, 1796.
12. Choi, H. J.; Park, S. J.; Kim, S. T.; Jhon, M. S. Diamond Relat Mater 2005, 14, 766.
13. Guo, M.; Chen, J.; Li, J; Tao, B.; Yao, S. Anal Chim Acta 2005, 532, 71.
14. Ramamurthy, P. C.; Harrell, W. R.; Gregory, R. V.; Sadanadan, B.; Rao, A. M. J Electrochem Soc 2004, 151, G502.
15. Tahhan, M.; Truong, V. T.; Spinks, G. M.; Wallace, G. G.; Smart Mater Struct 2003, 12, 626.
16. Zhou, Y. K.; He, B. L.; Zhou, W. J.; Huang, J.; Li, X. H; Wu, B.; Li, H. L. Electrochim Acta 2004, 49, 257.
17. He, Y. Mater Chem Phys 2005, 92, 134.
18. Xia, H.; Wang, Q. Chem Mater 2002, 14, 2158.
19. Xia, H.; Wang, Q. J Appl Polym Sci 2003, 87, 1811.
20. Posudievsky, O. Y.; Kurys, Y. I.; Pokhodenko, V. D. Synth Met 2004, 144, 107.
21. Kinyanjui, J. M.; Harris-Burr, R.; Wagner, J. G.; Wijeratne, N .R.; Hatchett, D. W. Macromolecules 2004, 37, 8745.
22. Sarma, T. K.; Chattopadhyay, A. J Phys Chem A 2004, 108, 7837.
23. Ahmad, N.; MacDiarmid, A. G. Synth Met 1996, 78, 103.
24. Bierwagen, G. P. Prog Org Coat 1996, 28, 43.
25. Herrasti, P.; Ocón, P. Appl Surf Sci 2001, 172, 276.
26. Cohen, S. M. Corrosion 1995, 51, 71.
27. DeBerry, D. W. J Electrochem Soc 1985, 132, 1022.
28. Dhawan, S. K.; Kumar, D.; Ram, M. K.; Chandra, S.; Trivedi, D. C. Sens Actuators B 1997, 40, 99.
29. Sapurina, I.; Riede, A.; Stejskal, J. Synth Met 2001, 123, 503.
30. Wan, M. X. Synth Met 1989, 31, 51.
31. Spinks, G. M.; Dominis, A. J.; Wallace, G. G.; Tallman, D. E. J Solid State Electrochem 2002, 6, 85.
32. Rout, T. K.; Jha, G.; Singh, A. K.; Bandyopadhyay, N.; Mohanty, O. N. Surf Coat Technol 2003, 167, 16.
33. Laco, J. I. I.; Villota, F. C.; Mestres, F. L. Prog Org Coat 2005, 52, 151.
34. Fahlman, M.; Jasty, S.; Epstein, A. J. Synth Met 1997, 85, 1323.
35. Schauer, T.; Joos, A.; Dulog, L.; Eisenbach, C. D. Prog Org Coat 1998, 33, 20.