

Synthesis of Iron-Polyaniline Nanocomposites and the Effect of Emulsifier

Sajjad Sedaghat

Islamic Azad University Malard Branch, Iran

Abstract: The objective of this study is to evaluate the emulsifier role in the synthesis of Iron - Polyaniline nanocomposite by in-situ oxidative polymerization of aniline and reduction of Iron ions into Fe nanoparticles. The polymerization of aniline was carried out in the presence of FeCl_3 as oxidizing agent. During the reaction aniline monomers undergo oxidation and form polyaniline (PANI) whereas the reduction of Fe^{+3} ions result the formation of Fe nanoparticles. Nano-sized Fe particles were prepared by controlled reduction of Iron precursor in presence of micro emulsion medium of two emulsifiers such as sodium dodecyl sulphate (SDS) and the anionic surfactant, dioctyl sullosuccinate (AOT) and in absence of emulsifier. Micro emulsion solutions act as both emulsifier and dopant to obtain stable nanocomposite. In this method of synthesis, the effect of emulsifier in the size of particles is investigated. PANI-SDS-Fe and PANI-AOT -Fe nanocomposites are characterized by FT-IR spectroscopy and scanning microelectronic microscopy (SEM).

Key words: Polyaniline • Nanocomposite • Fe Nanoparticles • Micro emulsion • Emulsifier

INTRODUCTION

Conducting polymer nanostructures combine the advantages of organic conductors and low dimensional systems and therefore should yield many interesting physicochemical properties and useful applications. During the last decade, considerable attention has been paid to the synthesis and evaluation of clay/polymer nanocomposites via the intercalation polymerization of special monomers such as aniline, pyrrole, thiophene or *N*-vinylcarbazole [1-3]. Among these synthetic materials,

Polyaniline (PANI) nanocomposites have attracted special attention, because by the intercalation polymerization, it is possible to obtain structure with a more ordered chain and better properties than those of bulk ones [4]. Nanomaterials, which are materials with structural units on a nanometer scale in at least one direction, are the fastest growing area in materials science and engineering. Material properties become different on the nanoscale: for example, the theoretical strength of materials can be reached or quantum effects may appear. Nanoparticles technology is of substantial interest for a large number of practical applications. There has been recent surge and interest in the synthesis and application of electroactive polymers with incorporated metal particles, practically in nanoscale [5-13]. Lamellar nanocomposites consisting of layered inorganic

compounds and conducting polymers display novel properties which result from the molecular level interaction of two dissimilar chemical components.

Most studies in the field were devoted to the preparation of polyaniline (PANI)/noble metal composites and ease of preparation. Conducting polymers find applications in fields like: sensors, electrocatalysts, microelectronics, electromagnetic shielding, rechargeable batteries and controlling systems [13-16]. Nanomaterials with a high surface area and porosities are known to show better performance electrode as materials for direct methanol fuel cell applications. The electroactive polymers may be particularly suitable as a matrix for hosting the metallic particles for catalytic applications, since these media provide an effective route for the flow of electronic charges. The nanofibilar morphology, significantly improves the performance of polyaniline in many conventional applications involving polymer interactions with its environment. The high conjugated polymeric structure of polyaniline produces new nanoscale phenomena that are not accessible with current in organic systems [17].

In-situ synthesis was achieved either through reaction of metal ions that are dispersed in polymer matrices or polymerization of a solution containing monomer and the metal nanoparticles. In-situ synthesis of Platinum loaded polyaniline nanowire in poly

(styrene sulfonic acid) is prepared using interfacial polymerization technique. Polyaniline as a conducting polymer is a desirable system to support the metal nanoparticles such as platinum, which can be dispersed on the dense surface of these supporting materials [18].

Recently, noble metal nanostructures have attracted substantial interest due to their unique properties that arise from quantum confinement effects and interplay between surface and bulk effects. In particular, size and shape provide an effective strategy for tuning their physical and chemical properties, including luminescence, conductivity, and catalytic activity. Scientists have achieved excellent control over particle size for several spherical metal and semiconductor compositions, which has led to their use as probes for biological diagnostics, LED and Raman spectroscopy-enhancing materials. Yet the challenge of synthetically controlling particle shape remains open. Although some physical deposition, thermal, electrochemical and photochemical methods have been developed for making variously shaped semiconductor and metal nanoparticles, they usually yield relatively small quantities of the desired particle shape and are not eco-friendly [19].

A micro-emulsion is a transparent liquid, thermodynamically stable, which contains water, a tenside and also some oil. When these are mixed to a certain concentration a micro-emulsion will result, forming nano-size droplets too small to be seen by the human eye. We are replacing the water with a metallic salt that does form nano particles after reduction and these are the ones that perform the catalytic activity. The droplets formed are called micells - they may be employed as "micro reactors" to obtain active particles in the 2 to 3 nm size range, of more even quality and in a better controlled manner than we could before.

One of the major benefits of micro-emulsions is that they, unlike other conventional dispersion formulations, are thermodynamically stable. In this respect they are somewhat similar to soluble concentrate (SL) formulations. However, micro-emulsions are often only stable within limited temperature ranges. For this reason particular attention should be given to the directions for formulation storage. Given that they form emulsions or dilute micro-emulsions on dilution into water, micro-emulsions are treated in a similar fashion to emulsifiable concentrate (EC) formulations, with some additional modifications to take account potential use problems relating to storage and use at high and low temperatures

It has been found that the novel materials exhibit improved mechanical, electrical and thermal properties due

to the synergistic effect of the organic and inorganic components. Micro emulsion processing technique has been employed to fabricate various nanocomposite materials [20,21]. At this paper we report a simple and green synthetic approach for production of Fe nanoparticles using In-situ oxidative polymerization of aniline and reduction of Fe^{+3} ions at room temperature. We also introduce a simple in-situ synthesis of Fe-polyaniline nanocomposite by utilizing the micro emulsion processing technique as an environmentally benign technique. The effect of two emulsifier (AOT and SDS) on the particle size and shape is reported in this paper.

$$E^0 \text{ of } \text{Fe}^{+3}/\text{Fe}^0 = 0.770 \text{ V}$$

$$E^0 \text{ of } \text{Pt}^{+4}/\text{Pt}^0 = 0.735 \text{ V}$$

Experimental

Materials: Aniline (99%, monomer), FeCl_3 , Sodium dodecyl sulphate (SDS) and (AOT) were purchased from Merck. All chemicals, solvents and reagents were used as received, except for aniline, which was double distilled before use.

Synthesis of PANI-SDS-Fe Nanocomposite: The synthesis reaction was performed in 100 mL of 0.1M SDS solution, in which the aniline monomers was added drop-wise and stirred for one hour to yield homogeneous transparent solution. 50 mL of a solution containing 0.05M FeCl_3 was added drop-wise to the previous solution to form nanocomposite. Nano-sized Fe particles were prepared by controlled reduction of Iron precursor in micro emulsion medium, stabilized with the surfactant (SDS). Micro emulsion solution acts as both emulsifier and dopant to obtain stable nanocomposite.

Synthesis of PANI-AOT-Fe Nanocomposite: The synthesis reaction is carried out as discussed in section 2.2 except that instead of SDS, AOT is used as emulsifier.

Characterization: A Perkin-Elmer model Spectrum GX Fourier Transform Infrared (FTIR) spectrophotometer was used to determine the infrared (IR) absorption spectra, in the wavelength range $4000\text{-}370 \text{ cm}^{-1}$. The samples were dispersed in potassium bromide (KBr) and compressed into pellets. The SEM used is XL30 model from Philips.

FTIR Spectroscopy of Nanocomposites: The FTIR spectra for the PANI-SDS-Fe nanocomposite is depicted in Fig. 1, The appearance of characteristic absorption band

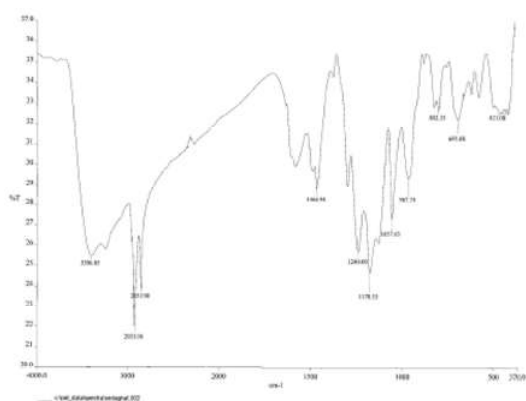
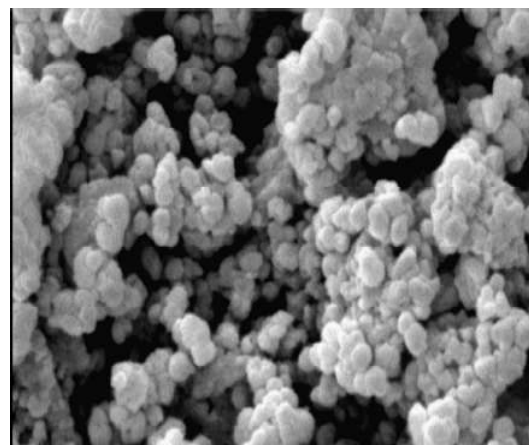


Fig. 1: Missing

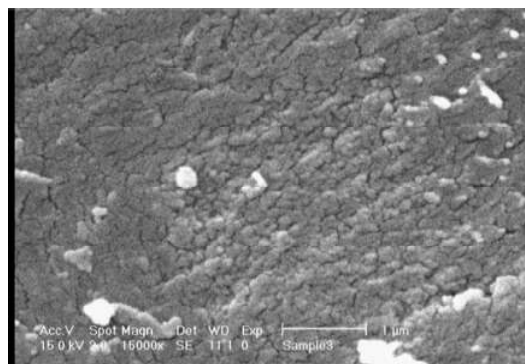


Fig. 2: FTIR spectra of PANI-SDS-Fe nanocomposite

around 1250 cm^{-1} , which is related to the C-N stretching in bipolaron structure, can be observed for the sample. These results indicate that polymer is highly doped and existed in conducting emeraldine salt form (ES). The broad absorption band ranges from 3000 to 3340 cm^{-1} , which is attributed to the protonation of amine functional group at polymer backbone and is observed for the highly doped



AOT



SDS

Fig. 3: SEM micrographs of the surface of pure polyaniline (a) and PANI-SDS-Fe (b).

PANI emeraldine salt. The absorption band near 2920 cm^{-1} is assigned to aliphatic C-H stretching of the polymer. The appearance of the absorption peak in the spectra is beyond our expectation as it indicates the existence of aliphatic alkyl functional group in the polymers, although none of such substances has been introduced in the system during the polymerization process. Hence, the appearance of the absorption peak may be corresponding to the long alkyl tail of the surfactant. It is well known that the surfactants can become the secondary dopants and absorbed as an outer layer surrounding the PANI particles.

Morphology: The SEM images of the inner layer surface morphology of the PANI-SDS-Fe and PANI-AOT-Fe nanocomposites are shown in Fig. 2. As can be seen, the polyaniline layer of the PANI-SDS-Fe has a porous

structure with different pore diameters, while on the outer surface of the composite film there are a lot of small pores. The porous structures of the inner and outer layers are asymmetrical. From Fig. 3b which shows the PANI-SDS-Fe nanocomposite, we find that the Fe particles disperse uniformly in the polyaniline layer. Fe particles are dispersed on the framework of the porous structure, and the holes of the polyaniline layer.

RESULTS AND DISCUSSION

Iron-Polyaniline nanocomposite has been synthesized employing the micro emulsion processing technique. The appearance of characteristic absorption bands around 310 and 425 in the UV-Vis spectra confirms the formation of conducting emeraldine salt (ES). The lower intensity polaron absorption for PANI-SDS-Fe Nan composites in the spectrum indicates that the doping state of the polymer has been improved. This method is simple, environmentally benign route for soluble polyaniline synthesis at room temperature and because there is no organic solvent used in this technique, so this can be called: green synthesis.

In this method of synthesis, the complete synthesis and purification procedure is carried out in an aqueous solution, which is environmentally benign.

CONCLUSION

Iron-Polyaniline nanocomposites is synthesized by in-situ and employing the micro emulsion processing technique. The data and analysis of the FTIR and SEM show that PANI-SDS-Fe composite has a porous asymmetrical structure with a bi-layer where the inner layer comprises polyaniline and the outer layer is composed of SDS. The appropriate content of polyaniline in the composite is a key factor for preparing the PANI-SDS-Fe composite better performance.

ACKNOWLEDGEMENT

The authors would be like to thank Islamic azad university for kindly supports.

REFERENCES

1. LeBaron, P.C., Z. Wang and T.J. Pinnavaia, 1999. Appl. Clay Sci., pp: 15-11.
2. Akane, O. and U. Arimitsu, 1995. Mater. Sci. Eng., C 3 pp: 109.
3. Carrado, K.A. and L. Xu, 1999. Micropor. Mesopor. Mater., pp: 27-87.
4. Do Nascimento, G.M., V.R.L. Constantino, R. Landers and M.L.A. Temperini, 2006. Polymer, pp: 47- 6131.
5. Wang, L., P. Brazis and M. Rocci and Chem Mater, 1998. 10, 3298.
6. Wang, L., M. Rocci and P. Brazis, 2000. J. Am. Chem. Soc., 122, 6629.
7. Alberti, G. and T. Bein, 1996. Comprehensive Supramolecular Chemistry Vol. 7, Elsevier, New York,
8. Gianellis, E.P., 1996. Adv. Mater., 8, 29.
9. Leroux, F.G. and J. Goward, 1997. Electrochem Soc, 144, 3886.
10. Wang, Y. and N. Herron, 1996. Science, 273, 632.
11. Li, H. and M. Joswicz, 1995. J. Electrochem. Soc., 142, 798.
12. Noufi, R., J. Electrochem, 1983. Soc., 130, 2126.
13. Jarjays, O. and P.H. Fries, 1995. Synth. Met., 69, 343.
14. Diaz, A.F. and J.A. Logan, 1980. J. Appl. Electrochem., 111, 111.
15. Ivanov, S. and V. Tsakova, 2002. J. Appl. Electrochem, 32, 701.
16. Ivanov, S. and V. Tsakova, 2002. J. Appl. Electrochem. 32, 709.
17. Wang, J.G., K.G. Neoch and E.T. Kang, 2003. Surf. Sci., 218, 231.
18. Heeger, A.J., 2002. Synth. Met., 125, 23.
19. Cho, M.S., Y.H. Cho, H.J. Choi and M.S. John. 2003. Langmuir. 19, 5875.
20. Kinyanjui, J.M. and D.W. Hatchett and J.A. Smith, 2004. Chem. Mater., 16, 3390.
21. Wessling, B., Synth. Met., 85, 1313.
22. Han, M.G., S.K. Cho, S.G. Oh and S.S. Im, 2002. Synth. Met., 126, 53.