Journal of Applied Chemistry

Synthesis and characterization of nanostructured polythiophene in aqueous medium by soft-template method

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Article history:
Received: 13 May 2013
Received in revised form: 7 August 2013
Accepted: 7 September 2013

Abstract

Polythiophene is a standout amongst the most valuable sorts of the conducting polymers that hold numerous odd physical and electrical lands for instance dissolvability, electrical conductivity and develop the ecologically and thermally stable materials. Distinctive assembling techniques have been advanced for conducting polymer nanostructures and near them, template method is a facile and encouraging method. Nanostructured polythiophene was prepared by soft-template method in the vicinity of sodium dodecyl sulfate (SDS) as an anionic surfactant, triethanolamine (TEA) as a co-surfactant and ammonium persulfate (APS) as an oxidant in aqueous medium. Moreover, the chemical structure of fabricated nanostructured polythiophene was investigated by fourier transform infrared (FTIR) spectroscopy. The morphology and particle size of the product was studied by scanning electron microscope (SEM) and atomic force microscope (AFM). Furthermore, dispersion state of nanostructured polythiophene in organic solvents was studied after being dried. The results indicate that nano-product has a favorable fiber-like-structure with a diameter in the range of 85–100 nm.

Keywords: Polythiophene, Soft template method, Chemical structure, Morphology.

1. Introduction

The vast majority of the regular conjugated polymers was unbendingly viewed as insulators or as semi-conductors, however in 1977 with the finding of the adaptation in the electrical conductivity of poly (acetylene) on doping, it has been recognized that they can have extensive electronic conductivities [1]. The most normal conducting polymers are conjugated polymers with heteroatoms in the primary chain (heterocyclic polymers) such as as polyaniline (PAni), polypyrrole (PPy), polythiophene (PTh) and their derivatives. Polythiophene and its derivatives own various supportive electrical and physical lands for instance dissolvability, electrical conductivity, versatility and alternates. The procurement of polythiophene as a conductive material has ended up being rather problematic. It has been connected as electrochromic devices, electroluminescent devices, solar cells, schottky barrier diodes, field-effect transistors (FETs), antistatic coatings, sensors, batteries, shielding materials and so forth [2,3,4].

Thiophene was uncovered by Viktor Meyer in 1883 as a contaminant in benzene [5]. In the partial refining of coal tar and petroleum, it was discovered in generally substantial amounts [6]. Thiophene is a colourless liquid at room temperature with a gently reminiscent possess an aroma similar to benzene. It is recognized aromatic, with the degree of aromaticity less than that of benzene. The participation of the lone electron pair on sulfur in the delocalized pi electron system is significant [7]. Thiophene is handled in numerous reactions including sulfur sources and hydrocarbons, particularly unsaturated hydrocarbons. For example; reactions of acetylene and elemental sulfur, were first attempted by Viktor Meyer. Particular thiophenes might be synthesized via the Gewald reaction, which includes the condensation of two esters in the vicinity of elemental sulfur [8].

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Polythiophene results from the polymerization of thiophene. The polymer is formed by connecting thiophene through its 2,5 positions [9]. Chemical synthesis of polythiophene was reported by two groups named Yamamoto and Dudek for the first time in 1980. Both synthesized polythiophene by metal-catalyzed polymerization of 2,5-dibromothiophene [10,11].

Aysegul et al., has synthesized polythiophene by chemical oxidative polymerization in the presence of three diverse surfactants (anionic, cationic and non-ionic) and ferric chloride as an oxidant in anhydrous medium. They discovered that the morphologies of the resulting polythiophene are enormously affected by the presence of the surfactant additives in the polymerization solution [12]. Gnanakan et al., prepared polythiophene nanoparticles by cationic surfactant assisted dilute polymerization method utilizing FeCl3 as oxidant to use as electrode material for high performances redox supercapacitors. It was found that the polythiophene acquired by this method had better capacitor performances than the same obtained by the conventional chemical and electrochemical polymerization methods because the materials in nano-size have high surface area with uniform porosity, gives better supercapacitor performances [13]. Zi wang et al., has synthesized polythiophene nanoparticles with regular spherical morphology, which were not ordinarily observed in traditional iron (III) catalyzed oxidative polymerization of thiophene in organic solvents, by copper (II) catalyzed oxidative emulsion polymerization with high yields in aqueous medium using sodium dodecyl sulfate as an anionic surfactant and hydroxyl peroxide. The results show that different copper salts have obvious influence on the rate of polymerization as well as the morphology and the properties of the resulting polythiophene such as surface conductivity, surface resistivity and thermal stability [14]. Senthilkumar et al., has synthesized polythiophene particles by iron (III) catalyzed oxidative polymerization in aqueous medium using thiophene as monomer, $FeCl_3$ as oxidant, H_2O_2 as co-oxidant and three various surfactants. The outcomes indicate that the surfactant may decrease the agglomeration of the polymers. The samples prepared with surfactant exhibit different morphology compared with surfactant free polythiophene. The polythiophene prepared in presence of Triton X-100 as a nonionic surfactant exhibited higher capacitance and faradic current values which confirm the possibility of utilizing the electrodes in redox supercapacitors [15].

Diverse fabricating strategies have been promoted for leading conducting polymer nanostructures, for instance template method, mechanical stretching, ultrasonic irradiation [16], dispersion polymerization and in addition physical systems such as electrospinning method [17]. Close them, template strategy is an incredible and compelling method and it is grouped by soft and hard templates [18]. Martin initially investigated a template-synthesis technique to prepare nanofibers or nanotubes and nanowires of conducting polymers utilizing commercially available porous membranes as templates [19]. Template method includes the incorporation of guests such as inorganic or organic ingredient inside the void spaces of a host material. These voids function as the template, disfiguring the shape, size, and orientation of the compound produced [20].The hard-template method, such as a porous anodic aluminum oxide (AAO) membrane, track-etched polycarbonate (PC) and zeolite, to guide the growth of the containers, leading to complete control of the morphology and diameter of the conducting polymer containers. Keeping in mind the end goal to acquire pure containers, this approach needs complicated manufactured steps, including the evacuating of the template after polymerization. Additionally, the quantity of the nanostructures produced by this method is restricted by the size of the template membrane. Subsequently, the potential impediment of utilizing hard templates constrained scientists to hunt down additional productive and effortless tracks to prepare conducting polymers. Around these recently advanced approaches, the soft-template method is acknowledged an effective instrument as an alternative strategy to hard-template synthesis. The playing point of utilizing soft-template materials, which is additionally called as self-assembly method is that they can be removed effortlessly after synthesis and leaving micro and nanostructures of the resulting polymer [18, 21]. Different soft templates such as surfactant micelles, oil droplets, liquid-crystalline phases, soap-bubble templates, have been reported for producing conductive polymers by self-assembly processes. Surfactants are common soft-template since they effectively structure thermodynamically stable and controllable nanometer-scale micelles in solution or at interfaces as a nanoreactor. The monomers filled in these micelles and by addition of oxidizing agent, polymerization reactions occured [18, 20]. Zhang et al., has reported the preparation of the Wire, ribbon, and sphere-like polypyrrole nanostructures by surfactants as soft-templates [22].

2. Experimental

2.1. Apparatus

A magnetic mixer model G-300, digital scale model PHMT-PSC20, scanning electron microscope (SEM) model KYKY-EM3200, fourier-transform infrared (FTIR) spectrometer model Shimadzu 4100, freez dryer model LTFD 5505 and atomic force microscope (AFM) model nano surf easy scan2 flex AFM were employed.

2.2. Chemicals and solutions

Materials used in this work were thiophene, ammonium persulfate (APS), triethanolamine (TEA), sodium dodecyl sulfate (SDS), N, N-dimethylformamide (DMF), acetone and methanol from Merck. All reagents were used without further purification and used as received. Double-distilled and deionized (DDI) water was employed throughout this work. Thiophene monomer was freshly purified by a simple distillation process prior to use.

2.3. Synthesis of nanostructured polythiophene

The reaction procedure is as follows: 2.5 mL fresh distilled thiophene, 1 g sodium dodecyl sulfate (SDS) and 9.5 mL triethanolamine (TEA) were mixed with 30 mL of DDI water in a reaction vessel containing a magnetic mixer. Simultaneously, ammonium persulfate (APS) was dissolved in 20 mL DDI water and was added into the reactant mixture solution. The molar ratio of APS to thiophene monomer was 1.15. The preliminary polymerization process was identified by the color change of the reaction mixture. The Polymerization was allowed to proceed for 24 h. Consequently, the resulting dark brown precipitate was collected by centrifugation and to separate the oligomers and impurities, product was washed several times with DDI water and methanol and dried by freez dryer.

3. Results and discussion

3.1. FT-IR study

The chemical structures of products were determined by FTIR spectroscopy (Figure 1), which has furnished significant information about the formation of nanostructured polythiophene. The FTIR transmission spectrum of the products exhibited characteristic vibration at 2916.16 cm^{-1} for C-H stretching vibration band. The bands at 1674.09 and 1404.08 cm^{-1} corresponding to C=C asymmetric and symmetric stretching vibrations of thiophene ring, respectively. The vibration bands observed at 1211.23 cm^{-1} and 1041.48 cm^{-1} are due to C–H bending and C–H in-plane deformation. Furthermore, the characteristic bands of polythiophene are seen at 763 cm-^{1} (C–S bending) and 694 cm^{-1} (C–S–C ring deformation stretching). The band at 3402.20 cm^{-1} originated from O–H stretching of water in KBr. Results of the FTIR studies clearly indicated polymerization of the monomer.

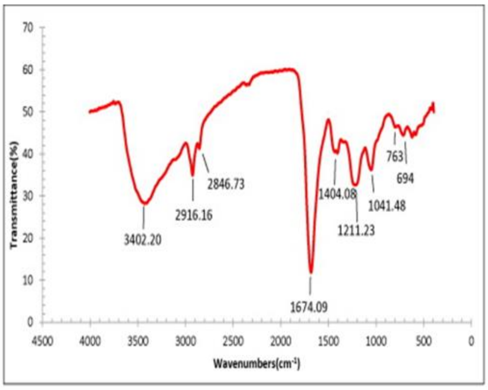

Figure 1. FTIR spectrum of nanostructured polythiophene.

3.2. Morphology investigation

Scanning electron microscopy was performed to investigate the dimensions and the morphology of nanostructured polythiophene. The scanning electron micrographs of nanostructured polythiophene are exhibited in Figure 2. The obtained products have an interesting fiber-like-structure with a diameter in the range of 85–100 nm.

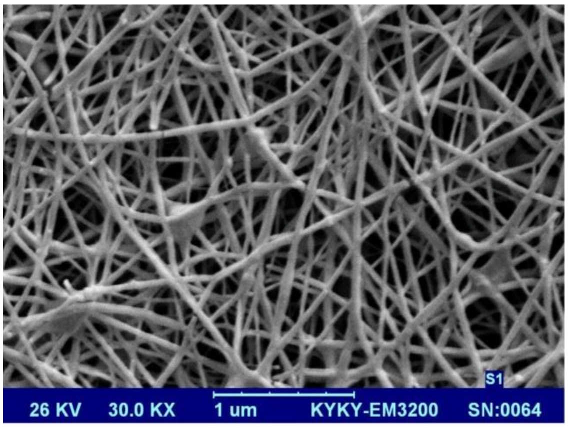

Figure 2. SEM micrographs of nanostructured polythiophene

This SEM image clearly demonstrates that the morphology of polythiophene can be controlled to fiber by this method. This is more helpful to distinctive applications.

3.3. AFM analysis

Atomic force microscopy (AFM) belongs to a group of scanning probe microscopy (SPM) instruments that are utilized to measure properties of surfaces. Figure 3 shows three-dimensional image of the surface of polythiophene. It indicates that the polymer formed aggregates with relatively rough surfaces.

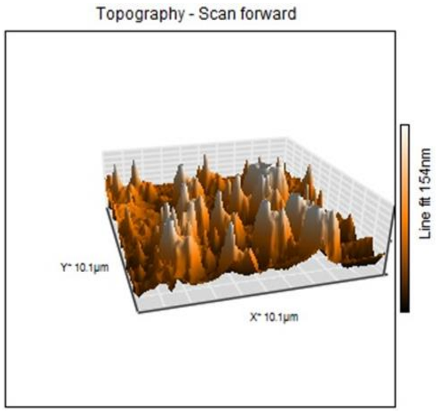

Figure 3. three-dimensional AFM image of polythiophene.

3.4. PT Dispersibility Test

Known amounts of obtained products (5 mg) was added into three beakers and then various organic solvents including N,N-dimethylformamide (DMF), acetone and methanol were introduced. Digital photos were taken three weeks later. Figure 4 showed the photographs of the dispersions of obtained polythiophene in various solvents.

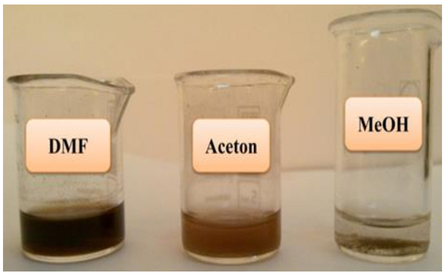

Figure 4. Dispersion state of nanostructured polythiophene in various organic solvents.

The dispersion state showed that the nanostructured polythiophene was well dispersed in DMF without any precipitation after 3 weeks. Also, it could be dispersed in acetone and methanol, however some precipitation was observed after 3 weeks.

4. Conclusions

We have demonstrated the successful synthesis of nanostructured polythiophene by soft template method utilizing sodium dodecyl sulfate (SDS) as an anionic surfactant, triethanolamine (TEA) as a co-surfactant and ammonium persulfate (APS) as an oxidant. The results of FTIR spectroscopy clearly proved formation of polythiophene. The morphology and structures of the product were analyzed by SEM. It exhibited that an interesting fiber-like-structure is obtained and the average diameter of the product was found to be in the range of 85–100. AFM investigation of product morphology revealed aggregates with relatively rough surfaces. Among all 3 solvents tested, nanostructured polythiophene showed the highest dispersibility in DMF and dispersed in acetone and methanol with some precipitation that was observed after 3 weeks. According to these findings, part of the future work could be directed on the application of such synthesized nanostructured polythiophene upon solar cells, sensors, batteries, removal of heavy metals from industrial waste waters and fuel cells.

Acknowledgements

The authors wish to express their sincere gratitude to the Nanotechnology Research Institute of Babol University for financial support.

References

[1] E. Antolini and E. R. Gonzalez, *Applied Catalysis A: General*, **365** (2009) 1.
[2] A. Acharya, S. Sahu, S. Balamurgan and G.S. Roy, *Lat. Am, J. Phys. Educ. Vol*, **5** (2011) 134.
[3] G. Schopf, G. Koßmehl, Polythiophenes: electrically conductive polymers, Springer Berlin, 1997.
[4] M. Ates, T. Karazehir and A. S. Sarac, *development*, **2** (2012) 224.
[5] V. Meyer, *Berichte der Deutschen chemischen Gesellschaft*, **16** (1883) 1465.
[6] W. C. Sumpter, *Chemical Reviews*, **34** (1944) 393.
[7] D. Lednicer, *Wiley Interscience*, **6** (1999) 187.
[8] R. Sabnis, D. Rangnekar and N. Sonawane, *Journal of heterocyclic chemistry*, **36** (1999) 333.
[9] J. Roncali, *Chemical Reviews*, **92** (1992) 711.
[10] T. Yamamoto, K. Sanechika and A. Yamamoto, *Journal of Polymer Science: Polymer Letters Edition*, **18** (1980) 9.
[11] J. W. P. Lin and L. P. Dudek, *Journal of Polymer Science: Polymer Chemistry Edition*, **18** (1980) 2869.
[12] A. Gök, M. Omastová and A. G. Yavuz, *Synthetic metals*, **157** (2007) 23.
[13] S. R. P. Gnanakan, M. Rajasekhar and A. Subramania, *Int. J. Electrochem.* **4** (2009) 1289.
[14] Z. Wang, Y. Wang, D. Xu, E. S.W. Kong and Y. Zhang, *Synthetic Metals*, **160** (2010) 921.
[15] B. Senthilkumar, P. Thenamirtham and R. Kalai Selvan, *Applied Surface Science*, **257** (2011) 9063.
[16] X. F. Lu, H. Mao, D. M. Chao, W. J. Zhang and Y. Wei, *J. Solid State Chem*. **179** (2006) 2609.
[17] A. MacDiarmid, W. Jones, I. Norris, J. Gao, A. Johnson, N. Pinto, J. Hone, B. Han, F. Ko and H. Okuzaki, *Synthetic metals*, **199** (2001) 27.
[18] Y.-Z. Long, M.-M. Li, C. Gu, M. Wan, J.-L. Duvail, Z. Liu and Z. Fan, *Progress in Polymer Science*, **36** (2011) 1415.
[19] G. Cao and D. Liu, *Advances in colloid and interface science*, **136** (2008) 45.
[20] J. Jang, Conducting polymer nanomaterials and their applications, in: Emissive Materials Nanomaterials, Springer, (2006) 189.
[21] H. D. Tran, D. Li and R. B. Kaner, *Advanced Materials*, **21** (2009) 1487.
[22] X. Zhang, J. Zhang, W. Song and Z. Liu, *The Journal of Physical Chemistry B*, **110** (2006) 1158.