Preparation and Characterization of Polyaniline Nanotubes

H. Shokry Hassan^{1,*}, M. F. Elkady^{2,3}, M. A. Abd El kawi⁴, M. F. Alian⁴

¹Electronic Materials Researches Department, Advanced Technology and New Materials and Research Institute (ATNMRI), City of Scientific Research and Technological Applications, Alexandria, Egypt

²Chemical and Petrochemical Engineering Department, Egypt-Japan University of Science and Technology, Alexandria, Egypt

³Fabrication Technology Department, Advanced Technology and New Materials and Research Institute (ATNMRI), City of Scientific Research and Technological Applications, Alexandria, Egypt

⁴Environmental Studies Department, Institute of Graduate Studies& Research, Alexandria University, Egypt

Email address:

Hassan.shokry@gmail.com (H. S. Hassan)

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Abstract: The present work reports slightly modification of the conventional chemical synthesis of polyaniline (PANI) to be nanotube structure without the need for any template or structural directing materials. PANI preparation was optimized by the oxidation of two different precursors: aniline and aniline hydrochloride with ammonium persulfate (APS) as oxidizing agent in various aqueous media of strong, weak acid and in alkaline medium at different pH values. Structural and morphological properties of the products are characterized by SEM, XRD and FTIR. Results showed the strong dependence of PANI nanotube on the acidity at certain pH value during the oxidation of aniline by APS. It is founded that, the optimum condition for preparation of PANI nanotube was obtained under oxidation of aniline monomer by APS in aqueous media of weak acid medium at pH five degree.

Keywords: Characterization, Conducting Polymer, Polyaniline Nanotube

1. Introduction

The advancement of science and technology provides the smaller and smaller dimensions with higher precision and enhanced performance. Currently, nanotechnology is concerned with fabrication and various applications of functional materials and structures in the range of 1nm to 100 nm using chemical and physical methods, nanoscale size control of material leads to superior physical and chemical properties with molecular and supermolecular structures [1-4].

Conducting polymers exhibit a wide range of novel electrochemical, chemical, electrical, magnetic, and optical properties that has led to their use in a diverse array of applications including sensors, biosensors, light-emitting diodes, electronics devices, microwave absorption and rechargeable batteries [5,6].

Among the conducting polymers, Polyaniline (PANI) has found significant attention in recent years which is used more extensively because of its easy preparation from aniline monomer with good thermal stability and it exhibits good

electrical, optical, magnetic, and chemical properties [7-10]. These features together with the low cost and wide availability of aniline and its derivatives make it an ideal candidate in many practical applications such as gas sensing, pH sensing, light-emitting diodes or corrosion protection. Switchable membrane, anti-corrosive coatings and thus poly aniline is used in this investigation [11-13].

Nano structures of PANI are of great current interest because they combine the properties of low- dimensional organic conductors with high surface area materials, this situation can lead to enhanced in unique chemical, electrical, magnetic, and optical properties [14, 15].

Various synthetic pathways are reported for the synthesis of PANI, but it is still highly desirable to develop novel and smart synthetic procedures for building PANI nanostructures, such as nano fibers/ wires/ rods/tubes [16].

In the present work, preparation and characterization of PANI nanotube has been studied.

2. Experimental

2.1. PANI Preparation

0.2 M Aniline monomer was dissolved in reagent grade water in a volumetric flask 50 ml solution, ammonium persulfate (0.25M) was dissolved in reagent grade water to 50 ml solution, both solutions were kept for 1h at room temperature then mixed in a beaker, briefly stirred then the reaction was allowed to proceed without agitation for 24h at room temperature.

The products were collected on filter paper, washed with reagent grade water and three 100 ml portions of 0.2M HCl, and similarly with methyl Alcohol and Acetone until the filtrate become colorless. Finally, the product was dried in air and then in vacuum at 60°C for 24h.

Samples were marked with: PHS, PHC, PHW, PS, PC, PA and PW, Where PHS, PHC and PHW samples are the polyaniline derived from aniline hydrochloride monomer in sulfuric acid, acetic acid and water aqueous media, respectively. PS, PC, PA and PW were poly aniline samples derived from aniline monomer in sulfuric acid, acetic acid, alkaline medium and water aqueous media, respectively. The previous marked samples coded with numbers according to different pH values as PC2 represent poly aniline sample derived from aniline monomer in acetic acid at pH value 2 of reaction media, PS3 represent polyaniline sample derived from aniline monomer in sulfuric acid at pH value 3 of reaction media, and so on.

2.2. Characterization

Structural, chemical, and morphological properties of the samples polyaniline that produced by chemical oxidation of aniline or aniline hydrochloride are characterized by XRD (X-ray Diffractometer model Schimadzu-7000, USA), FTIR (Fourier Transform Infrared Spectrophotometry model Shimadzu FTIR-8400 S, Japan over the wave length range 400-4000 cm⁻¹), and Scanning Electron Microscopy (Joel JSM 6360LA, JAPAN).

3. Results and Discussion

The SEM micrograph of polyaniline samples indicated in figure 1-a, 1-b it is observed that PC5 shows PANI super morphology nanotube, whereas rod PANI found in PCW and elongated PANI nanoparticles observed in PC2-PC4. Granular morphology is obtained in (PS2-PS5, PA10, PA12, PHC, PHS and PHW) due to no polymer chain entanglement during the polymerization process[9]. Thus, the role of the initial acidity and the acidity profile during the oxidation of aniline were soon recognized to be a key factor in the formation of PANI supermorphology nanostructures, the formation of PANI nanotubes in the oxidative polymerization of aniline with ammonium peroxy disulfate generally involves conditions of low initial acidity PC5 (reaction media with acetic acid at pH 5 degree). This agree with Miroslava and Jaroslav, report the role of initial weakly acidic as a directing factor in PANI

nanotube dominate; under strongly acidic or alkaline condition, granules are produce[16].

Thus, the significant key to fabricate PANI nanotube is to control the initial acidity during the oxidation of aniline monomer.

The average grain size of the polyaniline nanoparticles samples has been calculated by Scherrer's Formula:

$$D = K\lambda / \beta \cos\theta$$

where K is the particle shape factor (generally taken as 0.9), λ is the wave length of Cu α radiation ($\lambda = 0.15406$ nm), θ is the diffraction angle of the most intense peak, β are the experimental full width at half maxima (FWHM) of the investigated sample. The average grain sizes of each polyaniline nanoparticles samples obtained by this formula are tabulated in table1.

In order to understand the effect of precursor; aniline and aniline hydrochloride monomers, prepared samples using aniline and aniline hydrochloride for comparison purposes, start the reaction with various aqueous media of sulfuric, acetic and sodium hydroxide, execute the oxidation of monomer by APS oxidant [17, 18].

Table 1. Average grain size of polyaniline samples.

Sample name	Average grain size (nm)
PS2	40
PS3	50
PS4	45
PS5	20
PA10	55
PA12	55
PHC	45
PHS	45
PHW	35

PC5

PCW

PS2

PS3

PS

PS5

PA10

PA12

Figure 1-a. SEM micro images of polyaniline sample: (PC5, PCW, PS2, PS3, PS4, PS5, PA10, PA12)

PHS

PHC

PHW

PC2

PC3

PC4

Figure 1-b. SEM micro images of polyaniline Samples: (PHS, PHC, PHW, PC2, PC3, PC4)

X-ray diffraction characteristics can provide a great deal of information on structural aspects. XRD patterns of polyaniline samples that observed in figure 2.a, 2-b Show characteristic peak of poly aniline near $2\theta = 15^\circ$, 25° , 18.9° , this peaks manifest emeraldine salt form of PANI, the crystallinity of PANI can be ascribed to the repetition of benzenoid and quinoid rings in PANI chains. But the XRD pattern of PC5 sample show sharp and well defined peaks at $2\theta = 37.9^\circ$, 44.1° , 64.4° and 77.6° of the synthesized poly aniline sample that reveal the higher degree of crystallinity [10, 13]. XRD patterns of polyaniline samples derived from aniline monomer indicated that the PANI super morphology depend on acidity of reaction media for the oxidation of aniline monomer by APS as oxidant due to the aggregation of PANI nanoparticles from pH value 2 Degree to pH 5 degree to form elongated PANI nanoparticles, PANI nanotube and PANI rod.

XRD of PANI that produce in the oxidation of aniline monomer by APS oxidant with strong acid medium (sulfuric acid) show the crystallinity of PANI decrease at $2\theta = 37.8^\circ$, 44° , 64.5° and 77.5° compare to the formation of PANI from aniline monomer in acetic acid reaction medium, but in case of production of PANI nanoparticles from aniline monomer in alkali (sodium hydroxide) reaction medium exhibit higher crystallinity with formation of nanoparticles without aggregate of nanoparticles to form super morphology of PANI Nano particles [10]. XRD patterns that observed for PANI that produce with the oxidation of aniline hydrochloride monomer by APS oxidant in aqueous or acetic acid reaction medium are less amorphous than the pattern of PANI that obtained by the oxidation of aniline hydrochloride monomer in presence of strong acid (sulfuric acid) reaction medium. However, the crystallization property of PANI salts is affected by initial acidity of reaction medium during the oxidation of aniline monomer, the high crystalline products could display metallic behavior that more useful than amorphous products.

Figure 2.a. XRD spectrums of polyaniline samples: (PC5, PC4, PC3, PC2, PS5, PS4, PS3, PS2).

Figure 2.b. XRD spectrums of polyaniline samples: (PC5, PCW, PHW, PA10, PA12, PHS, PHC).

Figure 3. FTIR spectrum of polyaniline nanotube sample (PC5).

FTIR spectrum of polyaniline nanotube sample (PC5) that are given in figure 2.a, 2-b show the broad band at low intensity peak $3265\text{--}3320\text{ cm}^{-1}$ is attributable to the N-H stretching vibration due to the protonation of nitrogen, this confirms that sample nearly does not contain any free NH or OH group. The band at 1572 and 1489 cm^{-1} are attributed to C=N and C=C stretching mode of vibration for the quinonoid and benzenoid units of poly aniline. The C-N stretching mode of the benzenoid unit can be assigned to the band at 1310 cm^{-1} . The band at 1125 cm^{-1} is obtained from the quinoid unit of polyaniline C-C and C-H stretching of the benzenoid unit of poly aniline shows a band at 810 cm^{-1} . Hence peak assignment reveals that the produce polymer is polyaniline [18, 19].

4. Conclusion

The chemical oxidation of Aniline or aniline hydrochloride monomer by APS in presence of weak, strong acid and alkali produce polyaniline nanostructure, but the super morphology structure of polyaniline (rod, nanotube) are given by the oxidation of aniline monomer by APS in presence of weak acetic acid at pH values from 2 to 5 degree, the Nano particles aggregates to form PANI nanotube at pH 5 degree, the morphology of polyaniline nanotube that was observed in SEM, confirmed by FTIR and XRD reveals the higher degree of crystallinity of polyaniline nanotube with higher intensity peaks.

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