Open Access **Baghdad Science Journal** **P-ISSN: 2078-8665**
2020, 17(1):106-111 **E-ISSN: 2411-7986**

DOI: http://dx.doi.org/10.21123/bsj.2020.17.1.0106

Chemical Synthesis and Characterization of Conducting Polyaniline

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Received 25/4/2019, Accepted 1/10/2019, Published 1/3/2020

Abstract:

The polyaniline powder was chemically manufactured by direct oxidation of aniline. The resulting polymer was characterized by the results of optical, measurements by (FT-IR) spectroscopy, we have detected some of the absorption peaks located at 3498, 2858 cm^{-1}, which correspond N-H vibrations, and C-H expansion of the aromatic ring respectively as well as stretching vibrations of quinoid ring have been observed. Structural properties, such as the surface topography using an atomic force microscope (AFM), and Surface composition by (SEM) have been studied. The structure of some pellets of polyaniline powder have been examined by using analytical X-ray diffraction technique, the pattern of observed lines shows a crystalline nature and three large peaks observed.

Key words: Atomic force microscopy, Chemical synthesis, Conductive polyaniline, Scanning electron microscopy.

Introduction:

Polyaniline is an organic semiconductor polymer that has been discovered since more than 150 years. However, since the early 1980s, polyaniline has taken a strong interest from researchers due to the discovery of its electrical conductivity (1, 2, 3). It has adopted a basic place among the locations of the conductive polymers. Polyaniline is an unusual phenyl, its polymer structure is characterized by chemical elasticity, and the NH-series in the polymer chain is bounded by a phenyl ring from both sides(4) . It refers to a group of molecules that are conductive to the electrical conductivity and able to change from insulator to conductor through oxidation processes (5). Polyaniline can be produced by the process of aniline polymerization with many types of organic oxides and specific percentages of proton acids and under certain conditions of reaction (6). In fact, the total heteroatoms are stable while exposed to oxygen not as in polyacetylene. Therefore, the physical and chemical properties of these compounds make them particularly striking, and have a large electrical conductivity about 10^{-5} S / cm (7, 8). Also it has the scope of work in the field of Photovoltaic organic cells (9, 10), Gas sensors (11, 12), Solid electrical capacities (13), Electric windows and screens, and Batteries polymeric (14).

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Polyaniline has environmental stability as well as being easy to be vaccinated using protein acids (15, 16). We have synthesized and characterized polyaniline powder was obtained form in chemical via being used as conducting gas sensor for Acid–**base reaction material**

Materials and Method:

The chemical polymerization of emerald hydrochloride salt has been synthesized easily as a partially crystallized black-green precipitate, by oxidative polymerization of 0.2 M aniline with 0.25 M of the oxidizing agent ammonium peroxydisulfate $[(NH_4)_2S_2O_8]$ in an aqueous acid medium, this oxidative polymerization needs two electrons per one aniline molecule. Aniline was purchased from Sigma-Aldrich (465.6 mg), it was dissolved in distilled water in a volumetric flask1 of (25 ml). The flask 1 is then cooled with ice. Ammonium peroxydisulfate (1.426 g) was dissolved in water also of (25 ml) in flask 2, then a Hydrochloric acid was used with 1M /l (1.823 g) was dissolved in water and placed in (50 ml) volumetric flask then we divided this acidic solution into two portions of (25 ml), One of this portion was added to flask1 and the other one was also added to flask2. Then, we saved each baker separately for an hour at a room temperature degree. Thereafter, we mixed the two solutions slowly with magnetic stirring for a full day, as shown in Fig 1. By oxidizing the solution with added dropwise to

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P-ISSN: 2078-8665
E-ISSN: 2411-7986

the addition funnel while maintaining the constant temperature by addition of ice, when all the contents of the bulb are poured then, the mixture is colored after 3 to 5 minutes of colorless to a colloid solution of dark green precipitate. This is then washed with distilled water and then the hydrochloric acid solution, thence filtered under a vacuum and dried in an oven at (40 C °) for 48 hours. The procedures of polymerization are shown in Fig. 1. The synthesis powder doped polyaniline was dissolved with water only in the absence of hydrochloric acid to have undoped polyaniline.

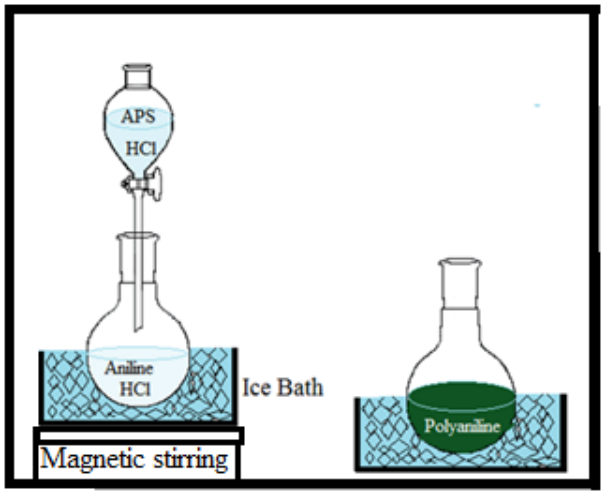

Figure 1. Chemical syntheses of polyaniline.

Preparation of Gas Sensors

Polyaniline can be used to manufacture a detector by connecting it to an electric circuit to measure its resistance by exposing it to vapor of a base such as ammonium hydroxide, recording its resistance and then exposed to acid vapor for the second time to measure its resistance again. For studying the reversible cyclic doping- dedoping, that corresponds charge - discharge states, the samples of polyaniline have been exposed to room temperature to the vapors of ammonia hydroxide and hydrochloric acid respectively . In other words the conductivity of polyaniline is a function of the rate of protons (17). Once polymerization is over, the precipitate solution of polyaniline, has been nominated by filtration, dried under vacuum, and washed over and over with HCl, taking a small piece of homogeneous adhering polymer and linked to the ends of avometer to measure its resistance, where primary resistance is measured at room temperature and then exposed to the vapor of NH_3, which pulls the protons of polyaniline and then become natural form or dedoping state. An increase in resistance readings over time (decrease in conductivity) and then exposed to the vapor of HCL acid vapor, where resistance readings decrease over time

Result and Discussion:

Infrared Spectroscopy (FT-IR)

FT-IR ensembles of polyaniline model primed by (0.2 M) of aniline via chemical polymerization are shown in Fig. 2. The assignments of the essential absorption bands are at (3498 cm^{-1}) are produced by N-H vibrations (18). The absorption bands at (2858 cm^{-1}) are consequent of the unbalanced C-H expansion of the aromatic ring (15). The pic at (2375 cm^{-1}) is related to stretching vibration of (O-H) group (19)**.** The crests at (1519, 1469, 1458, and 1423 cm^{-1}) produced from C=C stretching of quinoid ring and vibration of benzennoid ring (20, 21, 22). Bands appeared at (1300, 1375 cm^{-1}) are attributed to C–N stretching vibration in the alternate units of quinoid–benzenoid–quinoid rings and $C=N^+$ stretching to the quinoid structure respectively (22). The vibration band at (1238 cm^{-1}) can be assigned to C-N stretching vibration mode in benzenoid ring (23, 24). While the vibrations at (1141, 1111, 1076 and 1037 cm^{-1}) are characteristic to C-H bending vibration (25). Finally, the absorption peaks at (628, 675, 736, 759 and 871 cm^{-1}) formed C-H bending vibration out-of plane (20, 21, 25).

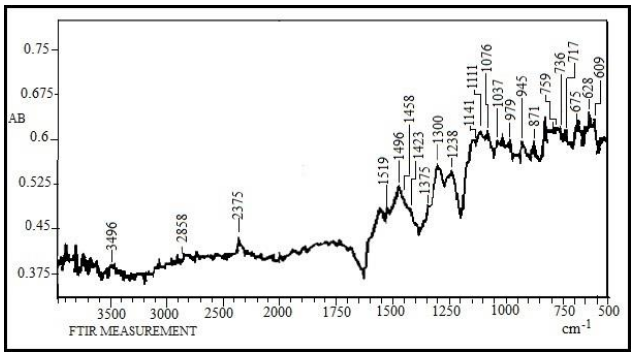

Figure 2. FT-IR bands of chemical polymerization of polyaniline.

Atomic force microscopy (AFM)

Figure. 3 shows the images of the atomic force microscope of a chemically prepared sample of PNAI powder. AFM technique gives us information about surface features of sample. Images have been taken to the survey area (10110 nm × 10151 nm). Fig. 3 (a) shows a two-dimensional imaging of the sample surface. The surface roughness rate (0.714 nm) and the mean square root (0.846) were found. Fig. 3 (b) shows a three-dimensional image of the sample surface, which shows granular interference, formed by grooves and part of which appears in large conglomerates and worm-like. Fig. 3 (c) shows a graph of the distribution of granular aggregates. Granules are equal to (135.54 nm). This indicates that the particles of the material are very

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P-ISSN: 2078-8665
E-ISSN: 2411-7986

large nanoparticles, and the rest of the sizes were found. The percentages of the remaining volumes were found to be 10% of the granule size (100nm) (26, 27, 28), 50% for (130 nm) and 90% for (170 nm).

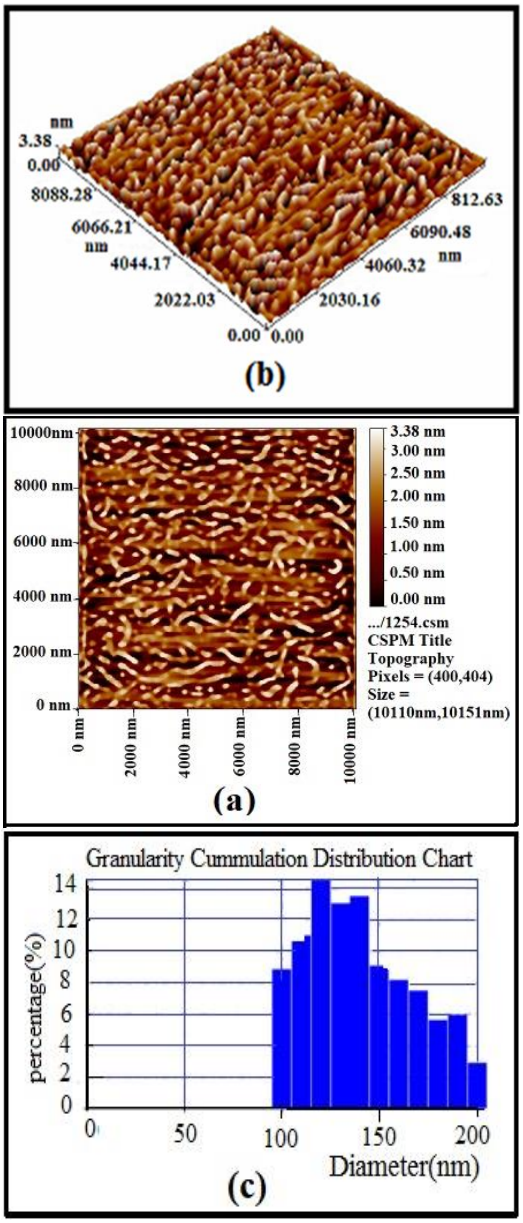

Figure 3. Atomic force microscopy images of the sample powder appears PNAI chemically (a) image analytical 2D, (b) Image 3D, (c) A chart of the distribution rate of particle size.

Scanning Electron Microscopy (SEM)

The SEM images of the PANI powder are shown ready chemically, with clusters and gathering of powder grains forming large spherical aggregates as shown in Fig. 4 (a), while Fig. 4 (b) shows a close-up image of one granule showing its formation in layers and layers of monoliths, some of which are made up of a spherical shape and the particle size of about (1μm) as mentioned in the literature (29).

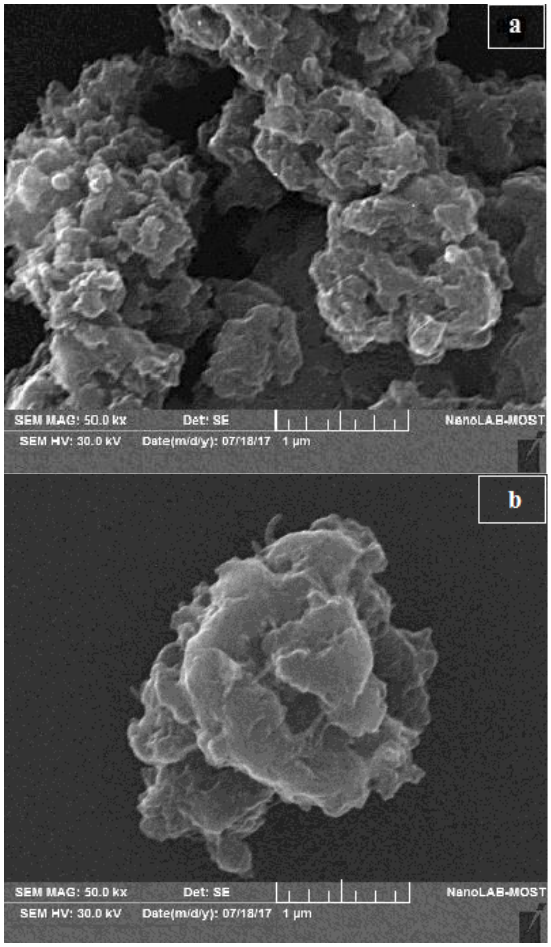

Figure 4. Shows SEM images of chemically prepared PANI powder, (a) image of PANI powder form, (b) rounded image of one granule.

X-ray diffraction analysis

Figure. 5 shows the x-ray reflection of the powder of polyaniline. It appears that the PANI is crystalline nature and shows three large peaks. This characteristic peak of PANI is attributed to the periodicity in perpendicular and parallel directions of the polymer chain. The peaks were observed at 2θ angle for reflection levels at 15°, 20.5° and 25.2°, corresponding to the following reflection levels (101), (020), (200) respectively, similar to those observed by others(30, 31). At the same time, the main peak shows a significant increase in intensity and can be attributed to an increase in the size of the crystals of the powder, and the crystalline volume was created using the Scherer's relationship of the polyaniline powder about 30.58 nm, which is comparable to previous research(2).

Baghdad Science Journal
P-ISSN: 2078-8665
E-ISSN: 2411-7986

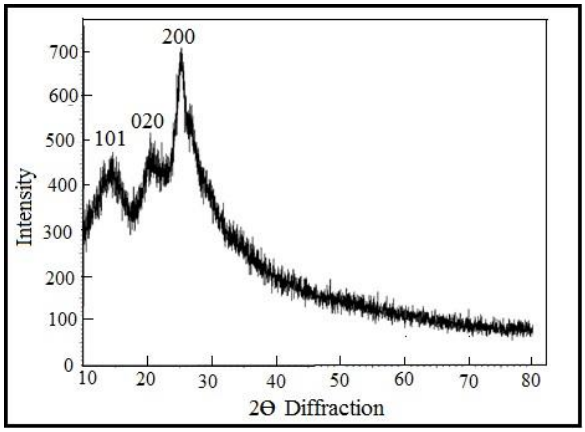

Figure 5. X-ray diffraction of polyaniline powder prepared by a chemical method.

Sensor Measurements

Fig.6 shows the characteristics measurements of the activated polyaniline, the exposure of polyaniline to ammonia gas vapors, which increases the resistance with time after exposing to ammonia gas vapors because ammonia withdraws the protons from polyaniline and thus removes the doping and the loss of conductivity, and when environment is displaced by air, the resistance almost gets back to its initial value. A similar behavior is presented in Fig.7 of the exposure of polyaniline to HCL, which increases the rate of doping with increasing exposure time. (32, 33, 34)

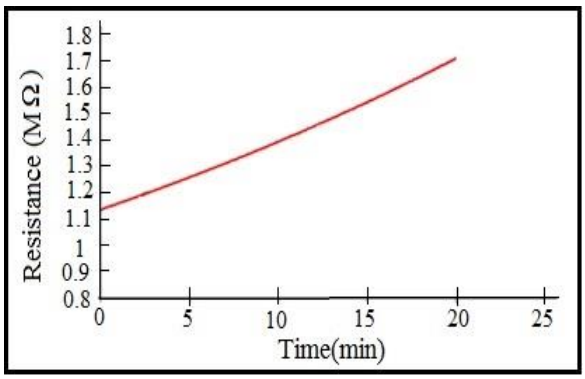

Figure 6. Shows the exposure of polyaniline to ammonia gas.

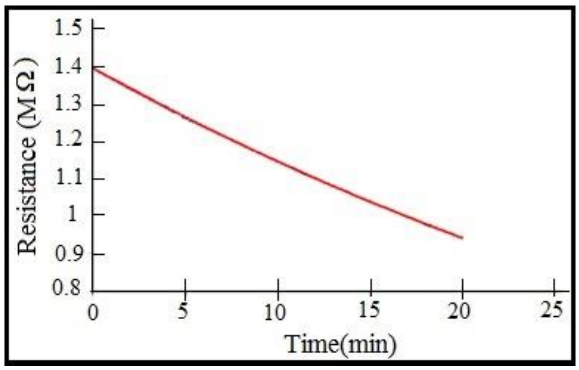

Figure 7. Shows the exposure of polyaniline to HCL.

Conclusion:

The polyaniline powder is prepared by the chemical method using acidic medium with ammonium persulfate, the AFM results show a particle size of about 135.54 nm, while the study shows SEM particle form agglomerated and dendritic. The study of the infrared spectrum of the polyaniline powder shows an increase in the intensity of the spectrum whenever the frequency is less**.** The X-ray diffraction measurement shows a particle size of about 30.58 nm.

Acknowledgements

The authors thank the Department of Physics, College of Science for Women, University of Baghdad for given that the required research capabilities.

Conflicts of Interest: None.

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2020, 17(1):106-111 **E-ISSN: 2411-7986**

التصنيع الكيميائي وخصائص البولي أنيلين الموصل

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قسم الفيزياء، كلية العلوم للبنات، جامعه بغداد، بغداد ، العراق.

الخلاصة:

تم تصنيع مسحوق البولي أنيلين كيميائيا عن طريق الأكسدة المباشرة للأنيلين. حيث تم توصيف البوليمر الناتج من خلال نتائج القياسات البصرية بواسطة طيف الأشعة تحت الحمراء (FT-IR) والخصائص التركيبية مثل دراسة تضاريس السطح باستخدام مجهر القوة الذرية (AFM) والتركيب السطحي بواسطة المجهر الإلكتروني الماسح (SEM) وحيود الاشعة السينية (X-ray).

الكلمات المفتاحية: مجهر القوة الذرية، التصنيع الكيميائي، البولي أنيلين الموصل، المجهر الالكتروني الماسح.