Synthesis and Spectroscopic Properties of Conducting Polymer Polyaniline (ES)

Amer N. J. Al-Daghman¹ K. Ibrahim¹ Naser M. Ahmed¹ Kareema M. Zaidan²
1.Institute Nano-Optoelectronic Research and Technology Laboratory (INOR)
School of Physics, University of Sains Malaysia, 11800 Pulau Pinang, Malaysia
2. Physics Department, Collage of Science, University of Basra, Basra, Iraq

Abstract

Polyaniline (PANI) was synthesized in Emaraldine salt form by the chemical oxidation method by using Ammonium persulfate (APS) as an oxidizing factor. The XRD pattern refer to that PANI is an amorphous nature with d-spacing 4.34 Å. The FE-SEM images show that the thin film of polyaniline at 500nm shows that is highly micro-porous. Similarly, the UV-Visible spectra of this polymer refer to two absorption peak at around 426nm and 805nm. These absorption bands are attributed to the transitions phase of $\pi \to \pi^*$ and Benzenoid to Quinoid respectively. The FT-IR spectrum of PANI shows strong bands representing the surface bondings of PANI and their vibration modes were also observed. PL photo-luminescent spectra of conducting Polyaniline (ES), one peak shows a broad spectrum with a maximum intensity at around 537nm, and the band gap energy at 2.3ev corresponds to the emission of polyaniline at solid state.

Keywords: Polyaniline (PANI-ES), XRD, FE-SEM, FTIR, UV, PL.

1. Introduction

The conjugated polymers were as futuristic new materials at over 30 years ago that would lead to the next generation of electronic and optical devices. The development of "plastic electronics" devices based on conjugated polymers has originated the states of these materials from academic curiosity to the rapidly growing new electronic industry. Among these conjugated polymers the polyaniline (PANI) possess excellent thermal and environmental stability. Polyaniline have been used in variety applications like diodes, solar cells, and in gas sensors (Ram MK. et al.2005). The polyaniline can be synthesized in to different sizes and shapes like nanofibers, nanorods, and in to thin films. Not only tunable morphology, polyaniline can be synthesized with tunable properties like stability of electrical conductivity and optical energy band gap.

A morphological and spectroscopic study of these polymers is an important subject to understand the transport process of these conjugated polymers such as polyaniline to apply them in electronic industry (Liu G. & Freund M.1997, Gupta K.et al. 2008). In this work we experimented to synthesis polyaniline, and study characterization of these synthesized polymers with help of different spectroscopic techniques.

2. Experimental Section:

2.1 Synthesis of Polyaniline:

Polyaniline was synthesized by oxidation chemical polymerization of aniline in the presence of hydrochloric acid (HCL) as a reaction exciting, and ammonium peroxydisulphate (APX) as an oxidant factor.

For the synthesis, we took 50ml beaker, 1M HCL, and 2ml of aniline (as a monomer) were added into a 250ml beaker equipped with a Teflon coated magnetic stirrer at about 0° temperature (ice bath). Then 5gm of ammonium peroxydisulphate ((NH4)2S2O8) aqueous solution in 50ml beaker 1M HCL was drop wise added into the above solution. The polymerization temperature 0° was maintained for 24h to complete the reaction. Then the precipitate obtained was filtered. The product was washed successively by 1M HCL followed by double distilled water until the wash solution turned to dark green color. The product PANI was dried by oven vacuum at 60° for 24h to get powder form polyaniline emeraldine salt (ES).

2.2 Characterization and Measurements:

X-ray diffraction studies were carried out using high resolution an HRXRD diffractmeter (Model: PANalytical X pert Pro MRD PW3040).

The XRD patterns were recorded in the range of $(2\theta : 10-70^\circ)$ with a step width of 0.02° and a step time 1.25 sec by using (CuK α) radiation (λ =1.5406A $^\circ$). The XRD patterns were analyzed by matching the observed peaks with the standard pattern provided by a JCPDS file. Fourier Transform Infrared (FT-IR) spectroscopy (Model: Perkin Elmer Spectrum Gx) of PANI was studied in the frequency range of

(400–4000 cm⁻¹). Morphological study of the thin films of PANI was carried out using field effect scanning electron microscopy (FE-SEM) (Model: FEI Nova NanoSEM 450) operating at 20 kV. UV-visible the spectra of the samples, which were recorded on a Shimadzu -1800 UV- Vis spectrophotometer.

www.iiste.org

3. Results and Discussion:

3.1 XRD analysis:

The X-ray diffraction pattern of PANI (ES) from (Fig 1) exhibit an only one wedi peak at $2\theta=22.68^{\circ}$. The average crystallite size is calculated by Debye Scherer equation:

$$D = \frac{K\lambda}{\beta\cos\theta} \tag{1}$$

Where: K is the shape factor (0.98); D is the average crystallite size; λ is the wavelength of X- ray radiation used (1.54Å); β is the full width at half maximum, θ is the diffraction angle. The pattern of thin film polyaniline that shows structure by the study of XRD peaks confirmed the semi-crystalline nature of the synthesis of the thin film polyaniline (Huang J.& Kaner R.2004, Deore BA et al. 2004)

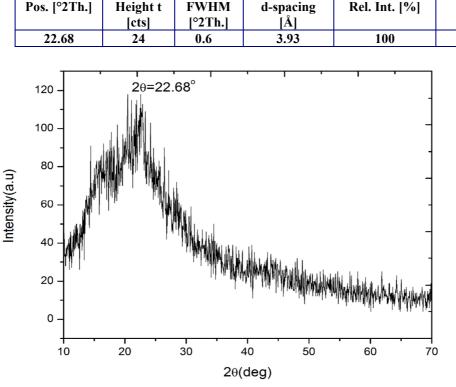
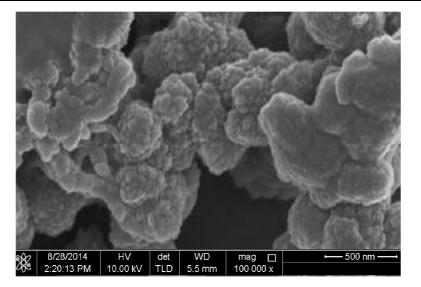


Table1. The XRD data of PANI (ES)

Figure 1. XRD pattern of gnitcudnocPANI (ES)

3.2 FE-SEM morphology:

FE-SEM morphology of PANI (ES), in the Fig(2) show the image at 500nm of the thin film of PANI, shows that the composite is highly spongy (micro-porous) nature and is able to increase the interfacial area (Matsumura M.& Ohno T. 1997, Xia H.& Wang Q.2002). The highly porous state of this material and the spherical morphology was confirmed with a FE-SEM study.

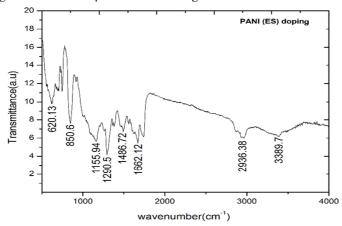


Figeru 2. FE-SEM morphology of PANI (ES)

3.3 FT-IR analysis :

Fig (3) shows the FT-IR spectra for the doped Polyaniline (ES), The origin of the vibration bands is as follows: at 3389 cm⁻¹ due to the NH stretching band vibrations, at 2936 cm⁻¹ due to a CH-stretching vibrations, at 620 cm⁻¹ due to CH out-of-plane bending vibration.

The CH out-of-plane bending mode has been used as a key to identifying the type of substituted benzene. The bands at 1662 and 1486cm^{-1} are attributed to C = N and C = C stretching modes of vibration for the quinonoid and benzenoid units of PANI. The peaks at 1295 and 1155cm⁻¹ are assigned to the C-N stretching mode of the benzenoid rings that of conducting protonated from PANi (Xia H.& Wang Q.2002). The bend at 850 cm⁻¹ originates out of the plane C-H bending vibration.



Figeru 3. FTIR Spectrum of depod Polyaniline (ES)

3.4 UV-vis Absorption analysis:

The absorption spectrum of the polyaniline doped (ES) film shows in Fig(4) at the visible spectrum, which is measured on a Shimadzu UV1700 ultraviolet visible spectrophotometer. There is two sharp absorptions peaks : one with max at 426 nm for transmittance (π - π *) of benzenoid ring and another at 805 nm, transmittance (polaron- π *) corresponding to molecular excite transition. This indicates that the synthesized polyaniline have been effectively doped with protonic acid from HCL doped. These two features are fingerprint of electronic conducting Polyaniline emeraldine salt. Should be considered to be a primary factor influencing the photo induced carrier mechanism of solar cells. We can solve that by increasing the absorption spectrum of polyaniline in the visible the zone by using a suitable doping materials (Jiaxing Huang & Richard B.)

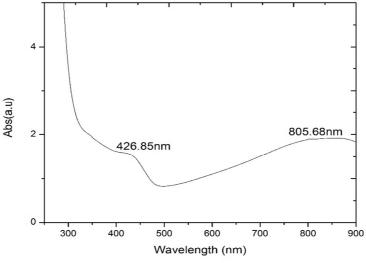


Figure 4. Absorption Spectrum of depod PANI (ES).

3.5 Photoluminescence analysis:

PL photoluminescent spectra of doped conducting polymer PANI (ES) of the thin films show at Fig (5). The peak show a wide spectrum with a maximum intensity around 538 nm, that with energy band gap $E_g=2.3$ ev corresponds to the emission of the polymer in the solid state, and demonstrating the optical properties at the polymer.

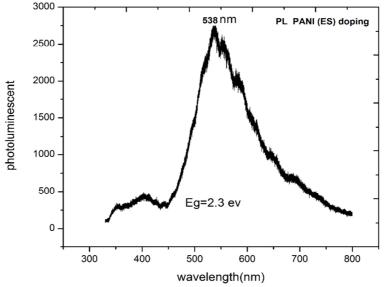


Figure.5 Potoluminecent spectra of depod Polyaniline (ES).

4. Conclusion

In this paper PANI (ES) was synthesized by chemical oxidative polymerization method .

The synthesized polymer was characterized by XRD, FESEM, FTIR and PL spectroscopic techniques. The X-ray diffraction pattern of PANI emeraldine salt form shows a sharp peak at 2θ =22.68° and d-spacing value obtained is 3.83 Å. Absorption spectrum of the polyaniline (ES) film shows a two absorptions peaks at 426,805 nm, corresponding to molecular exciton transition. The PL analysis shows the PANI emission peak at 538nm with direct band gap value obtained is 2.3eV. The FTIR characteristic peaks obtained confirm the formation of PANI(ES).

5. Acknowledgements

We gratefully acknowledge the support of the school of physics, USM, under short term grant No.203.PSF.6721001 and grant No.304/PFIZIK/6312076.

References

- Ram M K, Yang O, Lahsangarh V and Aldissi M. CO Gas Sensing from Ultrathin Nano- Composite Conducting Polymer Films. Sensors and Actuators B., 2005, 106:750-757.
- Liu G and Freund M S. New Approach for the Con-trolled Cross-Linking of Polyaniline: Synthesis and Characterization. Macromolecule., 1997, 30: 5660-5665.
- Gupta K, Jana P C, and Melkap A K. Magnetic Properties of CuCl2 Doped Polyaniline and Determination of Anisotropic Constant. Journal of Physical Science, 2008,12: 233-238.
- Huang J X, Kaner R B, J Am Chem Soc; 2004, 126, 851-5.
- Deore BA, Yu I, Freund MS. J Am Chem Soc; 2004, 126, 52-3.
- Matsumura, M., and Ohno, T. Adv. Mater. 9, 357 (1997).
- Xia, H. S., and Wang, Q. Chem. Mater. 14, 2158 (2002).
- Jiaxing Huang and Richard B. Kaner Handbook of Conducting Polymers Third Edition Conjugated Polymers, Edited by Terje A. Skotheim and John R. Reynolds Conjugated Polymers: Theory, Synthesis, Properties, and Characterization CRC Press Taylor & Francis Group.7-16.

The IISTE is a pioneer in the Open-Access hosting service and academic event management. The aim of the firm is Accelerating Global Knowledge Sharing.

More information about the firm can be found on the homepage: <u>http://www.iiste.org</u>

CALL FOR JOURNAL PAPERS

There are more than 30 peer-reviewed academic journals hosted under the hosting platform.

Prospective authors of journals can find the submission instruction on the following page: <u>http://www.iiste.org/journals/</u> All the journals articles are available online to the readers all over the world without financial, legal, or technical barriers other than those inseparable from gaining access to the internet itself. Paper version of the journals is also available upon request of readers and authors.

MORE RESOURCES

Book publication information: http://www.iiste.org/book/

Academic conference: http://www.iiste.org/conference/upcoming-conferences-call-for-paper/

IISTE Knowledge Sharing Partners

EBSCO, Index Copernicus, Ulrich's Periodicals Directory, JournalTOCS, PKP Open Archives Harvester, Bielefeld Academic Search Engine, Elektronische Zeitschriftenbibliothek EZB, Open J-Gate, OCLC WorldCat, Universe Digtial Library, NewJour, Google Scholar

