SYNTHESIS AND CHARACTERIZATION OF PANI-OA

¹Ravindra N. Khule, ²Sunil N. Botewad

^{1,2}Shri Shivaji Arts, Commerce and Science College, Kandhar, Dist. Nanded, Maharashtra-431714 (India).

Abstract: Polyaniline (PANI) is a versatile organic conducting polymers and it has enormous applications in the various fields. In present study we have been reported the synthesis of polyaniline-oxalic acid (PANI-OA) and its structural and optical properties. PANI-OA was synthesized via chemical oxidative polymerization method. The synthesized materials were characterized via X-ray diffraction (XRD), ultraviolet-visible (UV-vis.) and Fourier transform infrared (FTIR) spectroscopy. The XRD study of the PANI-OA shows the developed materials reveals the small crystallinity in the amorphous matrix. The UV-Vis. optical spectroscopy shows the two optical bands at 276 and 433 nm. The FTIR study exhibited the all expected peaks concerned to the PANI-OA.

Index Terms - Conducting Polymer, Polyaniline, Oxalic Acid, XRD, UV-Vis., FTIR.

1. INTRODUCTION:

Nowadays different types of materials have been synthesized and used for the various applications. Various synthesis techniques and characterization profoundly developed for the development the materials. Nanomaterials get more attraction in the present era however besides this conducting polymer makes more impact on the modern technology [1]. Generally, conducting polymers named as conjugated conductive polymers or organic polymeric conductors. In 1862, Letheby was firstly described the chemical oxidative polymerization of aniline and in 1962, Mohilner et al. studied it detailly [2]. The promising applicability or productivity of the conducting polymers start after the remarkable work carried out by Shirakawa and Heeger/MacDiarmid groups [2,3]. Generally conducting polymers comprised the C, H, and simple heteroatoms such as N and S, and different properties are being due to the π -conjugation. The chemical oxidative or electrochemical techniques can be used achieved the conductivity in the conducting polymers. Besides this doping process such as by reducing anionic or cationic species also can be used. Commonly, both oxidation and reduction process provide the conductive properties in the conducting polymers. The provided charges are highly delocalised over the monomer units in the polymers. The complete process workout like the doping process in the semiconductor [4-6].

Recently, various types of conducting polymers have been synthesized and used in different fields. Among the various types of conducting polymers polyaniline, polypyrrole, polyacetylene have studied mostly due to its extraordinary properties. Polyaniline is one of the conducting polymers which have the excellent properties such as better structural, optical and morphological properties and these properties can be tuned by using the proper synthesis technique [7,8]. As well as polyaniline have the high electrical conductivity, good thermal and environmental stability and it can be synthesized via inexpensive and facile synthesis technique. Due to these exceptional properties' polyaniline can be used in the applications such as gas sensing, solar cell, microelectronics, pharmaceutics, photovoltaic and catalysis etc. [9].

Thus, for the exploration of the structural, optical properties of the PANI-OA, herein we have been synthesized it and studied. The synthesized PANI-OA were studied with XRD, UV-Vis. FTIR characterizations techniques and explored the various properties.

2. EXPERIMENTAL:

2.1 MATERIALS:

Aniline was purified and all other chemicals used in present study n used without any further purification. Oxalic acid and ferric chloride were procured from Loba chemical India. Aniline was purchased from molychem India.

2.2 CHARACTERIZATION:

X-ray diffractometer (XRD) (Mini Flex II, Rigaku, Japan) with CuK α radiations of wavelength 1.5406 Å was used to study the structural properties. Ultra-violet-visible (UV-vis) portable spectrophotometer BLACK-Comet-SR (Stellar Net, USA) was used to explore the optical properties. Functional groups study was carried out by via FT-IR spectroscopy using α -ATR IR-spectrophotometer (Brucker, Japan).

2.3 SYNTHESIS OF PPY AND PPY-ZNO:

PANI-OA was synthesized via chemical oxidation method. Firstly, aniline 0.01 mol was mixed with 50 ml distilled water in beaker. In another beaker of 50 ml distilled water same concentration of $fecl_3$ was well dispersed by stirring. The oxalic acid 1 molar concentration was mixed in the aniline solution. Then the solution of $fecl_3$ was slowly added into the mixer of aniline and oxalic acid. The mixed of all stirred constantly for three hours at room temperature and filter with filter paper. The filtered powder then dried and used for the further characterization.

3. RESULT AND DISCUSSION: 3.1 STRUCTURAL PROPERTIES (XRD):

Fig. 1 shows the XRD pattern of polyaniline-oxalic acid. Generally, polyaniline shows the amorphous nature with small crystallinity. The XRD pattern of PANI-OA shows the diffracted peaks at an angle of $2\theta = 18.79^{\circ}$, 21.33° , and 28.40° , 34.79° , 35.98° and 47.46° . The observed peaks confirmed that the synthesised materials show the successful polymerization and highly crystallinity [10]. The peaks below the $2\theta = 30^{\circ}$ show better crystallinity of the synthesized PANI-OA. However, the synthesised material shows the crystalline nature most of the shows the non-crystallinity also. Due to the crystallinity nature the synthesised materials can show the better electrical conductivity than pure polyaniline.



3.2 OPTICAL STUDY: 3.2.1 UV-VISIBLE ABSORPTION:

Optical properties of the PANI-OA were evaluated by Ultraviolet–visible (UV-Vis.) spectroscopy. Fig. 2 shows the UV–vis. absorption spectrum of PANI-OA shows the two optical absorptions peaks at 276 and 433 nm. The absorption at 276 nm is corresponding to the $\pi \rightarrow \pi^*$ band transition and others at 433 nm is assigned to polaron band [11]. The optical properties of the synthesized materials show the better transparency in the materials which confirmed the lower bandgap also. The better optical properties of the can be applicable for the various applications in optoelectronics, solar cells etc.



3.2.1 FTIR SPECTROSCOPY:

Fig. 3 shows the FTIR spectrum of PANI-OA in the range 500- 3500 cm^{-1} . The peaks at 719 and 1234 cm⁻¹ corresponding to the C–N stretching and C–H out of plane vibration of 1,4-disubstituted benzene ring respectively. The characteristic peak in range of 1459 cm⁻¹ attribute for benzenoid ring vibration. The peaks at 3000-3500 cm⁻¹ are features of the PANI-OA material due to the extending frequency of –OH and NH groups. The peak around 1704 cm⁻¹ attribute for the stretching frequency of –COOH group due to the oxalic present in the polyaniline. The peaks at 1234 and 1343 cm⁻¹ are attributes due to the C–O group moieties present in oxalic acid. The peaks between 1400-1700 cm⁻¹ is obtained because of C=O group presence [12,13]. Thus, the all-corresponding peaks are observed corresponding to the PANI-OA which confirmed its proper formation.



Fig. 3 FTIR spectrum of PANI-OA

4. CONCLUSION:

The present report successfully prepared the PANI-OA and described the structural and optical properties. the chemical oxidative technique was reveled its compatibility to successful formation of conducting polymer. The XRD stud shows the crystalline properties of the developed PANI-OA and exhibited the developed materials is highly crystalline as compared to the pure PANI. The optical study shows the two absorption peaks at 276 and 433 nm which confirmed the very small optical bandgap as like semiconductor. The FTIR study confirmed the proper formation of PANI-OA material by showing all corresponding peaks related to it.

References:

- [1] Khan, I., Saeed, K., & Khan, I. (2019). Nanoparticles: Properties, applications and toxicities. *Arabian journal of chemistry*, *12*(7), 908-931.
- [2] Chandrasekhar, P. (1999). Basics of conducting polymers (CPs). In *Conducting Polymers, Fundamentals and Applications* (pp. 3-22). Springer, Boston, MA.
- [3] Inzelt, G. (2011). Rise and rise of conducting polymers. Journal of Solid State Electrochemistry, 15(7), 1711-1718.
- [4] Chandrasekhar, P. (2013). Conducting polymers, fundamentals and applications: a practical approach. Springer Science & Business Media.
- [5] Kar, P. (2013). Doping in conjugated polymers. John Wiley & Sons.
- [6] Xie, J., Zhao, C. E., Lin, Z. Q., Gu, P. Y., & Zhang, Q. (2016). Nanostructured conjugated polymers for energy-related applications beyond solar cells. *Chemistry–An Asian Journal*, 11(10), 1489-1511.
- [7] Kumar, D., & Sharma, R. C. (1998). Advances in conductive polymers. European polymer journal, 34(8), 1053-1060.
- [8] Ates, M. (2013). A review study of (bio) sensor systems based on conducting polymers. Materials Science and Engineering: C, 33(4), 1853-1859.
- [9] Wang, H., Lin, J., & Shen, Z. X. (2016). Polyaniline (PANi) based electrode materials for energy storage and conversion. Journal of science: Advanced materials and devices, 1(3), 225-255.
- [10] Rehman, S., Khan, A., Ullah, R., Anwar, N., Shah, L. A., Shah, N., ... & Ali, H. (2022). Synthesis and Characterization of Polyaniline Doped with Dodecyl benzenesulfonic and Oxalic Acids. *Russian Journal of Physical Chemistry A*, 96(1), S87-S94.
- [11] Hino, T., Seida, Y., Takahashi, T., & Kuramoto, N. (2006). Synthesis and characterization of polyanilines doped with several carboxylic acids and with a carboxylic acid equivalent. *Polymer international*, 55(2), 243-247.
- [12] Erdem, E., Saçak, M., & Karakişla, M. (1996). Synthesis and properties of oxalic acid-doped polyaniline. *Polymer international*, 39(2), 153-159.
- [13] Kulkarni, M. V., Viswanath, A. K., Marimuthu, R., & Seth, T. (2004). Synthesis and characterization of polyaniline doped with organic acids. *Journal of Polymer Science Part A: Polymer Chemistry*, 42(8), 2043-2049.