

Study the structural and electrical properties of prepared PANI/TiO₂ nanocomposites for electronic devices

R. A. Talib^a, K. A. Mohammed^{b,*}, D. K. Thbayh^{a,c}

^aPolymer research center, University of Basrah, Basra, Iraq

^bDepartment of Medical Physics, Hilla University College, Babylon, Iraq

^cInstitute of chemistry, University of Miskolc, 3515 Miskolc-Egyetemvaros, Hungary

Structural and electrical properties of pure Polyaniline (PANI), that doped with dodecyl benzene sulfonic acid (DBSA) and nanocomposite films Synthesized by insitu chemical polymerization method in the presence of TiO₂ nanoparticles. All the prepared samples have been investigated by x-ray diffraction (XRD), fuorier transformation infra-red (FTIR), and electrical conductivity studies. The results noticeably establish that the composites films have good crystallinity increase with increasing the TiO₂ content in the polymer matrix. Also, there are physiochemical interactions between PANI and TiO₂ nanoparticles that revealed by FTIR tests.

(Received January 11, 2022; Accepted May 12, 2022)

Keywords: PANI; TiO₂; Nanocomposite; electronic devices

1. Introduction

Polyaniline is among the most popular conjugated polymers on the market today [1]. Because of its great electric conductivity, small price, and easy of polymerization, polyaniline (PANI) is a popular conducting polymer in electronic and optoelectronic applications including sensor, organic solar cell, transistor, and Schottky diode [2]. The conductivity of a PANI Emeraldine Salt (ES) could be easily measured as a result of its sensitivity to various gases. That is why it was appropriate used in gas sensing applications [3]. Researchers have been focusing on heterogeneous-conducting polymer nanocomposites in recent years, particularly for organic/inorganic nanocomposite [4]. As a result, nanoscale additives are the most sought-after because of their intriguing properties. It is possible to enhance the electric and dielectric properties of host polyaniline materials by inserting nanoscale fillers [5]. Nano-titanium oxide (TiO₂) is an important semiconductor material, so it has a wide range of important applications owing to it is strong oxidizing power of the photo generated hole, chemical limpness, non-toxicity, low price, great index of refraction around 2.7 and extra beneficial surface properties [6]. May also can be used in many applications like photocatalytic [7], gas sensors [8], photoanodes for solar cells [9], dental fillers [10] and antibacterial [11]. Many Approaches may use for the production of PANI filled with TiO₂ nanocomposite materials, Template production [12], direct mixing [13] and Insitu polymerization which consider a very active way of production of polymeric nanocomposite which happens “in the polymerization mixture”. It includes the mixing of nanomaterials in a solutions blend holding a neat monomers, shadowed by polymerization. In this technique, the covalent link between the nanomaterials and polymer matrices happens [14].

In this paper, a PANi/TiO₂ hybrid was prepared via chemical in situ which PANi was polymerized by a simple chemical oxidative route, and described by using X-ray powder diffractio (XRD) technique , (FTIR) spectroscopy and FESEM The electrical characterization of the PANi/TiO₂ hybrid material was also discussed.

* Corresponding author: kahtan444@gmail.com

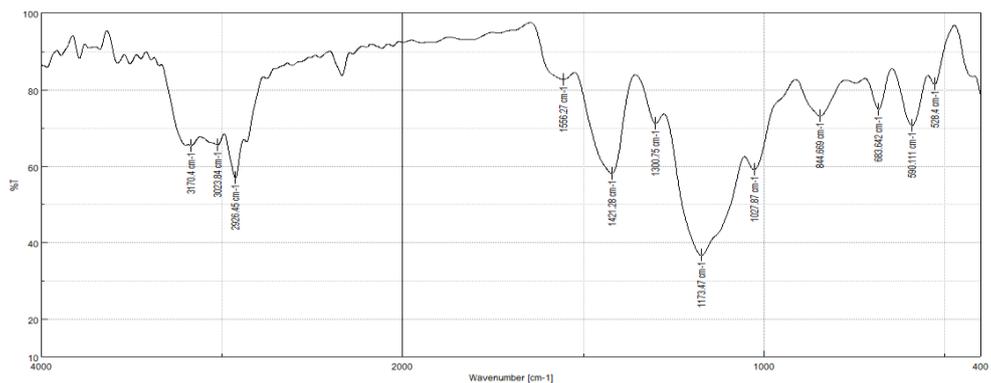
2. Experimental

2.1. Chemicals syntheses of DBSA-Doped PANi

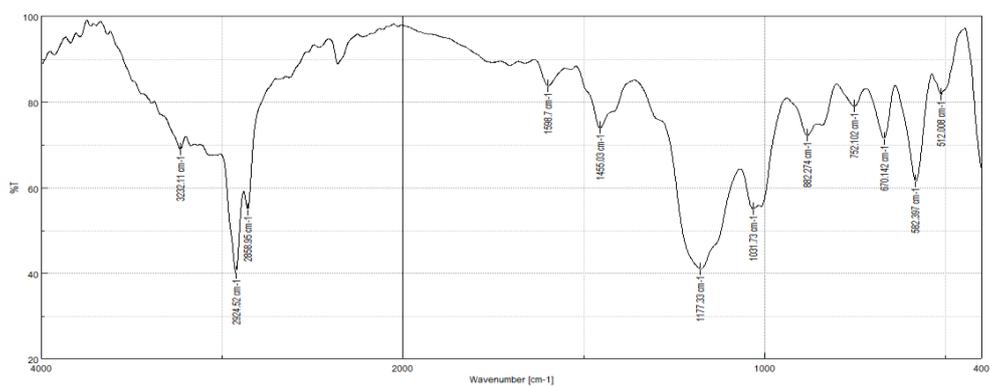
To prepare the doped polymer and the overlapping materials, the chemical polymerization method was used in the presence of an oxidizing agent in an acidic medium. The monomer used in the polymerization process is distilled aniline 1.5 ml of deionized water had been added into 1.14 gm of ammonium persulphate (APS), while 25 ml of haptan was added into 6.525gm of dodecyl benzene sulfonic acid (DBSA). 30 minutes at room temperature were spent stirring the solutions APS and DBSA until they were homogeneous in consistency and pointed to this solution by (A). Another solution was formed by dissolving 0.93gm of aniline in 5 ml of haptan and 0.5 ml of ethanol to generate another solution (B). The solutions A and B were mixed together for 24 hours at room temperature while being agitated. It was necessary to clean the precipitate by washing it in deionized water and methanol before drying it for 24 hours in a vacuum oven. Undoped PANi (EB-PANi) can harvest by washed some of PANi-DBSA by using ammonium solution. The nanocomposite synthesis had been done by same process above by addition TiO_2 to the aniline monomer (5% and 10% weight ratio from monomer) .

3. Results and discussions

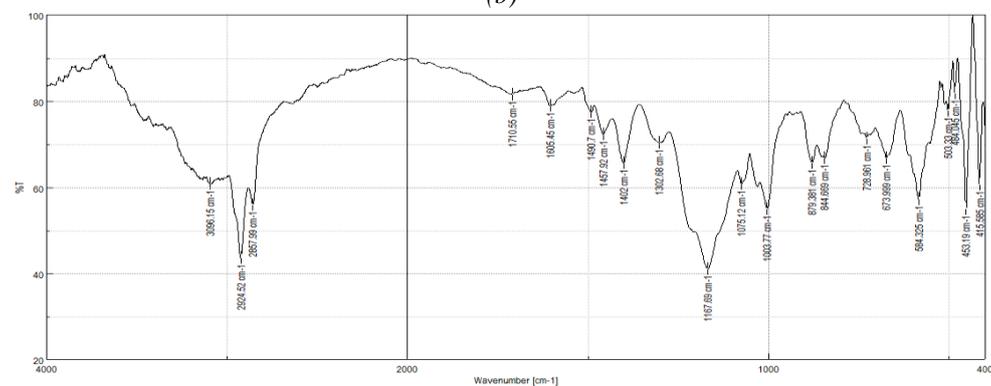
FTIR spectra of all synthesized samples were obtained in Fig. 1. The results of PANI-EB are in agreements with the spectra described by [15-17]. The spectrum of PANI-EB (spectrum a in Figure 1a) shows the phenyl C-H stretched at 3170 cm^{-1} . Stretch band of quinoid and benzenoid ring of the PANI polymer are detected at 1556 cm^{-1} and 1428 cm^{-1} , respectively. The stretching mode of the imine group (C=N) has been appeared at 1300 cm^{-1} . The peaks around 1173 and 844 are belong to C-H in-plane bending aromatic and C-H out-of-plan bending of 1, 4-ring respectively. The spectra of PANI-DBSA and PANI- TiO_2 (spectra in Figure 1b,c,d) have the same peaks that appeared in PANI-EB with small shifting in wavenumbers specifying the chemical interactions between polymer and TiO_2 .



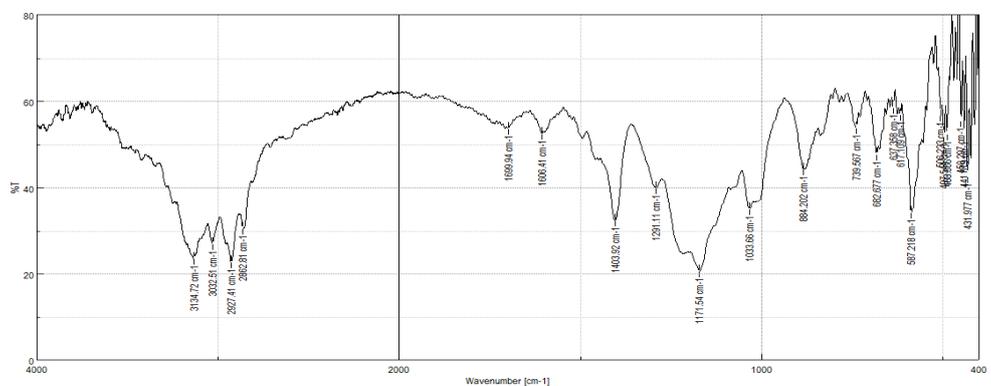
(a)



(b)



(c)



(d)

Fig. 1 Spectra of FTIR for (a) PANI-EB (b) PANI-DBSA (c) 5% TiO₂ (d) 10% TiO₂.

The recorded XRD peaks of PANI-EB, PANI-DBSA and PANI/TiO₂ nanocomposites are given in Fig. 2. The PANI positions of peaks in all the four established samples be present fit matching with the JCPDS card NO. 53-1891 [18,19]. Wide diffraction peak at 25° has been allocated to the spreading from the periodicity at right angles to chains of polymer PANI and the peaks before 25° can be credited as periodically equivalent to chains of PANI [20]. The presence of TiO₂ nanoparticles was confirmed by the XRD patterns of the composites (5 wt percent and 10 wt percent), which were both prepared using the same method. It was found that the distinctive peaks at 20, 25.3, and 28 were quite similar to those found in synthetic anatase and rutile TiO₂. [21,22].

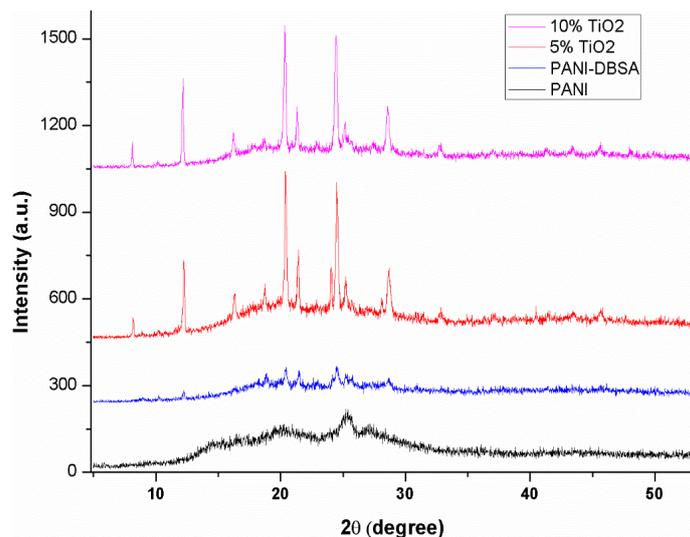


Fig. 2. The recorded XRD peaks of PANI-EB, PANI-DBSA and PANI/TiO₂.

Figure 3 show the I-V plot of PANI-EB, PANI-DBSA and PANI/TiO₂. The room temperature electric conductivity of PANI, PANI-DBSA and PANI/TiO₂ composite were calculated. The conductivity of PANI-DBSA was increased after doping with DBSA and decreased proportionally with the presence of TiO₂. The drop in conductivity of composite films is due to TiO₂ conductivity being lower than PANI-DBSA.

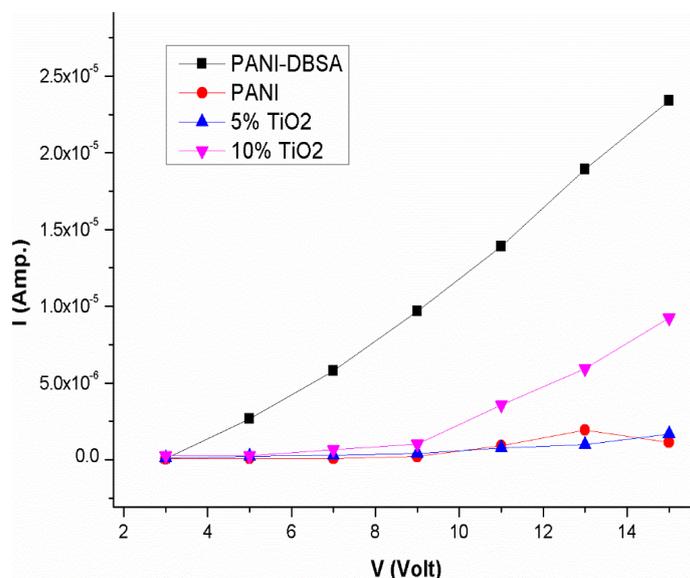


Fig. 3. I-V plot of PANI-EB, PANI-DBSA and PANI/TiO₂.

4. Conclusions

A hybrid composite material was prepared from a conductive polymer which is polyaniline doped by proton acid DBSA by chemical polymerization method. The physicochemical interaction between the polymer chains and titanium oxide nanoparticles proved by means of FTIR, the presence of which led to the improvement of crystallization of the polyaniline and that what the XRD results is revealed.

The electrical properties were also studied by a characteristic current voltage. The conductivity of PANI-DBSA was increased after doping with DBSA and decreased proportionally with the presence of TiO₂. The drop in conductivity of composite films is due to TiO₂ conductivity being lower than PANI-DBSA.

References

- [1] Mohammed, K. A., Ziadan, K. M., Al-Kabbi, A. S., Abdulzahr, D. S., Judi, H. K., & Hussein, H. M. (2021). The Role of Formic Acid as Secondary Dopant and Solvent for Poly (O-Toluidine) Intrinsically Doped with Camphor Sulfonic Acid. In *Materials Science Forum* (Vol. 1039, pp. 260-268). Trans Tech Publications Ltd.; <https://doi.org/10.4028/www.scientific.net/MSF.1039.260>
- [2] Ahilfi, D. N., Alkabbi, A. S., Mohammed, K. A., & Ziadan, K. M. (2020, November). Fabrication and Characterization of polyaniline/CdSe Device for Applications in Nano Structured Solar Cells. In *IOP Conference Series: Materials Science and Engineering* (Vol. 928, No. 7, p. 072069). IOP Publishing; <https://doi.org/10.1088/1757-899X/928/7/072069>
- [3] Diantoro, M., Masrul, M. Z., & Taufiq, A. (2018, April). Effect of TiO₂ nanoparticles on conductivity and thermal stability of PANI-TiO₂/glass composite film. In *Journal of Physics: Conference Series* (Vol. 1011, No. 1, p. 012065). IOP Publishing; <https://doi.org/10.1088/1742-6596/1011/1/012065>
- [4] Zhang, L., Liu, P., & Su, Z. (2006). Preparation of PANI-TiO₂ nanocomposites and their solid-phase photocatalytic degradation. *Polymer degradation and stability*, 91(9), 2213-2219; <https://doi.org/10.1016/j.polymdegradstab.2006.01.002>
- [5] Mo, T. C., Wang, H. W., Chen, S. Y., & Yeh, Y. C. (2008). Synthesis and dielectric properties of polyaniline/titanium dioxide nanocomposites. *Ceramics International*, 34(7), 1767-1771; <https://doi.org/10.1016/j.ceramint.2007.06.002>
- [6] Xing Z, Zhang J, Cui J et al (2018) Recent advances in floating TiO₂-based photocatalysts for environmental application. *Appl Catal B* 225:452-467; <https://doi.org/10.1016/j.apcatb.2017.12.005>
- [7] Burda, C., Lou, Y., Chen, X., Samia, A. C., Stout, J., & Gole, J. L. (2003). Enhanced nitrogen doping in TiO₂ nanoparticles. *Nano letters*, 3(8), 1049-1051; <https://doi.org/10.1021/nl034332o>
- [8] Song, Y., Xu, Y., Guo, Q., Hua, Z., Yin, F., & Yuan, W. (2021). MXene-Derived TiO₂ Nanoparticles Intercalating between RGO Nanosheets: An Assembly for Highly Sensitive Gas Detection. *ACS Applied Materials & Interfaces*, 13(33), 39772-39780; <https://doi.org/10.1021/acsami.1c12154>
- [9] Krishnapriya, R., Nizamudeen, C., Saini, B., Mozumder, M. S., Sharma, R. K., & Mourad, A. H. (2021). MOF-derived Co²⁺-doped TiO₂ nanoparticles as photoanodes for dye-sensitized solar cells. *Scientific reports*, 11(1), 1-12; <https://doi.org/10.1038/s41598-021-95844-4>
- [10] Chuang, Y. C., Chang, C. C., Yang, F., Simon, M., & Rafailovich, M. (2021). TiO₂ nanoparticles synergize with substrate mechanics to improve dental pulp stem cells proliferation and differentiation. *Materials Science and Engineering: C*, 118, 111366; <https://doi.org/10.1016/j.msec.2020.111366>
- [11] Alomary, M. N., & Ansari, M. A. (2021). Proanthocyanin-Capped Biogenic TiO₂ Nanoparticles with Enhanced Penetration, Antibacterial and ROS Mediated Inhibition of Bacteria Proliferation and Biofilm Formation: A Comparative Approach. *Chemistry-A European Journal*,

- 27(18), 5817-5829; <https://doi.org/10.1002/chem.202004828>
- [12] Xiong S, Wang Q, Xia H (2004) Template synthesis of polyaniline/TiO₂ bilayer microtubes. *Synth Met* 146:37-42; <https://doi.org/10.1016/j.synthmet.2004.06.017>
- [13] Chen F, An W, Li Y et al (2018) Fabricating 3D porous PANI/TiO₂-graphene hydrogel for the enhanced UV-light photocatalytic degradation of BPA. *Appl Surf Sci* 427:123-132; <https://doi.org/10.1016/j.apsusc.2017.08.146>
- [14] Jangid, N. K., Jadoun, S., Yadav, A., Srivastava, M., & Kaur, N. (2021). Polyaniline-TiO₂-based photocatalysts for dyes degradation. *Polymer Bulletin*, 78(8), 4743-4777; <https://doi.org/10.1007/s00289-020-03318-w>
- [15] Massoumi, B., Badalkhani, O., Gheybi, H., & Entezami, A. A. (2011). Poly (N-octadecylaniline) synthesis and its electrochemical parametric characterizations.
- [16] Nguyen, H. D., Nguyen, T. H., Hoang, N. V., Le, N. N., Nguyen, T. N. N., Doan, D. C. T., & Dang, M. C. (2014). pH sensitivity of emeraldine salt polyaniline and poly (vinyl butyral) blend. *Advances in Natural Sciences: Nanoscience and Nanotechnology*, 5(4), 045001; <https://doi.org/10.1088/2043-6262/5/4/045001>
- [17] M.M. Abutalib, Insights into the structural, optical, thermal, dielectric, and electrical properties of PMMA/PANI loaded with graphene oxide nanoparticles, *Phys. B Condens. Matter*. 552 (2019) 19-29; <https://doi.org/10.1016/j.physb.2018.09.034>
- [18] Subramanian, E., Ramalakshmi, R. D., Vijayakumar, N., & Sivakumar, G. (2012). Hybrid composite materials of anatase titania and conducting polyaniline: properties and chemical sensor application.
- [19] Amaechi, I. C., Nwanya, A. C., Ekwealor, A. B., Asogwa, P. U., Osuji, R. U., Maaza, M., & Ezema, F. I. (2015). Electronic thermal conductivity, thermoelectric properties and supercapacitive behaviour of conjugated polymer nanocomposite (polyaniline-WO₃) thin film. *Eur. Phys. J. Appl. Phys*, 69, 30901; <https://doi.org/10.1051/epjap/2015140441>
- [20] Vijayalakshmi, S., Kumar, E., Ganeshbabu, M., Venkatesh, P. S., & Rathnakumar, K. (2021). Structural, electrical, and photocatalytic investigations of PANI/ZnO nanocomposites. *Ionics*, 27(7), 2967-2977; <https://doi.org/10.1007/s11581-021-04041-w>
- [21] Thamaphat, K., Limsuwan, P., & Ngotawornchai, B. (2008). Phase characterization of TiO₂ powder by XRD and TEM. *Agriculture and Natural Resources*, 42(5), 357-361.
- [22] He, J., Du, Y. E., Bai, Y., An, J., Cai, X., Chen, Y., ... & Feng, Q. (2019). Facile formation of anatase/rutile TiO₂ nanocomposites with enhanced photocatalytic activity. *Molecules*, 24(16), 2996; <https://doi.org/10.3390/molecules24162996>