

GREEN SYNTHESIS OF Co_3O_4 /POLYANILINE NANOSTRUCTURES FOR STRUCTURAL, MORPHOLOGICAL, AND ELECTRICAL STUDIES

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ABSTRACT

In this work, Polyaniline (PANI)-Cobalt oxide (Co_3O_4) nanoparticles (NPs) were synthesized via in-situ polymerization. The PANI- Co_3O_4 hybrid nanocomposites (NCs) morphology revealed a granular structure with a hole in the middle of the spectrograms, as determined using XRD, FTIR, SEM, and TEM. Superior electrical properties are shown by Polyaniline/ Co_3O_4 (50%)'s Alternating Current (AC) conductivity. Direct Current (DC) conductivity is temperature dependent, which is related to chain length and 50 wt. % greater conductivity. It is promising material for fabricating optoelectronic devices.

Keywords: PANI, Cobalt Oxide, XRD, SEM, Conducting Polymer.

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INTRODUCTION

A wide range of industries, including military equipment, defensive clothing, automotive, aviation, photosensitive devices, and catalysis, have made extensive use of hybrid NCs made of polymers and inorganic nano oxides. It results from the blending of inorganic and natural hybrid materials, which endows them with exceptional properties.¹⁻⁴ In order to be used in a variety of application sectors, these hybrid nanocomposites need to possess good mechanical qualities, water repellence, fire resistance, chemical and radiation resistance, and environmental stability. Considering that their properties vary greatly from those of PANI and Co_3O_4 NPs, which may be explained by the PANI and Co_3O_4 NPs interfacial contacts⁶⁻¹¹, NCs composed of PANI and Co_3O_4 are increasingly being studied. In order to produce hybrid nanocomposites, the present work emphasizes dispersing Co_3O_4 NCs in a polyaniline matrix. Inorganic oxide Co_3O_4 NPs were produced using a solution combustion method and then embedded in a Polyaniline matrix. Diverse characterisation approaches were used to analyze the synthesized NCs.

EXPERIMENTAL

Synthesis of Polymers

Polyaniline is produced by mixing ammonium persulfate ($(\text{NH}_4)_2\text{S}_2\text{O}_8$) with an aqueous solution of aniline. After filtering out the resultant greenish-black precipitate, acetone was used to clean it. After designing the PANI precipitate, it was dried for 24 hours at around 80°C in an air oven.

Bio-Mediated Co_3O_4 Nanoparticles Synthesis

Aloe-Vera (A.V.) gel was used as biological fuel in the low-temperature solution fire technique to produce Co_3O_4 NPs. 2.14 grams of cobalt nitrate hexahydrate and 15 milliliters of A.V. gel were added to a ceramic crucible and carefully mixed. Next, the response mixture was heated to 400 degrees Celsius in a preheated muffle furnace. Co_3O_4 NPs are produced by the combustion of the fuel and metallic nitrates.

Synthesis of PANI/ Co_3O_4 Hybrid NCs

PANI was combined with Co_3O_4 NCs by an in-situ polymerization process. To reach equality, 0.1M aniline and 1 M. of HCl were mixed and agitated for about 15 minutes. The Co_3O_4 NCs were gently dispersed by adding them to the previously described mixture at the proper weight percentage. Polymer blend was gradually mixed while the oxidizing agent, 0.2M ammonium persulfate, was incorporated drop by drop to finish the polymerization process.⁵ After that, the combination was kept for four hours at ice

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temperature. Following filtration, acetone and deionised water were used to rinse the precipitate. To get a constant mass, it underwent a 24-hour thermal treatment using a hot air oven at 80°C. As shown in Fig.-1, this technique was used to produce PANI/Co₃O₄ NCs varying (wt.% %) of Co₃O₄ (10, 20, 30, 40, and 50 wt.%%).

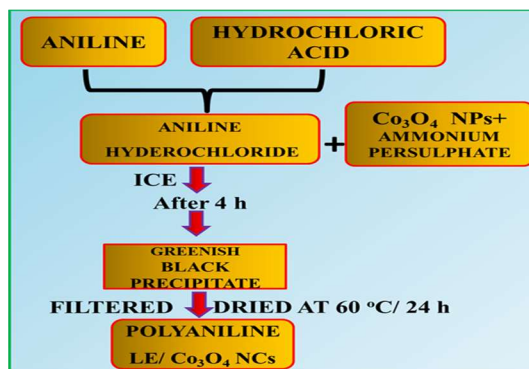


Fig.-1: Synthesis Flowchart of PANI/Co₃O₄ NCs

RESULTS AND DISCUSSION

PXRD Analysis

Figure-2 shows PANI, Co₃O₄ NPs, and PANI/Co₃O₄ NCs (10–50 wt.% %) PXRD patterns. PANI NPs have a prominent peak at a Bragg angle of 24° (2θ).¹³⁻¹⁶ In the present NCs, the incorporation of Co₃O₄ NPs diminishes the wide peak of PANI. According to the ICDD card No. 73-1519 standard¹⁵, the Co₃O₄ XRD patterns lattice parameters, which show a basic cubic structure, are a = b = c = 4.1678. The lattice parameters of the (200) X-ray diffraction of cubic structured Co₃O₄ in PANI/Co₃O₄ (10-50 wt.%) polymer NCs were found to be a = b = c = 4.183 Å using existing relations. The PANI/ Co₃O₄ hybrid NCs showed a significant increase in the lattice parameters of Co₃O₄. The basic building block (unit cell) of the crystalline Co₃O₄ material is somewhat extended as a consequence of the adsorption of PANI atomic chains on its surface. The change in crystallite size of the most prominent peaks (200) planes in X-ray diffraction patterns of PANI/ Co₃O₄ hybrid NCs can also be ascribed to the presence of such interactions. PANI/Co₃O₄ hybrid NCs and Co₃O₄ crystallite dimensions are computed for the (200) visible peaks using Scherrer's formula:

$$D = \frac{0.9\lambda}{\beta \cos \theta} \quad (1)$$

Here, D represents the typical crystallite size, β represents the peak's FWHM⁵. Cobalt oxide (Co₃O₄) crystallite size in PANI/Co₃O₄ NCs increases from 22 nm to 37 nm along the (200) plane. PANI atomic chains are absorbed on the Co₃O₄ surface in PANI/Co₃O₄ NCs, indicating an expansion of the crystallinity of Co₃O₄.

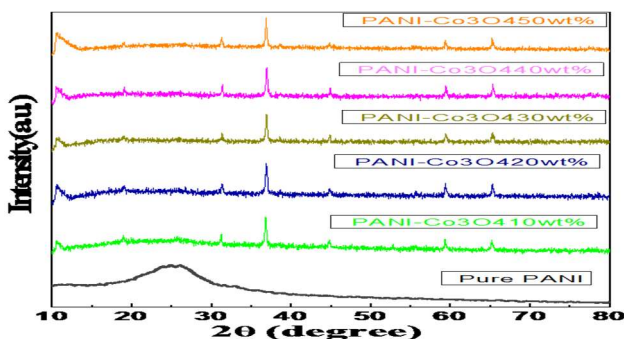


Fig.-2: PXRD Patterns Pure PANI and PANI/ Co₃O₄ NCs

Organizational and Morphological Studies

The surface morphology of current polymer/metal oxide composites is shown in Fig.-3. Co_3O_4 NPs have a nano-crystalline surface morphology (Fig.-3b), while pure PANI has a granular surface geomorphology with holes in the middle of the spectrographs (Fig.-3a). Figure-3c displays the morphology of the PANI/ Co_3O_4 nanocomposites that were prepared (10–50 weight percent). When the PANI matrix's Co_3O_4 content is raised by 50 weight percent, the morphology displays crowded groups (Fig.-3c).

Table-1: Estimated Average Crystallite Size, PANI/ Co_3O_4 (10-50 wt% %) NCs.

Co_3O_4 (wt %)	Crystallite size (nm) by Scherer's method
10	23
20	29
30	30
40	33
50	34

Permeable linked nanospheres are produced when Co_3O_4 (50 weight percent) NCs are further incorporated into the PANI matrix (Fig.-3.c). Figure-3(d-e) Co_3O_4 content is visible in the PANI matrix according to SEM EDX spectra. As seen in Fig.-4(a) to 4(d), respectively, the TEM analysis offers additional insight into the form and Pure PANI and Co_3O_4 NPs in PANI/ Co_3O_4 hybrid NCs construction. According to Fig.-3 (a-d), the synthesized PANI/ Co_3O_4 50 weight percent NCs had a diameter of 38 nm to 40 nm. These findings are consistent with the PXRD patterns obtained. The PANI/ Co_3O_4 50weight% % NCs inter-planar space is shown in Fig.-3(c-d) between 0.28 nm and 0.32 nm.

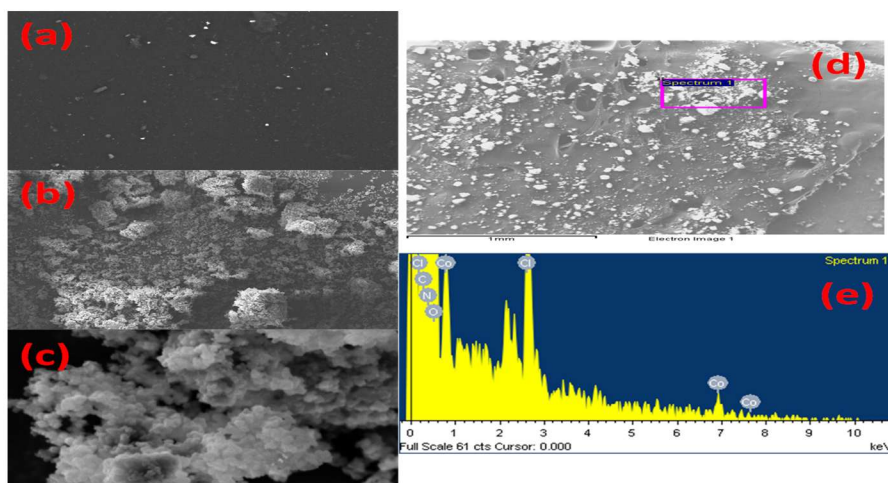


Fig.-3: Pure PANI SEM Micrographs, (b) Co_3O_4 NPs, (c) PANI/ Co_3O_4 NSs, and (d-e) PANI/ Co_3O_4 Nanostructures (NSs) EDX Spectra

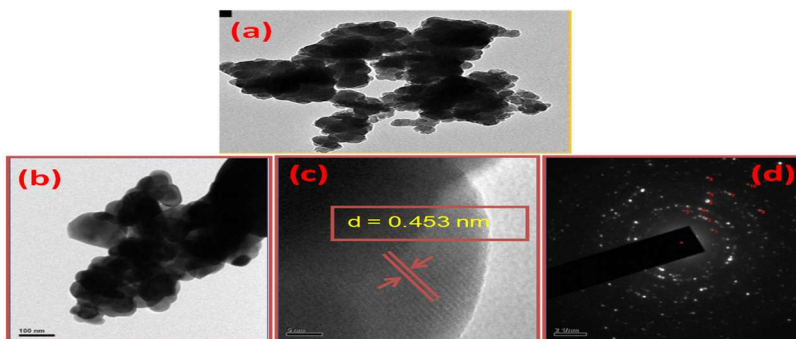


Fig.-4: TEM of (a) PANI, (b) Co_3O_4 NPs, and (c,d) PANI/ Co_3O_4 (50 wt% %) NSs

Electrical Conductivity

A. C. Conductivity

PANI/Co₃O₄ NCs frequency-dependent AC conductivity is shown in Fig.-5.5. PANI/Co₃O₄ NCs residual conductivity doesn't change until 2×10^7 Hz, at which point it increases at high frequencies. The IR graph indicates that chain length may be related to the maximum conductivity perceived in PANI/Co₃O₄ (50 wt%) samples. Increased conductivity gift be caused by stronger charge polarization.^{3,5}

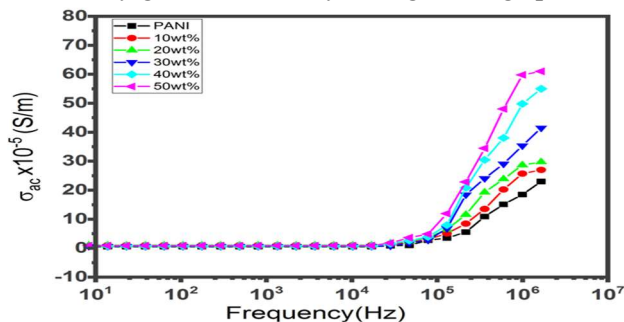


Fig.-5: PANI/Co₃O₄ NCs AC Conductivity

D.C. Conductivity

The range of DC conductivity for (Co₃O₄) in polyaniline as a function of temperature is shown in Fig.-6. It's observed that the measurement of these nanocomposites' DC conductivity rises exponentially with temperature.¹³ Dispersion of Co₃O₄ NPs with bigger particle sizes, which partially obstruct hopping's charge carriers, may also be responsible for the conductivity decrease that is observed.¹⁴⁻¹⁶ PANI/Co₃O₄ NCs temperature-dependent DC conductivity is shown in Fig.-6. Up to 100°C, PANI/Co₃O₄ NCs' conductivity is stable; at higher temperatures, it starts to increase. The PANI/Co₃O₄ (50 wt% %) samples' high conductivity may be caused by the length of the chain. The reason for increased conductivity might be enhanced charge polarization.

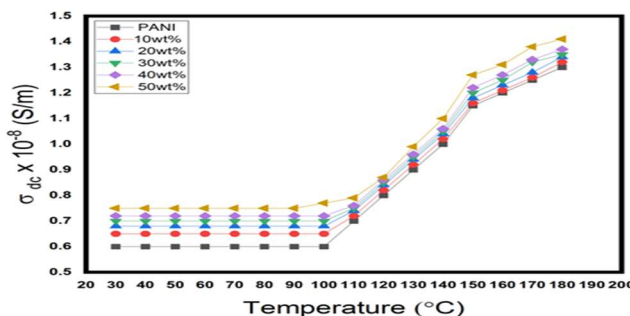


Fig.-6: PANI/Co₃O₄ NCs DC Conductivity

CONCLUSION

PANI/Co₃O₄ NCs were effectively produced by an in-situ polymerization approach. Co₃O₄ nanoparticles cubic phase and amorphous nature of pure PANI are validated through PXRD patterns, while the morphology of pure PANI and the mixtures were carefully examined using TEM micrographs. Comparing PANI/Co₃O₄ (50 weight percent) to the other NCs, the AC Conductivity shows better electrical properties. According to the IR graph, samples and chain length could be related. Augmented conductivity may result from improved charge polarization. The IR graph indicates a possible relationship between the chain length and the excessive temperature-dependent DC conductivity observed in samples of PANI/Co₃O₄ (50wt%). Elevated conductivity may result from improved charge polarization. In summary, the results show that the present PANI/Co₃O₄ hybrid NCs are promising materials for the fabrication of optoelectronic devices, and the materials that are intended for these NCs are semiconductors.

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CONFLICT OF INTERESTS

There is no conflict of interest, according to the authors.

AUTHOR CONTRIBUTIONS

The present work is related to *SDG-12: Responsible Consumption and Production*. All the authors contributed significantly to this manuscript, participated in reviewing/editing and approved the final draft for publication. The research profile of the authors can be verified from their ORCID ids, given below:

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REFERENCES

1. Anandrao S. Kulkarni, Hajeebaba K. Inamdar, M. Sasikala, M.V.N. AmbikaPrasad, *The International Journal of Analytical and Experimental Modal Analysis*, **13**,16(2021), <http://doi.org/18.0002.IJAEMA.2021.V13I3.200001.0156859021628>
2. J. Venkatreddy, Narsappa Reddy, B. R. Reddy, P. Naresh, B. Lavanya, M.V.N.A. Prasad, Hajeebaba K. Inamdar, *AIP Conference Proceedings*, **2269**(1), 030094(2020), <http://doi.org/10.1063/5.0019605>
3. Bharati Basavaraj, Hajeebaba K. Inamdar, M. Sharanabasamma, *AIP Conference Proceedings*, **2269**(1), 030109(2020), <http://doi.org/10.1063/5.0019777>
4. Hajeebaba K. Inamdar, Narsappa Reddy, S. Abdul Khader, Pallati Naresh, M.V.N. Ambika Prasad, G.S. Durga Prasad, *Composites Communications*, **14**, **21**(2019), <http://doi.org/10.1016/j.coco.2019.04.004>.
5. Mahadeva, Hajeebaba K. Inamdar, Chakradhar Sridhar B., *Materials Today: Proceedings*, **68**(3), 424(2022), <https://doi.org/10.1016/j.matpr.2022.06.575>.
6. Hajeebaba K. Inamdar, M.V.N. Ambika Prasad, R.B. Basavaraj, M. Sasikala, S.C. Sharma, H. Nagabhushana, *Optical Materials*, **88**, 458(2018), <http://doi.org/10.1016/j.optmat.2018.11.042>
7. D. Navami, R.B. Basavaraj, G.P. Darshan, Hajeebaba K. Inamdar, S.C. Sharma, H.B. Premkumar, H. Nagabhushana, *Optical Materials*, **88**, 479(2019), <http://doi.org/10.1016/j.optmat.2018.11.058>
8. Gilroy JJ, Gill JA, Butchart SHM, Jones VR, Franco, *Ecology Letters*, **19**(3),308(2016), <http://doi.org/10.1111/ele.12569>
9. C. E. Studds, B. E. Kendall, N. J. Murray, H. B. Wilson, D. I. Rogers, R. S. Clemens, *et al.*, *Nature Communications*, **8**(1),14895(2017), <http://doi.org/10.1038/ncomms14895>
10. J. Kamp, S. Oppel, A. A. Ananin, Y. A. Durnev, S. N. Gashev, N. Hölzel, *et al.*, *Conservation Biology*, **29**(6),1684(2015), <http://doi.org/10.1111/cobi.12537>
11. L. J. Koudelka, J. Jiráček, P. Mošner, L. Montagne, G. Palavit, *Journal of Materials Science*, **41**, 4636(2006), <https://doi.org/10.1007/s10853-006-0031-x>
12. P. Venkateshwararao, G. Raju, P. Prasad, C. Laxmikanth, N. Veeraiah, *Optik*, **127**(5), 2920(2016), <https://doi.org/10.1016/j.ijleo.2015.12.056>
13. S. C. Colak, I. Akyuz, F. Atay, *Journal of Non-Crystalline Solids*, **432**, 406(2016), <https://doi.org/10.1016/j.jnoncrysol.2015.10.040>
14. S. Kabi, *Solid State Ionics*, **334**, 65(2019), <https://doi.org/10.1016/j.ssi.2019.01.036>
15. M. Daefalla, M. Tawat, Jamel Basha Adlan, Mat Johr Abdullah, *Journal of Non-Crystalline Solids*, **357**(10), 2152(2011), <https://doi.org/10.1016/j.jnoncrysol.2011.02.011>
16. A. Megha, K. Salorkar, V. K. Gour, Deshpande, *Journal of Alloys and Compounds*, **865**,158926(2021), <https://doi.org/10.1016/j.jallcom.2021.158926>

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