International Journal of Chemical Studies

P-ISSN: 2349–8528
E-ISSN: 2321–4902
www.chemijournal.com
IJCS 2024; 12(1): 46-50

Received: 01-11-2023
Accepted: 08-12-2023

Kusum Lata
Department of Chemistry, Baba Mastnath University, Asthal Bohar, Rohtak, Haryana, India

Jyoti
Department of Chemistry, Baba Mastnath University, Asthal Bohar, Rohtak, Haryana, India

Ravi Kumar Rana
Department of Chemistry, Baba Mastnath University, Asthal Bohar, Rohtak, Haryana, India

Corresponding Author:
Ravi Kumar Rana
Department of Chemistry, Baba Mastnath University, Asthal Bohar, Rohtak, Haryana, India
Email id: hit.ravirana@gmail.com

Synthesis and characterization of polyaniline-copper oxide nano-composites

Kusum Lata, Jyoti and Ravi Kumar Rana

DOI: https://doi.org/10.22271/chemi.2024.v12.i1a.12396

Abstract
Polyaniline-based metal oxide composites offer unique features that make them useful in many technical domains. This research synthesizes and characterizes these composites to reveal their structural, morphological, anxd functional properties. Combining metal oxide nanoparticles with the conductive polymer polyaniline multiplies material and application capabilities. The oxidizing agents and reaction conditions must be carefully controlled during aniline monomer oxidative polymerization. This allows for composite qualities to be tailored to sensor, energy storage, and catalytic technology challenges. Copper oxides are inherently p-type semiconductors with narrow band gaps and possess numerous desirable features that can be used in a wide range of applications. This research presents the production of CuO nanoparticles and the fabrication of polyaniline-CuO Nano composites using five distinct proportions of CuO nanoparticles. The samples underwent characterization using X-ray diffraction (XRD) and scanning electron microscopy (SEM). Utilizing electrochemical impedance spectroscopy (EIS) and CV to determine their potential use in sensors and energy storage devices.

Keywords: Polyaniline, composites, copper oxide, nanoparticles

Introduction
The complimentary properties of conductive polymers and metal oxide nanoparticles have made composites made by mixing these materials a hot topic in the field of advanced materials. Considerable research has been dedicated to studying polyaniline, a conductive polymer, because to its exceptional electrical conductivity, environmental durability, and straightforward manufacturing process [1]. The addition of metal oxide nanoparticles to polyaniline allows for easy modification of these composites, which have great promise for applications in sensing, electronics, and energy storage, among many other areas. To achieve a well-defined and optimized material structure, metal oxide composites based on polyaniline are synthesized and characterized using a multi-step approach. Conductivity, stability, and reactivity are all enhanced thanks to the careful selection of metal oxides and the unique properties of polyaniline. This comprehensive approach has the ability to address issues in various technological domains, including energy storage, sensor technology, and catalysis [2].
Polyaniline, a conductive polymer, is typically made via oxidative polymerization of aniline monomers. The oxidizing agent and reaction conditions utilized have a significant impact on the structure and properties of the resulting polymer. The conductive properties of polyaniline are derived from its π-conjugated backbone, which enables charge mobility within the polymer matrix [3]. Metal oxide nanoparticles added to the polyaniline matrix modify the composite's characteristics and add new functions. You can make metal oxides like copper oxide in situ during polymerization, or you can make them separately and then combine them. Improved performance characteristics are the result of the complementary qualities of metal oxides and polyaniline [4].

Characterization Techniques
A thorough characterization of these composite materials is necessary to comprehend their functional, morphological, and structural characteristics. Composites' chemical bonding and structural composition can be uncovered using methods such as (XRD) and (FTIR). Researchers can gain a better understanding of particle size, distribution, and surface features through morphological examination utilizing (SEM) and (TEM) [5].

In order to proceed, we determine the composite's chemical composition using (EDS) and (XPS). The Four-Probe Method of conductivity can be used to measure the electrical characteristics of polyaniline since it is electrically conductive. Tensile testing and other mechanical testing procedures are used to analyze mechanical properties, whereas (TGA) is used to determine thermal stability [6].

The potential sensor and energy storage device applications of the composites are explored using electrochemical techniques like (EIS) and (CV). Optoelectronic device applications can be better understood by analyzing materials' optical properties with UV-Visible Spectroscopy [7].

(Prashanth *et al*., 2021) describes the process of creating and analyzing polyaniline (PANI) and PANI/Copper oxide (PANI/CuO) nanocomposites. Polyaniline (PANI) was manufactured by a chemical process, while a mechanical mixing approach was employed to prepare the PANI/CuO Nanocomposite. The produced materials underwent characterization using FTIR, XRD, SEM, and electrical conductivity analysis employing the four-probe method. Additionally, their methanol gas sensing properties were evaluated. FTIR spectra validate the existence of distinct peaks that are indicative of PANI. The XRD spectrum confirms the existence of copper oxide nanoparticles in PANI, while the SEM micrographs illustrate the dispersion of these nanoparticles inside the PANI matrix. The electrical conductivity of PANI has decreased when different weight percentages of CuO were included. The gas sensing capability of PANI-CuO was shown to be higher than that of pure PANI [8].

(Hemalatha *et al*., 2019) presents the fabrication of composites consisting of Polyaniline/Cu-doped materials. This study synthesized Polyaniline/CuO-doped composites by conducting an in situ polymerization of Aniline monomer in the presence of CuO that was doped with ammonium per sulfate (APS) as an oxidant. Polyaniline was modified by using various amounts (10-50 wt %) of CuO metal oxides. The finished product was thoroughly analyzed using PXRD, SEM, and XRD techniques, which revealed the presence of CuO particles in Polyaniline. The shape of the resulting product exhibits porous and agglomerated particles, which can be attributed to a significant release of gas during the synthesis process. The current investigation illustrates that the generated samples are highly beneficial for electrochemical storage applications [9].

Materials and Methods

The chemicals used, such as copper (II) nitrate, aniline, ammonium persulfate, ammonia solution, acetone, ethanol, and concentrated HCl, were of high purity and suitable for analysis. The experiment employed double distilled water.

Synthesis of Polyaniline

We employed oxidative polymerization of aniline in our work. Two separate flasks were used to create a solution consisting of 0.5 M aniline and 0.5 M ammonium persulfate in 0.5 M hydrochloric acid. The two substances were gradually combined using magnetic stirring, resulting in the gradual transformation of the colorless solution into a green hue. The mixture was allowed to stand undisturbed for a few hours to allow the powder to settle, after which it was filtered using a Buchner funnel. A dark green paste-like residue was obtained. Subsequently, the paste underwent a thorough rinsing with acetone to eliminate soluble aniline molecules with low molecular weight, followed by complete drying of the paste. The dry material was ground into a fine powder using a Passel motor, resulting in a conductive PANI powder. The powder was then sealed for further processing.

Synthesis of CuO nano particles

6 grams of copper turnings were collected in a 100 milliliter beaker, followed by the progressive addition of 24 milliliters of HNO_3. The copper turnings underwent oxidation, resulting in a highly concentrated solution that transitioned from a greenish color to a brownish-green color. The concentrated solution exhibits a bluish-green color. Nevertheless, upon dilution with 600ml of distilled water, the substitution of nitrate ions by water molecules occurred in the coordination sites around the copper ions, leading to a change in the solution's hue to blue. The solution was incrementally augmented with a 10% sodium chloride solution and stirred. The copper hydroxide precipitate was gathered, filtered, and then treated to several rinses with distilled water. Ultimately, it was subjected to air drying at ambient temperature. The material underwent calcination at a temperature of 400 °C for a period of 2 hours. The resultant sample, exhibiting a black hue, was gathered for additional processing.

Synthesis of PANI-CuO nano composites

The synthesis of five separate nano-composite samples of PANI-CuO was conducted using the following procedure: The measured mass of CuO was added to the mixture of aniline and hydrochloric acid and stirred for a period of one hour. Afterwards, ammonium persulfate was added to the mixture and stirred at a lower temperature for a period of six hours. The solution was subsequently filtrated, and the resulting verdant paste was initially cleansed with acetone, followed by a subsequent rinse with distilled water. The paste was later dehydrated by air-drying for two days, and then further dried in an oven at a temperature of 70 °C for eight hours. The resultant sample was a bottle-contained dark green powder, intended for later processing. Upon the polymerization of aniline, the resulting sample was found to have a copper oxide (CuO) content of 10wt%. The procedure was duplicated to generate PANI-CuO nano composites with weight proportions of 15%, 20%, 25%, and 30%.

Results and Discussion

“The XRD patterns of pure PANI and nano CuO are shown in Figures 1 and 2, respectively. The XRD pattern of pure PANI indicates that it is amorphous, with three broad peaks visible at 2θ values of 15°, 20°, and 25°.” Figure 2 displays the crystalline structure of the sample. The presence of peaks at 2θ values of 25.76° and 29° indicates a monoclinic structure for the CuO nanoparticles. The CuO nanocrystalline's average crystallite size at 20 nm can be determined using Scherrer's formula.

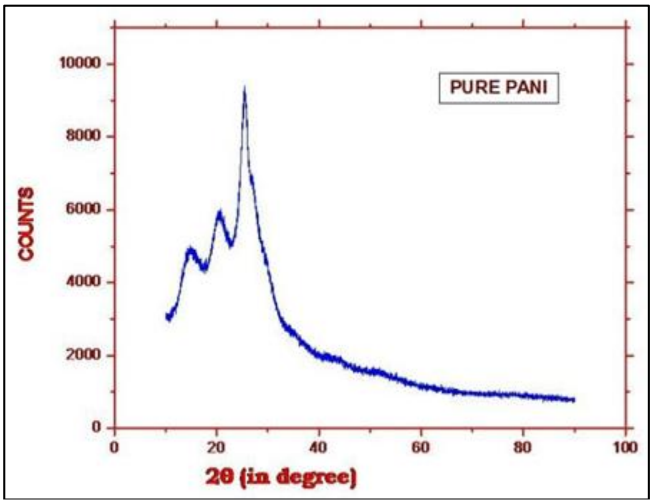

Fig 1: XRD of pure PANI

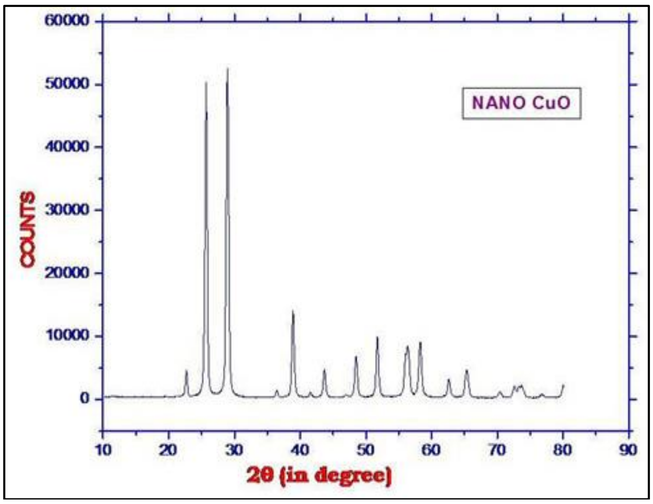

Fig 2: XRD of nano particles of CuO

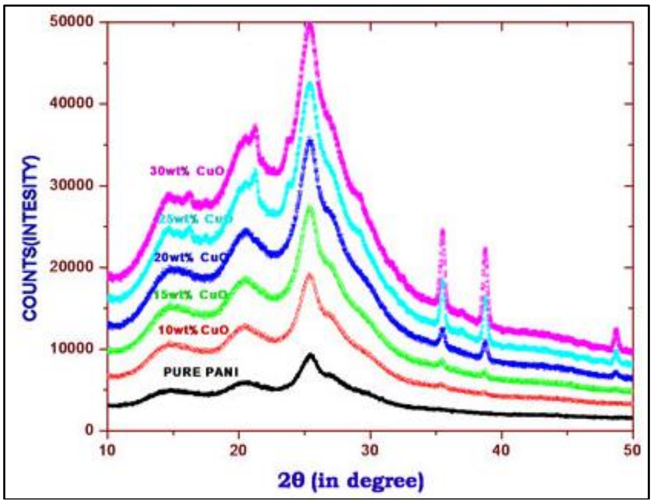

Fig 3: XRD of pure PANI and the nano PANI-CuO nanocomposites

"The XRD patterns of PANI-CuO nanocomposites with varying weight percentages (10%, 15%, 20%, 25%, and 30%) of CuO are displayed in Figure 3." "The five created composites share a same peak at $2\theta=25^{o}$, suggesting that the PANI maintains its identity during the composite phase. The peaks at $2\theta = 35.42^{o}$, $2\theta = 38.75^{o}$, and $2\theta = 48.62^{o}$ have higher heights as the weight % of CuO nanoparticles rises." As the proportion of CuO nanoparticles increases, the nanocomposite progressively moves from the amorphous to the crystalline phase. The Scherer formula was used to determine the average crystallite size of the nanocomposites, which is shown in Table 1.

Table 1: "Average particle size of prepared samples"

"PANI-CuO Nanocomposite"	Diameter (nm)
"10 wt % of CuO"	14.79
"15 wt% of CuO"	12.06
"20 wt % of CuO"	11.44
"25 wt % of CuO"	14.13
"30 wt % of CuO"	10.77

Figures 4(a-g) show the SEM pictures of the five nanocomposites, pure PANI, and CuO nanoparticle. The pure polyaniline Scanning Electron Micrograph (SEM) picture, as shown in Figure 4(a), demonstrates the amorphous nature and well-connected grains. The SEM picture of CuO nanoparticles in Figure 4(b) demonstrates the uniform dispersion of spherical particles. The SEM picture of the 10wt% PANI-CuO composite is shown in Figure 4(c). The CuO oxide particles are not evenly distributed, and the grains have an uneven shape. "The SEM images of the 15 wt%, 20 wt%, 25 wt%, and 30 wt % PANI-CuO composites are shown in Figures 4(d), (e), (f), and (g). An increase in the weight percentage of CuO causes the composite materials to become more crystallinity."

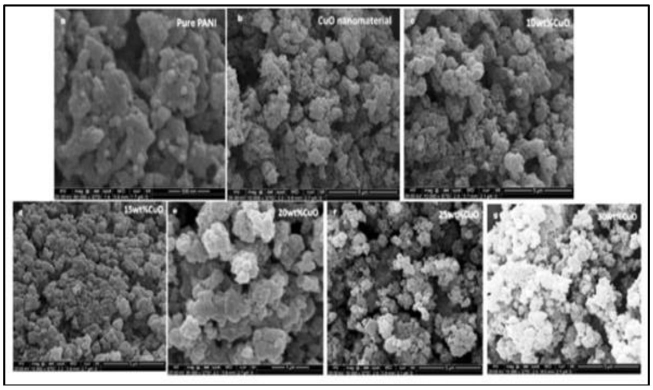

Fig 4 (a-g): SEM images of Pure PANI, CuO Nanoparticles and PANI-CuO nanocomposites of different weight percentages (10%, 15%, 20%, 25%, & 30% of CuO)

Cyclic voltmeter

The cyclic voltammetric analysis of the polyaniline/CuO nanocomposite reveals an oxidation peak at 0.3502 V and a reduction peak at -0.3672 V. These peaks suggest the presence of an interaction between polyaniline and CuO nanoparticles.

The computed capacitance values derived from the CV curves are displayed in the subsequent table. The capacitance values demonstrate an increase in response to doping.

Table 2: The computed capacitance values derived from the CV curves are displayed in the subsequent table.

Materials	Average Current µ A	Scan rate V	Capacitance µ F
CuO	70	0.025	280
PANI	120	0.025	480
PANI -CuO	220	0.025	880

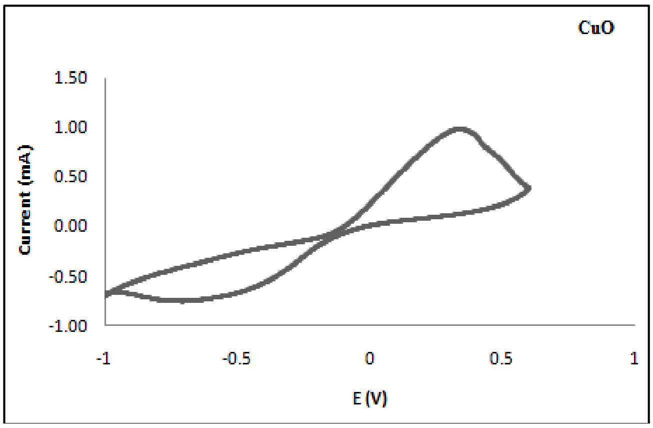

Fig 5(A): Cyclic Voltammogram of CuO Nanoparticle

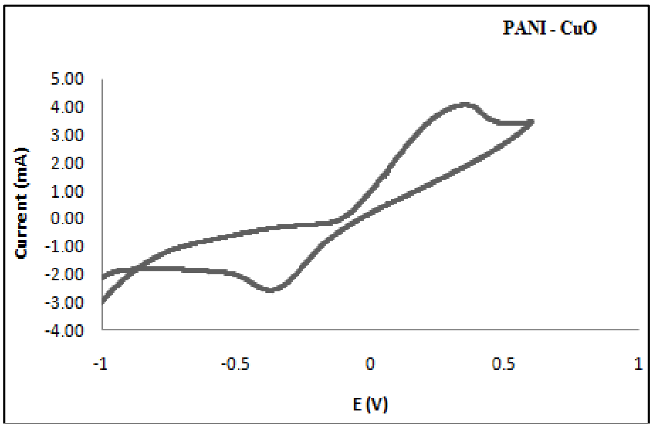

Fig 6(C): Cyclic Voltammogram of PANI-CuO nanocomposite

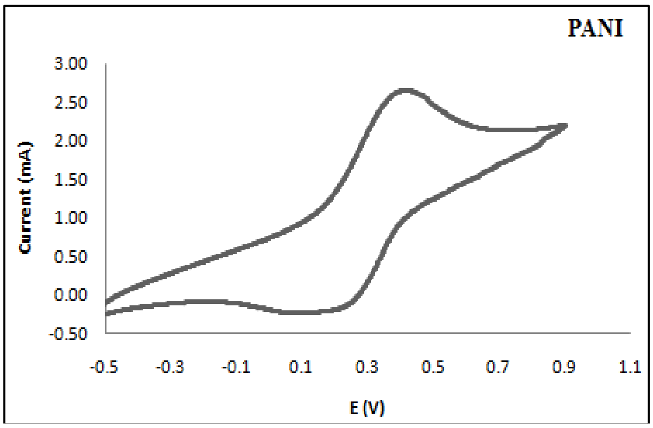

Fig 6(B): Cyclic Voltammogram of PANI

Electrochemical Impedance Spectroscopy

IES and CV are two electrochemical techniques that can be used to study the properties and behavior of polyaniline-copper oxide nano-composites. IES measures the impedance of a material as a function of frequency, which can reveal information about the charge transfer, diffusion, and capacitance of the material. CV measures the current response of a material as a function of applied potential, which can reveal information about the redox reactions, electron transfer kinetics, and electro activity of the material. These techniques can be used to synthesize, characterize, and optimize the performance of polyaniline-copper oxide nano-composites for various applications, such as sensors, batteries, super capacitors, and solar cells

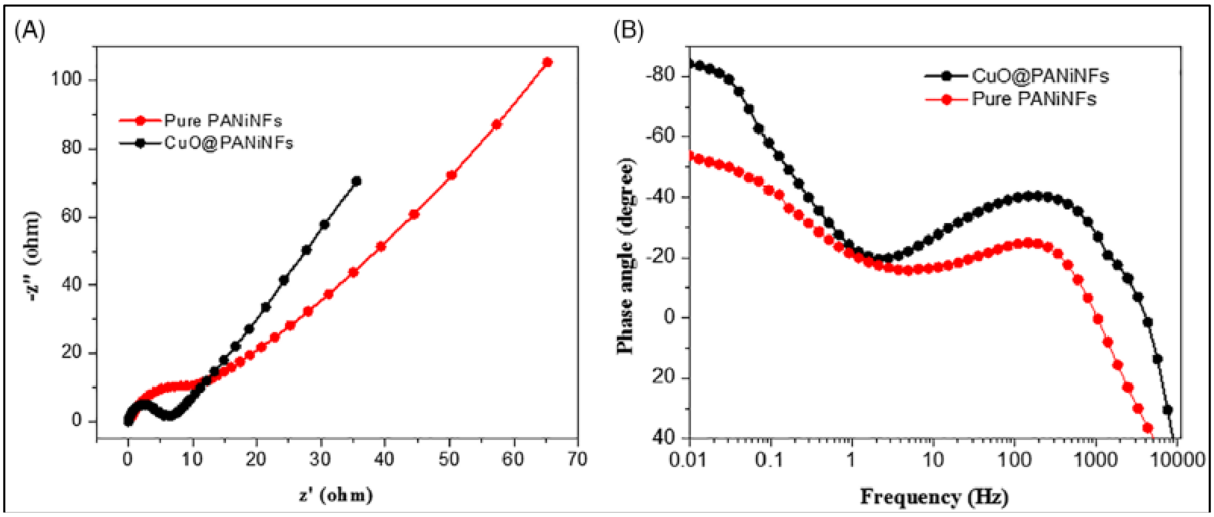

Fig 7: (A) Electrical impedance spectroscopic curves and (B) Bode plots pure polyaniline Nanofibers and copper oxide-decorated polyaniline Nanofibers Nano composite electrodes

An outstanding pseudo capacitive performance is shown by the Nano composite, as evidenced by the fact that the electrode of CuO @ PANiNFs (84.2) is remarkably close to that of an ideal super capacitor (90). As a consequence of the synergistic combination of PANiNFs with electro active CuO nanoparticles, as well as the alteration of their structure and shape, the electrochemical performance of the CuO @ PANiNFs electrode was significantly improved. This was accomplished by modifying the particles' structure and shape.

Conclusion

The synthesis of polyaniline-copper oxide (PANI-CuO) nano composites marks a significant achievement in the exploration of advanced materials. The X-ray diffraction (XRD) patterns obtained during the study revealed compelling insights into the crystallization process, showcasing distinct alterations as a function of varying weight percentages of CuO nanoparticles. Notably, the degree of crystallinity exhibited a discernible augmentation in PANI-CuO Nano composites, a trend mirroring the increased incorporation of CuO nanoparticles.

The XRD analysis not only provided a quantitative measure of crystallinity but also served as a key indicator of the structural evolution within the composite materials. The shifting patterns underscored the intricate interplay between polyaniline and copper oxide, shedding light on their cooperative influence on the overall crystalline structure.

Furthermore, the SEM (Scanning Electron Microscopy) images employed for morphology analysis added another layer of understanding to the synthesized materials. The microscopic examination revealed a noteworthy aspect of the Nano composites the distribution of CuO nanoparticles within the polymer matrix. As the weight percentage of CuO increased, the SEM images distinctly portrayed a more homogeneous dispersion of nanoparticles throughout the PANI matrix. This uniform distribution is pivotal for optimizing the synergistic effects between the polymer and metal oxide components, influencing the overall performance and properties of the composite.

PANiNFs' synergistic interaction with electro active CuO nanoparticles and their structural and shape alterations increased the electrode's electrochemical performance, putting it near an ideal super capacitor (90).

These findings not only validate the success of the synthesis process but also underscore the meticulous control exercised over the composition, revealing a systematic relationship between the CuO content and the resultant morphological characteristics. The observed homogeneity in nanoparticle dispersion holds promise for enhanced functionalities and improved performance in various applications.

References

1. Nadaf LI, Venkatesh KS. Polyaniline-Copper Oxide Nano-Composites: Synthesis and Characterization. Mater Sci Res India; c2015. Available from: doi:10.13005/msri/120204
2. Beygisangchin M, Rashid SA, Shafie S, Sadrolhosseini AR, Lim HN. Preparations, properties, and applications of polyaniline and polyaniline thin films—a review. Polymers (Basel). [Online]. 2020;13(12):2003. Available from: doi:10.3390/polym13122003
3. Boeva ZA, Sergeyev VG. Polyaniline: Synthesis, properties, and application. Polym Sci - Ser C; c2014. Available from: doi:10.1134/S1811238214010032
4. Shubha LN, Kalpana M, Rao PM. Study of chemically synthesized polyaniline / copper oxide Nanocomposites. In: Frontiers in Chemical Research and Analysis; c2015.
5. Raja MD S. Synthesis and Characterization of Polyaniline-Copper (II) Oxide Nanocomposite. [Online]. 2015. Available from: [insert URL if available]
6. Sangamesha MA, Pushpalatha K, Shekar GL. Synthesis and Characterization of Conducting Polyaniline/Copper Nanocomposites. Indian J Adv Chem Sci. 2014;2(3):223-227.
7. Ramirez JMH, Pérez-Bustamante R, Merino CAI, Morquecho AMA. Characterization Techniques; c2020. p. 129-165. Available from: [insert URL if available]
8. Nagaraja M, Prashanth S, Pattar J, Mahesh HM, Rajanna K. Polyaniline-CuO nanocomposite: Electrical, structural and sensor properties. In: Materials Today: Proceedings; c2021. Available from: doi:10.1016/j.matpr.2021.08.154
9. Venkatesh KS, Synthesis H. Charcaterization of polyaniline / CuO doped composites for electrical studies. J Emerg Technol Innov Res. 2019, 6(1).