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RESEARCH

Polyaniline/$CoNiO_2$ Nanocomposite: Synthesis, Characterization and Thermal Study

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ABSTRACT

Nano-sized inorganic oxide materials dispersed polymers constitute a special class of composite materials that improve the properties of the base polymer. The way of designing the composite materials by fine dispersion of inorganic nanofillers in polymers leads to special properties and applications. Metal oxide-based polymer nanocomposite materials integrate the science and technology of materials in terms of enhanced properties in comparison with basic materials. A bimetallic oxide material like nanosized cobalt nickelate ($CoNiO_2$) is considered as an inorganic filler in polyaniline for its composite material. $CoNiO_2$ was synthesized by microwave-assisted route using polyvinyl alcohol (PVA) as a fuel. The in-situ chemical oxidation polymerization method was adopted for the synthesis of nanosized cobalt nickelate dispersed polyaniline nanocomposite (PANI/$CoNiO_2$) sample. Structural characterization of the derived nanocomposite sample was studied by employing X-ray diffraction (XRD) tool and morphology by Scanning Electron Micrograph (SEM) tool respectively. Fourier transform-Infrared (FT-IR) instrumentation is used to know the bonding nature of the sample. The presence of metal oxygen confirms the sample. Absorption behavior was analyzed by UV-vis study. The presence of metal components is confirmed by EDX analysis. The thermal behavior of the prepared polymer composite sample was carried out to know its thermal behavior.

KEYWORDS

$CoNiO_2$, PANI/ $CoNiO_2$, XRD, SEM, FT-IR, EDX, Thermal studies.

INTRODUCTION

The extrapolation of Science and Technology by bimetallic oxide nanomaterials-based polymer composites in terms of its applications [**1**]. Dispersion of the bimetallic oxide nanomaterials into the polymer matrix constitutes special class of polymeric materials called polymer nanocomposites [**2-3**]. In particular, conducting polymer composite materials are attracted to recent researchers due its electrical applications [**4-5**]. These conducting composite materials are synthesized by the addition of suitable compositions of conducting polymers like Polyaniline, Polythiophene, etc with bimetallic oxide materials for desirable properties and applications [**6-7**]. Literature review indicates that many researchers have performed desired experiments and studied extensively on conducting polymer composites due to their various applications [**8-10**]. Conducting based polymer nanocomposite materials exhibit technological importance and hence high commercial demand in the market [**11**]. The creation of metal oxide nanoparticles dispersed in polymer nano composites without the use of surfactants [**12-17**], where the oxide nanomaterials are introduced during the in-situ polymerization process by chemical oxidation. Uniform distribution of metallic oxide in polymer matrix takes place without the use of surfactant [**18-19**]. Nano sized inorganic filler like bimetallic oxides dispersed organic polymer base phase composite materials are considered as an important material in various fields [**20-21**]. The characteristics of organic polymer components and inorganic oxide materials work in concert with the polymer composite materials to develop additional properties. Such polymer composite materials synthesis is the most common technique for adding inorganic building components, such as metal oxide nanoparticles, to the matrix of organic polymers. Composites for inorganic-organic polymer-based nanocomposite composites are highly attracted too many technologists for various particular applications [**22-24**].

Spinel $CoNiO_2$ compound shows the many desired uses because of its electrical, mechanical, thermal, and chemical characteristics [**25**]. It also showed superior adsorbent performance for various adsorbates due to its highly porous nature. Sample reflects high specific area which was synthesized by suitable method. Various unconventional synthetic techniques for bimetallic oxides, such as co-precipitation, combustion, thermal breakdown, hydrolytic sol-gel, and mechano-chemical processes, have been established [**26-27**]. But conventionally, the $CoNiO_2$ The self-propagating solid-state combustion reaction makes the sample CoO and NiO powders using polymer fuel. Nano sized $CoNiO_2$ material composed with polyaniline may leads additional force of attraction varies bonding nature of the composites sample in comparison with its plain polymer [**28**]. In-situ polymerization with cobalt nickelate core with PANI method is most adoptable method for the formation of polymer composites. The synthetic efforts are based on the well-known process of creating a variety of polymer nanocomposite by dispersing metal oxide in an organic polymer matrix [**29**]. Oxide nanomaterial and polymer nanocomposites with molecular mixing at phase boundaries and homogeneity affect characteristics and uses [**30-31**]. Scientific approaches with technology together can develop nanosized bimetallic oxide-based polymer nanocomposite materials for various need-based applications [**32**]. The strong interaction is developed between metallic oxides and polymer is made to design new class of composite materials [**33-34**]. The present work is reporting that, combustion route using PVA as a fuel for the synthesis of nanosized $CoNiO_2$ sample. Chemical oxidation polymerization method was used for the synthesis of PANI/ $CoNiO_2$ nanocomposite and was well characterized by various characterization tools. Thermal study of the prepared composite was carried out to know its thermal behaviour.

EXPERIMENTAL

Materials and Methods

AR grade chemicals are used in the present experimentation and are purchased from Merck (Mumbai, India). Glass wares are washed properly with chromic acid are used. Self-propagating combustion route was used for the synthesis of $CoNiO_2$ sample. In-situ chemical oxidation polymerization method was adopted for the preparation PANI/ $CoNiO_2$ nanocomposite.

Preparation of CoO and NiO

Cobalt chloride ($CoCl_2$) was mixed with PVA in the weight ratio 1:5 and grounded well in a pestle and mortar which forms a combustion-able reaction mixture. The resultant solid mixture was transferred into a china dish and heated in open-air atmosphere until the carbonaceous gases completely evolved. Then, it is transferred into a silica crucible and ignited at around 800°C in a muffle furnace. During the combustion process, it was observed that initially PVA melted, then frothed and finally ignited to give CoO as a residue. On cooling to room temperature followed by acetone washing gives CoO product. This reaction occurs with the evolution of large volume of gases and ignites with self-propagation combustion reaction. Similar procedure was adopted in the synthesis of NiO nanomaterials using nickel salt with PVA [**35**].

Preparation of $CoNiO_2$

Cobalt nickel oxide was synthesized by weighing CoO, NiO and PVA in the ratio 1:1:5 and grounded well in a pestle and mortar to form a reaction mixture. The resultant solid was transferred into china dish and pre heated in open air atmosphere. Continue the heat treatment until the complete evolution of white dense fumes and carbonaceous product. In a muffle furnace, ignite the reaction mixture for approximately 30 minutes at 1300°C. It was noted that PVA melted and frothed during the reaction, eventually forming CoNiO2 as the end product [**36**], which is shown in **Fig. 1**. The experimental scheme is given in **Scheme 1** and possible reactions are given below

$$CoO + NiO \rightarrow CoNiO_2$$

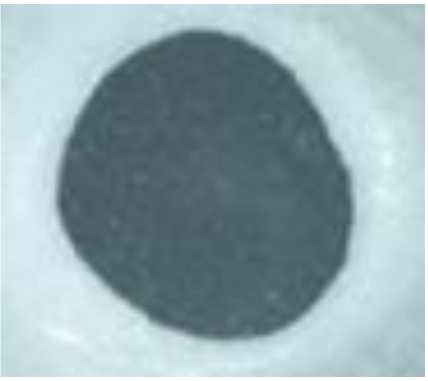
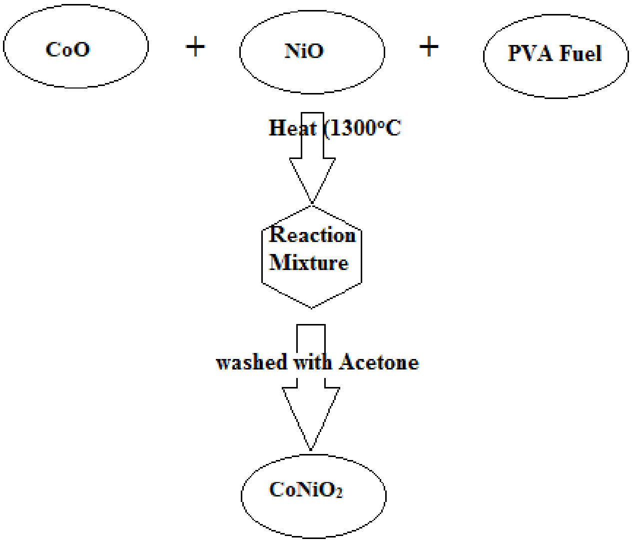


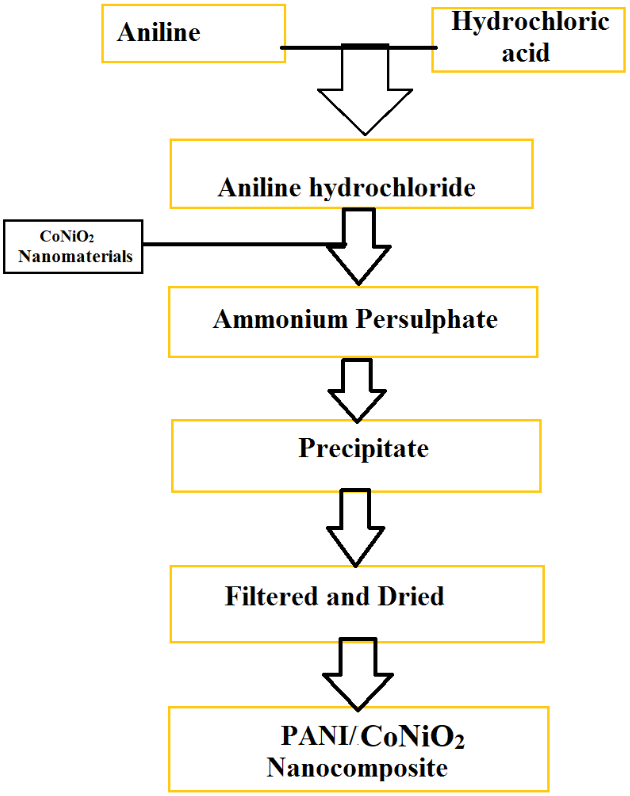
Fig. 1. Optical image of $CoNiO_2$nanomaterial.



Scheme 1. Synthetic scheme of $CoNiO_2$ nanomaterials.

Preparation of PANI/ $CoNiO_2$ nanocomposites

In-situ chemical oxidation polymerization method is employed for the synthesis of PANI/$CoNiO_2$ nanocomposites using ammonium persulphate as a strong oxidizing agent. In the same container, 0.5 g of aniline is dissolved in 20 ml of chloroform solvent, and 0.1 M of ammonium persulphate is dissolved in 1 M of HCl. Ready $CoNiO_2$ nanomaterial is added gradually to the aqueous and organic phase mixture mentioned above. The slow formation of the dark green coloration is caused by oxidation. Give the mixture around twenty-four hours to undergo a full oxidation reaction. Washing with ethanol first, then water, eliminated any unreacted aniline. Following multiple washings, the resulting polymer nanocomposite was purified and dried for approximately 36 hours at 40°C in a vacuum oven [**37**]. The complete synthetic mechanism of PANI/ $CoNiO_2$ Material for nanocomposite is shown in **Scheme 2**.



Scheme 2. Synthesis of PANI/ $CoNiO_2$ nanocomposite.

Characterization Techniques

The generated samples' structural characteristics were thoroughly examined using powder X-ray diffraction patterns, which were captured on a JEOL JDX-8P X-ray diffractometer using CuKα radiation (1.54 Å) at 30 kV. In order to investigate the bonding nature of the samples, Fourier transform infrared (FT-IR) spectra were acquired using a Perkin-Elmer FT-IR (Model No. 1000) at a resolution of 4 cm-1 in the 4000-400 cm-1 range. Using a bright field transmission electron microscopy picture acquired from the JOEL 100 CX operating at 190 KeV, the sample's morphology was examined. The morphology of the samples is scanned using a JEOL JSM-6380 LA scanning electron microscopy instrument. Energy dispersive X-Ray microanalysis (EDAX) was used to create the same instrument in order to determine whether metals were present in the samples. The filtrate's absorption was measured using a UV-visible spectrophotometer (Milton-Roy Spectronic 1201). Thermal behaviours of the nanocomposite sample were studied by thermo gravimetric analyses (TGA) of the sample and were recorded using NETZSCH STA 409PC tool. Heating rate of 10^0C/min under Argon atmosphere is maintained to obtain TGA data of the sample.

Table 1. FT-IR data of PANI, $CoNiO_2$ and PANI/$CoNiO_2$ nanocomposite.

Sample Description	Peak position (cm^{-1})	Mode of vibration
Pure $CoNiO_2$	566	May be M-M bonding (Ni-Co) vibration
	669	Co-O and Ni-O vibration (Metal-Oxygen)
	710	
	1320	Stretching vibrations of C=C and C-O
	1399	
	1510	
	3145	O-H stretching of water
PANI/ $CoNiO_2$	655	Co- O and Ni-O vibration
	705	
	1060	Bending vibration of the C-H plane
	1090	
	1120	
	1219	C-O stretching
	1245	characteristic of the conducting protonated form of PANI
	1230	C-O-C stretching (C-N) Stretching
	1310	
	1488	CH_2 bending
	1566	C=N quinonoid ring
	3010	C-H stretching
	3225	O-H stretching of water, which might be brought on by moisture absorption

RESULTS AND DISCUSSIONS

FT-IR Studies

Obtained FT-IR data of as prepared $CoNiO_2$ and PANI/ $CoNiO_2$ nanomaterials is tabulated in **Table 1**. It is observed from the table that, the sample $CoNiO_2$ shows O-H stretching of water is compatible with the absorbance at 3145 cm-1, which could be the result of moisture absorption during sample testing. C-O and C=C stretching vibrations are represented by peaks at 1320–1510 cm-1. The low energy bands (1000–400 cm-1) associated with the stretching and bending modes of M–O bonds (Co-O, NiO) can be used to corroborate the spinel-type structure. Furthermore, the bending and stretching modes of metal-oxygen (M-O-M) are associated with the absorbance bands below 1000 cm^{-1} confirming the formation of $BaZrO_3$ sample. Further, the table shows composite vibrations at 1566 and 1488cm^{-1} are caused by the C=N and C=C stretching modes of vibration, respectively, for the PANI quinonoid and benzenoid units. The sample's benzenoid ring's C-N stretching mode is represented by two peaks at 1310 and 1230 cm-1. The characteristic of the conducting protonated form of PANI is the peak located at 1230 and 1245 cm-1 [**38**]. Vibrations in the 1000–1120 cm-1 range are classified as C–H plane bending vibrations. The presence of CoNiO2 (M-O) is responsible for the two peaks in the nanocomposite spectra that were seen at 655 and 710 cm-1 and Co-Ni (M-M) in the PANI/$CoNiO_2$ nanocomposite confirms the formation of the nanocomposite.

X-ray diffraction study

X-ray diffraction tool is used to study the crystallinity and chain packing of the synthesized polymer nanocomposite. The literature reports that plain PANI has a distinctive peak at 2θ = 280 and a conducting nature with a partly crystalline structure [**39**]. **Fig. 2(a-b)** shows the XRD pattern of prepared plain PANI and PANI/$CoNiO_2$ nanocomposite respectively. A broad peak at 2θ at 28^0 is due to the presence of PANI as mentioned above and also indicates the partial crystalline nature of the sample. Further, the nanocomposite pattern displays a lot of Bragg's reflections, which are caused by the presence of dispersed $CoNiO_2$ filler and the development of crystallinity in the sample. Organization of Crystallinity in the simple PANI is caused by CoNiO2 nanomaterial matrices, and the composite pattern indexes this according to the JCPDS file of $CoNiO_2$ (10-0188). The production of the PANI/CoNiO2 nanocomposite is confirmed by the presence of both PANI and cobalt nickel oxide reflections in the sample.

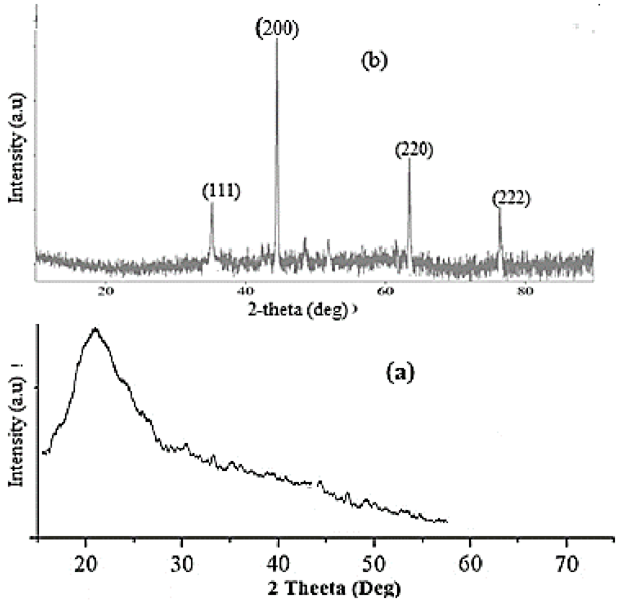


Fig. 2. XRD pattern of (a) PANI (b) PANI/ $CoNiO_2$ nanocomposite.

Scanning Electron Micrograph study

Fig. 3(a-c) shows the SEM image of prepared PANI/ $CoNiO_2$ nanocomposite. The image shows irregular particles and most of the particles are closed netting with each other to form a crystalline nature. Development of The PANI's crystallinity is caused by cobalt nickel oxide granules, which can also be seen in the picture. The sample also displays closed netting and spherical tiny particles. Certain particles have an extremely compact and close-knit structure with each other. Such morphology is treated as applicable oriented morphology in various fields.

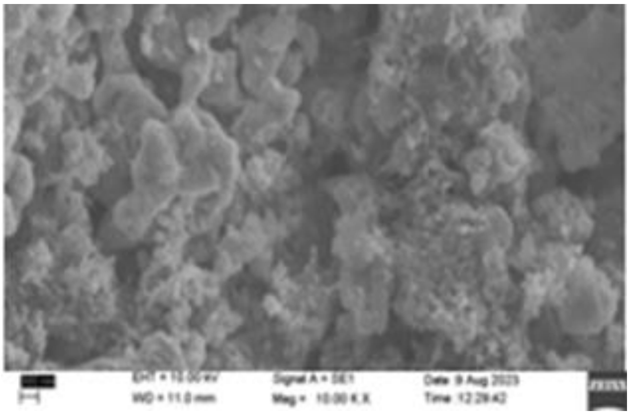


Fig. 3. SEM image of PANI/ $CoNiO_2$ nanocomposite.

EDX Studies

The presence metal in the PANI composite sample can be analysed by EDX technique. **Fig. 4** shows EDX pattern of as synthesized PANI/ $CoNiO_2$ nanocomposite sample. The pattern demonstrates the existence of Co and Ni atoms at detectable locations with oxygen signals. These distinctive metal and oxygen absorption peaks in the pattern validate the PANI/CoNiO2 nanocomposite's creation.

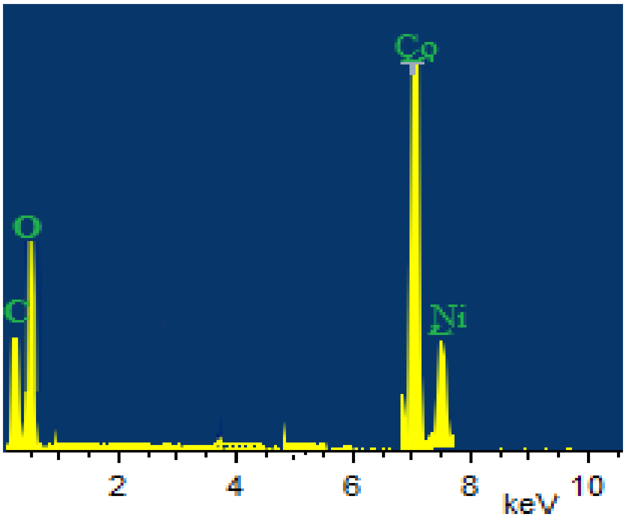


Fig. 4. EDX pattern of PANI/ $CoNiO_2$ nanocomposite.

UV-Vis study

The **Fig. 5** shows UV absorption spectra of PANI/ $CoNiO_2$ nanocomposite sample. It is observed in the figure that, due to localized polarons, which are features of the protonated PANI, and the prolonged tail, which signifies composite development, the greatest absorption peak at 330 nm shows the creation of the polymer nanocomposite. The said absorbance band also indicates the particles were polydispersity. In addition, it reflects the characteristics of surface plasmon resonance of prepared nanocomposite. The good developments of the band indicate that the nanocomposite was successfully framed. The broad size distribution of the polymer is also noted, which supports the production of the PANI/CoNiO2 nanocomposite.

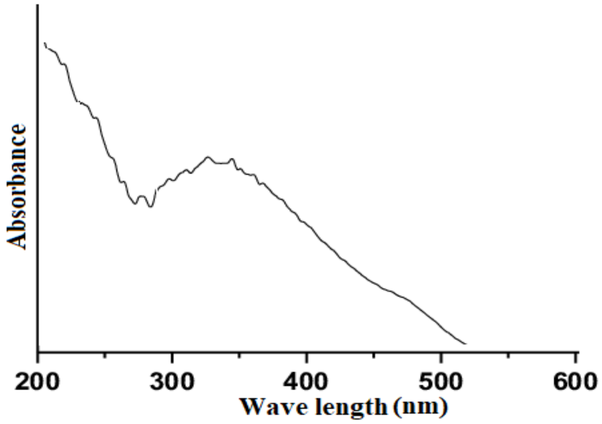


Fig. 5. UV-vis spectrum of PANI/ $CoNiO_2$ nanocomposite.

Transmission Electron Microscopy

TEM image of as prepared PANI/$CoNiO_2$ nanocomposite sample is shown in **Fig. 6**. Irregular particle morphology can be viewed, and particles fall under nano dimension. A few Particles are spherical and arranged in tight assembly representing the dispersed metal oxide particles in PANI matrix. The image also represents the high crystalline nature of the composite sample by particle mapping. In addition, the image reflecting with globular arrangement indicates the applicable morphology in various fields.

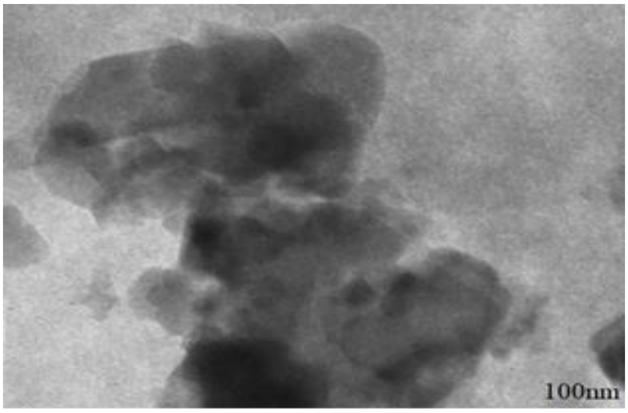


Fig. 6. TEM image of PANI/$CoNiO_2$ nanocomposite.

Thermal study

Thermal behaviour of the prepared sample was studied by TGA analysis and obtained TGA trace of the composite is shown in **Fig. 7**. PANI/CoNiO2 nanocomposite thermal degradation demonstrates the first mass loss at lower temperatures, i.e., 10 to 120ºC, as the early step of weight loss was observed due to evaporation of water moiety in the sample. When temperatures fall between 120°C and 240°C, there is a second weight loss that might be caused by the organic moiety that was assembled with the sample breaking down. In addition, the breakdown of PVA is also considered. In the third region, the weight loss up to 400 ºC and it is expected that the only material changes that occur at this stage are in the crystal structure [**40**]. The last weight loss is due to the complete decomposition of the composite sample.

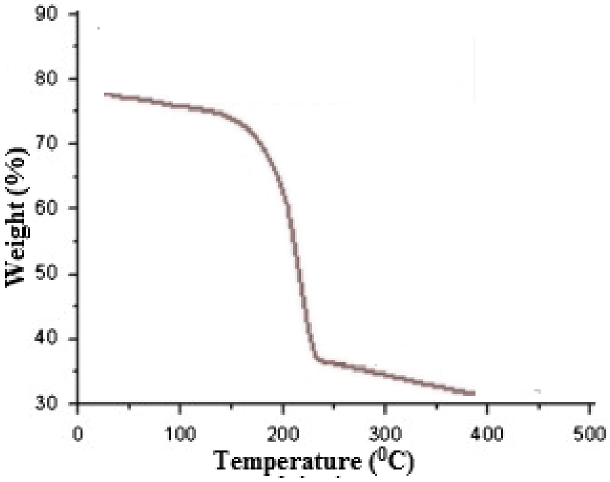


Fig. 7. TGA trace of the PANI/$CoNiO_2$ nanocomposite.

CONCLUSION

The effective experimentation leads the some of the major conclusions. Microwave-assisted synthetic route for $CoNiO_2$ finds simple and phase-confirmed product. Chemical oxidation polymerization of aniline monomer using an oxidizing agent followed by $CoNiO_2$ nanomaterials is found to be simple and the same may be used for the synthesis of other polymer composites. High crystallinity development in the partially crystalline polyaniline is achieved by this synthetic route. The Thermal analysis reveals that the matrixation of CoNiO2 nanoparticles with PANI reduces the rate of breakdown.

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CONFLICTS OF INTEREST

“There are no conflicts to declare”.

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