Synthesis and Characterization of Polymer-Based Poly Aniline Nickel Oxide Nanocomposites by Sol-Gel method and their photocatalytic Activity

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Abstract:

Utilizing $NiCl_2$ as a precursor, PANO (Polyaniline Nickel Oxide Nanocomposite) was manufactured using the Sol-Gel approach using in-situ chemical oxidation polymerization. This procedure involves utilizing $K_2S_2O_8$ as an oxidant in an acidic medium with various concentrations of NiO 0.1, 0.2, 0.3, 0.4, and 0.5 moles at RT. XRD, FTIR, SEM, and TEM were used to characterize the produced PANO nanocomposites. Through the photo-degradation of $KMnO_4$ dye, polymer NiO nanocomposite exhibited more promising photocatalytic activity than nitrogen-doped TiO_2 for photocatalytic degradation under a UV-Visible light source. Synthesized nanocomposites exhibited ferromagnetic and semiconducting properties. According to the obtained outcomes, produced nanocomposite could be used as an efficient photocatalyst.

Keywords: Polyaniline-Nickel Oxide, nanocomposites, Sol-Gel method, Spectroscopic methods, and Photocatalytic activity.

1. Introduction:

Hybrid organic and inorganic materials known as polymer nanocomposites have at least one filler phase dimension that is less than 100 nm [1]. Exfoliation adsorption, melt intercalation, template synthesis, and in situ polymerization intercalation are the four main approaches used to create polymer nanocomposites [2-6]. The alteration of fundamental polymers like polyaniline-nickel oxide nanocomposites has recently drawn a lot of study interest. Because of their high surface area to volume ratio and reduced target analyte diffusion distance, polyaniline-Nickel Oxide-based nanocomposites have great sensitivity and

a rapid response time, which are important characteristics for a range of applications, including photocatalytic activity [7].

The most extensively used conductive polymers are polyaniline-nickel oxide nanocomposites because of their reversible redox, pH-switching, sensing, and ease of manufacturing [8]. However, it has subpar physical and thermal stability, similar to most of these materials. In a spinning process, Polyaniline Nickel Oxide nanocomposites are exclusively created from spinning solutions because it is impossible to use melt processes like extrusion [9]. Researchers have become interested in the PANO because of its appealing qualities that can be used in a variety of applications [10–12]. In order to create polymer-based nanocomposites that can be employed as photocatalysts, filters, protective fabrics, and medicinal substrates, PANO nanocomposite has been successfully generated using the Sol-Gel technique [13]. To the best of our knowledge, this study is the first to present a useful technique for fabricating desired nanocomposites using in-situ reduction of aniline, N, N-dimethyl formamide containing nickel chloride with magnetic stirring and heating. This method for making PANO nanocomposites with various Nickel chloride solution concentrations is unique, simple, quick, and economical.

Morphology and structural elucidation of PANO by FTIR, SEM, TEM, and X-Ray Diffraction. This is furthermore applied in the field of photocatalysis.

2. Experimental:

2.1 Materials:

After two distillations, aniline (S. D. Fine-Chem Ltd., 99.5%) was utilized. Other chemicals, including nickel carbonate (99%), potassium persulfate (99%), ethanol (99.9%), sulfuric acid (98.9%), starch, and N- and N-Dimethyl formamide, were purchased from a local business. The ammonia used was of AR quality. De-ionized water was utilized in this experiment.

2.2 Synthesis method of PANO nanocomposites:

Step-1(Preparation of Nickel Oxide Nanoparticles)

The mixture of 100 ml of starch solution and 0.1 M nickel carbonate was continuously stirred as ammonia was added drop by drop. The solution was left to settle overnight once the ammonia was fully incorporated, and the sample's color changed from green to grey. Whatman filter paper is used to filter the acquired sample. Collect a sample of

NiO nanoparticles and wash it in ethanol and deionized water to get rid of any contaminants. Then it was dried in hot air furnaces at 750˚C.

Step-2(Preparation of Poly aniline Nickel Oxide Nanocomposites)

Synthesized NiO nanoparticles undergo in-situ chemical oxidative polymerization to create the PANO matrix. Take 1 ml of aniline and dissolve it in 1M H2SO4 solution. Stir the mixture for an hour using a magnetic stirrer. Add the previously prepared 10 ml of sonicated NiO solution. Heat the reaction mixture while stirring continuously for 2 hours. Add the potassium persulfate dropwise and stir continuously for 3 hours. When the color changes from blue to blackish green, we know that polymerization has taken place and PANO nanocomposites have been created. The sample was collected after the solution had been maintained overnight in a dark area. Using ethanol and deionized water, clean the sample. It was possible to create nanocomposites of polyaniline and nickel oxide at different mole concentrations (0.1, 0.2, 0.3, 0.4, and 0.5).

3. RESULT AND DISCUSSIONS:

3.1 Transmission Electron Microscopy (TEM):

An acceleration potential of approximately ca 2 A◦ is used with a point resolution and 300 kV of TEM. The microscope column was employed, which has a number of lenses including a condenser lens, an objective lens, and a projection lens. In general, an electron cannon installed on top of a TEM produces the electrons, which are subsequently accelerated to user-selected high energy, often between 100 and 300 kV. The source of an electron is a material with a low work function for electron emission. Using TEM, the PANO Nanocomposites' dimensions and forms were investigated. Images of the various morphologies of the generated PANO Nanocomposites are shown in **Fig.1** and **Fig.2.**The formation of spherical nanoparticles made of PANO nanocomposites is influenced by the aniline's rate of polymerization. We utilized the TEM method to see how well nanocomposites dispersed light. Since TEM can image materials at the nanoscale scale in **Fig.3**, it offers the most direct means to study the states of polyaniline nickel oxide nanocomposites exfoliation. In the matrix, we discovered a uniform distribution of polymer nanocomposites together with a few tiny agglomerates. We estimate the uniform size of the polyaniline nickel oxide nanocomposites to be 200 nm based on the TEM images in **Fig.3** and **Fig.4.**

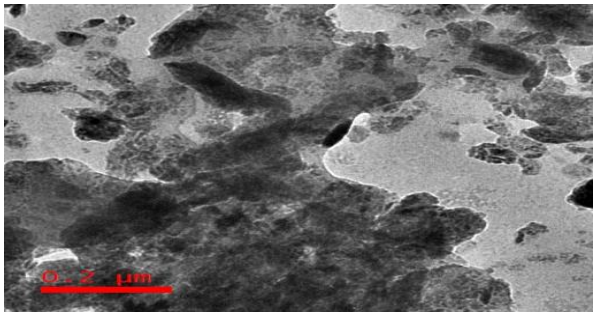

Figure.1

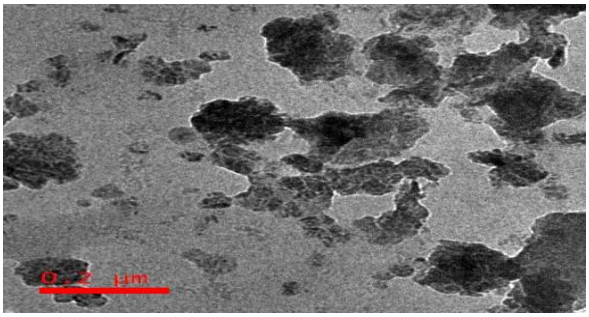

Figure.2

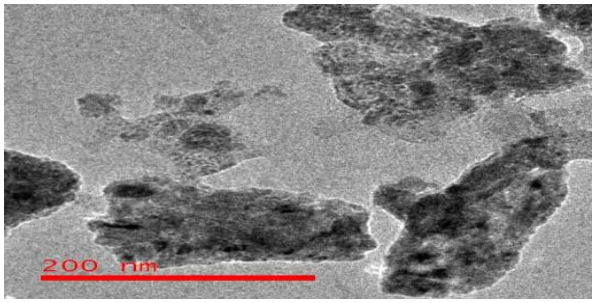

Figure.3

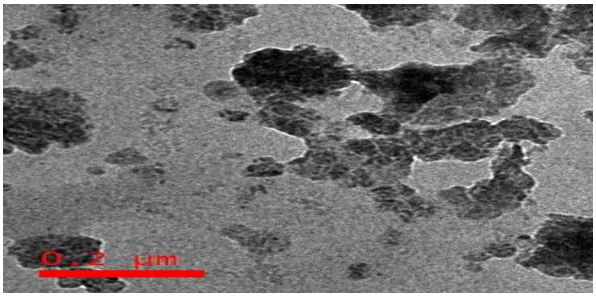

Figure.4

TEM-images of Polymer-based Polyaniline Nickel Oxide (PANO) nanocomposites.

3.2 Scanning Electron Microscopy (SEM):

Numerous distinct SEM picture types are produced when an electron beam strikes a sample, and these images are then used to discover or examine the morphology and topology of the sample. Elements, sizes, and states may all be analyzed with SEM. These photos consist of X-rays, Auger, secondary, and backscattered electrons. Because an SEM's magnification may vary by up to 6 orders of magnitude, or from 10 to 500,000 times, it can be used to generate a high-resolution image of surface characteristics and draw inferences about the distribution of various chemical components within the sample.

SEM examination was used to examine the size and morphology of Polyaniline-NiO nanocomposites, and the findings are displayed in **Fig. 5.** Additionally, the Polyaniline NiO adopts the NaCl structure, with octahedral Ni^{2+} and O_2 sites, as seen in the SEM picture of the as-synthesized Polyaniline-NiO nanocomposites. The "rock salt structure" is the most prevalent theoretically straightforward structure. The surface of the PANO nanocomposites is shown in **Fig.6**, demonstrating their effective production. SEM research was done to determine the surface morphology of 200 nm PANO nanocomposites based on polymers**.**

Fig.7 shows SEM micrographs of a polymer-based nanocomposite made of polyaniline nickel oxide. SEM analyses demonstrate that PANO nanocomposite is in its purest form, with brilliant white nanocomposite particles. The Scanning Electron Microscopy image displays a consistent structure and size for polymer-based Nickel Oxide nanocomposites. The samples with medium concentrations had a better size distribution, according to **Fig. 8.** This is a result of the particles being less aggregated in the samples' medium concentrations.

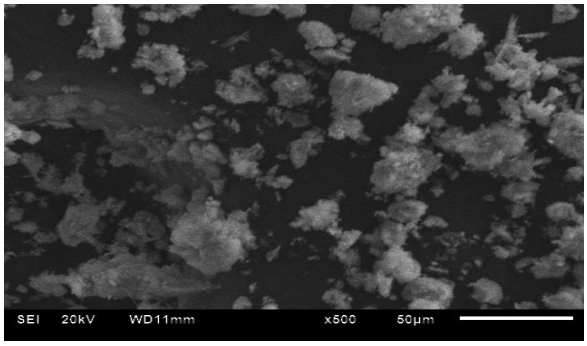

Figure.5

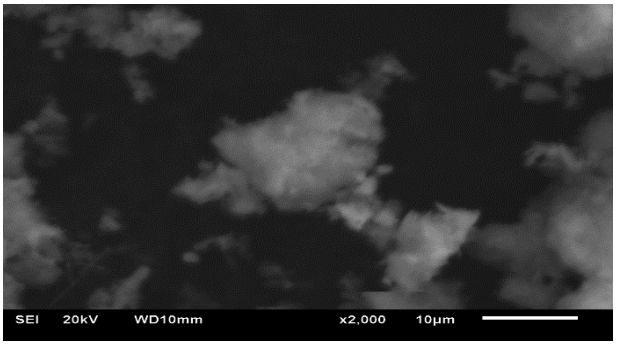

Figure.6

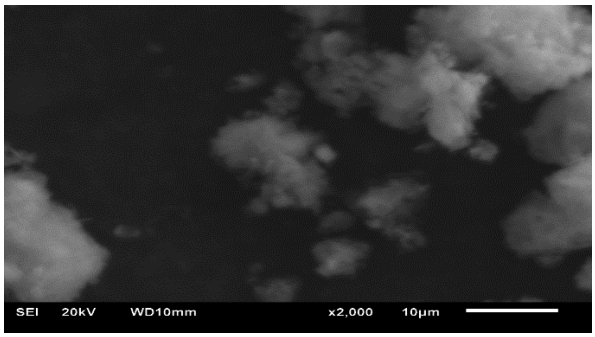

Figure.7

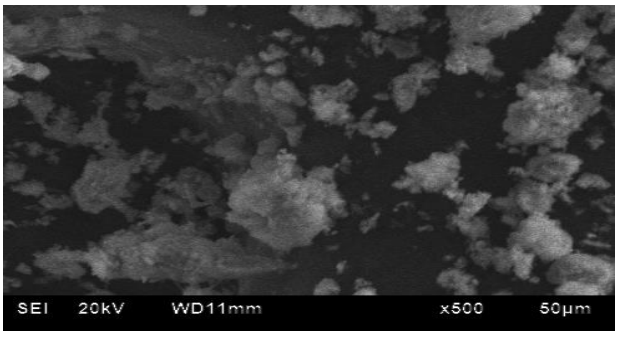

Figure.8

SEM-Images of Polymer-based Polyaniline Nickel Oxide (PANO) nanocomposites.

3.3 X-ray Diffraction Studies (XRD):

Fig. 9 and **10** depict the X-ray diffraction patterns of PANO nanocomposites. When compared to nickel oxide, which displays crystalline peaks at 2θ = 37·53°and 43·60°that have been recognized as peaks from the single-phase cubic structure of NiO, the PANO nanocomposites exhibit two distinctive wide peaks at 2θ = 21.31° and 26.23°. The PANO nanocomposites' crystallite size was discovered to be 200 nm. The two wide peaks are found at 2θ = 21.31° and 26.23°. The XRD pattern of **Fig. 9** demonstrates that PANO has a partially crystalline structure. Crystalline peaks of PANO nanocomposites together with crystalline

peaks of NiO show that interfacial interactions occur between the XRD patterns of PANO and the XRD patterns of NiO crystallites.

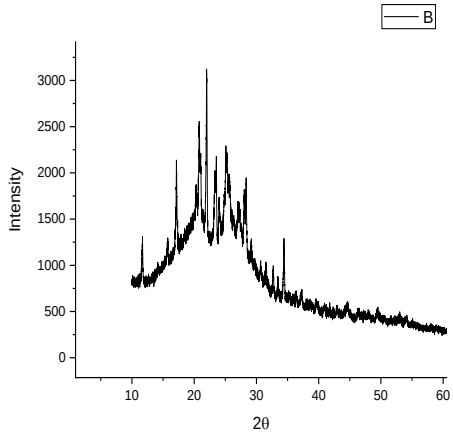

Figure.9

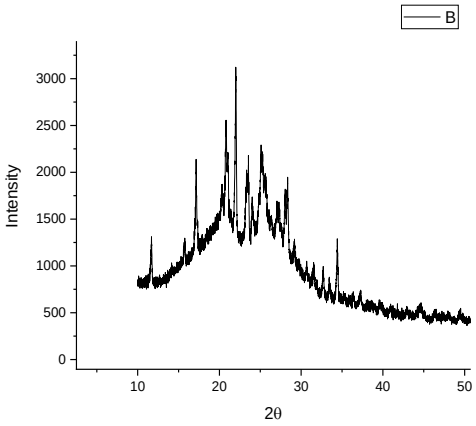

Figure.10

XRD-Spectra of Polymer-based Polyaniline Nickel Oxide (PANO) nanocomposites.

3.4 Fourier Transform Infrared Spectroscopy (FTIR):

Table-1 lists the FTIR peaks for the polymer-based polyaniline nickel oxide nanocomposites and their likely designations. FTIR peaks at 2975 cm-1, 2923 cm-1, and 2852 cm-1, which matched the published FTIR spectra for PANO nanocomposites in **Fig. 11**, corroborated the existence of polyaniline in the PANO nanocomposite recovered following repeated extraction with DMF.

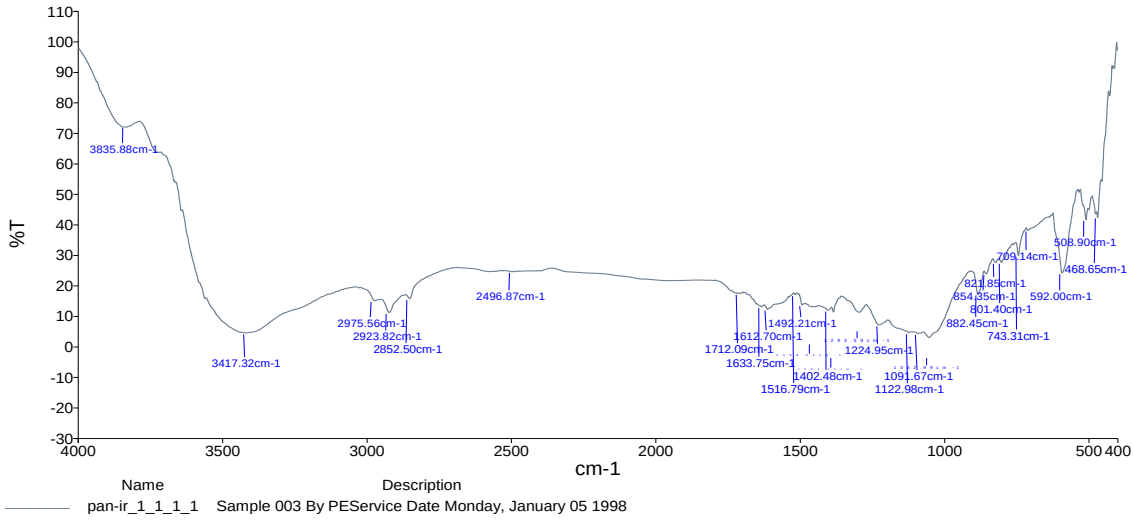

Figure.11

FTIR-Spectra of Polymer-based Polyaniline Nickel Oxide (PANO) nanocomposites.

Table-1. FTIR absorption characteristics of PANO nanocomposites

PAN	**PANO Nanocomposite in cm^{-1}**	**Assignments**
2939	2975	C-H Stretching vibration
2245	2923	C=N Stretching vibration
1454	2852	C-H bending vibration

3.5 Photo-catalytic activity of PANO nanocomposites:

Because potassium permanganate is a common chemical that is inexpensive and accessible in labs, it was utilized in the photo-degradation of a concentration of 0.5 M dye to produce PANO nanocomposites, which showed high photocatalytic activity. It was taken and placed on a Petri plate to dissolve the potassium permanganate in the distilled water. Prepare samples of PANO nanocomposite at various concentrations, add them to a solution of (KMnO4), and then expose them to UV light (between 300 and 800 nm) sources. **Fig.12** shows the connection between the absorbance of KMnO4 vs UV-irradiation depending on the duration in minutes (20, 40, 80, and 100 minutes). The sample's absorbance after being annealed at 550 °C using PANO nanocomposites. The photo-generated electron-hole pair was produced less on the surface of the polymer nanocomposite catalyst, which has poor crystallinity and an imperfect crystal structure, and this result showed in **Fig. 12** that the integrity and regularity of PANO nanocomposite's structure have critical influences on the photo-degradation rate.

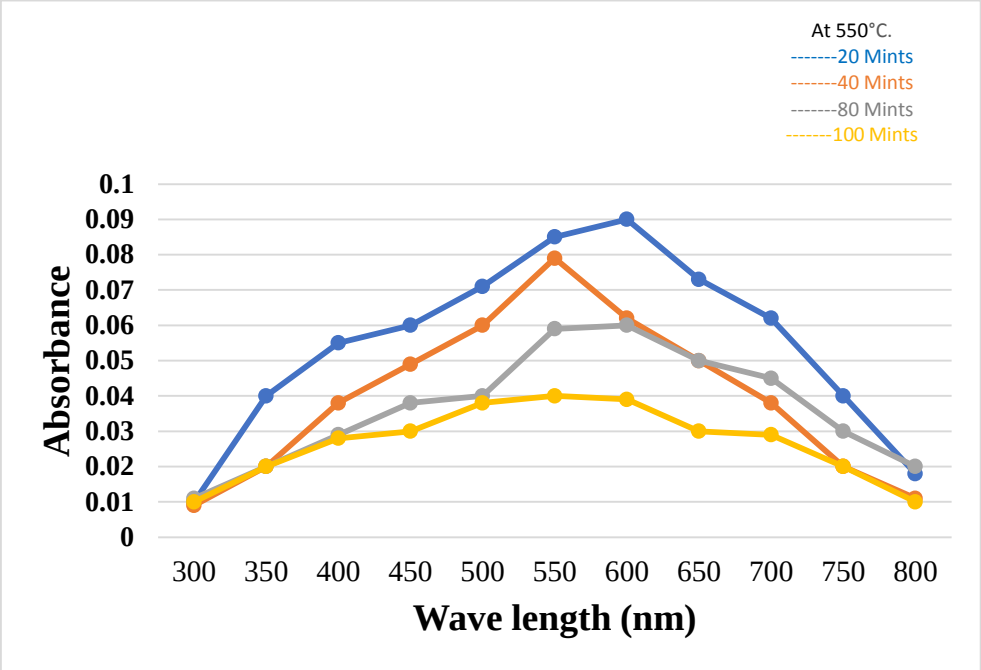

Figure.12

Photocatalytic analysis data of PANO nanocomposites

Table-2. Experimental values for photocatalytic application of PANO nanocomposites

S.No	Wavelength(nm)	Absorbance (100 mins)	Absorbance (80 mins)	Absorbance (40mins)	Absorbance (20 mins)
1.	300	0.01	0.011	0.009	0.01
2.	350	0.02	0.02	0.02	0.04
3.	400	0.028	0.029	0.038	0.055
4.	450	0.03	0.038	0.049	0.06
5.	500	0.038	0.04	0.06	0.071
6.	550	0.04	0.059	0.079	0.085
7.	600	0.039	0.06	0.062	0.09
8.	650	0.03	0.05	0.05	0.073
9.	700	0.029	0.045	0.038	0.062
10.	750	0.02	0.03	0.02	0.04
11.	800	0.01	0.02	0.011	0.018

Conclusion:

Oxidatively induced polymerization using the bottom-up Sol-Gel methodology has effectively produced polymer-based PANO nanocomposites and NiO nanoparticles. We have described the morphology, and topology, size of PANO nanocomposites 200 nm by TEM, SEM, whereas in the case of the cubic crystalline structure of nanocomposites illustrated by XRD. The polymer PANO nanocomposite's chemical grafting was validated by FTIR. UV-Visible spectral data reveals that at wavelength 600 nm with good absorbance at 20 mins and furthermore found to be photocatalytic activity and suitable for semiconducting material.

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