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Optical and Electrochemical Properties of Nio Doped Pirlindole(Pin)

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ABSTRUCT

The characterization of PIN/NiO nanocomposites are the main topics of this investigation. By using ferric chloride oxidant in the chemical Oxidative polymerization process, polyindole/Nickle oxide was produced. Electrochemical impedance, cyclic voltammetric investigations, Fourier transform infrared spectroscopy, and ultraviolet visible spectroscopy were also used to characterize the produced nanoparticles. Using UV-vis spectroscopy, the intricate optical characteristics of the generated samples were investigated. The polymeric samples as produced showed absorption at wavelengths between 220 and 300 nm. Following Nickle Oxide doping, the optical band gap was found to vary above 4.4 eV to 2.7eV. It is clear that the dopant increases conductivity since the UV-vis spectrum shows that the band gap of the doped PIN decreases. FTIR Spectroscopy was used to examine the surface binding of functional compounds on nanocomposite. In order to better understand the frequency response characteristics of the nanocomposites as the material of electrodes for electrochemical supercapacitors, electrochemical impedance spectroscopy (EIS) studies were performed. Lastly, the cyclic voltammetry (CV) method was used to examine the electrochemical behavior.

1.INTRODUCTION

Polymer matrix-based nanocomposites have emerged as a key topic of current study and development in the broad field of nanotechnology [1]. The favorable electrical characteristics, environmental stability, and simplicity of synthesis of conjugated polymers, such as polyaniline, polypyrrole, and polythiophene (Ferraro, 1987), have drawn a lot of interest [2], [3]. Solitons, Bipolarons, and Polarons are responsible for the fundamental conduction process in conducting polymers [4]. Tourillon et al. [5] published the first study on the electrochemical production of polyindole. Since their high homogeneity, flexible processing, and adjustable physical characteristics (mechanical, magnetic, optical, electric, and electronic), polymeric nanocomposites implanted with inorganic nanoparticles have piqued attention.[6] Air stability and a conductivity of around 10-3–10-1 S cm-1, depending on the kind of dopant ions and the manufacturing method, are characteristics of polyindole. Usually, given the right circumstances, indole may be anodic oxidized to produce this [7]. Different transition metal oxides, including materials ranging in size from micrometers to nanometers, such as copper, iron, nickel, cobalt, and zinc, are now the subject of study attention because of their potential uses in photonics, sensors, catalysis, systems to deliver drugs, optical switching devices, and other fields [8]. Because conducting polymer/metal oxide nanocomposites have better characteristics than both pure conducting polymer and metal oxide, they have recently been regarded as a distinct class of materials [9]. By polymerizing indole combined with NiO nanocomposite, the study's goal was to create conducting polymer nanocomposites for electrocatalytic applications.

2. EXPERIMENT

MATERIALS

The precursors Nickle chloride ($NiCl_2.6H_2O$), indole monomer, Ferric chloride and Sodium hydroxide (NaOH) were purchased from Aldrich. All solutions were made up with deionised water.[10]

A. SYNTHESIS OF POLYINDOLE

The monomer indole (0.03M) was dissolved in 100ml of hot water, and then dropwise additions of ferric chloride (0.06M) as an oxidant were added to the mixture while stirring and heating it to 80°C. Polymerization caused the reaction mixture's color to shift from colorless to dark green. To get rid of the unreacted indole monomer, ferric chloride, the reaction liquid was filtered and rinsed with water after two hours. After gathering, polyindole was allowed to dry at the natural temperature.[10]

B. SYNTHESIS OF NIO NANOCOMPOSITE

After two hours of refluxing the Nickle Chloride ($NiCl_2$. $6H_2O$, 0.2M) solution while stirring, sodium hydroxide (NaOH, 0.4M) was gradually added. The precipitate of Nickle hydroxide was then filtered and cleaned with water and ethanol to get rid of any remaining impurities. After drying at 60°C, NiO nanocomposite were collected and calcined at 360°C for five hours.

C. NiO DOPED PIN NANOCOMPOSITES SYNTHESIS

After dissolving the monomer indole (0.03M) in 100 ml of hot water at 80°C, the mixture was heated and agitated while dropwise quantities of ferric chloride (0.06M) as an oxidant were added. The monomer solution was kept hot and stirring after 1g of NiO nanocomposite were added. After three hours, the polyindole/NiO nanocomposite was thoroughly cleaned with water. The NiO-doped Polyindole nanocomposite was dried at room temperature.[10]

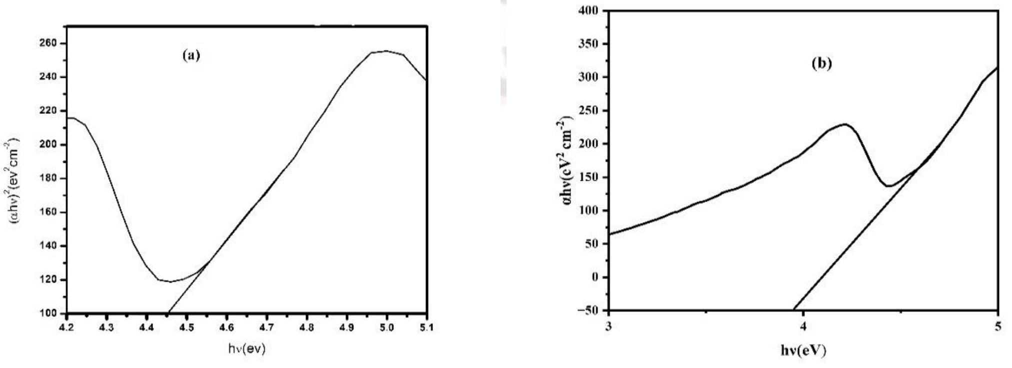
3. RESULTS AND DISCUSSION

3.1. UV-VIS ABSORBANCE

Figure 1 displays the UV-visible spectra for PIN, NiO, and PIN/NiO. Absorption is the process by which an electron changes into an excited state by absorbing the energy of a photon. The band gap, extinction coefficient, refractive index, and contamination states may all be found out by studies on optical absorption. The absorbance of PIN range from 278 nm. PIN/NiO also exhibits an absorbance peak at 342 nm. The band gap of PIN, NiO and PIN/NiO were shown in Figures 1(a), (b) and (c), respectively. The band gap was calculated by extrapolating the energy axis. The band gap's optical values for PIN/NiO and pure PIN were shown in the following table:

Materials	Band gap (eV)
PIN	4.45
NiO	3.94
PIN/NiO	2.42

According to the table, when NiO was doped with PIN, the band gap between both valence and conduction bands decreases.



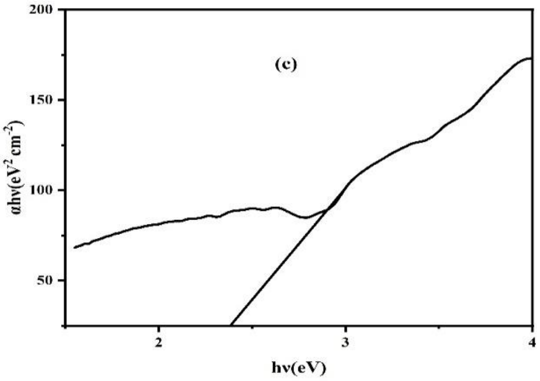


FIG .1. Tauc's Plot of (a)PIN (b) NiO (c) PIN/NiO

3.2. FTIR STUDIES

FTIR spectra of PIN/NiO and Polyindole were shown in Fig 2. The typical out-of-plane distortion of the CH bond in the indole benzene ring is responsible for the sharp band at 747 cm-1 [11], [12]. The peak located at 1332 cm-1 illustrates the pyrrole ring's stretching modes [13], [14]. As per reference [15], the distinct spectral band situated at 1456 cm-1 and 1381 cm-1, respectively, may be attributed to the C–N and C=N stretching vibration modes. The presence of C-N vibration modes supports the idea that the nitrogen atom in indole is not involved in the polymerization process. Peaks at 1594 and 1619 cm-1 show the C-C stretching vibration of the indole benzenoid ring [16]. The strongest infrared band is the N–H stretching vibration, which is located at 3380 cm-1. The peak at 600 cm-1 demonstrates a significant interaction between the NiO nanoparticles and the polymer and is consistent with the normal NiO nanoparticle signal.

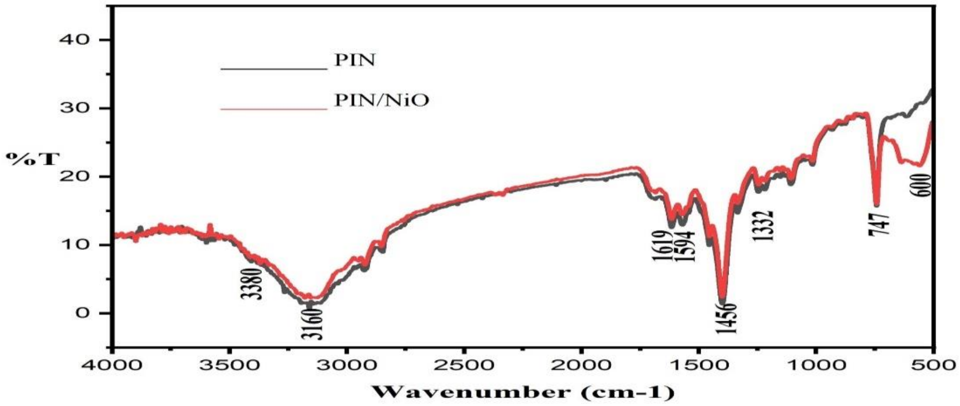


FIG.2. FTIR SPECTRUM of PIN/NiO

3.3. THERMAL ANALYSIS

The impact of the fillers on the polymer matrix's thermal degradation was investigated by TG studies, the results of which are shown in Fig. 3. The two consecutive weight loss phases that are seen for PIN and its composites between 100 and 175°C are ascribed to the structural elimination of oligoindole molecules and moisture [17]. For PIN and its composites, the minor derivative thermogravimetric (DTG) peaks between 200 and 400°C suggest that there were also some weight loss stages in this temperature range. Decomposition of the dopant molecules, such as radicals and solvents, may be the source of these weight losses [18][19]. Two and one endothermic peaks were identified in the DTG analysis of polyindole and polyindole doped with nickel oxide, respectively, at 341.5°C, 450.5°C, and 539°C.

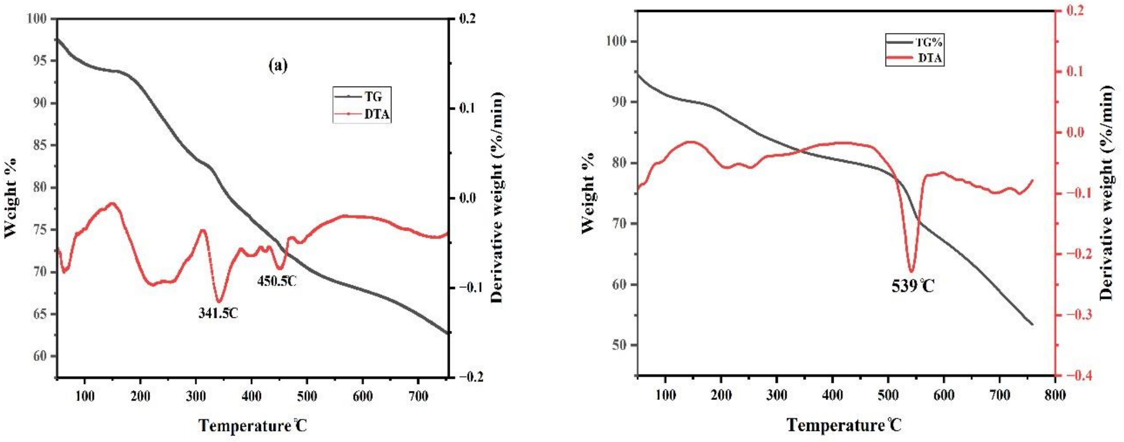


FIG 3.TGA/DTA of (a) PIN (b) PIN/NiO

3.4. ELECTROCHEMICAL PROPERTY

One of the most useful electroanalytical methods for examining the redox behavior of electroactive species is cyclic voltammetry. A CHI 650C electrochemical workstation with a traditional three electrode cell was used to perform electrochemical measurements of cyclic voltammetric investigations at room temperature. Three electrodes were used in the cell assembly: a counter electrode made of Pt-wire, a working electrode made of Modified NiO Oxide (also known as Polindole, NiO-doped Polyindole nanocomposite, or GCE for short). The reference electrode was silver/silver chloride (Ag/AgCl) electrode.[20]

The supporting electrolyte were

1. 0.1M H_2So_4
2. 3M KOH
3. 1M Na2So4.

3.4.1. CYCLIC VOLTAMMETRY

Cyclic voltammetry (CV) was used to examine the electrochemical performance of a Nickle oxide modified glassy carbon electrode throughout the whole potential range of +1.5 to -1.5 volt [20]. As the scan speeds were raised, all electrodes' current responsiveness improved. When the scan rates were increased from 10 to 100 mV/s, there was a gradual shift in the peaks to higher potentials and variations in the peak current height. The relation was used to compute the electrodes' specific capacitance, or C_{SC}, based on the CV data.

$$C_{\mathrm{SC}}=\frac{1}{\upsilon\ m\,(Va-Vc)}\int_{Vc}^{Va} I\,dV$$

Where I is the current response, υ indicates the voltage scan rate, and (Va-Vc) is the anodic to cathodic potential range. The specific capacitance was calculated using the electrode m's electrochemically active mass. As shown in Fig. 9, the cyclic voltammetric behavior of PIN/NiO nanocomposites for various electrolytes revealed an oxidation peak and a reduction peak. The specific capacitance of the H_2So_4 electrolyte and KOH electrolyte samples decreases when the scan rates are increased from 10 to 100 mV/s (Fig. 8(f)). This is because, at greater scan speeds, there are diffusion limits and insufficient time for the ions to reach the outer layer of the electrode. When the NiO doping was increased, the specific capacitance decreases linearly. At scan speeds of 5-100 mV/s, the specific capacitance for the undoped sample drops from 360.58 to 126.63 mF/g for H_2So_4 electrolyte and82.29 to 38.20 mF/g for KOH electrolyte, while for the NiO samples doping it drops from 200.33 to 71.36 mF/g for H_2So_4 electrolyte and 45.65 to 1.94 mF/g. However, when NiO doping polyindole are increased, the specific capacitance of the Na_2So_4 electrolyte increases linearly. Table displayed a specific capacitance that was determined.

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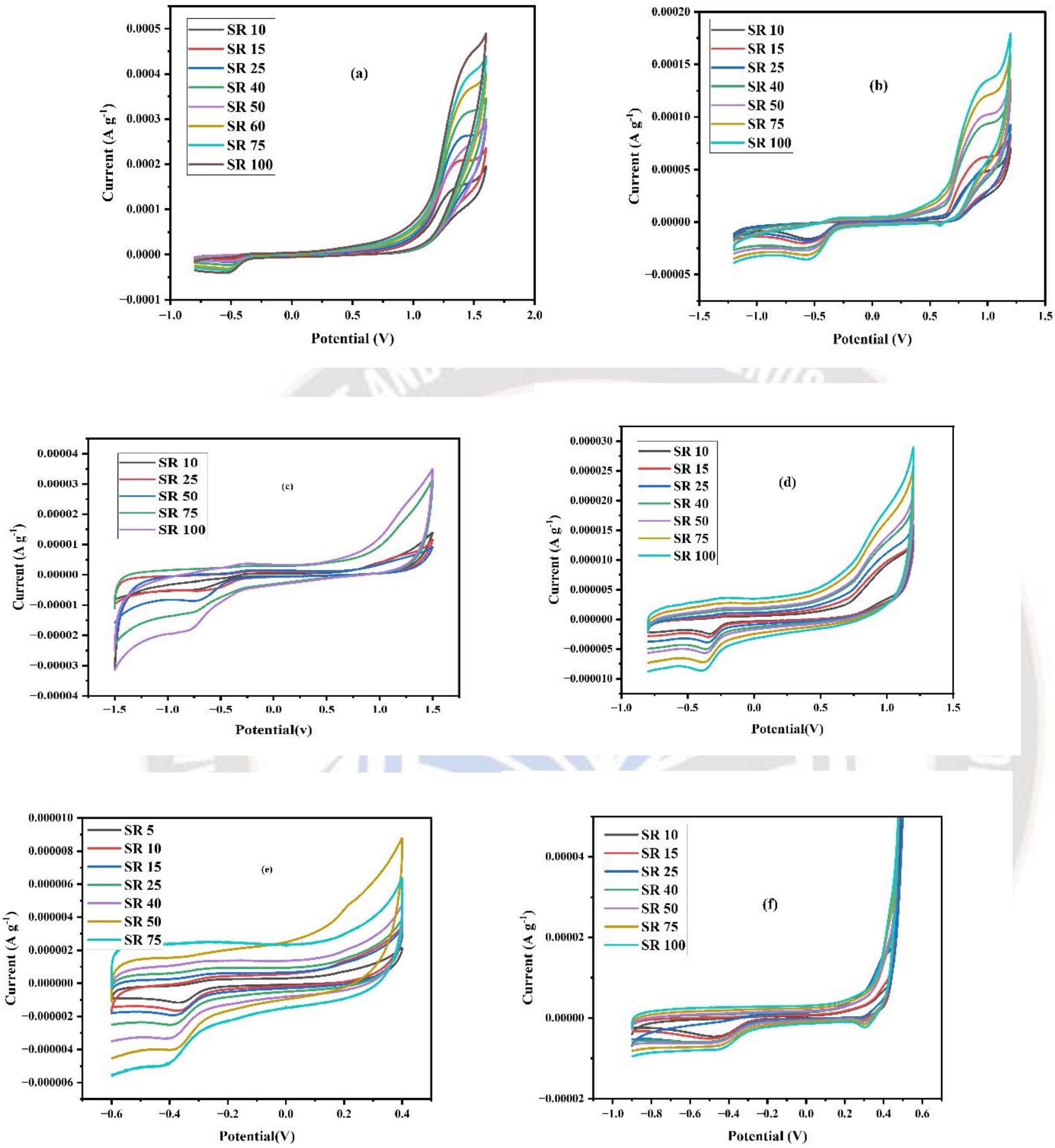

FIG.4. H_2SO_4 electrolyte of (a) PIN (b) PIN/NiO.. Na_2SO_4 electrolyte of (c) PIN (d) PIN/NiO. KOH electrolyte of (e) PIN (f) PIN/NiO.

Table 1. Specific Capacitance of H_2SO_4 Electrolyte

Scan Rate (mV/s)	PIN (mF/g)	PIN/NiO (mF/g)
10	360.58	200.33
15	350.04	198.12
25	270.77	96.97
40	206.7	118.57
50	151.13	102.65
75	147.70	83.04
100	126.63	71.36

Table 2 Specific Capacitance of KOH Electrolyte

Scan Rate (mV/s)	PIN (mF/g)	PIN/NiO (mF/g)
10	82.29	45.65
25	47.14	33.17
50	33.02	23.95
75	43.39	21.21
100	38.20	1.94

Table 3 Specific Capacitance of Na_2SO_4 Electrolyte

Scan Rate (mV/s)	PIN (mF/g)	PIN/NiO (mF/g)
10	26.17	54.29
15	23.07	46.77
25	20.06	38.30
40	18.16	32.31
50	22.06	29.49
75	16.69	26.26

The electrodes' number of active sites (N) was determined using the equation [21],

$$N = (C \times M \times \Delta V) / F$$

where C is the specific capacitance (F/g), M is the molecular weight (g/mol), V is the potential window (V), and F is the Faraday's constant (96,500 C/mol). The number of active sites involved in the redox reaction at varying scan rates corresponding to 10-100 mV/s were displayed in a table. The N of all samples at low scan rates is higher than that at high rates because the ions have enough time to reach the electrode surface, indicating content utilization [21]. When doping NiO, a decrease in the number of active sites results in a decrease in specific capacitances.

When peak currents of PIN/NiO correlated with the square root of scan rate, a straight line is observed (Fig.5). These facts reveal that the adsorption process controls the voltammetric redox behavior of mixed metal oxide nanocomposites. The plot of peak current versus different scan rate for PIN/NiO mixed oxide exhibits a straight line (Fig. 5), indicating a good adherent behavior on electrode surface.

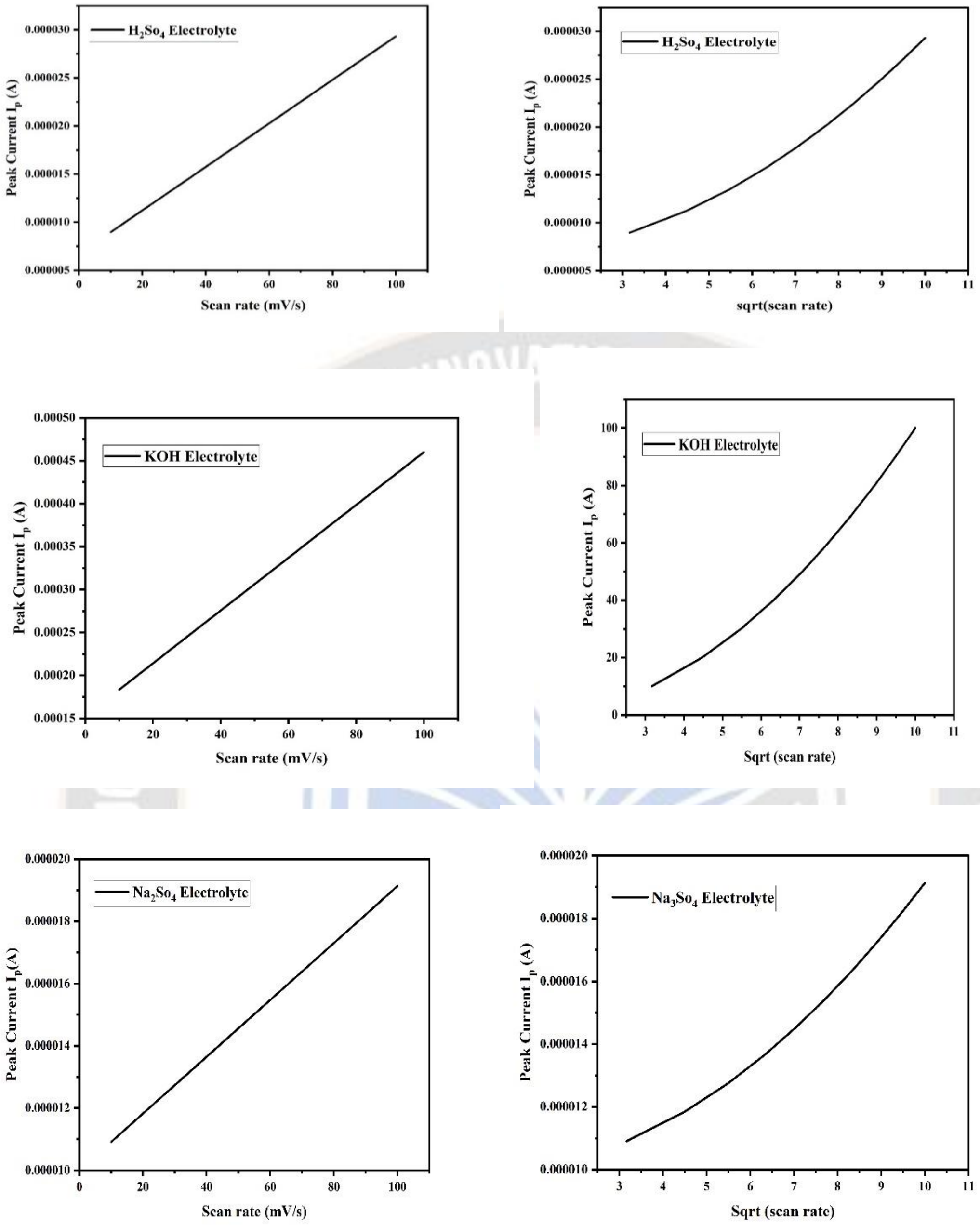

Fig 4. Scan rate vs Peak current and Sqrt(scan rate) vs Peak current

Fig 5 shows that the H_2So_4 Electrolyte expert the higher specific capacitance compared to another two electrolyte.

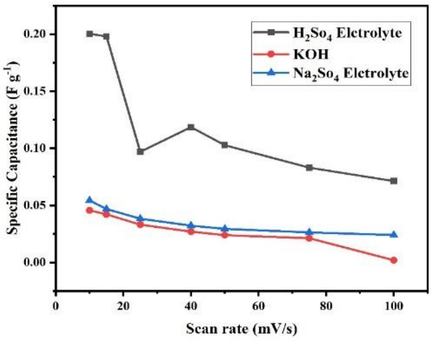

FIG 5. Scan rate vs Specific Capacitance

3.4.2. ELECTROCHEMICAL IMPEDANCE SPECTROSCOPY (EIS)

Electrochemical impedance spectroscopy (EIS) was used to further assess the electrochemical performances of the recommended electrodes in the 0.01 Hz–1 MHz frequency range. Plots of the Bode curves for the electrode materials were made. To investigate the capacitive functioning of the samples, the low-frequency Bode plot slope was used. The optimal capacitive behavior is indicated by a slope value around 1.0.

3.4.2.1.H_2So_4 ELECTROLYTE

Figure (6a) displays the Bode plot, which illustrates how the Bode phase changes as a function of applied frequency. For a perfect resistor (n = 0), the phase angle θ may be 0°, but for a perfect capacitor (n = 1), it can range from 90° [20]. The slope of the frequency against |Z| plot yields the value of n. The phase angle of 81.1° in the case of PIN/NiO nanocomposites indicates the material's pseudo capacitive properties. A slope value R^2=0.84 was likewise obtained from the plot of log |Z| vs log f (Hz) (Fig.6b), indicating the pseudo capacitive behavior of NiO doped Polyindole[20].

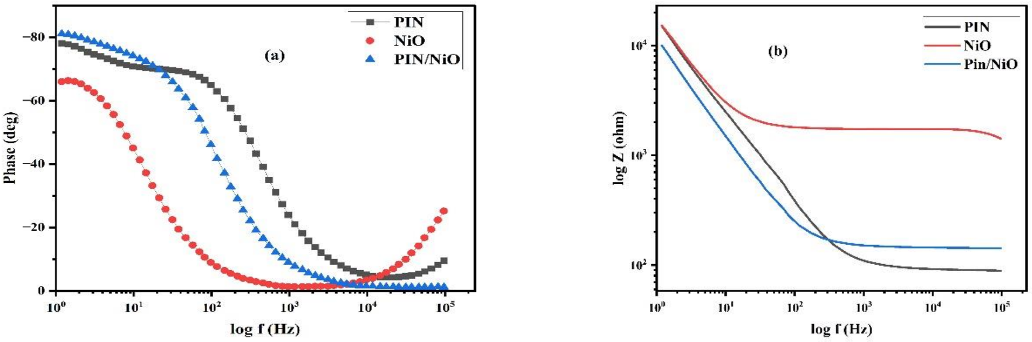

FIG 6. Bode plot of H_2So_4 Electrolyte

3.4.2.2.KOH ELECTROLYTE

According to Fig. 7a Bode plot (-phase angle (degree) vs. log f(Hz), Nickle oxide doped Polyindole has a superior pseudocapacitive behavior because its bode phase angle is closed at 84.7°. According to the Bode plot seen in Figure 7b, a slope value of 0.98 (R^2=1) in the low frequency zone. It displays a pseudo capacitor's characteristic.

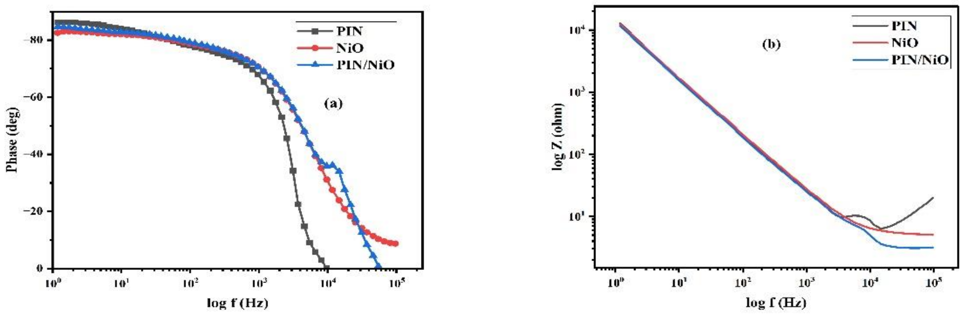

FIG 7. Bode plot of KOH Electrolyte

3.4.2.3. Na_2So_4 ELECTROLYTE

According to the Bode plot (-phase angle (degree) vs. log f(Hz) shown in Figure 8a, the NiO-Polyindole nanocomposite's bode phase angle is closer to (83.9°), which is more than that of Better results are shown by nano Nickle oxide (79.8°) and polyindole (62.3°). compared to nano NiO and polyindole, pseudocapacitive behavior. According to the Bode plot seen in Fig. 8b, at the slope NiO-Polyindole nanocomposite values are 0.9(R^2=1) at the area of low frequency. It displays the attribute of a fictitious capacitor.

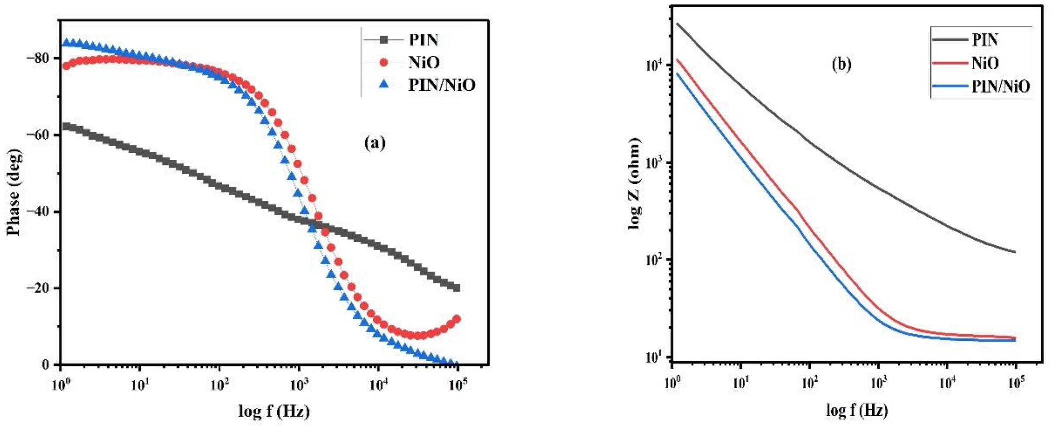

FIG 8. Bode plot of Na_2So_4 Electrolyte

CONCLUSION

By using the chemical oxidative polymerization approach, NiO nanoparticles, polyindole, and polyindole-NiO nanocomposite were effectively created. The descriptions of Samples were made using FTIR, UV Spectroscopy, and Thermal analysis examination. FTIR analysis showed that the 600 cm-1 peak, The C-N bond's vibration mode is 1387 cm-1, and 1456 cm -1 (the benzene ring's stretching mode) were allocated to the distinctive indication of a note worthy NiO interaction polymeric nanoparticles with polyindole. According to UV-Vis study, the optical band gap and absorbance of PIN are 4.45 eV and 237 nm, respectively, where as PIN/NiO has an optical band gap anof 2.42 eV. Studies on electrochemistry have also been conducted he brittle electrode covered Nickle Oxide Polyindole. The nanocomposite demonstrated superior capacitive capabilities. Having a large specific capacitance in the range of -1 to +1V in Na_2So_4 electrolyte at 1M. This performance of capacitance was because of the combined benefits of a big surface area and high pseudo-capacitive reaction caused by NiO's presence Polyindole nanocomposite. Consequently Nickle Oxide Polyindole Nanocomposite was thought to be an appropriate electrode components of supercapacitors. The chemically mediated capacitance produced nanocomposite indicates that they have potential application.

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