

Structural, Morphology, Transport and Humidity Sensing Properties Study of Calcium Titanate (CaTiO_3) Doped Polyaniline Composite.

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Abstract:

In the present work, calcium titanate (CaTiO_3) doped polyaniline (PANI) composites ($\text{PANI}/\text{CaTiO}_3$) were prepared by chemical oxidative in situ polymerization technique with the ammonium persulphate as oxidising agent. Various composites have been prepared by varying the level of additive material CaTiO_3 . The phase and morphology of all the synthesized samples were analyzed using basic characterization techniques such as X-ray diffraction (XRD) and scanning electron microscopy (SEM). The AC electrical conductivity of the samples was measured using the impedance technique within a frequency range of 1KHz to 1MHz at room temperature and found that 50 wt% shows high conductivity compared to other composites. Additionally, the dc electrical transport property of the composites was investigated within a temperature range of 40-200°C and found that 50 wt% shows high conductivity compared to other composites. The change in electrical resistance of both PANI and $\text{PANI}/\text{CaTiO}_3$ composites was measured when exposed to 10 %Rh to 90 %Rh. Both samples exhibited a rapid resistance change upon exposure to humidity, with the $\text{PANI}/\text{CaTiO}_3$ composite demonstrating higher change in resistance and suitability for humidity sensing compared to PANI.

Key words: —Composites, conducting polymers, polyaniline, calcium titanate, conduction mechanism.

1. Introduction:

The need for advancement and development of scientific materials to obtain better materials and materials has increased due to the wide application of technology [1-2]. The physical properties of nanocomposites are unique and they have a wide range of applications in different areas. Successfully combining the characteristics of parent constituents into a single material can result in novel properties of nanocomposites. In the modern period, composite materials that combine inorganic elements with the addition of organic-conjugated polymers, boasting exceptional characteristics such as high electrical conductivity, dielectric constant, minimal dielectric loss, robust thermal and chemical stability, have gained improved prospects for use in rechargeable batteries, sensors, thermoelectric gadgets, microwave absorbers, and capacitors [3-5]. Sensors constructed from the ABO₃-type of composite oxide materials possess a notable benefit in their stability. The perovskite arrangements within these compounds remain intact even when certain types of perovskite structures experience a shortage of an A-site element. Despite the straightforward nature of the initial perovskite arrangement, this group of compounds exhibits an incredible diversity in their structural alterations and forms across a broad spectrum of physical and chemical characteristics. The perovskite structure of CaTiO_3 is found in its solid-state form within the realm of solid state inorganic chemistry. This arrangement harbors a wide range of compounds.

Also, the polyaniline (Pn) has been explored as a promising material for many gas sensing applications, due to its controllable electrical conductivity and interesting redox properties associated with the chain nitrogen's. In Pn the charge delocalization can provide multiple active sites on its backbone for the adsorption and desorption of gas analyte. However, with respect to the gas species, the polyaniline is not as sensitive as metal oxides and also its poor solubility in organic solvents which limits the applications of polyaniline. The polyaniline is more suitable as a matrix for synthesis of CP's composites. Polyaniline is prominetely conductive polymers , and also highly promising materials due to its excellent optical, electrochemical, and ease of synthesis. Furthermore PANI is very potential material towards gas sensing uses because of its environmental stability and regulated electrical conductivity and well defined readox behaviour [6-8]. Nevertheless, the PANI's solubility, processability, morphology, and conductivity are all significantly impacted by doping it with organic acids like dodecylbenzene sulphonic acid (DBSA), sodium dodecyl sulphate, and p-toluene sulphonic acid [9-11].

Recent studies have uncovered a fascinating discovery. When a perovskite compound was formed with a deficiency of A-site, such as $\text{La}_{0.88}\text{MnO}_3$ [12] and $\text{Pr}_{0.6}\text{Sr}_{0.3}\text{MnO}_3$ [13], the perovskite structures of these compounds remained intact, yet they displayed unique physical characteristics. As a result, the benefits of using ceramic-based nano composite sensors are enhanced in terms of chemical, thermal, and mechanical stability. The current present research is centered on creating polyaniline nano ceramic sensor composites from the perovskite family through in-situ polymerization methods. Because of their significant thermal, optical, and electrical properties, calcium titanate (CaTiO_3), barium titanate (BaTiO_3), and strontium titanate (SrTiO_3) are a few well-known perovskite-structured oxides that have been studied with conductive polymers [14-15]. Because of its wide bandgap (3–3.5 eV), low cost, abundance, non-toxicity, excellent chemical and thermal stability, and ecofriendliness, CaTiO_3 has been considered one of the more versatile materials among them [16].

The combination of PANI and CaTiO_3 in the presence of organic acid is likely to exhibit modified structural, optical, dielectric and electrical properties [17]. According to the report, PANI/ CaTiO_3 composites were prepared by chemical oxidative polymerization, and the results showed a strong dependence of electrical conductivity and dielectric constant on the weight percentage of CaTiO_3 [18]. In-situ oxidative polymerization was used to prepare PANI/ CaTiO_3 composites, which were found to have improved electrical properties and charge mobility for use in Schottky diodes. Additionally, for the purpose of using humidity sensors, surface-modified PANI/ CaTiO_3 composites prepared in the presence of sodium dodecylbenzene sulphonic acid showed improved response recovery time and sensing [19-20].

Furthermore, there isn't a thorough analysis in the literature of the structure-property correlation of PANI/ CaTiO_3 hybrid composites when DBSA is present for Humidity sensing devices.

2. Experimental section:

2.1. Materials used:

The chemical reagents utilized in the synthesis process were aniline (99%), ammonium persulfate (APS) (99%), hydrochloric acid (HCl), Calcium carbonate (CaCO_3), Titanium dioxide (TiO_2) and calcium titanate (CaTiO_3) of analytic grade. All the aqueous solutions were prepared using double-distilled water. The calcium titanate (CaTiO_3) was used to prepare composites via chemical oxidative polymerization method.

2.2 Chemical synthesis of calcium titanate (CaTiO_3).

The solid state method was used to prepare the calcium titanate (CaTiO_3). Calcium titanate powders were prepared from calcium carbonate (CaCO_3) and titanium dioxide (TiO_2) by solid state reactions under controlled conditions. In a typical experimental procedure, stoichiometric amounts of titanium dioxide (TiO_2) and calcium carbonate (CaCO_3) were grounded in agate mortar for a period of about half an hour. Then the resultant product was stirred in ethanol and calcined in muffle furnace at 1400C for a period of about 3 h while being packed in alumina crucible according to the already mentioned procedure [21-23].

2.3 Preparation of polyaniline:

The 0.25 M of aniline and 1N of HCL is mixed and stirred for 1 hour at room temperature. at constant RPM for the completion of the reaction. Then the 0.2 M of ammonium persulfate was prepared separately and added drop wise in the above mixer for 1 hour at temperature 1 to 5°C. This solution was stirred continuously stirred in magnetic stirrer for 8 hrs to get homogenous mixer. After completion of the reaction, dark green solution was obtained and precipitate formed. The precipitate formed and separated out by filtering by using vacuum pump and washed with deionised water with acetone and 1N HCL to remove other additives present in the PANI. The obtained final suspension was dried in oven at 50° C for 24 hrs. The final product was grinded into powder.

2.4 Preparation of polyaniline-calcium titanate composite:

The 0.25 M of aniline and 1N of HCL is mixed and stirred for 1 hour at room temperature. at constant RPM for the completion of the reaction. Then the 0.2 M of ammonium persulfate was prepared separately and added drop wise in the above mixer for 1 hour at temperature 1 to 5°C. Calcium titanate powder of 10%, 20%, 30%, 40% and 50% additive weight percentage is dissolved in the mass fraction to the above solution. This solution was stirred continuously stirred in magnetic stirrer for 8 hrs to get homogenous mixer. After completion of the reaction, dark green solution was obtained and precipitate formed. The precipitate formed and separated out by filtering by using vacuum pump and washed with deionised water with acetone and 1N HCL to remove other additives present in the PANI. The obtained final suspension was dried in oven at 50° C for 24 hrs. The final product was grinded into powder [24]. The synthesized composites so obtained above are crushed into fine powder in an agate mortar in the presence of acetone medium

3. Results and discussion:

3.1 XRD spectra:

The XRD spectra for the pure polyaniline samples were recorded in the range of 20° to 90° and have been depicted in figure-1. Careful analysis of X-ray diffraction of polyaniline exhibits a broad peak at 2θ angles around 26° can be assigned to the scattering from polyaniline at interplanar spacing and which is characteristics of the van der Waals distances between stacks of polyaniline ring and which corresponds to (200) diffraction planes of pure PANI. This broad peak shows that polyaniline is amorphous structure contains crystalline regions and low degree of crystallinity [25].

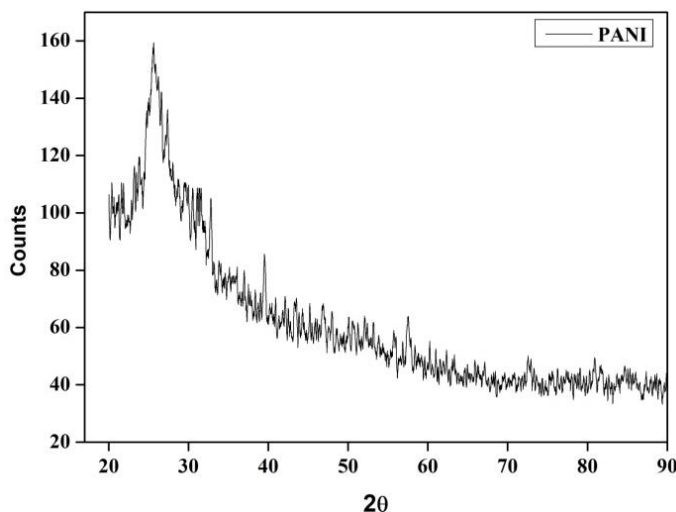
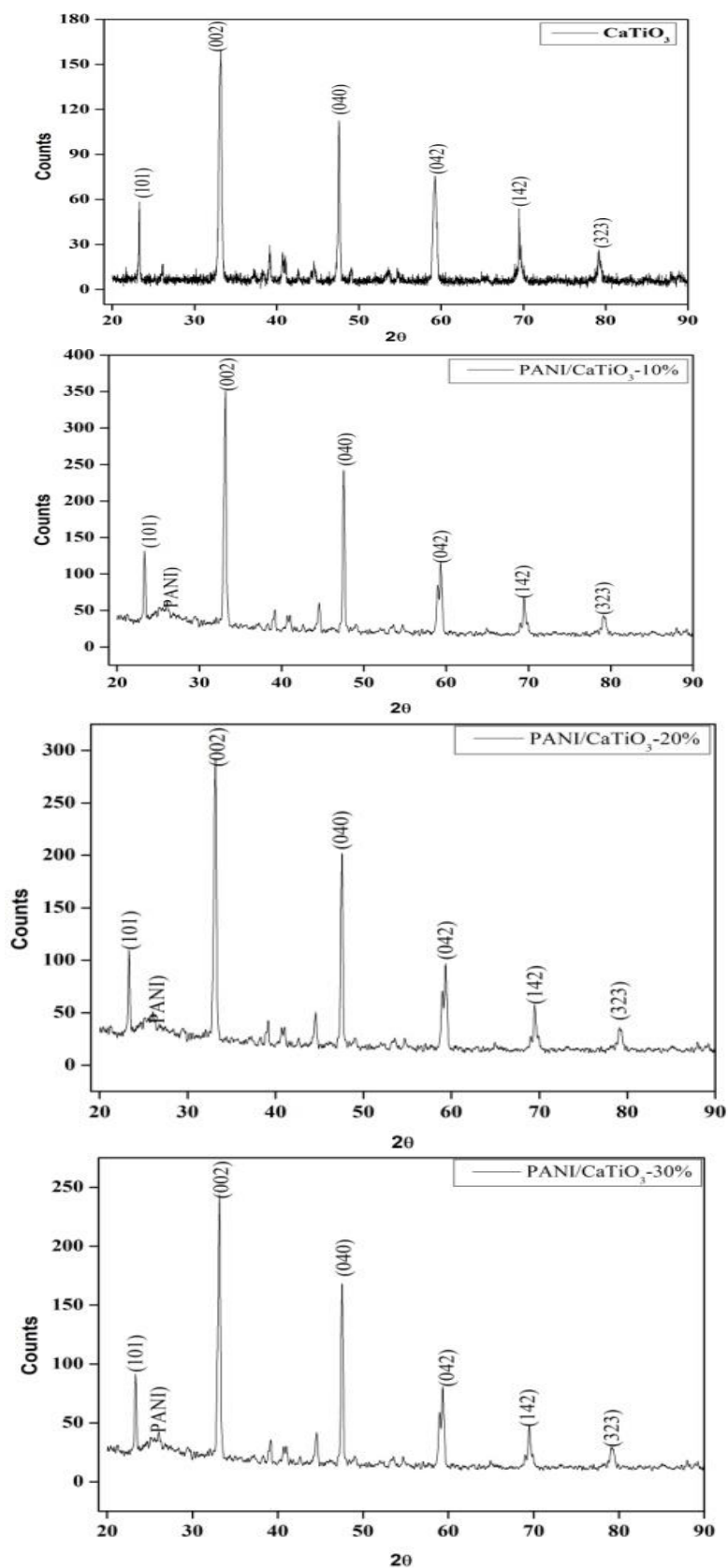


Figure-1: XRD spectra of polyaniline



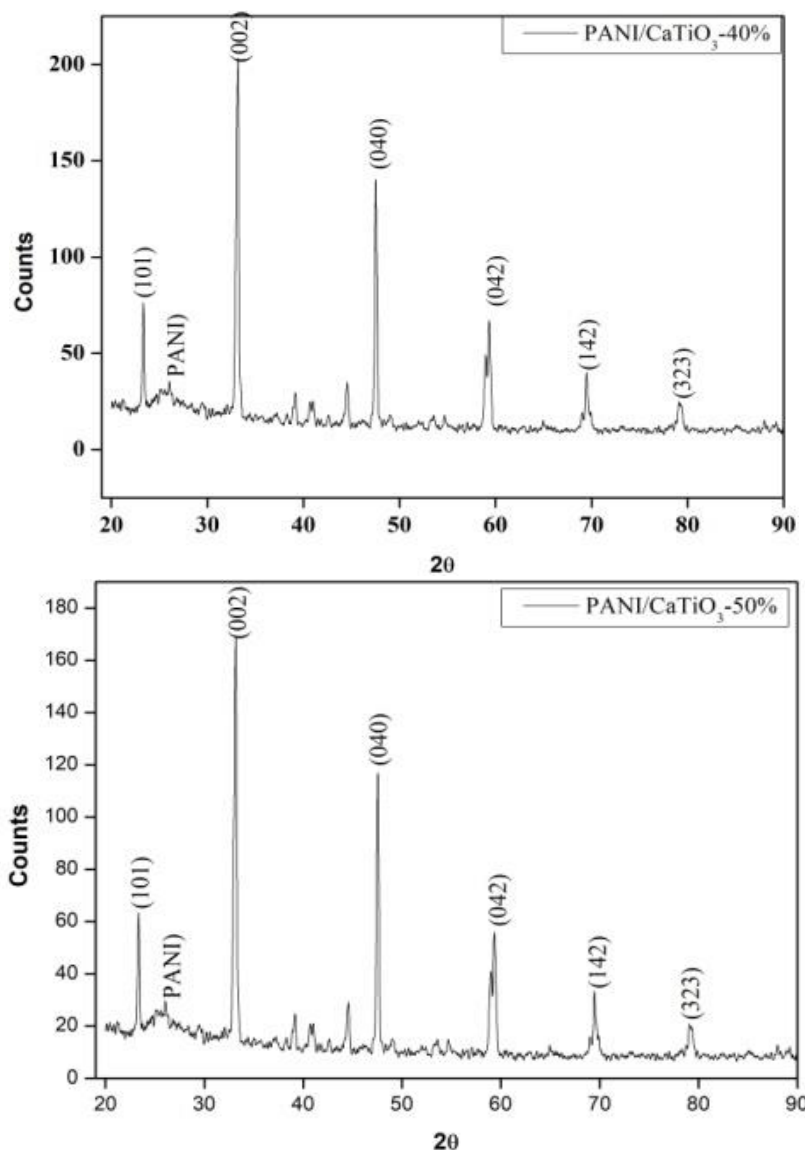


Figure-2: XRD spectra of (a) CaTiO_3 , (b) PANI/ CaTiO_3 -10%, (c) PANI/ CaTiO_3 -20%, (d) PANI/ CaTiO_3 -30%, (e) PANI/ CaTiO_3 -40%, (f) PANI/ CaTiO_3 -50% composites

The XRD spectra for the CaTiO_3 composites were recorded in the range of 20° to 90° and have been depicted in figure-2 (a). The XRD pattern of CaTiO_3 shows the characteristic peaks identified 2θ angles 23.29° , 33.19° , 47.57° , 59.29° , 69.49° and 79.19° corresponding to the hkl planes (101), (002), (040), (042), (142) and (323) for the phase of the CaTiO_3 and which are well matched with the reported literatures [26] and standard JCPDS data card No. 42-0423.

The XRD spectra for the PANI/ CaTiO_3 composites were recorded in the range of 20° to 90° and have been depicted in figure-2 (b-f). The XRD spectra of PANI/ CaTiO_3 composite exhibits the diffraction peaks belongs to both CaTiO_3 and PANI which describes the withholding of PANI in the composite material. The XRD spectra of prepared PANI/ CaTiO_3 composite exhibits well defined diffraction peaks obtained at different 2θ angles 23.29° , 33.19° , 47.57° , 59.29° , 69.49° and 79.19° corresponding to the hkl planes (101), (002), (040), (042), (142) and (323) for the phase of the CaTiO_3 and which are well matched with the reported literatures and standard JCPDS data card No. 42-

0423. The XRD spectra of composite also exhibit diffraction peak at 25° corresponding to PANI. No characteristic peaks other than CaTiO_3 were observed. The average crystalline size was calculated by using Scherrer's formula $D = K\lambda / \beta \cos \theta$ (where $\lambda = 1.54060 \text{ \AA}$, θ is the Bragg angle, K is the Debye Scherrer constant and β is the peak full width at half maximum of the peak. The average crystallite size of CaTiO_3 composite was found to be 30 nm.

3.2 SEM micrographs:

The SEM micrographs for the PANI, CaTiO_3 and PANI/ CaTiO_3 composite samples being magnified at 5000 times have been depicted in figure-3, 4(a) and 4(b-f) respectively. The morphology of the polyaniline appears to be irregular shapes, relatively low porous structure, non fibrous with high densities and few oval-shaped particles randomly distributed micro size round shape particles with uniformity on the surface as well as a few agglomerations. When compared to SEM micrographs PANI samples, the SEM images of the CaTiO_3 show that the crystalline CaTiO_3 particles have smaller particle sizes and are composed of a significant amount of aggregated particles. It has been shown that the morphology of composites containing CaTiO_3 particles differs from that of PANI. The morphology of polymers is generally influenced by a number of elements, including the synthesis technique, the circumstances of the polymerization reaction, the type of dopant, and the surfactant structure [27]. The less agglomerated and more ordered chains arrangements were observed in the SEM micrographs of the PANI/ CaTiO_3 composites due to the interaction between the PANI and CaTiO_3 . The interconnected particles were observed in the composite morphology which suggests the increase in the crystalline domain in the amorphous material.

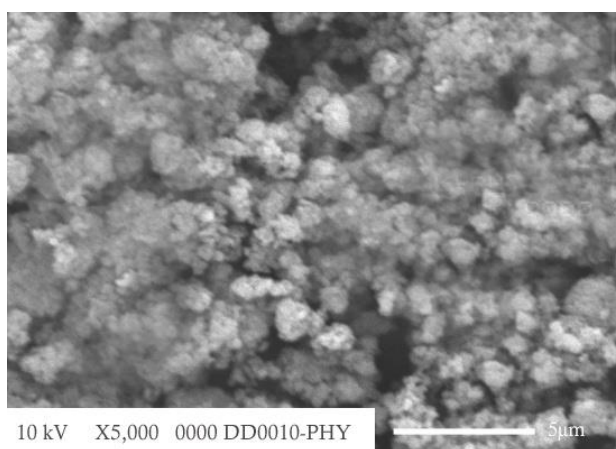
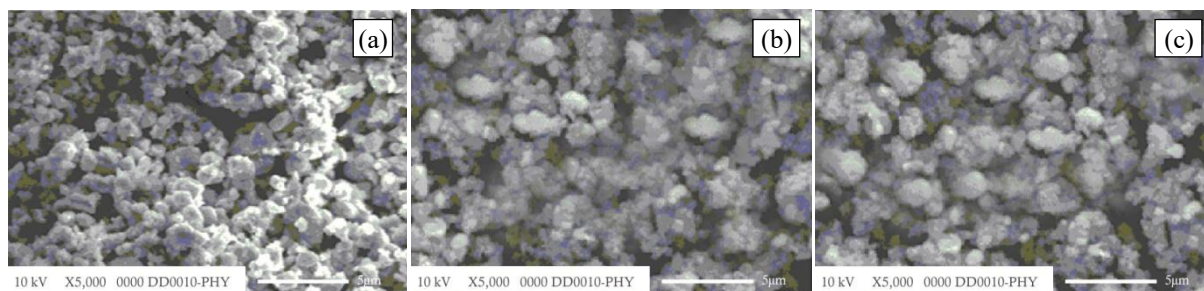


Figure-3: SEM micrographs of PANI



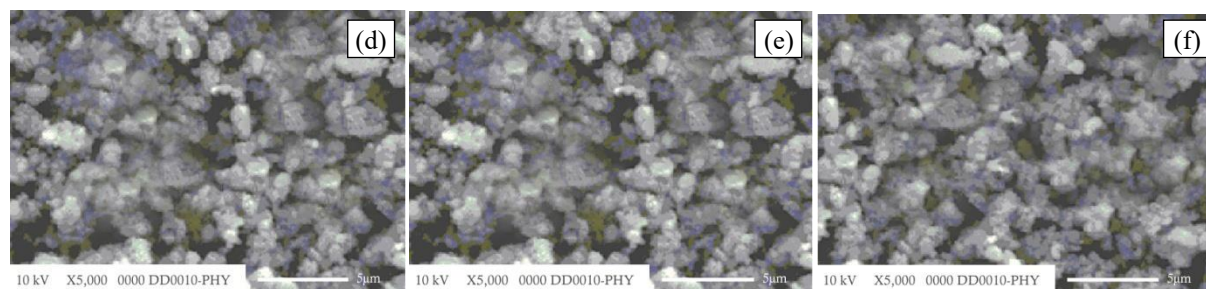


Figure-4: SEM micrographs of (a) CaTiO_3 , (b) PANI/ CaTiO_3 -10%, (c) PANI/ CaTiO_3 -20%, (d) PANI/ CaTiO_3 -30%, (e) PANI/ CaTiO_3 -40%, (f) PANI/ CaTiO_3 -50% composites

3.3 AC electrical conductivity:

The transport properties of the polymer is directly depends on the conductivity of the doping agent, filler particles, the crystallinity of the material, degree of protonation, order of crystalline domains, temperature, frequency and the quality of the electrical network formation between the additive and the macromolecular chain [28]. The total electrical conductivity in amorphous semiconductors generally consists of AC and DC conductivity, which are dependent on temperature and angular frequency [29]. The ac conductivity measurements have been conducted by a typical two probe method. The frequency dependent ac electrical conductivity of PANI and PANI/ CaTiO_3 composite was depicted in figure-5 and 6 respectively. The conductivity of both samples increases with increase in frequency obeying the universal power law. The conductivity of the composite increases with increase in the content of calcium titanate in the PANI matrix. This increase in the conductivity of PANI/ CaTiO_3 composite may due to the even distribution of calcium titanate particles and which is evident from XRD results that the increase in the crystallinity. AC conductivity increases with increase in the wt% of CaTiO_3 perovskite. The enhancement in conductivity could be associated with the development of more effective conductive pathways at the interface, which aids in the movement of charge carriers throughout the polymer matrix. The ac-conductivity is shown to be constant for all samples up to 10^4 Hz, after which it increases sharply with frequency dependences that follow a universal power law. It is connected to the function of polarizability. A common pattern for hopping conduction is the low-frequency behavior [30-31]. The conductivity of the composite material found increasing from 2.42×10^{-4} S/cm for 10wt% at 1KHz with increase in the content of CaTiO_3 and reaching 5.51×10^{-4} S/m in the 50wt% at 1MHz. Further ac conductivity decreases as doping increase up to 50wt%. Further the decrease in conductivity for 10 to 50 wt% may be attributed due to the trapping of charge carrier hop [32].

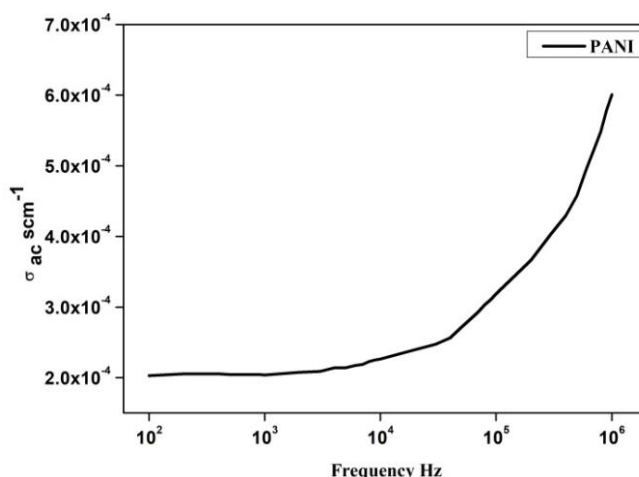


Figure-5: AC electrical conductivity of PANI

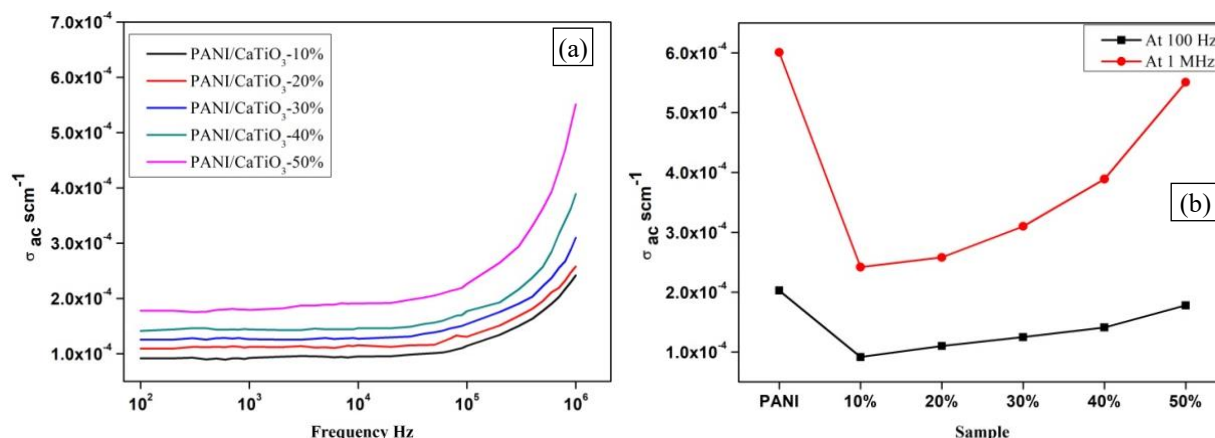


Figure-6: AC electrical conductivity (a) PANI/CaTiO₃ composite, (b) as function of wt% of CaTiO₃.

3.4 DC electrical conductivity

The temperature dependent dc electrical conductivity was recorded to describe the charge transport mechanism in the polymer composites. The variation in the dc conductivity with change in temperature of PANI and PANI/CaTiO₃ composites was conducted and represented in figure-7. The DC conductivity increases with increase in temperature as well as increase in weight percentage of CaTiO₃ in PANI matrix. This indicates the CaTiO₃ particles gives positive influence on composite towards increase in conductivity. It is found that the conductivity rises in two stages. In the first stage, the conductivity rises slowly between 40 and 120 °C. Because there may not be enough activation energy needed to accelerate the charge carrier from one conducting site to another. Additionally, from 120 to 220 °C, the conductivity increases significantly in the second stage. The increase in the conductivity at higher temperature due excitation of electrons to the conduction band at higher temperature [33]. Figure 7(b) indicates the dc conductivity as function of different wt% of CaTiO₃. The result shows that the CaTiO₃ has positive influence on the temperature dependent conducting property of the PANI. Among all the composites, 50 wt% shows the high conductivity of 3.32×10^{-4} S/cm which is due to the tunnelling of charge carriers. However, compared to other compositions, the high conductivity at higher temperatures is caused by the tunneling phenomenon linked to charge carrier hopping [34]. The conductivity of the composite material found increasing from 1.15×10^{-4} S/cm for PANI at 200°C with increase in the content of CaTiO₃ and reaching 3.32×10^{-4} S/cm in the 50wt% at 200°C.

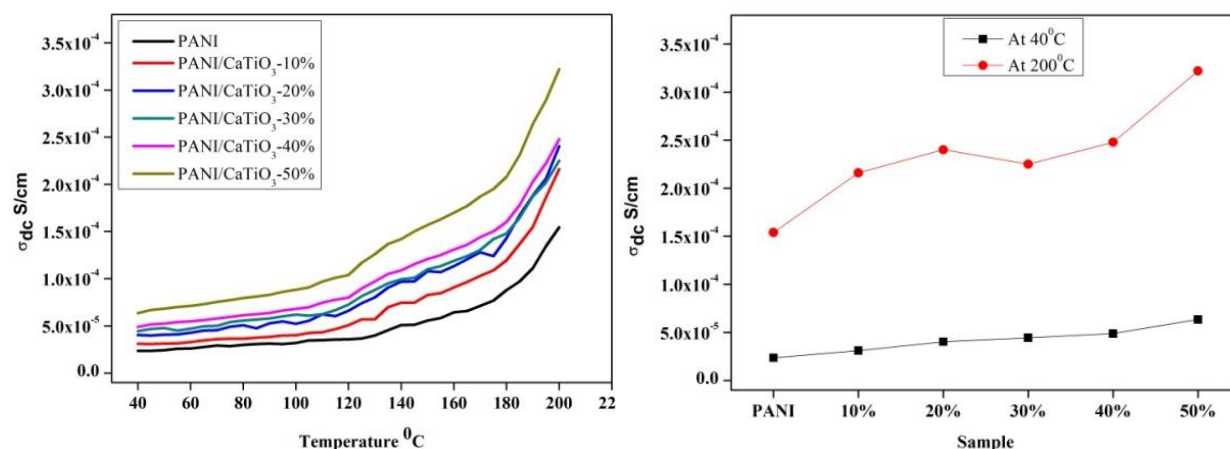


Figure-7: DC electrical conductivity (a) PANI/CaTiO₃ composite, (b) as function of wt% of CaTiO₃.

3.5 Humidity sensing studies:

Figure 8 shows the schematic diagram of the humidity sensing test chamber. It consists of air-tight chamber container with two openings at the left and right side of the chamber. The left side inlet of the humidity source and the right side outlet is connected to a rotary pump for evacuation. The chamber house having dc fan in order to distribute the gas molecules uniformly all over the chamber. The fabricated sensor pellet was placed over the sample holder in air tight chamber. The test chamber was maintained at temperature 28°C throughout the experiment. The change in the electrical resistance of the samples as function of %RH was noted using digital LCR meter.

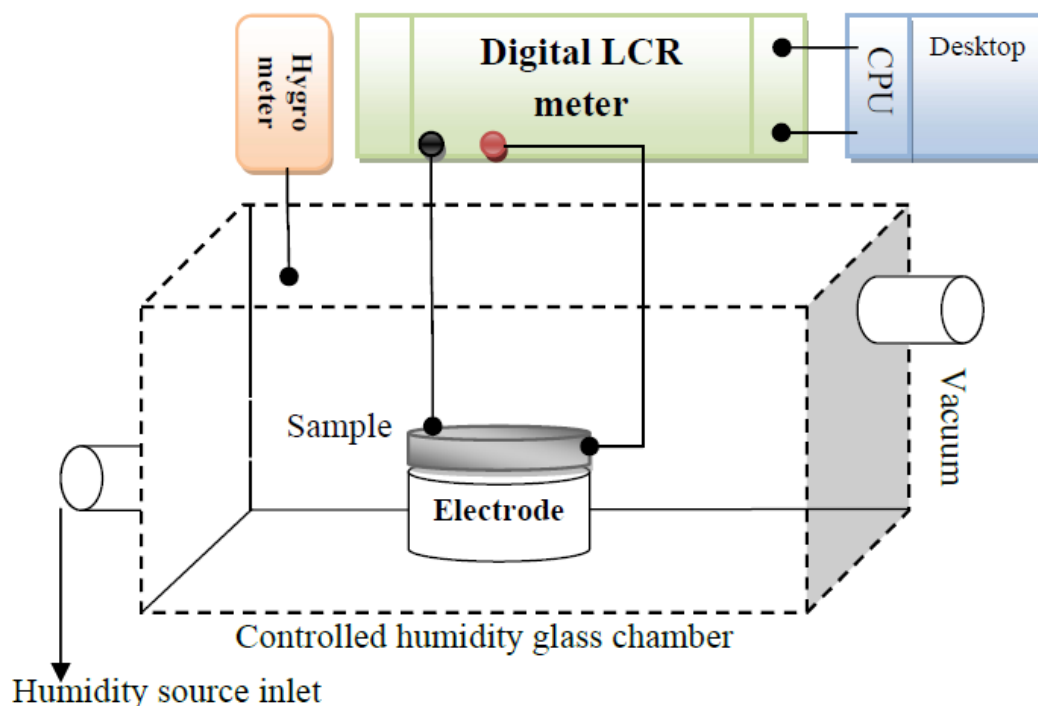


Figure-8: Block diagram of Humidity sensor set up

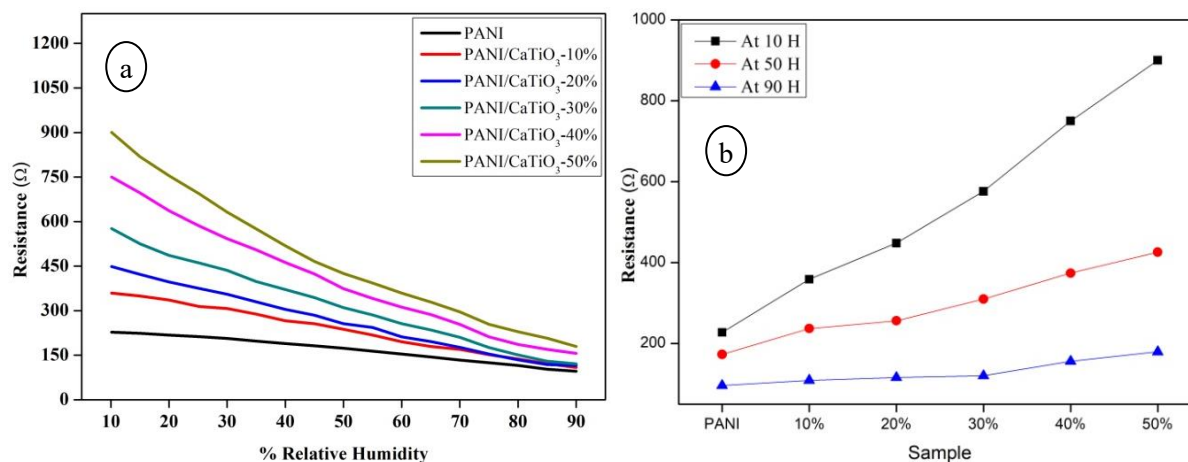


Figure-9: Variation of resistance as function percentage relative humidity of polyaniline/CaTiO₃ composites at different

In order to test the humidity sensing ability of PANI and PANI/CaTiO₃ composite at room temperature (RT) was studied by calculating change in the resistance of sensing samples with %RH toward humidity exposure presented in figure 9.

It is observed that the decrease in the resistance of the PANI with increase in the percentage of relative humidity from 10 to 90 %RH. In case of PANI/CaTiO₃ composite were also studied in the range of 10 to 90%RH, resistance has phenomenally decreased linearly by one order of magnitude. It is evident that the PANI and PANI/CaTiO₃ composite describe a linear response towards the relative humidity from 10 to 90% RH. The decrease in the resistance of the sample with increase in the relative humidity may ascribe to the trapping of water molecule in the voids formed in between polymer and CaTiO₃ particles [35]. The observed uniform linear decrease in resistance at lower and higher RH by the composites is mainly due to the hybrid nano-structure of the composite [36]. The variation of resistance plotted against sample at 10, 50 and 90%RH are shown in figure 7(b). The resistance found increasing with increase in the content of CaTiO₃ in the polyaniline matrix and then it decreases as the relative humidity increases. From results it is also observed that the prepared PANI/CaTiO₃ composite have presented better linear sensing even at lower relative humidity. It is evident from figure 7(b) that at lower relative humidity was observed for 10 percentage relative humidity compared to 50 and 90 percent of relative humidity. This observed remarkable change is considered to be significant compared to that of many other composites for which linear sensing response is observed only at higher RH even though the sensing response is very high. [37-38]. The change in the resistance of the composite decreases suddenly at higher humidity may suggests the composite materials may absorb more vapour from long conduction path. It is also evident from plot that the PANI and composite presenting large change in resistance but above 60%RH, the polymer becomes unstable and starts degrading as results change in resistance almost constant

4. Conclusion:

The calcium titanate was prepared using solid state method and PANI/CaTiO₃ composites by chemical polymerization of aniline in the presence of CaTiO₃ particles. Further the detail structural and morphological characterizations of the PANI & composite were investigated using XRD & SEM technique. XRD pattern of pure PANI describes the existence of broad peak at $2\theta \approx 26^\circ$ suggests the amorphous character of the prepared PANI and XRD pattern of PANI/CaTiO₃ composite shows the presence of CaTiO₃ particles in the PANI with crystalline peaks of CaTiO₃. Careful study of SEM micrographs revealed morphology of the polyaniline appears to be irregular shapes, relatively low porous structure, non fibrous with high densities and few oval-shaped particles randomly distributed, micro size round shape particles with uniformity on the surface as well as a few agglomerations. The ac conductivity of both samples increases with increase in frequency obeying the universal power law and also increases with increase in the content of calcium titanate in the PANI matrix. The ac conductivity of the composite material found increasing from 2.42×10^{-4} S/cm for 10wt% at 1KHz with increase in the content of CaTiO₃ and reaching 5.51×10^{-4} S/m in the 50wt% at 1KHz. The DC conductivity increases with increase in temperature as well as increase in weight percentage of CaTiO₃ in PANI matrix. This indicates the CaTiO₃ particles gives positive influence on composite towards increase in conductivity. The dc conductivity of the composite material found increasing from 1.15×10^{-4} S/cm for PANI at 200°C with increase in the content of CaTiO₃ and reaching 3.32×10^{-4} S/cm in the 50wt% at 200°C. The decrease in the resistance of the PANI with increase in the percentage of relative humidity from 10 to 90 %RH. In case of PANI/CaTiO₃ composite were also studied in the range of 10 to 90%RH, resistance has phenomenally decreased linearly by one order of magnitude. The resistance found increasing with increase in the content of CaTiO₃ in the polyaniline matrix and then it decreases as the relative humidity increases. From results it is also observed that the prepared PANI/CaTiO₃ composite have presented better linear sensing even at lower relative humidity. Thus, composites shows better sensing properties and exhibits good linearity in sensing response curve. Therefore, the composite can be a promising material for humidity sensing applications.

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