Studies on structural, morphology and electrical conductivity of titanium dioxide doped polyaniline (TiO$_2$/PANI) nanocomposite

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Abstract:

Polyaniline (PANI)/TiO$_2$ nanocomposite samples with various dopant percentages of TiO$_2$ were synthesized at room temperature using a chemical oxidative polymerization method. The doping effect of TiO$_2$ was characterized and evaluated by X-ray diffraction (XRD) and scanning electron microscopy (SEM) technique. X-ray pattern confirms the formation polyaniline and as the TiO$_2$ percentage was increased, the amorphous nature disappeared and the composites became more strongly oriented and SEM study shows that TiO$_2$ nanoparticles have a strong effect on the morphology of composites with average grain size of 10-20nm nm. The electrical conductivity measurements indicate that the conductivity of composites at low TiO$_2$ content is much higher than that of the PANI, while with the increasing contents of TiO$_2$, the conductivity shows an orderly decrease. DC conductivity increasing as content of TiO$_2$ and temperature in increased.

1. Introduction:

Now a day's conducting polymers has been observed as a rising field of research and versatile materials for technological applications and therefore attracts many researchers and academicians for the development of multifunctional conducting polymers. Polyaniline (PANI) refers as an important conducting polymers and it has been the first conducting polymer established itself as a novel commercialization material owing to its excellent characteristics [1]. Polymer based metal/metal oxide composites are currently attracted for various applications. Among the synthetic polymers, polyaniline is utilized maximum because of its high conductivity, ease of preparation, good environmental stability and variety of nanostructured morphology [2-4]. Polyaniline can be prepared in three redox forms: pernigraniline, leucoemeraldine and emeraldine. The emeraldine form of polyaniline, usually referred to as emeraldine base (EB), is either neutral or doped, with imine nitrogen protonated by an acid. Doping and dedopoing with acid and base can interchange EB and emeraldine salt (ES) forms of polyaniline. EB is regarded as the most useful form of polyaniline due to its high stability at room temperature, ease of synthesis, less expensive, environmental stability and simple doping/dedoping chemistry [6]. Chitosan can be prepared by deacetylation of chitin using sodium hydroxide [7]. During this process, the acetyl groups are converted into amine groups [5-6]. Some forms of PANI can

be 'doped', chemically or electrochemically to produce highly conducting PANI powders and films with a substantial increase in electrical conductivity of the order of 10^{10} to 10^{12} [7-9].

Xu. et al. have noticed that the electrical conductivity of PANI/TiO_2 nanocomposites varies with a low TiO_2 content than that of neat PANI. Titanium oxide (TiO_2) is an n-type semiconductor with very interesting material for many different applications in both microelectronic and optoelectronic devices. It has good mechanical flexibility and environmental stability, and its conductivity can be controlled with acid/base (doping/undoping) balance. It has potential applications in many fields, such as lightweight battery electrodes, electromagnetic shielding devices, anticorrosion coatings, and sensors. Consequently, it is hoped to obtain new materials with complementary behavior between PANI and TiO_2. PANI/TiO_2-based structures have received much attention owing to their high current production in an external circuit by exciton dissociation at the TiO_2 and conjugated polymer interface. Although many studies on composite materials of PANI/TiO_2 have been reported, most of the research on these polymers is still focused on material preparation and morphology characterization, such as size and shape of the oxide particles, degree of dispersion, type of interaction, and interface between the organic and inorganic phase [10].

2. Materials and Method:

i. Preparation of Polyaniline

Aniline solution of 0.2M is mixed with 1N of solution of hydrochloric acid at room temperature. This mixer was stirred by magnetic stirrer for 2 hrs at constant RPM for the completion of the reaction. The solution of 0.2 M of ammonium persulfate $(NH_4)_2S_2O_8$ was added drop wise into the mixer. This reaction mixer was continuously stirred in magnetic stirrer for 8 hrs in room temperature. The precipitate formed and separated out by filtering and washed with deionised water with acetone. The obtained final suspension was dried in oven at 50° C for 24 hrs. The final product was grinded into powder.

ii. Preparation of TiO_2/PANI:

Aniline solution of 0.2M is mixed with 1N of solution of hydrochloric acid at room temperature. This mixer was stirred by magnetic stirrer for 2 hrs at constant RPM for the completion of the reaction. The solution of 0.2 M ammonium persulfate $(NH_4)_2S_2O_8$ was added drop wise into the mixer. Titanium dioxide (TiO_2) powder for different additive weight percentage (10%, 20%, 30%, 40% & 50%) is dissolved in the mass fraction to the above solution with vigorous stirring in order to keep the TiO_2 homogeneously suspended in the solution and stirring of final solution was continued for another 8 hours at room temperature. After 8 hrs the precipitate was separated out by filtering and washed with deionised water with acetone. The obtained final suspension was dried in oven at 50°C for 24 hrs. The final product was grinded into powder.

3. Characterization:

i. X-ray diffraction:

XRD patterns of PANI/TiO$_2$ nanocomposite samples were obtained using an advance diffractometer (for 2θ range from 10° to 80°) with monochromatic CuKα radiation (λ=1.54 A) to identify the crystalline nature of the samples. Figure-1 is the X-ray diffraction patter of pure polyaniline. Usually polyaniline is amorphous in nature. The broad peak was observed in the 2θ ranging from 25-27°, which is the main characteristics peak of polyaniline and the broadness of the peak clearly shows the sample is amorphous, indicating that PANI exhibited some degree of crystallinity. Figure-2 is the X-ray diffraction pattern of TiO$_2$/PANI composites (10%, 20%, 30%, 40% & 50%). From pattern it is observed that, the intensity of the peaks is increasing as doping increases in the polyaniline matrix up to composite 40% and further it decreases which suggest that TiO$_2$ is completely dispersed in the polyaniline matrix and confirms the formation of composite. Also the broadness of the peak is decreasing as doping increases which suggest the conversion of amorphous sample to semi crystalline sample. Hence the crystallinity of the sample is increasing as doping increases. The crystalline size of the PANI are estimated to be approximately 1-3nm. The size of the particles is increasing as TiO$_2$ content increases in the polyaniline and average crystalline size of the composite are estimated to be approximately 5-10nm are calculated by using Debye -Scherrer formula,

$$(D=K\lambda/(\beta \cos\theta)$$

Where D is average crystalline size, λ is wavelength of the X-ray, K is crystallite shape factor a good approximation is 0.9, **β** is the full width at half the maximum (FWHM) of the X-ray diffraction peak and 2θ is the Braggs' angle (deg.).
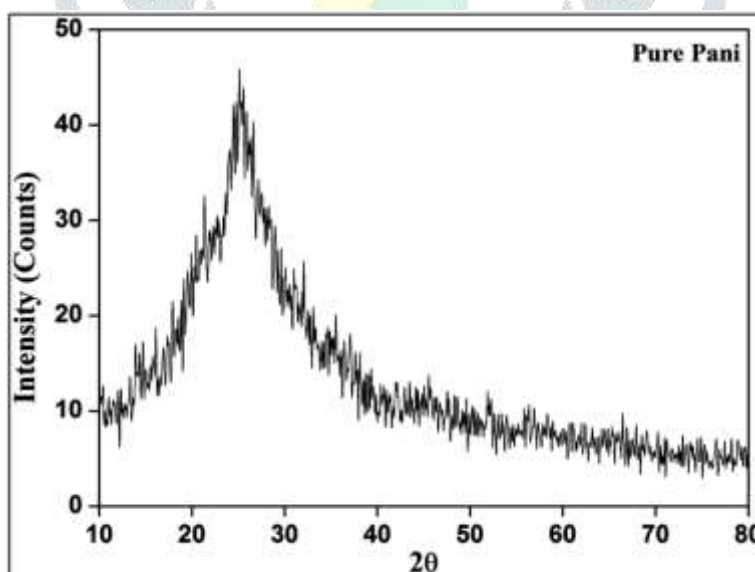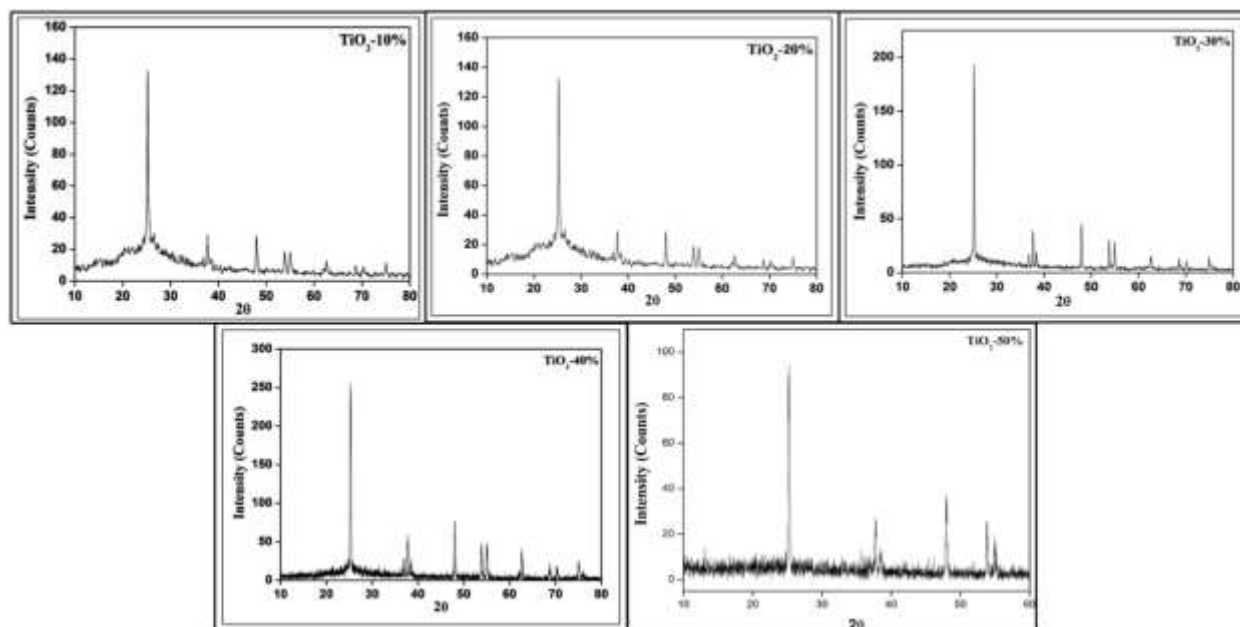

Figure-1: XRD pattern of Pure PANI

Figure-2: XRD pattern of TiO2/PANI (10%, 20%, 30%, 40% & 50%) nanocomposite

ii. Scanning Electron Microscope:

Figure-3 illustrates the surface morphology of pure polyaniline and Figure-4 illustrates the surface morphology TiO$_2$/PANI (10%, 20%, 30%, 40% & 50%) respectively. The SEM image of PANI shows uniform morphology with semi-crystalline like structure. In the nanocomposites, some of the TiO$_2$ particles seemed to be embedded in the polymer matrix and started coalescing (a tendency to coalesce and form agglomerates) due to the surface absorption property of PANI, which led to an oriented morphology (clear view of oriented structure). Morphological examinations revealed that, with higher TiO$_2$ contents, round TiO$_2$ particles with few adherent PANI were observed, due to preferential orientation of aniline on TiO$_2$ particles. The SEM image of TiO$_2$/PANI reveals that the dopant metal oxide particles are dispersed in PANI which also justifies the successful composite formation and mainly composed of irregularly arranged granular, nonporous, aggregated surface morphologies with diverse sizes. The average grain size was calculated as 10-20nm.
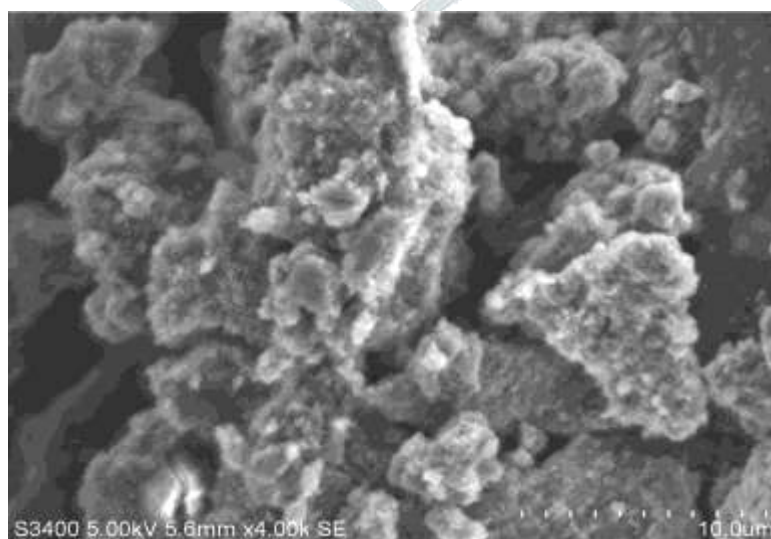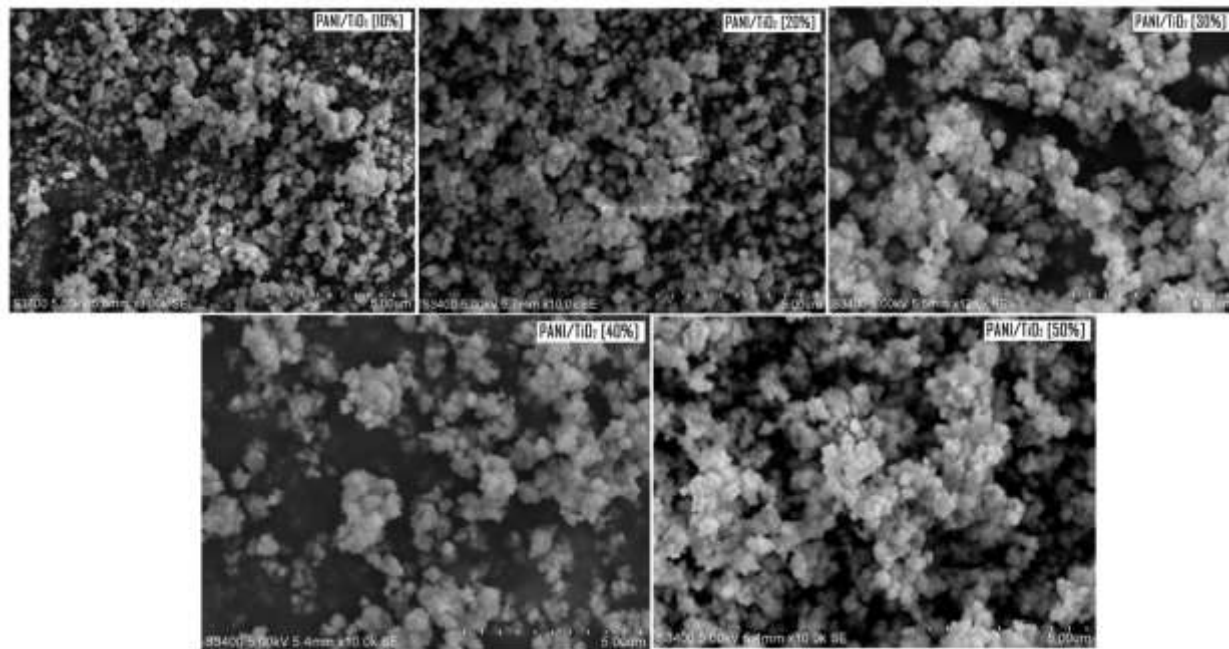

Figure-3: SEM image of Pure PANI

Figure-4: SEM image of TiO$_2$/PANI (10%, 20%, 30%, 40% & 50%) nanocomposite

4. Electrical Properties:

i. AC conductivity:

Figure-3 is the variation of ac conductivity of pure polyaniline as function of frequency. The value of ac conductivity increases as frequency increases from 1KHz – 1MHz. The frequency dependent conductivity for disordered materials such as polymers can be due to interfacial polarization at contacts and grain boundaries of the sample [11]. The value of ac conductivity was found to be 6.12×10^{-9} S/m at 1KHz frequency and which increases as frequency increased & reaches the value 8.88×10^{-5} S/m at 1MHz frequency. Previously reported that, the ac conductivity of pure polyaniline was found to be approximately 3×10^{-7} S/m at 1 KHz and it increases to 6.5×10^{-6} S/m at 1 MHz [12].
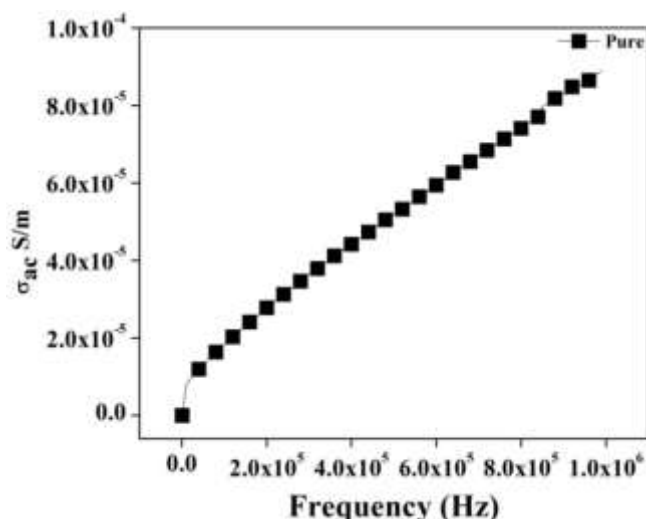
Figure-5: AC conductivity of Pure PANI as a function of frequency

Figure-4 is the variation of ac conductivity of TiO₂/PANI (10%, 20%, 30%, 40% & 50%) nanocomposite as a function of frequency. In all the cases ac conductivity increases as frequency increases and it decreases as content of TiO₂ increases in the polyaniline matrix. It is observed that, the ac conductivity of all the composites are higher in value compared to the value of pure polyaniline at measured frequency 1KHz. This may be due to the extended chain length of polyaniline which facilitate the hopping of charge carriers when the content of TO₂ is up to 10-50 wt% [13-14]. Further observed that, the ac conductivity of all the composite is less compared to pure polyaniline at measured frequency 1MHz. Further the decrease in conductivity for composite may be attributed due to the trapping of charge carrier hop [15].
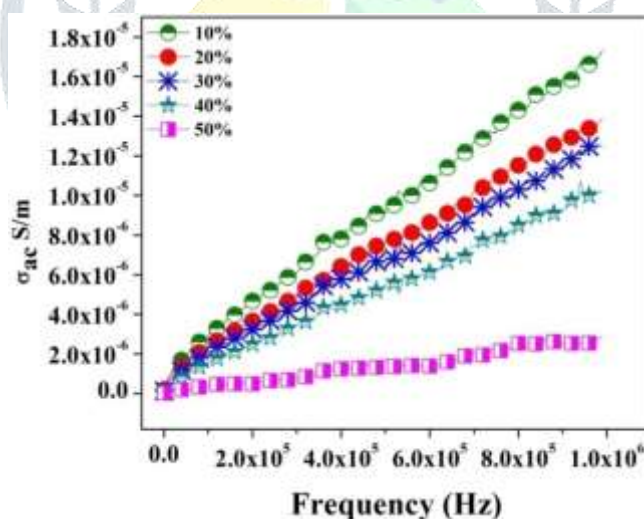

Figure-6: AC conductivity of TiO₂/PANI (10%, 20%, 30%, 40% & 50%) nanocomposite as a function of frequency

ii. DC conductivity

Figure-7 is the variation of dc conductivity of polyaniline and TiO₂/PANI (10%, 20%, 30%, 40% & 50%) nanocomposite as a function of temperature. The dc conductivity increases as temperature increases and showing semiconductor behaviour. Also the dc conductivity increases as content of TiO₂ increases in the polyaniline. It is observed from figure that, conductivity of PANI showing in two phases i.e., the

conductivity in the range 30 °C – 140 °C and 150 °C to 200 °C. The first phase conductivity is almost constant which may be due to inter-chain transport of charge carriers, i.e., hopping of charge carriers between the polymer chains and is usually observed at intermediate temperature. But, at high temperature region, (phase two) there is an sudden increase in the conductivity with increase in temperature due to intra-chain transport of charge carriers which can be described by the band conduction mechanism and is usually it is observed at high temperatures as reported by authors in their previous work [16-18].
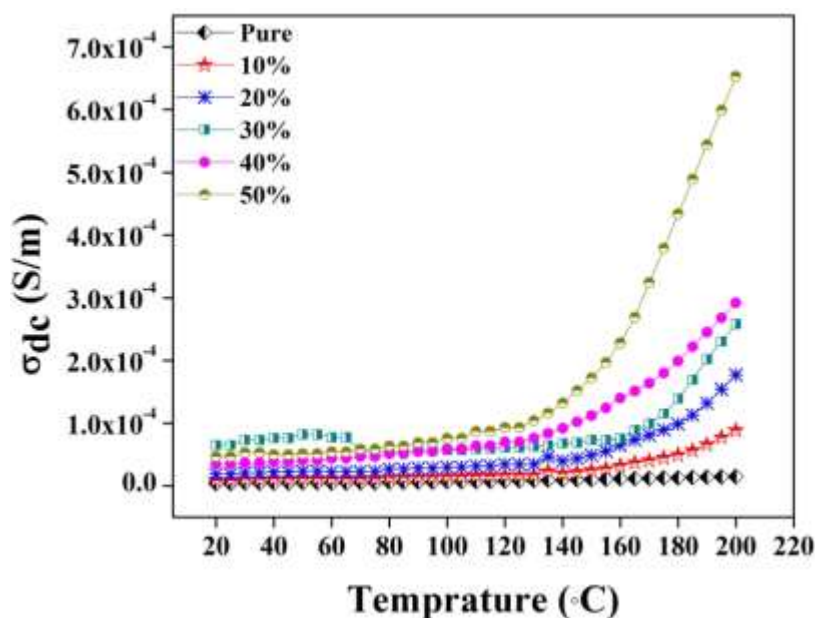

Figure-7: DC conductivity of PANI & TiO2/PANI (10%, 20%, 30%, 40% & 50%) nanocomposite as a function of temperature

5. Conclusion:

PANI/TiO$_2$ nanocomposite samples with various dopant percentages of TiO$_2$ were synthesized using in situ chemical oxidative polymerization method at room temperature. The structural and morphology studies of PANI/TiO$_2$ support the efficient interaction of PANI/TiO$_2$ nanoparticles. XRD can be attributed to the substantive internalization between PANI/TiO$_2$ nanoparticles. The SEM images helped to draw the conclusion that the doping of TiO$_2$ had a effect on PANI morphology, and with increased TiO$_2$ content, the composites showed a transformation in morphology from typical granular and nonporous PANI particles. The increased conductivity was attributed to the formation of a better charge transport network in the relatively insulating PANI matrix. The investigation of PANI/TiO$_2$ nanocomposites confirmed their stability and suitability for solar cells and optoelectronics devices.

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