Optical Behavior of PANI/Sno$_2$ Nanocomposites

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Abstract

This article reports the synthesis of Polyaniline (PANI) in Emeraldine form by in situ chemical oxidation method by using Ammonium persulphate as an oxidizing agent and a simultaneous synthesis of polyaniline (PANI)/SnO_2 nanocomposites. The UV-Vis absorption spectra were studied to explore the optical behavior after incorporating SnO_2 nanoparticles into PANI matrix. The absorption bands for the PANI/SnO_2 sample were observed at ~370nm, ~550 nm and ~910 nm wavelengths. This, however shows significant shifts in the absorption spectral to higher wavelength when comparing the absorption spectrum of both PANI and PANI/SnO_2. These bands may well correspond to π-π^* transition, polaron-π^* transition and polaron-π transition, respectively. This could be attributed to the successful interaction of the SnO_2 with the polymer chain. Hence, such shifts in absorption peak positions are related to the presence of the SnO_2 in the matrix of PANI. The Attenuated Total Reflectance (ATR) spectrum of PANI/SnO_2 provided the characteristic absorption peaks at 3227.54cm^{-1}, 1569.03cm^{-1}, 1496.71cm^{-1}, 1444.86cm^{-1}, 1289.13cm^{-1}, 1145.65cm^{-1}, 821.57cm^{-1}, 506.68cm^{-1}, and 412.08cm^{-1} due to the provision of information about the changes in the chemical structure of polymer. ATR spectra also give indication that the incorporation of SnO_2 in the matrix of PANI seems to be effective for the improvement of the physicochemical properties of conducting polymers.

Keywords: PANI, nanocomposite, chemical oxidation, SnO_2, ATR spectra

Introduction

Nanocomposites of polymers and metal nanoparticles have received significant attention due to the potential possibilities to create suitable materials for different types of microelectronic devices (Huang et al., 2006; Sridevi et al., 2011). These composites are of a particular class of materials initiated from the combinations of two or more compounds by a suitable technique. Therefore, this technique has a unique physiochemical properties and huge potential for wide applications. Also, polymeric nanocomposites differ from the conventional wholesome polymers with respect to some of the physical and chemical properties. For this reason, they are very useful in many applications (Pfaendner, 2010). The inclusion of metallic nanoparticles in polyaniline (PANI) is of great interest because of the strong electronic interaction between the nanoparticles and the polymer matrix (Smith et al., 2005a; Smith et al., 2005b). Hence, it is a booster to the polymers' conductivity. In view of this, the synthesis of different nanocomposites using metal nanoparticles and conducting polymers such as PANI would provide a range of interesting characteristics and many new features in nano-technological applications (Bhadra et al., 2009; Manawwer et al., 2012).

Therefore, the present work reports, the synthesis of Polyaniline (PANI) in Emeraldine form by in situ chemical oxidation method by using Ammonium persulphate as an oxidizing agent and a simultaneous synthesis of polyaniline (PANI)/SnO_2 nanocomposites.

Experimental Procedures

Synthesis of PANI

- 125ml of Ammonium persulfate (APS) and 100ml of aniline into different beakers.
- Added APS in a drop wise fashion to aniline over a period of 20 minutes using a syringe.
- The mixture was left at room temperature for 24 hours.
- The mixture was filtered so as to obtain the PANI precipitate, and was washed with distilled water several times.
- The precipitate was mixed with NH_4OH to convert the PANI Emeraldine Salt (ES) form to PANI Emeraldine Base (EB) form.
- It was filtered again to get rid of excess aniline and NH_4OH
- The precipitate was dried at about 70 ^{o} C in an oven to get the PANI powder.

Preparation of PANI Pellet

- Weigh 250 mg of the already treated KBr salt.
- Measure 2.5 mg of already prepared PANI.
- Mix the KBr and PANI, and grinded it thoroughly in a crucible using a pestle for at least 20 minutes.

- Make a pellet from the mixed KBr and PANI by applying a pressure of about 6-8 tons.

Preparation of PANI/KBr Pellet

- Weigh and heat 5 g of KBr at 100 º C for 2 hours.
- Measure 250 mg of the KBr and grinded it thoroughly in a crucible using a pestle for at least 20 minutes.
- Make a pellet with the ground 240 mg of KBr by applying a pressure of about 6-8 tons.

Synthesis of SnO_2 Nanoparticles

Mixed 4 g of Anhydrous Tin Chloride ($SnCl_2.2H_2O$) with 100 ml of distilled water and top it up with 100 ml of distilled water. The solution was stirred using a magnetic stirrer and 20 ml of NH_4OH was added under stirring for at least 1 hour. The solution begins to form a yellowish precipitate after sometime. More NH_4OH was added while checking the pH of the solution to ensure it was conveniently above 10.

Preparation of PANI/SnO2 Nanocomposites

a) With 0.2 g of PANI Powder

- 0.2 g of already prepared PANI powder was mixed with 55 ml of the solution containing $SnCl_2.2H_2O$ and NH_4OH under continuous stirring for at least 20 minutes at room temperature.
- The mixture was allowed to settle for 12 hours with the powder at the bottom and a clear solution on top.
- The solution was poured away and the precipitate was washed with more distilled water.
- This was done until a neutral pH wash obtained to ensure the removal of excess NH_4OH.
- The precipitate was dried in an oven at 80 º C for 6 hours.
- 0.1g of PANI/SnO_2 was dissolved in methanol under constant stirring for 4 hours.
- The mixture was then filtered, poured into a curvet and a UV-Vis spectrum of the filtrate was taken.

b) With 0.4 g of PANI Powder

- 0.4 g of already prepared PANI powder was mixed with 55 ml of the solution containing $SnCl_2.2H_2O$ and NH_4OH under continuous stirring for at least 20 minutes at room temperature.
- The mixture was allowed to settle for 12 hours with the powder at the bottom and a clear solution on top.

- The solution was poured away and the precipitate was washed with more distilled water.
- This was done until a neutral pH wash obtained to ensure the removal of excess NH_4OH.
- The precipitate was dried in an oven at 80^o C for 6 hours.
- 0.1g of PANI/SnO_2 was dissolved in methanol under constant stirring for 4 hours.
- The mixture was then filtered, poured into a cuvette and a UV-Vis spectrum of the filtrate was taken.

c) With 0.8 g of PANI Powder

- 0.8 g of already prepared PANI powder was mixed with 55 ml of the solution containing $SnCl_2.2H_2O$ and NH_4OH under continuous stirring for at least 20 minutes at room temperature.
- The mixture was allowed to settle for 12 hours with the powder at the bottom and a clear solution on top.
- The solution was poured away and the precipitate washed with more distilled water.
- This was done until a neutral pH wash obtained to ensure the removal of excess NH_4OH.
- The precipitate was dried in an oven at 80 ^{o}C for 6 hours.
- 0.1g of PANI/SnO2 was dissolved in methanol under constant stirring for 4 hours.
- The mixture was then filtered, poured into a cuvette and a UV-Vis spectrum of the filtrate was taken.

UV-Visible Spectra of PANI/SnO_2

PANI/SnO_2 composites were dissolved in methanol under constant stirring for 4 hours, and the mixture was then filtered. The UV-Vis spectrums of the filtrates were recorded on a UV-Visible spectrophotometer.

ATR Spectroscopy

The ATR spectra of the PANI powder, samples with KBr and PANI/SnO_2 composites were recorded using Perkin Elmer Spectroscope Version 10.03.09.

Results and Discussion

UV-Visible Spectra

The UV-Vis spectra taken for all the samples were presented in Figures 1 -6. The absorption bands for the PANI/SnO_2 sample are observed at ~370 nm, ~550 nm, and ~910nm wavelengths showing significant shifts in the absorption spectral to higher wavelengths. These bands may well correspond to π-π* transition, polaron-π* transition and polaron-π transition, respectively. This could be due to the successful interaction of the SnO_2 with the polymer chain. Hence, such shifts in the absorption peak positions are linked to the presence of the SnO_2 in the matrix of PANI.

ATR Spectra

The Attenuated Total Reflectance (ATR) spectrum of PANI/SnO_2 provided the characteristic absorption peaks at 3227.54cm^{-1}, 1569.03cm^{-1}, 1496.71cm^{-1}, 1444.86cm^{-1}, 1289.13cm^{-1}, 1145.65cm^{-1}, 821.57cm^{-1}, 506.68cm^{-1}, and 412.08cm^{-1}. The ATR spectra was recorded and depicted in Figures 7 - 11 of the samples show specific stretching vibrations of PANI and PANI/SnO_2 nanocomposites as given in Table 1.

TABLE 1: CHARACTERISTIC ABSORPTION PEAKS OBTAINED FROM ATR SPECTRA

Wavenumber (cm^{-1})	**Functionality**	**%Transmission PANI/SnO2 0.2, 0.4, 0.8 g PANI**	**% Transmission PANI**
531-506	Sn-O-Sn bonds and free oxi-hydroxides	55.52, 56.36, 57.05	------
817-821	C-H out of plane bending vibrations	86.78, 78.27, 80.00	42.52
1140-1145	N-Q-N stretching.	85.62, 72.71, 80.34	40.60
1289-1291	C-N stretching	87.27, 84.93, 78.51	42.36
1444-1445	C-C aromatic ring stretching of the benzoid diamine unit.	90.93, 82.12, 82.46	44.90
1494-1497	C-C stretching of the quinoid and benzenoid rings	85.77, 74.70, 73.22	41.69
1569-1586	C-N stretching of the quinoid and benzenoid rings	90.20, 80.55, 82.21	49.04
3226-3227	N-H stretching	93.05, 86.29, 88.30	62.2

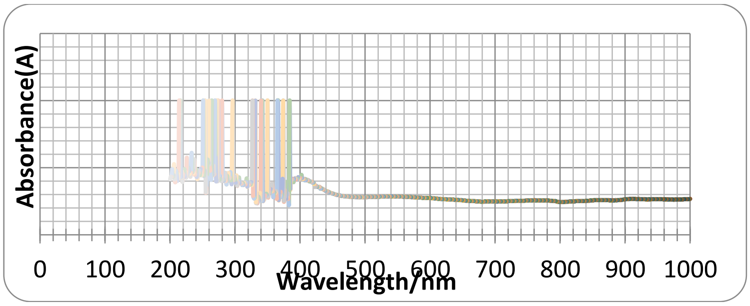

Figure 1. Absorbance Vs Wavelength Plot of 0.2g PANI/SnO_2

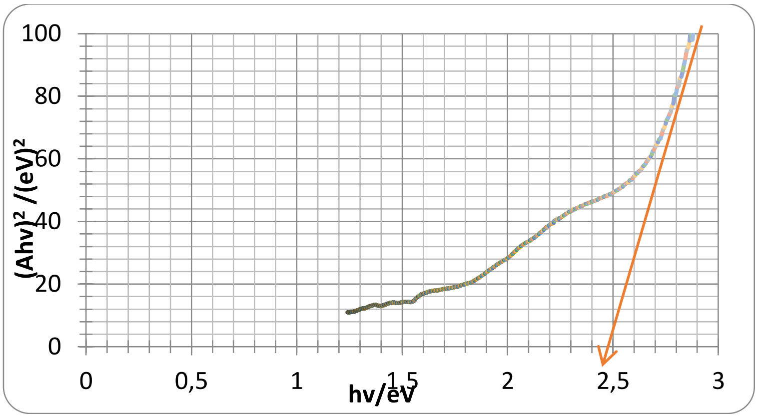

Figure 2. **(Ahυ)^2 vs hυ** of 0.2g PANI/SnO$_2$

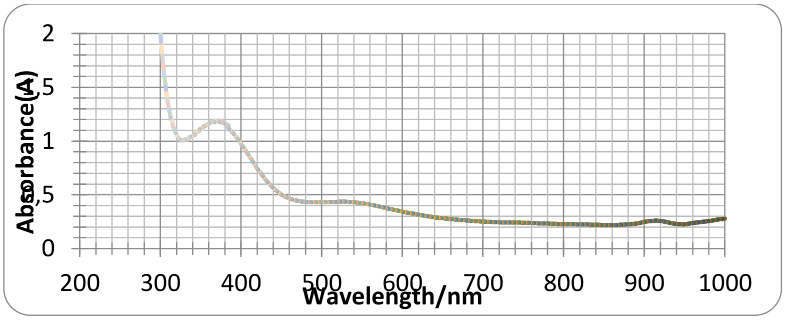

Figure 3. Absorbance vs Wavelength plot of 0.4g PANI/SnO$_2$

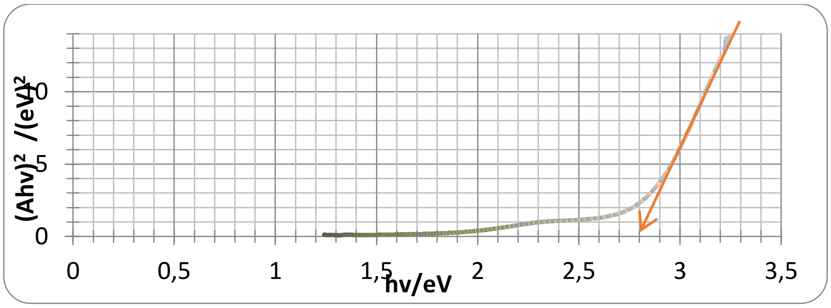

Figure 4. **(Ahυ)^2 vs hυ** of 0.4g PANI/SnO$_2$

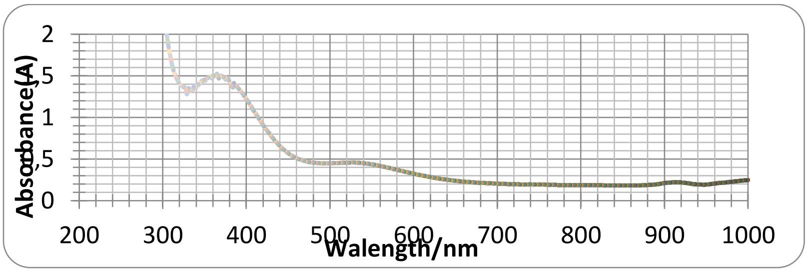

Figure 5. Absorbance vs Wavelength plot of 0.8g PANI/SnO$_2$

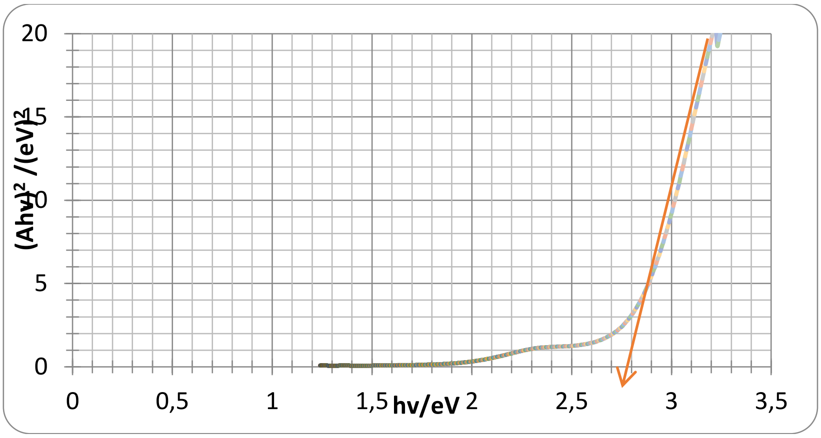

Figure 6. (Ahυ)^2 vs hυ of 0.8g PANI/SnO$_2$

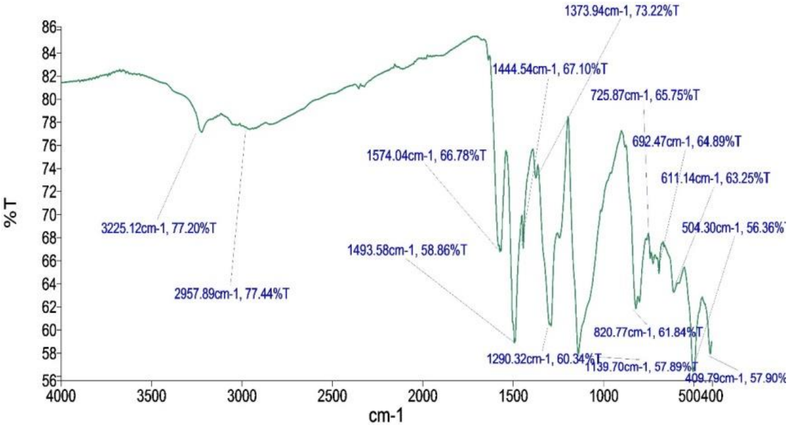

Figure 7. ATR spectrum of PANI

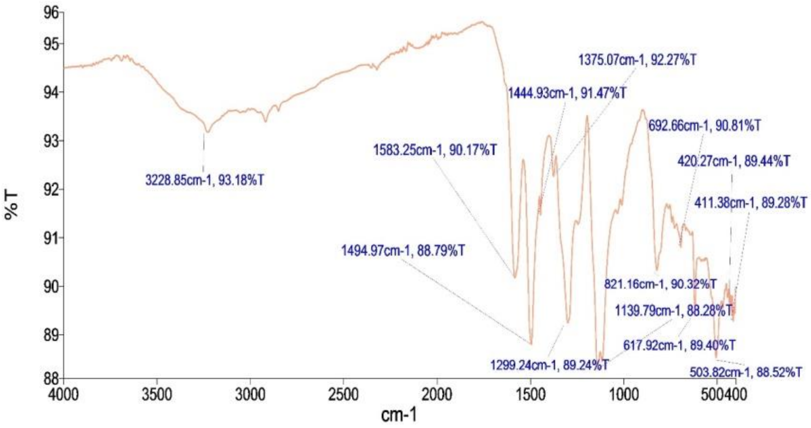

Figure 8. ATR spectrum of PANI KBr

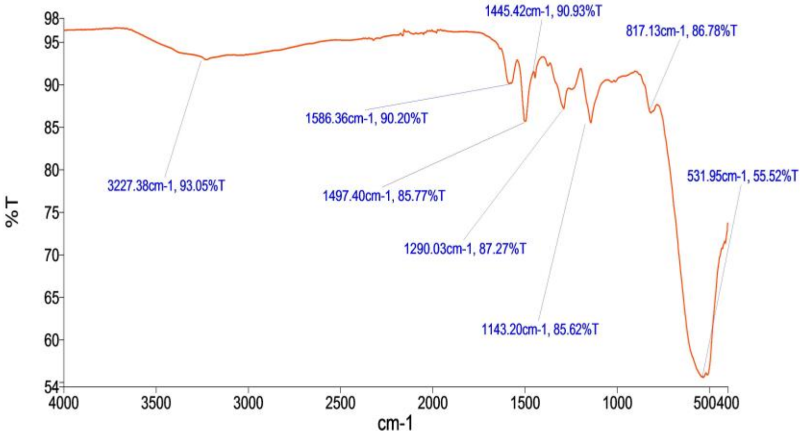

Figure 9. ATR spectrum of 0.2g PANI/SnO_2

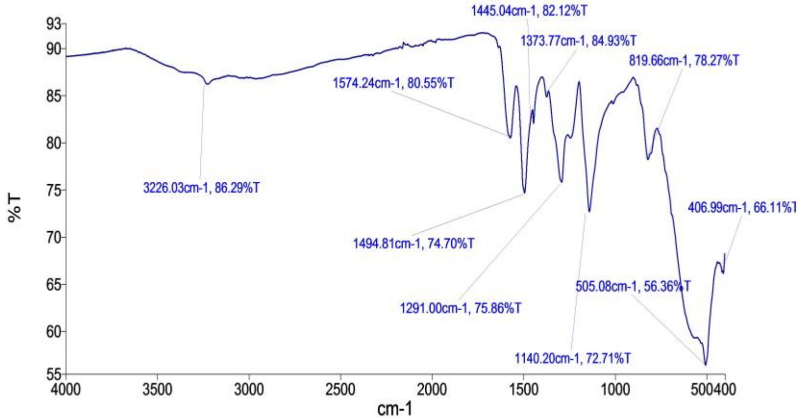

Figure 10. ATR spectrum of 0.4g PANI/SnO_2

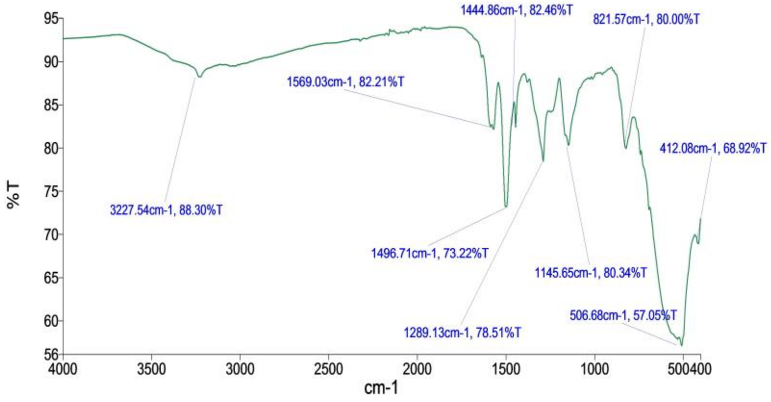

Figure 11. ATR spectrum of 0.8g PANI/SnO_2

Conclusion

The changes in the absorption peaks of PANI/SnO_2 composites might be due to the successful integration of the SnO_2 within the polymer chain. Such shifts in the absorption peak positions are related to the presence of the SnO_2 in the matrix of PANI. The % Transmission in Attenuated Total Reflectance (ATR) spectra PANI/SnO_2 clearly shows the presence of SnO_2 in the polymer chain. This provides indication that the incorporation of SnO_2 in the matrix of PANI will be very useful for the improvement of the physicochemical properties of conducting polymers.

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