PANI, SNO_2 DOPED PANI AND WO_3 DOPED PANI: SYNTHESIS AND CHARACTERIZATION

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Abstract:

Polyaniline (PANI) was synthesized in the lab by a simple chemical synthesis route. In this route, polymerization of aniline was carried out by using oxidizing agent ammonium peroxydisulphate at room temperature. Also SnO_2 (10%, 20% and 50%) doped PANI and WO_3 (10%, 20% and 50%) doped PANI were prepared by a simple and low cost solid state grinding method. In which, grinded SnO_2 and grinded WO_3 were mixed with in two different half parts of synthesized PANI powder. The PANI, SnO_2 doped PANI and WO_3 doped PANI were characterized by UV spectroscopy. The electrical conductivity of PANI , SnO_2 doped PANI and WO_3 doped PANI were also investigated with the help of a simple lab prepared two probe I-V characteristics set up. The results show that electrical conductivity of synthesized PANI can be enhanced by adding dopant SnO_2 (10%) where as conductivity reduces to lower values for further 20% and 50% doping of SnO_2. Also, it was observed that electrical conductivity of PANI can be enhanced by adding dopant WO_3 in different proportions (10%, 20% and 50%), but 20% doping of WO_3 shows highest increase in conductivity of PANI as compared to 10% and 50% doping of WO_3.

Key words: PANI, doped PANI, SnO_2, WO_3, electrical conductivity etc.

Introduction:

Conducting polymers have elicited much interest among researchers because of their reasonably good conductivity, stability, ease of preparation, affordability and redox properties compared to other organic compounds. In particular, the electronic and electrochemical properties of conducting polymers have made them find applications in photovoltaic cells, organic light emitting diode and sensors [1-4].

Recently, conducting polymer especially polyaniline (PANI) shows great potential as it is easy to synthesize [5, 14-15] flexibility, good environmental stability and it has remarkable optical and electrical properties due to its particular features such as low band gap and π-*π transition due to which the electron can be excited from highest occupied molecular orbital (HOMO) to lowest unoccupied molecular orbital (LUMO) [3, 5-9].

Many researchers have prepared metal oxide doped with conducting polymers such as TiO_2, ZnO, MoO_3,CeO_2, CoO_2 and Cu_2O doped with PANI to enhance their electrical or optical properties. Such Polyaniline composites with metal oxides have many applications in electrical and electronic devices like light emitting diodes, solar cells and photo detectors [10-13].

In this work, the PANI was synthesized by chemical polymerization method. The synthesized PANI powder is divided in two parts. Then grinded SnO_2 powder was added to half part of pure PANI in different proportions and mixed well to obtain powders of PANI + SnO_2 (10%), PANI + SnO_2 (20%) and PANI + SnO_2 (50%). Then also grinded WO_3 powder was added to remaining half part of pure PANI in different proportions and mixed well to obtain powders of PANI + WO_3 (10%), PANI + WO_3 (20%) and PANI + WO_3 (50%). The pellets of pure PANI and doped PANIs were prepared by using a hydraulic press. The UV and IV characterization of the prepared pellets were investigated.

Experimental

Synthesis of PANI

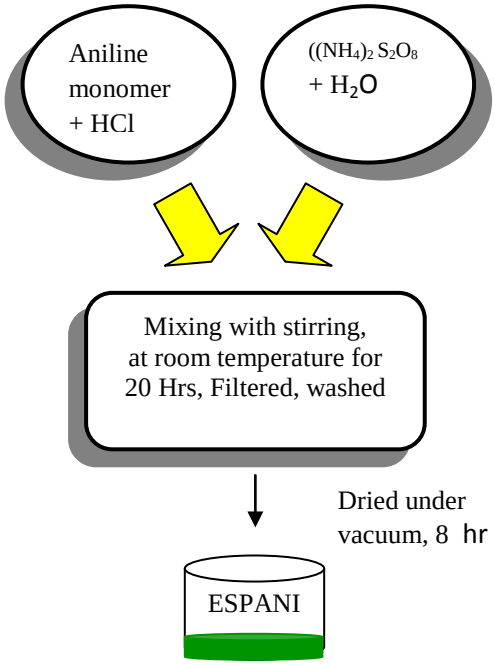


Fig.1. Schematic diagram of chemical polymerization method

In this work, the Polyaniline (PANI) powder was synthesized by chemical polymerization method. The aqueous solution of Hydrochloric acid (HCl) was used as a protonic acid medium and monomer aniline was used. Ammonium peroxydisulphate ($(NH_4)_2\ S_2O_8$) was used as a oxidizing agent. The monomer aniline was double distilled prior to use.

Fig.1. shows schematic of chemical polymerization method. Freshly distilled aniline monomer is used for synthesis of polymer. For the chemical synthesis of polyaniline, two solutions were prepared with appropriate volume concentration. In first solution, 1M HCl and 0.1 M aniline are dissolved in distilled water and second one is, the aqueous solution of 0.02 M ammonium peroxydisulphate ($(NH_4)_2\ S_2O_8$). The monomer solution is kept under constant stirring at room temperature for ½ hour. After that the oxidant solution was added to the monomer solution drop by drop. Then this polymerization process was carried out up to 20 hrs. After this process, the solution was filtered and washed with distilled water repeatedly to remove the impurities. This powder was dried under dynamic vacuum for constant weight. After that we get poly aniline powder having mixed phase. Then the so synthesized PANI was devided in to two equal parts.

Preparation of SnO_2 doped PANI powder:

AR grade pure SnO_2 powder (2 gm) was grinded by mortar and pestle for 5 hours. Then this powder is added in lab synthesized half part of PANI in different proportions such as 10%, 20% and 50% and mixed well to obtain doped PANI with above mentioned proportions.

Preparation of WO_3 doped PANI powder:

AR grade pure WO_3 powder (2 gm) was grinded by mortar and pestle for 5 hours. Then this powder is added in lab synthesized half part of PANI in different proportions such as 10%, 20% and 50% and mixed well to obtain doped PANI with above mentioned proportions.

Preparation of Pellet:

Now to study the conducting properties of above prepared powders, four pellets were prepared. Pellets of PANI, PANI + SnO_2 (10%), PANI + SnO_2 (20%), and PANI + SnO_2 (50%) powders were prepared by using a die under pressure of 4 tons for 15 sec with the help of a hydraulic press. Also pellets of PANI, PANI + WO_3 (10%), PANI + WO_3 (20%), and PANI + WO_3 (50%) powders were prepared by using a die under pressure of 4 tons for 15 sec with the help of a hydraulic press.

Characterization

UV characterization of prepared pellets:

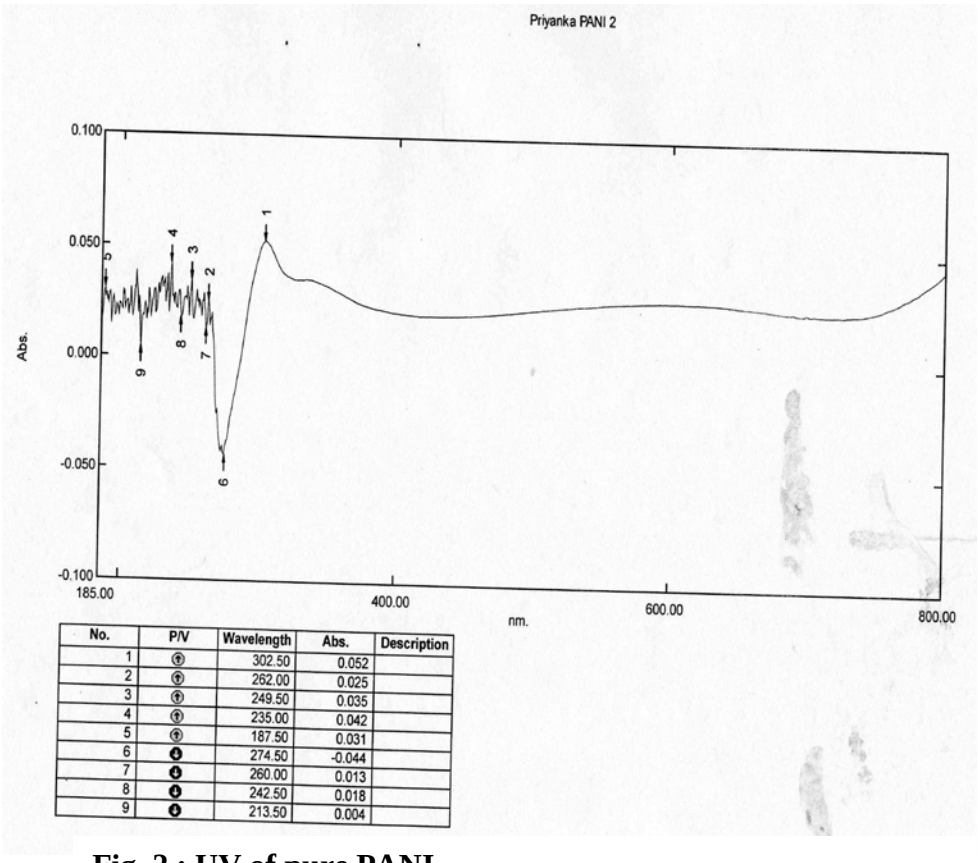
The synthesized powders of PANI, PANI+SnO_2(10%), PANI+SnO_2 (20%), PANI+SnO_2(50%), PANI + WO_3 (10%), PANI + WO_3 (20%), and PANI + WO_3 (50%)were characterized by UV-visible spectrophotometer (Schimadzu UV-visible spectrophotometer 2600) by using N Methyl 2- Pyrrolidone (NMP) solvent, in UV Visible range (185 – 800 nm)

I-V Characteristics of Prepared Pellets:

The I-V characteristics of prepared pellets of PANI, PANI + SnO_2 (10%), PANI +SnO_2(20%), and PANI+SnO_2(50%) were investigated by a simple two probe method with the help of a simple lab prepared set up with a digital multimeter and regulated d. c. power supply (0-30 V). Also, The I-V characteristics of prepared pellets of PANI, PANI + WO_3 (10%), PANI + WO_3(20%), and PANI+ WO_3(50%) were investigated by same two probe method and with same lab prepared set up.

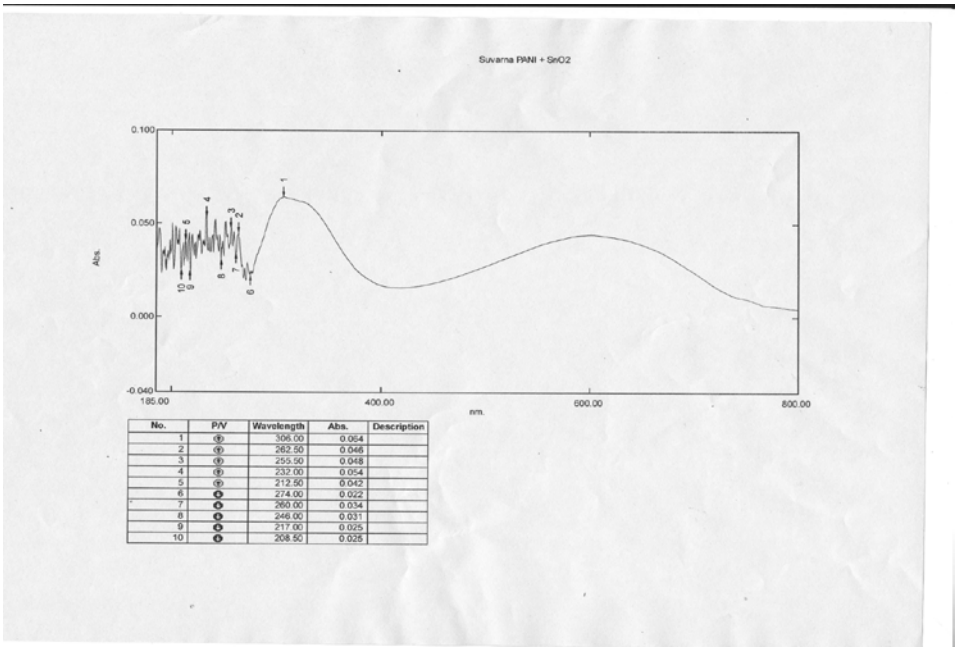
Results and Discussion

UV characteristics of Pure PANI and SnO_2(10%)doped PANI:



No.	P/V	Wavelength	Abs.	Description
1	↑	302.50	0.052	
2	↑	262.00	0.025	
3	↑	249.50	0.035	
4	↑	235.00	0.042	
5	↑	187.50	0.031	
6	↓	274.50	-0.044	
7	↓	260.00	0.013	
8	↓	242.50	0.018	
9	↓	213.50	0.004	

Fig. 2 : UV of pure PANI



No.	P/V	Wavelength	Abs.	Description
1	↑	306.00	0.064	
2	↑	262.50	0.046	
3	↑	255.50	0.048	
4	↑	232.00	0.054	
5	↑	212.50	0.042	
6	↓	274.00	0.022	
7	↓	260.00	0.034	
8	↓	246.00	0.031	
9	↓	217.00	0.025	
10	↓	208.50	0.025	

Fig.3: UV of SnO_2 (10%) doped PANI

The powders of PANI and SnO_2 doped PANI where characterized by using UV visible spectrophotometer. The UV spectrum was recorded by using solvent NMP in the UV range 185 to 800 nm. It is observed all samples show UV bands at about 300 nm due to presence of emeraldine salt from of PANI. These spectra have good resemblance with earlier reported work.

UV characterization of PANI and PANI+ WO_3 (20%):

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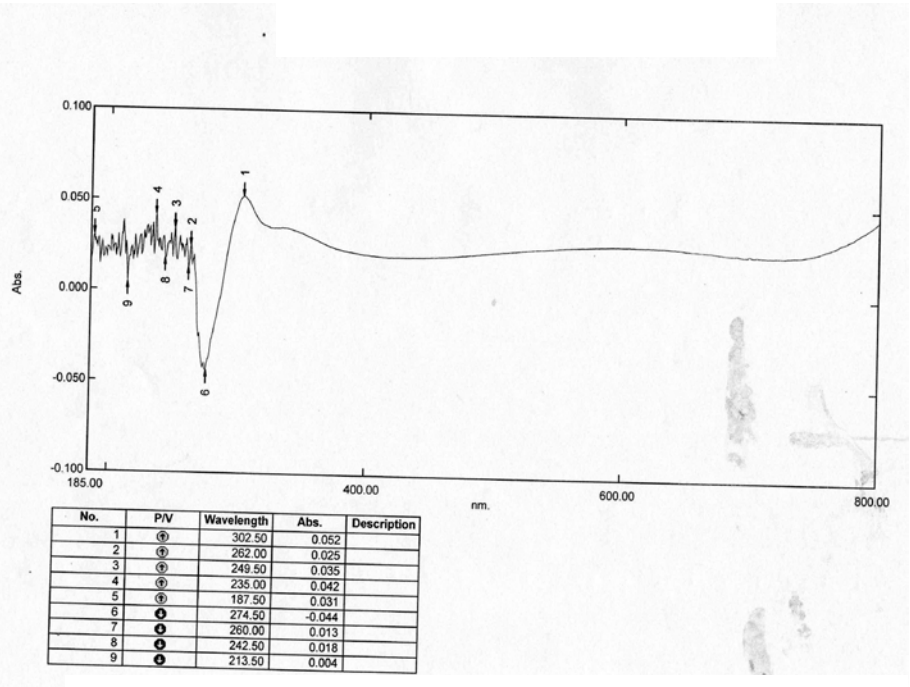
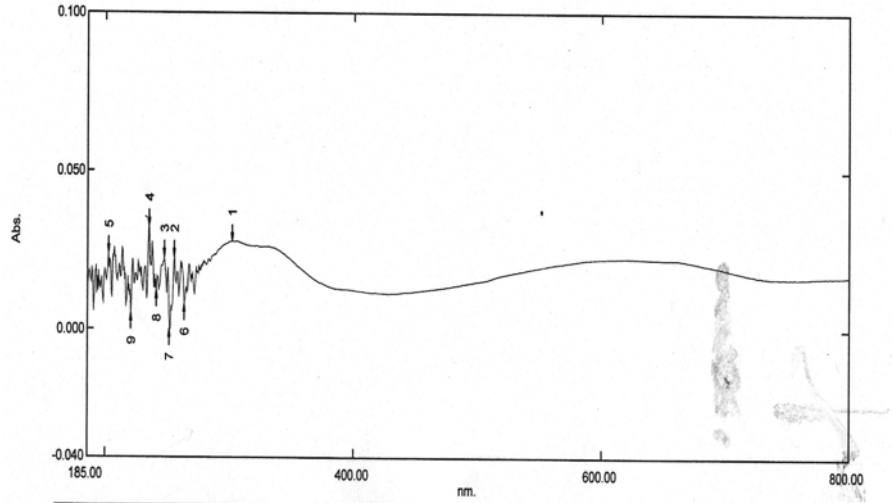


No.	P/V	Wavelength	Abs.	Description
1	↑	302.50	0.052	
2	↑	262.00	0.025	
3	↑	249.50	0.035	
4	↑	235.00	0.042	
5	↑	187.50	0.031	
6	↓	274.50	-0.044	
7	↓	260.00	0.013	
8	↓	242.50	0.018	
9	↓	213.50	0.004	

Fig. 4 : UV of pure PANI



No.	P/V	Wavelength	Abs.	Description
1	↑	302.00	0.028	
2	↑	255.50	0.023	
3	↑	247.00	0.023	
4	↑	234.50	0.033	
5	↑	202.00	0.024	
6	↓	263.50	0.008	
7	↓	251.50	0.000	
8	↓	240.50	0.012	
9	↓	220.00	0.005	

Fig. 5: UV of doped PANI with WO_3(20%)

The powders of PANI and WO_3 doped PANI where characterized by using UV visible spectrophotometer. The UV spectrum was recorded by using solvent NMP in the UV range 185 to 800 nm. Fig 4 and 5 shows UV of PANI and WO_3 (20%) doped PANI. It is observed that all samples show UV bands at about 300 nm due to presence of emeraldine salt from of PANI These spectra have good resemblance with earlier reported work.

Prepared Pellets:

Pellets of PANI, PANI + SnO_2 (10%), PANI + SnO_2 (20%), and PANI + SnO_2 (50%) powders were prepared by a hydraulic press. Required Pressure: 4 ton for 15 sec. Thickness of each pellet ~ 2 mm, Diameter of each pellet ~ 8mm. Also, pellets of PANI, PANI + WO_3 (10%), PANI + WO_3 (20%), and PANI + WO_3 (50%) powders were prepared by a hydraulic press. Required Pressure: 4 ton for 15 sec. Thickness of each pellet ~ 2 mm, Diameter of each pellet ~ 8mm.

I-V characteristics of Pure PANI and SnO_2 doped PANIs

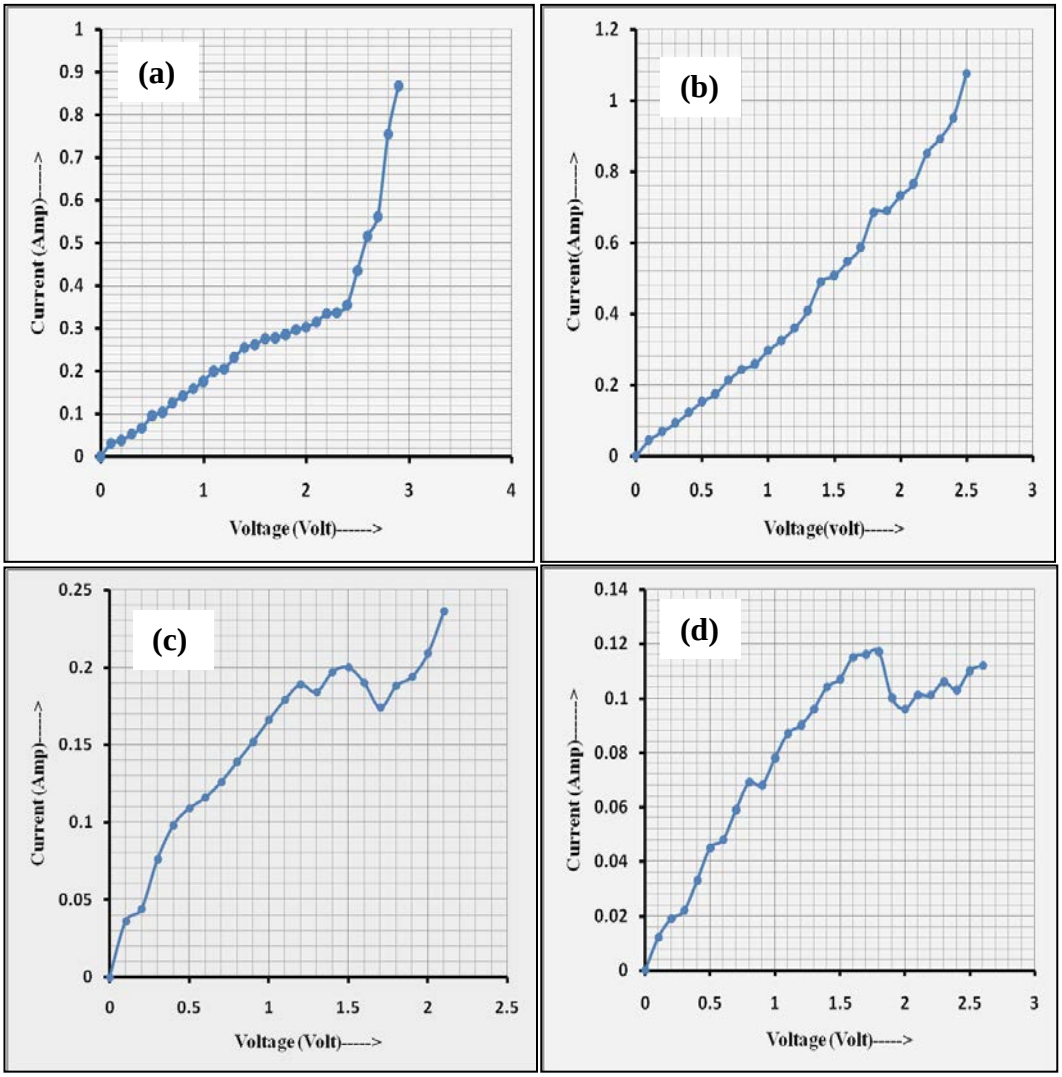


Fig.6: I-V characteristics of (a) Pure PANI (b) PANI+SnO_2(10%) (c)PANI+SnO_2(20%) (d) PANI+SnO_2(50%)

Pellet	Conductance (Slope from graph) ohm^{-1}	Resistance (1/slope) ohm
Pure PANI	0.1378	7.2768
PANI + SnO_2 (10%)	0.427	2.34001
PANI + SnO_2 (20%)	0.0927	10.7874
PANI + SnO_2 (50%)	0.0671	14.9031

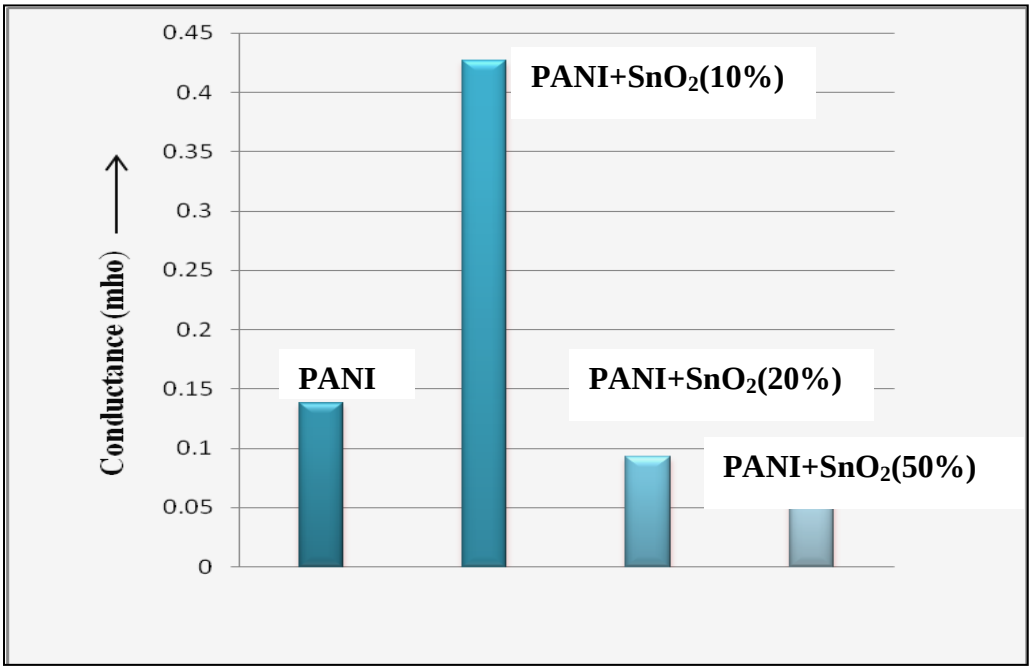


Fig.6: Variation in conductance of pure PANI and doped PANIs

Fig .6 (a), (b), (c) and (d) shows the I-V characteristics prepared pellet of the synthesized PANI, PANI + SnO_2 (10%), PANI + SnO_2 (20%), and PANI + SnO_2 (50%) respectively. Table I shows corresponding slope, conductance and resistance of the pellets of synthesized PANI, PANI + SnO_2 (10%), PANI + SnO_2 (20%), and PANI + SnO_2 (50%). It confirms the conductivity of synthesized PANI powder and all other doped PANIs. Fig.6 shows variation conductance of pure PANI and doped PANIs.

Fig 7. shows comparison of I-V characteristics of all prepared pellets of the synthesized PANI and SnO_2 doped PANI. From graph it was found that the conductivity of pellet **PANI+SnO_2(10%)** is found to be increased as compared to pellet of **pure PANI.** This is because as p-type semiconductor (PANI) in contact with n-type semiconductor (SnO_2), the electron from valence band of SnO_2 will extract and adds to LUMO of PANI thus has increased its conductivity [16]. However, conductivity of pellet **PANI+SnO_2 (20%)** and conductivity of pellet **PANI+SnO_2 (50%)** is found to be decreased as compared to pellet of **pure PANI.** It may be due to agglomerated SnO_2 and thus blocks the conductive pathway of PANI in composites [17]. It was found that, conductivity is as follows: PANI +SnO_2 (10%) > PANI > PANI +SnO_2 (20%) > PANI+ SnO_2 (50%).

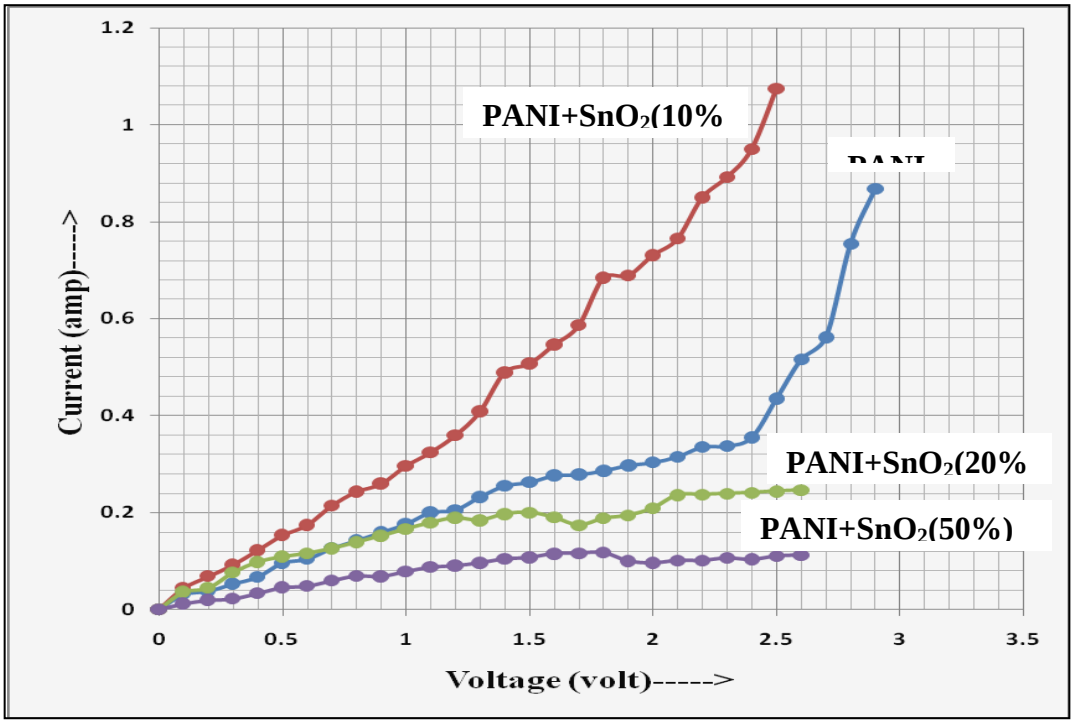


Fig.7: Comparison of I-V characteristics of pure PANI and doped PANIs

I-V characteristics of Pure PANI and WO_3 doped PANIs

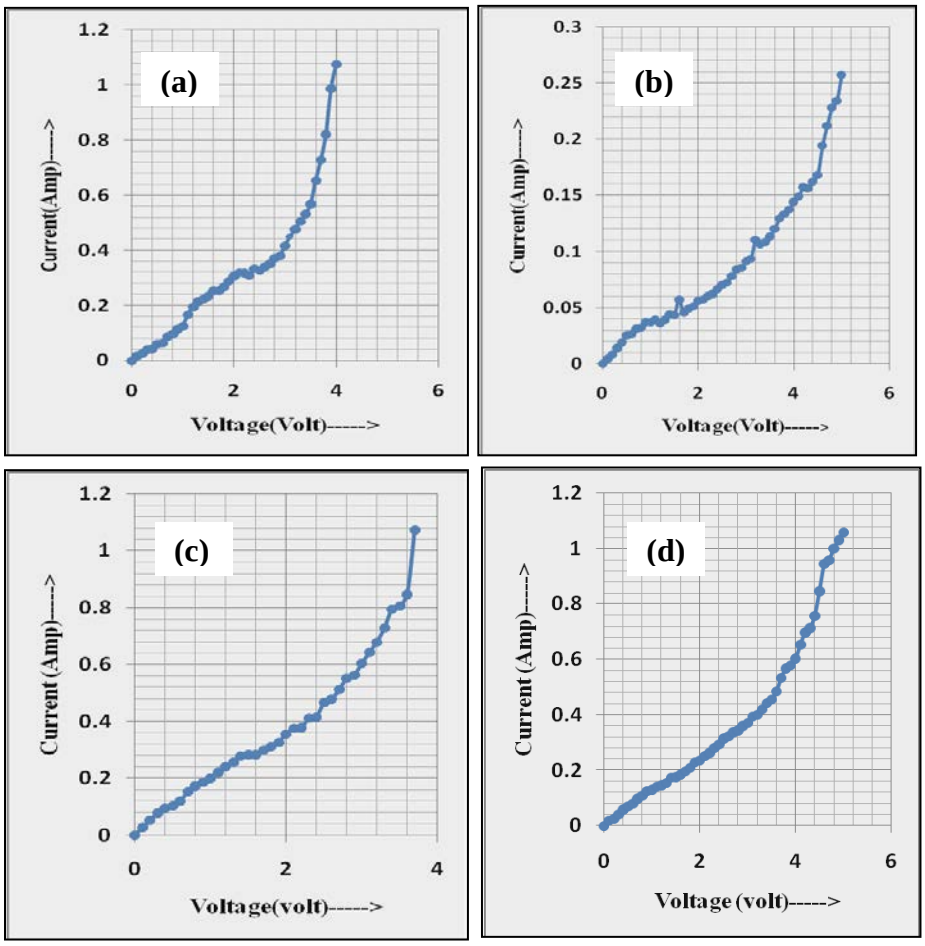


Fig. 8: I-V characteristics of (a) Pure PANI (b) PANI+WO_3 (10%) (c)PANI+ WO_3 (20%) (d) PANI+ WO_3 (50%)

Table II

Pellet	Conductance (Slope from graph) ohm^{-1}	Resistance (1/slope) ohm
Pure PANI	0.4	25
PANI + WO_3 (10%)	0.16	6.25
PANI + WO_3(20%)	**0.178**	**5.61**
PANI + WO_3 (50%)	0.130	7.69

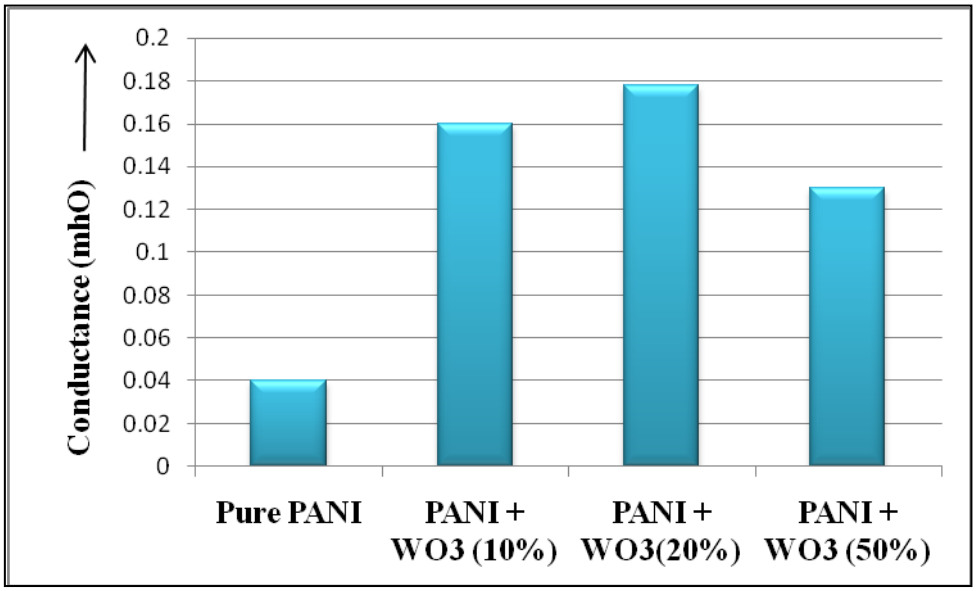


Fig. 9: Variation in conductance of pure PANI and doped PANIs

Fig .8 (a), (b), (c) and (d) shows the I-V characteristics prepared pellet of the synthesized PANI, PANI + WO_3 (10%), PANI + WO_3 (20%), and PANI + WO_3 (50%) respectively. Table I shows corresponding slope, conductance and resistance of the pellets of synthesized PANI, PANI + WO_{32} (10%), PANI + WO_3 (20%), and PANI + WO_3 (50%). It confirms the conductivity of synthesized PANI powder and all other doped PANIs. Fig.9 shows variation conductance of pure PANI and doped PANIs.

Fig 10. shows comparison of I-V characteristics of all prepared pellets of the synthesized PANI and SnO_2 doped PANI. From graph it was found that the conductivity of all pellets of PANI doped with WO_3 is found to be increased as compared to pellet of pure PANI. But the conductivity of pellet of PANI+ WO_3 (20%) is highest as compared to conductivity of PANI+ WO_3 (10%) and PANI+WO_3 (50%). Addition of WO_3 increases electrical conductivity, because as p-type semiconductor (PANI) comes in contact with n-type semiconductor (WO_3), the electron from valence band of WO_3 will extract and adds to LUMO of PANI thus has increased its conductivity [16]. However, conductivity of pellet of PANI+ WO_3 (10%) and conductivity of pellet PANI+WO_3 (50%) is found to be decreased as compared to pellet of pure PANI. It may be due to starting of agglomeration of WO_3 and which starts blocking the conductive pathway of PANI in composites [17]. It was found that, conductivity is as follows:

PANI + WO_3 (20%) > PANI + WO_3 (10%) > PANI+ WO_3 (50%) > PANI

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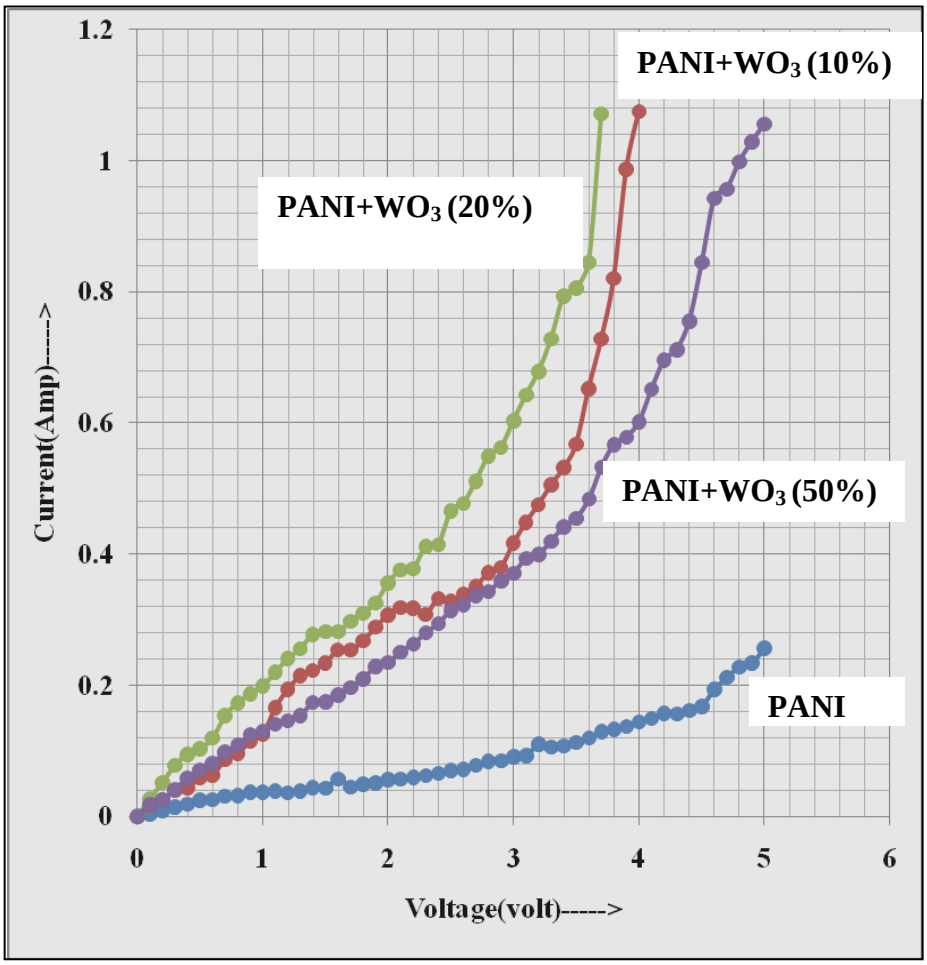

Fig.10: Comparison of I-V characteristics of pure PANI and doped PANIs

Conclusions

1. The conducting powder of PANI can be synthesized at room temperature by simple chemical synthesis route by using ammonium peroxydisulphate ($(NH_4)_2 S_2O_8$) as a oxidizing agent.
2. The conducting powder of PANI+SnO_2 (10%), PANI +SnO_2(20%) and PANI+SnO_2 (50%) can be prepared by adding crushed powder of SnO_2 in suitable proportion.
3. The pellets of synthesized PANI, PANI+SnO_2(10%), PANI+SnO_2(20%) and PANI+SnO_2 (50%) can be prepared by using hydraulic press.
4. The I-V characteristics of pellets of synthesized PANI, PANI+SnO_2(10%), PANI +SnO_2 (20%) and PANI +SnO_2 (50%) can be obtained.
5. It was found that the conductivity of pellet **PANI+SnO_2(10%)** is found to be increased as compared to pellet of **pure PANI** where as conductivity of pellet **PANI+SnO_2 (20%)** and conductivity of pellet **PANI+SnO_2 (50%)** is found to be decreased as compared to pellet of **pure PANI.**
6. The conducting powder of PANI+ WO_3 (10%), PANI + WO_3 (20%) and PANI+ WO_3 (50%) can be prepared by adding crushed powder of WO_3 in suitable proportion.
7. The pellets of synthesized PANI, PANI+ WO_3 (10%), PANI+ WO_3 (20%) and PANI+ WO_3 (50%) can be prepared by using hydraulic press.
8. The I-V characteristics of pellets of synthesized PANI, PANI+ WO_3 (10%), PANI + WO_3 (20%) and PANI + WO_3 (50%) can be obtained.
9. It was found that the conductivity of all pellets of **PANI doped with** WO_3 is found to be increased as compared to pellet of **pure PANI, where as**

conductivity of pellet of PANI+ WO_3 (20%) is highest as compared to conductivity of PANI+ WO_3 (10%) and PANI+WO_3 (50%).

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