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Electrochemical Synthesis of Polyaniline Conducting Composite Films Using Various Dopants

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ABSTRACT

The synthesis of conducting composite films is novel concept as well as challenging technology in thin film. In proposed work conducting composite films were electrochemically synthesized by using various dopants such as zinc sulphate, silver nitrate, potassium chromate and potassium dichromate, ferrous sulphate etc. These composite films were characterized and analysed by various characterization techniques such as X-ray, FTIR, SEM and UV-Vis. Spectroscopy. Conductivity of the films were measured by four probe methods and compared.

Keywords: Electrochemical, Composite films, conductivity, dopants

I. INTRODUCTION

The study of conducting polymer film is innovative concepts as well as the challenges for new technologies [1]. The composite films has unexpected properties like electrical conductivity, simple processibility, a variety of conducting polymer Polyaniline (PANI), polypyrrole (PPY), poly(phenylene)s (PP), Poly(p-phenylene) (PPP), polyacetylene (PA), poly(p-phenylenevinylene) (PPV), poly(3,4-ethylene dioxythiophene) (PEDOT), polyfuran (PF) and other polythiophene (PTh) derivatives, etc, have a special interest in the field of nano science and nanotechnology [2-5] The Polyaniline is a conducting polymer of the semi flexible class polymer family. Among all the over classes polyaniline is of much significance worldwide because of its unique properties. The synthesis of polyaniline was firstly shown in the mid 19th century by Henry Lethe by the working on the electrochemical and chemical oxidation products of aniline in acidic media [6]. The electrochemical study of Polyaniline composite films synthesized with various dopants like potassium chromate, potassium dichromate, silver nitrate, zinc oxide and ferrous sulphate has been carried out. The electrochemically synthesized PANI/ZnO film and films with other dopants were characterized by electrochemical technique, the ultraviolet (UV), Fourier transform infrared spectroscopy (FTIR), scanning electron microscope (SEM) and four probe technique for conductivity measurement. This comparative study observed that as compared to PANI/K_2CrO_4, PANI/$K_2Cr_2O_7$, PANI/$AgNO_3$ and PANI/$FeCl_3$ films.

II. METHODS AND MATERIAL

In experimental procedure the freshly prepared 0.1 N aqueous solution of aniline and pyrrole in double distilled water and proper concentration of dopants and electrolyte. The pH of aqueous medium was maintained by using phosphate buffer solution. The electrochemical polymerization of aniline and pyrrole was characterized by galvanostatic method in one compartment there is a three electrode system electrochemical cell. In electrochemical cell, the three electrode system was used among that platinum foil was used as a counter electrode (cathode), the indium tin oxide coated glass plate was used as a working electrode (anode) whose resistance is 50Ω and silver-silver chloride (Ag/AgCl) as a reference electrode. All these electrodes were immersed in an electrochemical cell having 50 ml proper concentration reaction medium was used for each reaction [7-9]. The pH of electrolyte is measured by calibrated ELICO LI120 pH meter. The electrochemical characterization was carried out by galvanostatic method, by maintaining a current constant overall reaction. Experimental process, various composite polymer films has prepared by electrochemical synthesis for taking proper concentration of monomer, electrolyte and dopants and maintain the various process parameters.

TABLE 1. Monomer ,electrolyte, dopant concentrations

Sr. No.	Monomer/ concentration	Dopant/ concentration	pH	Current density mA/cm²	Polymerization Potential (mV)
1	Aniline (0.1M)	K_2CrO_4 (0.05 M)	2.5	0.5	670
		$K_2Cr_2O_7$ (0.0025M)	1.5	0.5	676
		$FeCl_3$ (0.05 M)	2.5	0.5	700
		$AgNO_3$ (0.004 M)	2	0.5	672
		ZnO (0.2M)	3.5	0.5	650

III. RESULTS AND DISCUSSION

The electrochemically synthesized composite films of PANI with different dopants and electrolyte are prepared with proper concentrations, which affecting its morphology and some of its properties. The previous investigated work electrochemical polymerization of aniline was carried out in micellar solutions of camphor sulphonic acid and cetyltrimethyl ammonium bromide [10]. It was observed that the effects of various synthesis parameters on electrochemical polymerization of aniline and measured potentials at constant current density 0.5mA/cm².

1. The influence of pH in electrochemical synthesis of various composite films

The PANI composite polymer films were synthesized by various pH and measured the polymerization potentials. The figure 1.shows influence of pH (1, 1.5, 2.5,3). We have recorded low polymerization potential of PANI/K_2CrO_4 at pH 2.5and high polymerization potential of PANI/$FeCl_3$at pH 2.5 and current density was 0.5mA/cm².

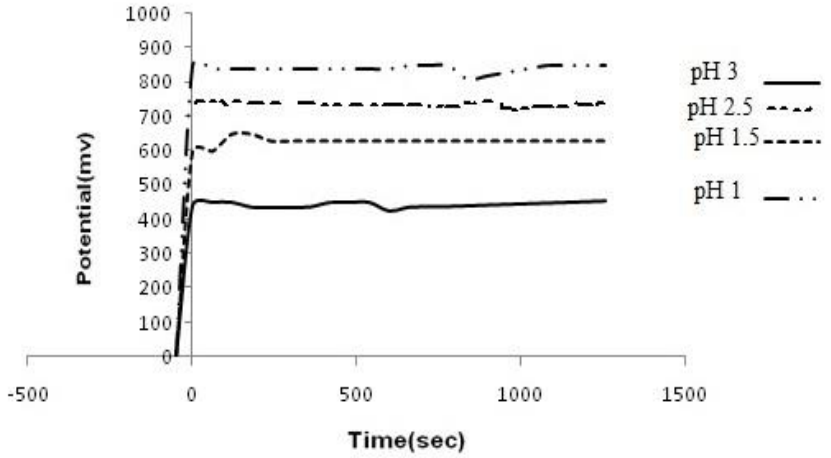


Figure 1.Influence of pH in PANI with different dopants.

2. The Ultra-violet spectroscopy of composite films

Figure 2 (a-e) shows UV spectroscopy of electrochemically synthesized composite polymer films. The measurement of the band gap of nanomaterials and thin films by using UV spectroscopy, the band gap is the energy difference between valence band and conduction band. It gives the conductivity of materials. The peak shows absorption of sample, following graphs shows UV spectrum of PANI composite films with different dopants.

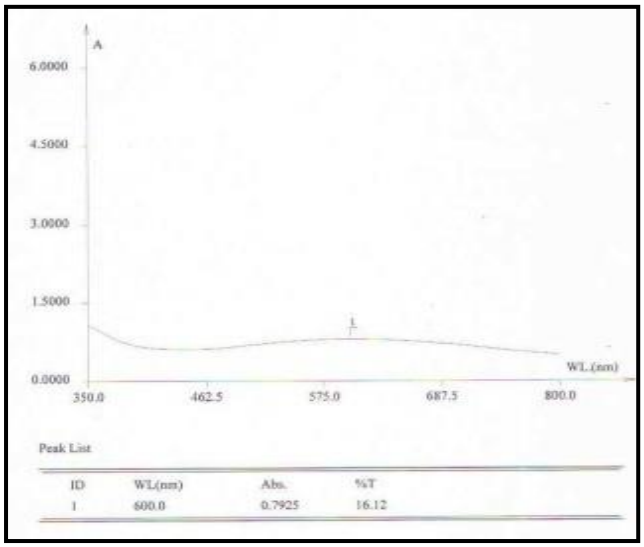
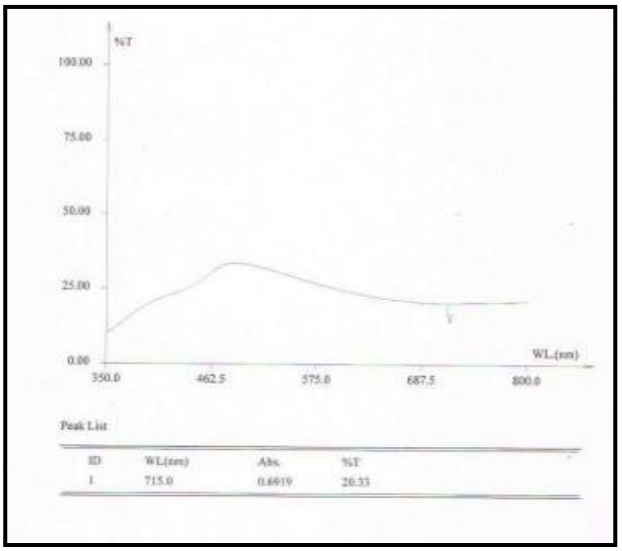
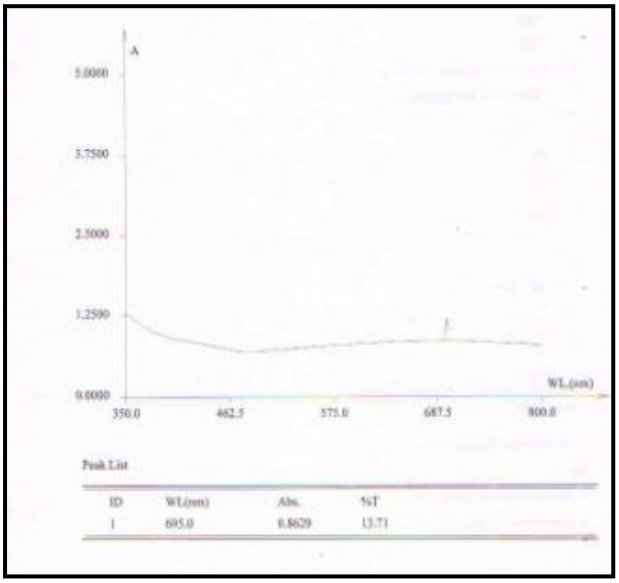


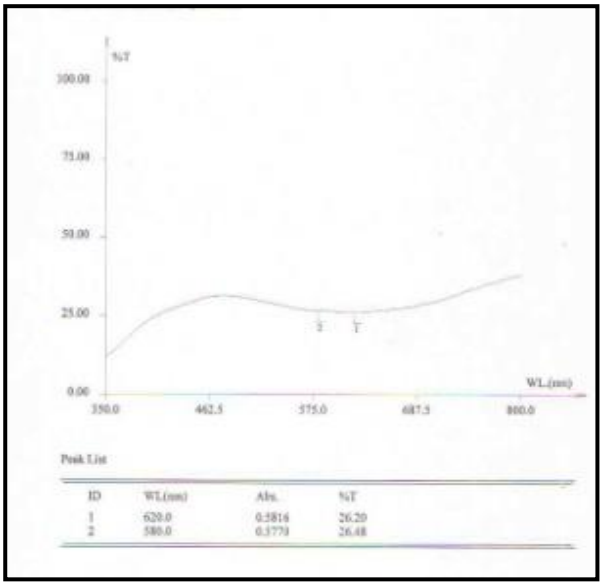
Figure 2. a)PANI/$K_2Cr_2O_7$ (WL-600 nm)



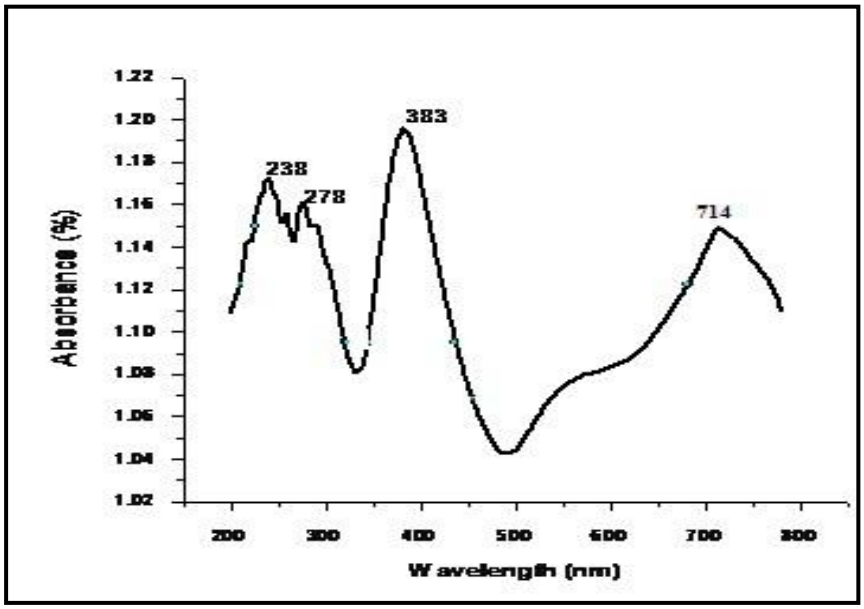
b) PANI/$AgNO_3$ (WL-715 nm)



c) PANI/$FeCl_3$ (WL-695 nm)



d) PANI/K_2CrO_4 (WL-580 nm)



e) PANI/ZnO (WL-383 nm)

3. The conductivity measurement of composite films

The four probe technique (S.E.S. Instrument Pvt. Ltd. Rookie) was used for the measurement of electrical conductivity of PANI/$K_2Cr_2O_7$, PANI/K_2CrO_4, PANI/$FeCl_3$, PANI/$AgNO_3$ and PANI/ZnO composite polymer films prepared on ITO coated glass plate by electrochemical synthesis. The four probe method is one of the standard and most widely used methods for the measurement of resistivity of semiconductors.

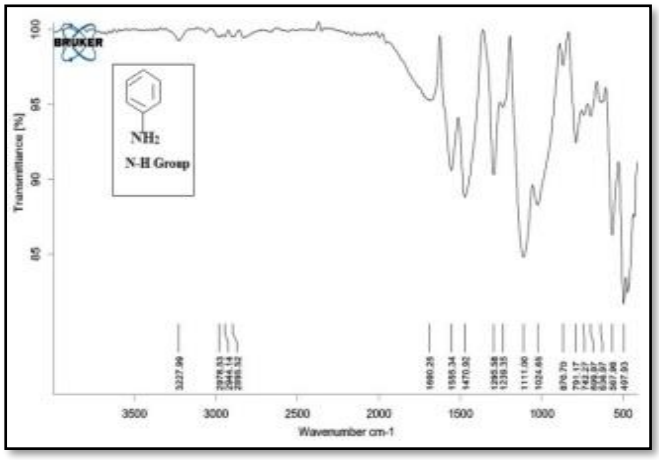
Table 2 shows conductivity of various composite polymer films, along which PANI/$FeCl_3$ and PANI/AgNO3 polymer film shows high conductivity at polymerization potential 700 mV and 672 mV respectively for current density 0.5 mA/cm^2 at pH 2 and 2.5

TABLE 2: Band gap energy and conductivity of composite films

Sr.No.	Composite polymer films	Band gap Energy (eV)	Conductivity (S/cm)
1	PANI/K_2CrO_4/ITO	2	0.0154
2	PANI/$K_2Cr_2O_7$/ITO	2.07	0.0162
3	PANI/$FeCl_3$/ITO	1.78	0.0172
4	PANI/$AgNO_3$/ITO	1.73	0.0180
5	PANI/ZnO/ITO	2.52	0.0175

4. Fourier Transforms Infrared Spectroscopy of Composite Films

Figure 3 (a-c) shows the FTIR spectra of PANI with $K_2Cr_2O_7$, $FeCl_3$ and K_2CrO_4 composite polymer films. The peaks at 870.7$cm^{-1}$and 1024$cm^{-1}$are attributed to C-H wagging, the characterization peaks at 1555.34$cm^{-1}$and 1470.92cm^{-1}correspounds to the C=C stretching, whereas peaks at 1709.33$cm^{-1}$and 1338cm^{-1}represent the C=N and C-N bonds respectively. The occurrence of small peaks at 3227cm^{-1}, 3254cm^{-1} and 3325$cm^{-1}$of figure (a-c) is assigned to presence of N-H stretching vibrations respectively [11].



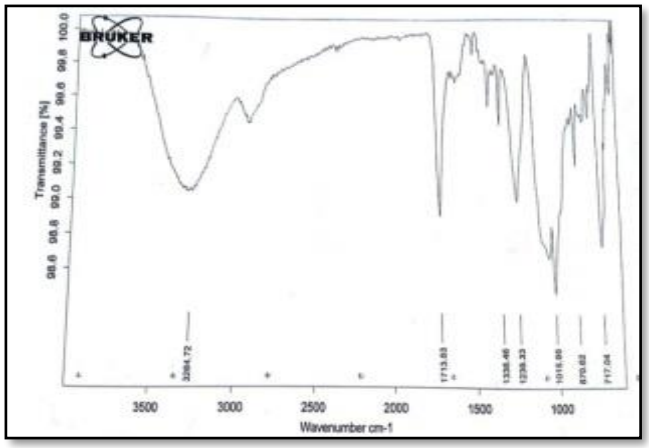
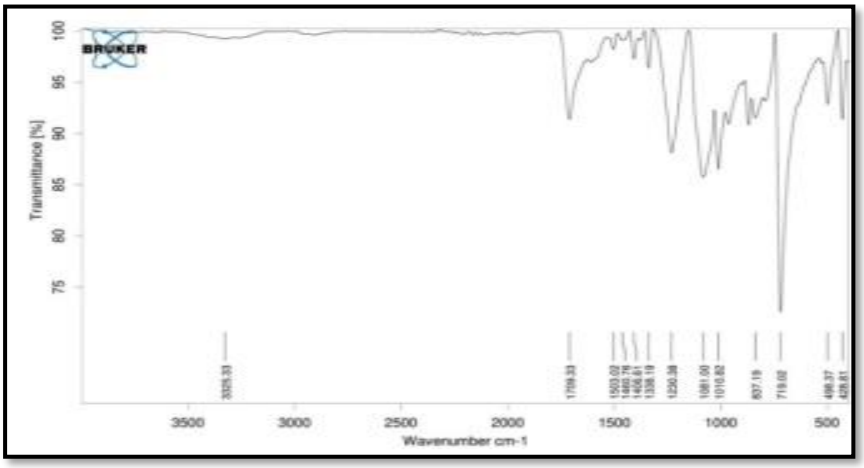


Figure 3. a)FTIR of PANI/$K_2Cr_2O_7$(N-H 3227) b) FTIR of PANI/$FeCl_3$ (N-H 3264)



c) FTIR of PANI/K_2CrO_4 (N-H 3325)

5. Study of x-ray spectroscopy of PANI composite films

The X-Ray diffraction of PANI shows amorphous in nature. In figure 4 broad peak was observed at about 2θ

=21.8^0.The broad peak is characteristic of amorphous PANI and are due to the scattering from PANI chains at the inter planer spacing.

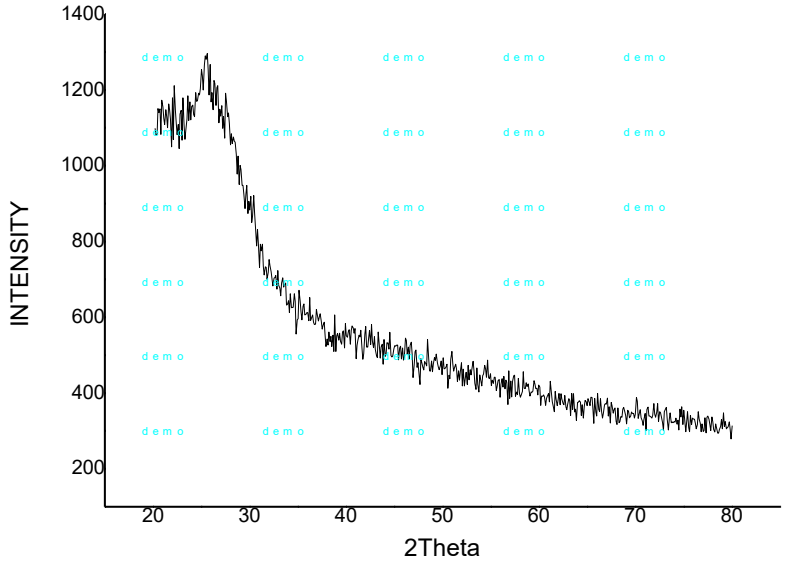
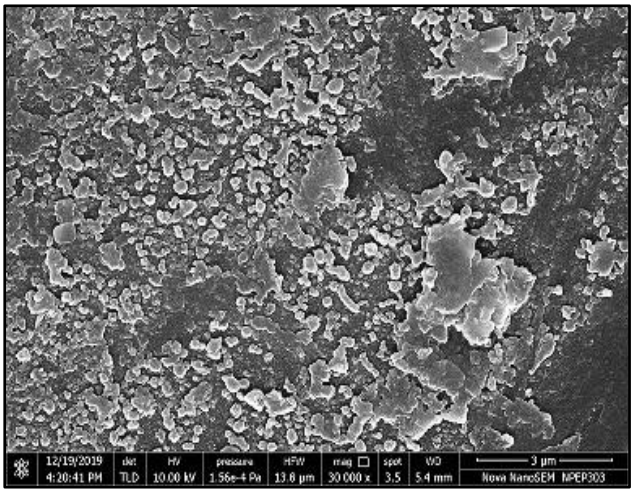


Figure 4. X-ray spectroscopy of PANI composite films

The X-ray spectroscopy analysis of PANI composite films used for measurement of polymer chain separation S and average crystallite size D. For PANI composite film, (θ = 25.31) chain separation was given as S = 43.52 nm, and average crystalline size is calculated it is given as D = 63.15 nm.

6. Scanning electron microscopy of composite Films

The figure 4. (a-e) shows scanning electron microscopy image of PANI composite composite films using various dopants such as potassium dichromate, potassium chromate, silver nitrate, ferrous sulphate and zinc oxide. The images show porous and globular in structure.



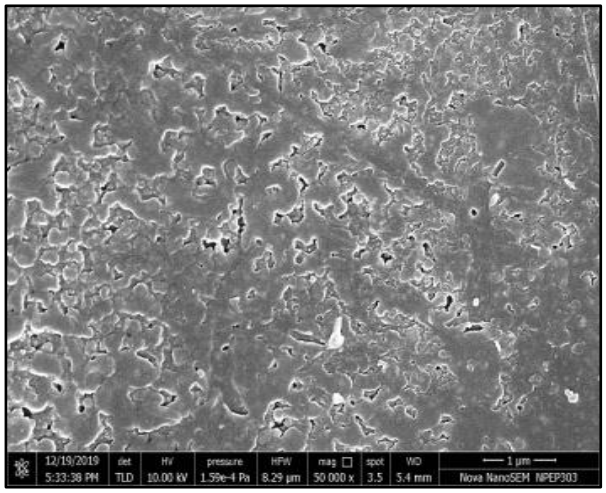
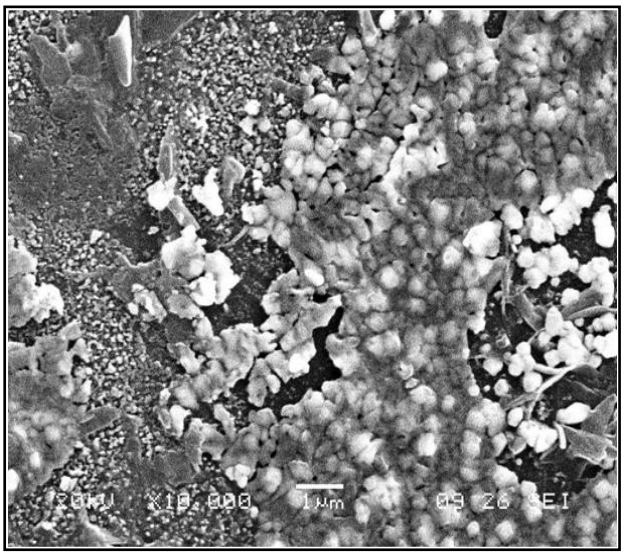
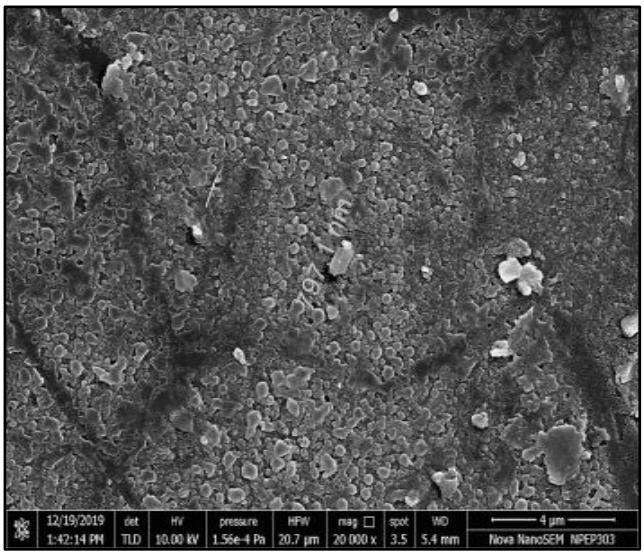


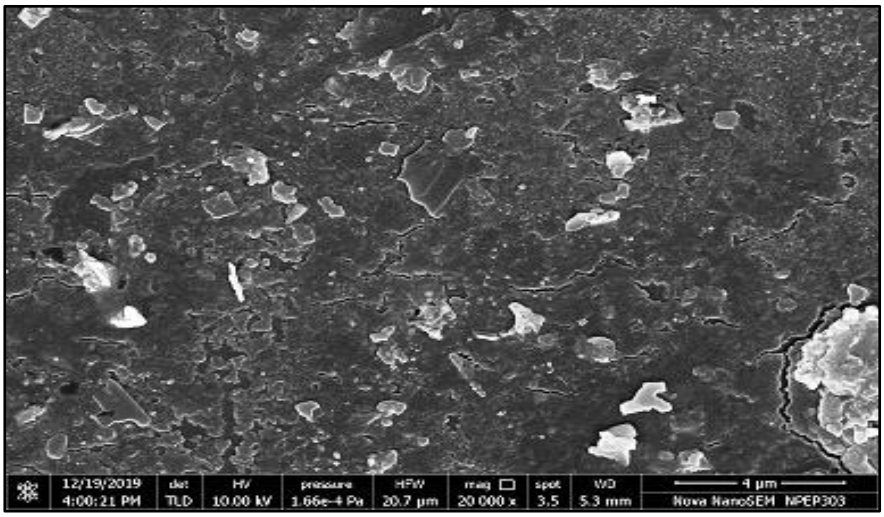
Figure 4. a) SEM image of PANI/$K_2Cr_2O_7$ **b) SEM image of PANI/K_2CrO_4**



c) SEM image of PANI/$AgNO_3$



d) SEM image of PANI/$FeCl_3$



d) SEM image of PANI/ZnO

IV. CONCLUSION

The electrochemically synthesized composite films with various dopants were compared by its conductivity. The conductivity of PANI/$FeCl_3$ and PANI/$AgNO_3$ composite films were higher than other dopants but all composite films shows conductive. Here PANI/$FeCl_3$ better composite film for fabrication of sensor because it is simple, low cost and highly stable. These composite film also provide a polymer matrix having a good porosity, high conductivity, uniform surface morphology and good mechanical and environmental stability.

V. REFERENCES

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