Research Article

Effect on Poly($C_6H_5NH_2$) Emeraldine Salt by FeCl$_3$ and KMnO$_4$ as Secondary Dopants

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Abstract

Polyaniline in its emeraldine salt form was synthesized by chemical method from aniline monomer in the presence of HCl mixed with LiCl and Ammonium-persulphate (APS) as oxidant. Then a portion of samples was de-doped with NH$_3$ solution and another equal portion was separately post doped with secondary dopants such as FeCl$_3$ and KMnO$_4$ respectively. Finally the dried samples of polyaniline prepared in all its three different forms were characterized by ultraviolet – visible (UV-Vis) spectroscopy, Fourier- Transform Infrared (FTIR) spectroscopy and electrical conductivity measurement. FT-IR and UV-Vis spectra confirmed the expected structural modification upon doping, undoping and post doping processes of the polymer. The influences of secondary doping on the electrical conductivity were also investigated from their spectroscopic data and the dramatic rise in conductivity was said to be induced from the secondary doping is attributed by structural rearrangement from a compact-coil form of PANI to a more expanded conformation. The result also shows that secondary doping increased the π conjugation. Their measured electrical conductivities were from 0.02 for undoped, 156 for primary doped form and increasing from 158 to 210 S/cm for those secondary doped polyaniline.

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Introduction

Conductive polymers are peculiar in nature that they conduct current without having a partially empty or partially filled band. The conjugation arising from chemical unsaturation of the carbon atom in conducting polymers is the main cause for charge transport. The presence of localized electronic

states of energies less than the band gap arising due to the changes in the local bond order have attributed to the possibility of new types of charge conduction phenomenon in these conjugated polymers [1].

Polyaniline (PANI) has been investigated extensively for over 100 years, has attracted special interest as a conducting material, and become the most prominent subject of study. Such popularity, in both theoretical and practical aspects, is a consequence of its unique properties: existence of various oxidation states, electrical and optical activity, low cost monomer, the polymerization reaction is straightforward and proceeds with high yield. PANI has an excellent environmental stability [2].

A first fairly detailed description of this product which was earlier known as 'aniline black' was provided by Green and Woodhead

[3]. The later discoveries on polyaniline dealt with its electrical conductivity and other properties like electrochemical redox activity, reversible doping/dedoping, electrochromism etc. [4] These diverse and important features seem to be promising in wide area of practical applications in rechargeable power sources, sensors, magnetic shielding, electrochemical capacitors, electro-chromic devices, corrosion protection etc. Further attention has been focused on PANI due to two prime reasons: (i) It can be synthesized easily both by electrochemical and chemical oxidation processes and (ii) it shows a particular sensitivity to the proton activity of its environment [5].

In reality; "polyaniline" is a name for whole family of polymers, which can be described by the formula presented in Figure 1.
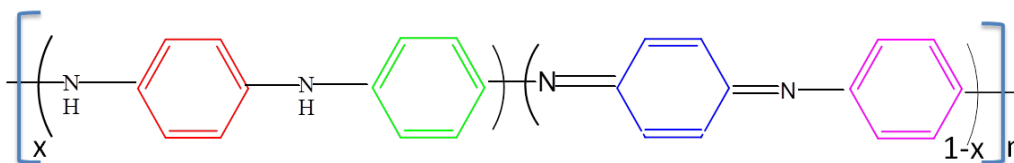

Figure 1 General formula for different forms of polyaniline base

Correctness of the formula presented above was proved, among others, by spectroscopic studies of Wudl and co-workers [6, 7]. Green and Woodhead were the first to depict PANI as a chain of aniline molecules coupled head-to-tail at the para position of the aromatic ring. They have proposed a linear octameric structure for PANI [8, 9].

Polyaniline, a typical phenylene based polymer, has a chemically flexible – NH– group in the polymer chain flanked by phenyl rings on either sides. The diversity in physicochemical properties of polyaniline is

traced to the – NH– group. The difference in the composition of amine and imine segments of polyaniline generates several oxidation states of this material ranging from completely reduced leucoemeraldine to completely oxidized pernigraniline states. The different forms of polyaniline can be readily converted to one another by simple redox methods. Out of several possible oxidation states, the 50 % oxidized emeraldine salt state shows electrical conductivity [6].

Polyaniline is unique among inherently conducting polymers in that it can be rapidly

converted between base and salt forms by treatment with acid or base. These reversible redox and pH switching properties together with the electrical conductivity of its emeraldine salt form, its ease and cheapness of synthesis, and its good environmental stability, have led to its becoming the most extensively studied conducting organic polymer over the past decade, and a wide range of potential applications are currently being developed [10].

Polyaniline has an electronic conduction mechanism that seems to be unique among conducting polymers, because it is doped by protonation as well as undergoing the p-type doping [11, 12]. This results in the formation of a nitrogen base salt rather than the carbonium ion of other p-doped polymers [13]. Many of the unusual properties of polyaniline were resulted because of the A-B nature of the polymer configuration, whereas most other conducting polymers are of the A-A type. Furthermore, the B component is the basic N heteroatom, which is involved with the conjugation in polyaniline more than the heteroatoms in similar polymers such as polypyrrole (PPY) [13]. Therefore, the conductivity of PANI depends on both the oxidation state of the polymer and its degree of protonation.

Among the various oxidation states of the PANI its "emeraldine" form can be doped to the highly conducting state. It consists of amine (–NH–) and imine (=N–) sites in equal proportions. The imine sites are protonated by acids HA to the bipolaron (dication salt) form. However, this undergoes a further rearrangement to form the delocalized polaron lattice, which is a polysemiquinone radical-cation salt. Although theoretical calculations have predicted that the bipolaron state is energetically more favored than the polaron

[13], it is widely agreed that polarons are the charge carriers responsible for the high conductivity in polyaniline [14-18]. It has been proposed that the presence of coulombic interactions, dielectric screening and local disorder in the polyaniline lattice act to stabilize the delocalized polaron state. It has also been shown that bipolaron states do exist in polyaniline, but they are few in number and are not associated with the conducting regions of the polymer [18, 19].

The study of conducting polymers received a major wave of momentum in the 1990s when Heeger et al. discovered secondary-doping effects in PANI systems [20, 21]. Their studies showed that exposure of camphor sulfonic-acid-doped PANI to m-cresol can increase the conductivity of the original polymer from $1-2$ Scm^{-1} to nearly 400 Scm^{-1}. Given the ability to dramatically improve PANI's conductivity, these solvents were commonly termed as 'secondary dopants' for PANI [22].

Recently, much interest has been shown in enhancing the order and consequent conducting properties of conducting polyaniline salts via post-polymerization treatment with an appropriate "secondary dopant". In particular, much attention has focused on the influence of m-cresol solvent or vapor on the properties of the emeraldine salt PANI. (+)-HCSA obtained by doping emeraldine base (EB) with racemic (+)-10-camphorsulfonic acid [23-26].

The conductivity of PANI-HA emeraldine salts is dependent on the temperature as well as humidity and hence, polymer water content [27, 28]. In general, attachment of functional groups decreases the conductivity, whereas the formation of copolymers between aniline and functionalized aniline results in polymers with intermediate conductivity. In addition, the preparation conditions [29, 30], particularly as

they relate to the formation of structural defects [31] and the polymer morphology [32, 33], influence conductivity. It has also been reported that the conductivity of PANI is dependent on the solvent it is cast from or exposed to. This phenomenon has been referred to as "secondary doping" [34, 35]. The solvent causes a change in the polymer conformation that result in increased conductivity.

Materials and Methods

All the chemicals used in this work were of Analytical grade. Aniline, $C_6H_5NH_2$ (99. 5% , Aldrich ,was purified by double distillation under vacuum and stored in a refrigerator) and Ammonium persulphate, $(NH_4)_2S_2O_8$ (98%,Technopharmchem, was stored in a refrigerator and used as supplied) whereas N-methylpyrrolidinone (NMP) (99.5%, Aldrich), Acetone ($\geq$99.9%, Aldrich), Methanol, CH_3OH (Anhydrous, 99.8% , Aldrich), Ammonia solution, NH_3 (27%, Merck), Hydrochloric acid, HCl (37%, Fluka), Lithium chloride, LiCl (anhydrous, $\geq$99.0%, Ubichem) and Sulfuric acid, H_2SO_4 (95-98%, Fluka) used as supplied.

Sample preparation

Polyaniline hydrochloride (PANI-ES) sample was chemically synthesized by following standard procedure for the polymerization of aniline by using aniline, ammonium peroxydisulfate (APS), and the appropriate dopant (HCl, contains dissolved LiCl). More precisely, a doubly distilled 0.20M aniline was dissolved in to 100 mL volumetric flask containing acidic solution of (1.0 M HCl, 5.0 M LiCl) prepared in de-ionized water. The

solution was stirred for 1 hr in the plastic beaker and a resulted color less solution cooled to -20°C for 30 minutes. Then the solution was transferred to 500 mL round bottom flask located in the reaction setup that maintained at 0°C in ice bath and 0.25M Ammonium peroxydisulfate (APS) was added slowly(1ml drop/min) above the solution. Then mixtures were stirred for 5 hours at a temperature maintained between 0-2°C and pH = 0-1 after that the mixture was left for polymerization room temperature for 48 hrs. After 48 hrs the resulting dark green PANI precipitate was collected on a filter, washed with distilled water, again with three 100 mL portions of 0.2M HCl and similarly with acetone. Polyaniline (emeraldine) hydrochloride powder was dried in air and then in oven at 60°C for 3 and 5 hrs respectively. Finally, the dried powder of PANI-ES was grinded to fine powders and preserved for undoping and secondary doping sample preparations.

Doping and De-doping (Insulating) in Polyaniline

ES- powder of polyaniline was dissolved in the concentrated 4.0 M H_2SO_4 in the crucible glass and stayed on post doping for 72 hrs at room temperature and then heated in the oven at 60 ℃ for additional 72 hrs. Finally, the green color fine powder were obtained and preserved for sample analysis. To prepare an insulated polyaniline of (PANI-EB) 0.2 g dry ES was dumped into 1.0 M NH_4OH solution (at pH = 8-9) and stirred for 4 hrs. The resulting blue color PANI precipitate was collected on a filter, washed with distilled water, again with methanol. Polyaniline (emeraldine base) powder was dried in vacuum then in air.

Secondary doping of polyaniline with salts of transition metals

Anhydrous $FeCl_3$ (0.1625 g, 1.0 mM) was dried in high vacuum at 30 ℃ for 3 hours. Dry $FeCl_3$ was dissolved in acidic methanol solution (pH~1). Polyaniline -ES (0.200 g) powder was mixed with dopant solution and stirred for 2 hrs. The doped mixture was kept for 15 hrs at room temperature in the glass crucible and dried in the oven at 60℃ for 5 hrs. Finally, the green-blue powders of polyaniline was formed and then the dried re-doped polyaniline powders were grind to fine powders and preserved for sample preparations. 0.158 g anhydrous $KMnO_4$ separately dissolved in the small volume of concentrated sulfuric acid solution (pH< 1) and then follow the same procedure adopted with $FeCl_3$.

Characterizations of polyaniline

The synthesized samples of polyaniline were characterized by UV-Vis spectroscopy and FT-IR spectroscopy. FT-IR spectra were recorded using Thermo Nicolet V-200 FTIR spectrometer by KBr pellet method in the region 400 to 4000 cm^{-1}. Optical absorption spectrum was taken using a double beam spectrometer (T80 UV/VIS, PG Instruments, Ltd.) and sample holder quartz glass with wave length scanned between 190nm-1100nm.

Conductivity measurements

Electrical conductivity was measured by using the digital multimeter with lead metal roads inserting in the solutions and also using pH-ISE by Conductivity Meter model-250. Then, the current-voltage (I-V) measurements were obtained using the two-point probe method and resistivity measurements were carried out.

Results and Discussion

UV-Vis spectra for undoped polyaniline (PANI-EB)

UV-Vis spectra of black color undoped polyaniline (PANI-EB) powder in solvent NMP turns to bright blue color solution has two absorption peaks at 328 and 630 nm. The absorption at 328 nm has been suggested to arise from excitation of the benzene segment including amine structures in polyaniline, whereas the peak at 630 nm arises from the quinoid structure including imines [5].

On the other hand the UV-Vis spectra (Figure 2) of PANI doped with 1.0M HCl in solvent NMP has two absorption peaks at 430 and 850 nm. This is attributed when the nitrogen atoms in imine groups are protonated; nitrogen and its neighboring quinoid ring become a semiquinoid radical cation, generation of these two absorption peaks due to the presence of polaron/bipolaron band transition [6, 7]. Decreasing of undoped polyaniline absorption in the 630 nm is proportional to increasing of doped polyaniline absorption in the 850 nm.
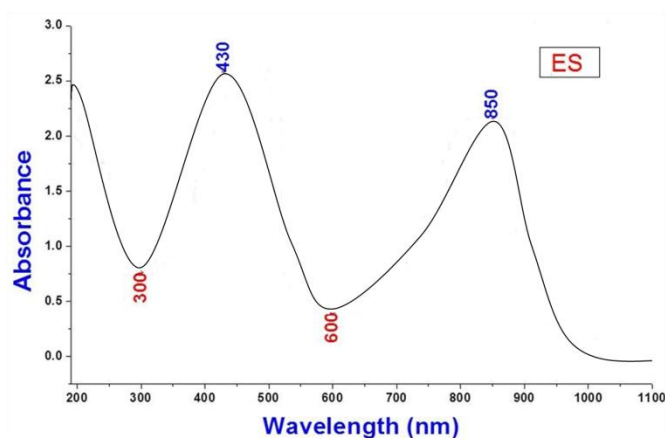
Figure 2 UV-Vis Spectra of Polyaniline-HCl (PANI-ES) in the NMP solution

At high protonation level 630 nm band completely disappears. Therefore, adding acidic solution NMP into polyaniline solution, both 330 nm $(\pi_B - \pi^*)$ and 630 nm $(\pi_B - \pi_Q)$ absorptions decrease in intensities. Simultaneously, two new absorptions appear at 430 and 850 nm, which are attributed to polarons/bipolarons in protonated polyaniline [8].

UV-Vis spectra of secondary doped polyaniline with salts of transition metals

Polyaniline complexation with salts of transition metals was manifested by a green-blue coloration of the reaction medium. Again the UV-Vis spectra of polyaniline secondary doped with salts of transition metals (Figures 3, 4) also indicate almost similar to the ES form of polyaniline. Thus when transition metal salts are mixed with polyaniline they undergo complex formations as PANI-Cl-M^{n+} (where M^{n+} is the transition metal ions) in the same way as PANI-ES complexed with $FeCl_3$ presented in Figure 5.
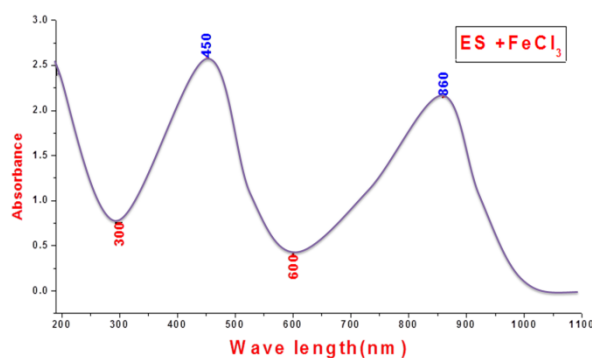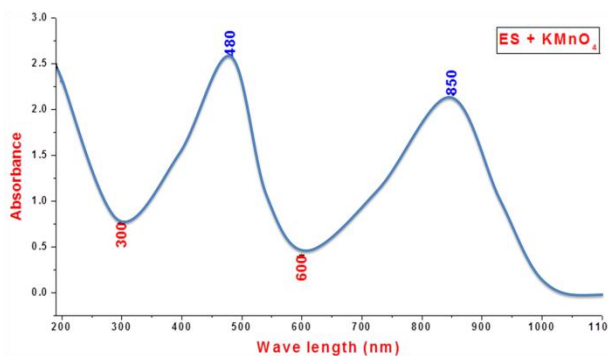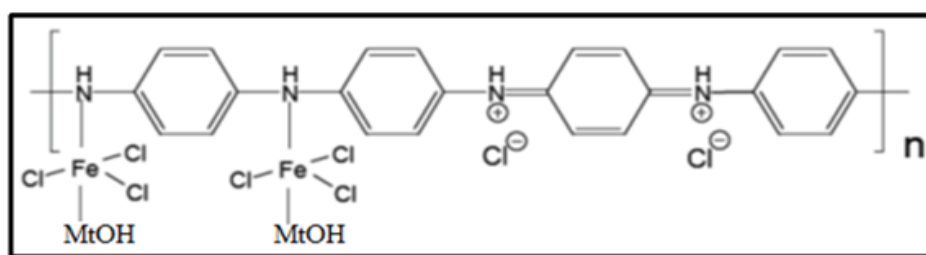

Figure 3 UV – Vis spectra of PANI secondary doped with $FeCl_3$

Figure 4 UV-Vis spectra of PANI secondary doped with KMnO$_4$

Figure 5 PANI-ES re-doped with FeCl$_3$ in the acidic methanol solution (MtOH)

On the other hand, there was a slight improvement in the conductivities of polyaniline re-doped with those transition metals salts this is also expects from the post modification process might improve the deformed structure of PANI – ES due to an ion of those salts substitute on the phenyl ring. In the same way their solubility's were also highly improved in the most organic solvents like Chloroform, NMP, DMSO as compared with ES this is also attributed to the effects of post modification by the secondary doping process. Expected electronic change in all prepared samples of PANI can be mathematically explained by calculating the band gaps from their UV-Vis spectra. The energy $h\upsilon$ of the photon is related to the wavelength λ of UV-Vis radiation by the following relation [36-38].

$$\Delta E \ = \ h\,\upsilon \ = \ E(LUMO) - E(HOMO) \ = \ \frac{1.24}{\lambda(\mu m)}\ eV \quad --- 1$$

Where h is Planck's constant ν frequency of light and c velocity of light. The calculated band gap for each case is reported in (Table 1).

Table 1 Conductivity and computed energy gap of the undoped and primary and secondary doped polyaniline samples.

Dopants	Conductivity (S/cm)	HOMO-LUMO (Energy gap), eV
Polyaniline undoped	0.02	2.45
Polyaniline doped with HCl, ES	156	2.34
ES - $FeCl_3$	168	2.12
ES - $KMnO_4$	210	1.97

Infrared (IR) Spectroscopy of polyaniline

IR studies were carried out in order to confirm the presence of lithium chloride in the polyaniline/ pre-doping polyaniline and post-doping with different dopants. The powder samples of undoped polyaniline were dissolved in NMP and the rest primary and secondary samples were dissolved in chloroform to record the spectra. For PANI, it is most useful for obtaining qualitative information regarding the average oxidation states. IR spectroscopy can distinguish between benzenoid rings and quinoid rings in the 1300 to 1600 cm^{-1} region of the spectrum; this region of the spectrum is most useful for distinguishing between oxidation states in the undoped polymer, as the quinoid stretches disappear on doping.

Figure 6, shows comparative IR spectras of PANI along with doped by secondary dopants as recorded through spectrometer. Our results show that no pronounced peaks have been observed in the spectra region 1750 – 2750 cm^{-1}, but there is a shift in the responses after doping the samples with HCl and LiCl as a primary dopant and re-doping this samples with $FeCl_3$ and $KMnO_4$ as a secondary dopants separately.
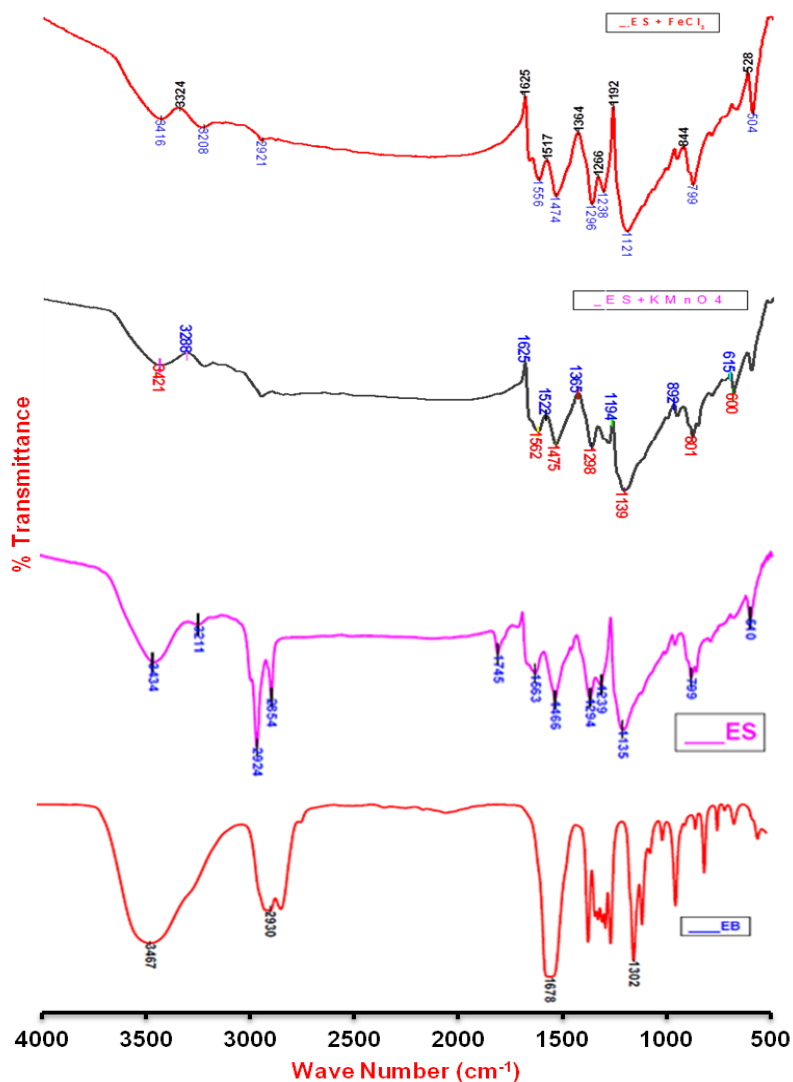
Figure 6 FTIR of Undoped, primary doped PANI- HCl (ES), secondary doped with $FeCl_3$ and $KMnO_4$

Giving rise to a good comparison between the doped and undoped polymer, the medium intensity band at 1591 cm^{-1} (as in undoped PANI) is assigned to the C–N stretching of secondary aromatic amine, which shifts to 1518 cm^{-1} in doped samples. The band at ~616 cm^{-1} observed for undoped and doped PANI samples is the characteristic peak of C–H out of plane bending vibration of benzene ring. The medium band observed (in doped samples) around 1586 cm^{-1} is the characteristic peak of nitrogen quinoid ring and is absent in polyaniline undoped sample. The vibration band at 616 cm^{-1} is assigned to the benzene ring distribution, whose intensity increases with increase in dopants.

IR spectra of emeraldine salt re-doped with the salts of transition metal (Figure 6) shows almost the same spectra as ES especially with $FeCl_3$ due to the same Cl$^-$ group as HCl doped ES but for the case of Mn^{7+} there are additional peaks nearly at 600 which are expected to be the presence of MnO_4^- ions.

Conductivity measurements

The electrical conductivity were measured using digital multimeter with lead metal roads inserting in the solutions and also using pH-ISE [39]. Then, the current-voltage (I-V) measurements were obtained at room temperature using the two-point probe method and resistivity measurements were carried out by using equation 2 given below. The reported conductivity values were the averages of four pair of reading of sample solutions.

$$\sigma = 1/\rho = \frac{\omega I}{VA} \quad ------- 2$$

Where: ρ = resistivity ($\Omega.cm$), σ = conductivity (S/cm), V = potential difference (mV), I= applied constant current (mA) and ω = thickness (cm).

The resulted conductivity values of all the samples of polyaniline in NMP were summarized in Table 1.

The doping of conducting polymers implies charge transfer, the associated insertion of a counter ion and the simultaneous control of Fermi level or chemical potential. The electrical conductivity of conducting polymers results from mobile charge carriers introduced into π-electronic system through doping. At low doping levels these charge carriers are self-localized and form non-linear configuration. Because of large inter-chain transfer integrals, the transport of charge is believed to be principally along the conjugated chains, with inter-chain hopping as a necessary secondary condition. In PANI, there are nearly degenerate ground states, the dominating charge carriers are polarons and bipolarons. It is observed transition metal doped PANI shows charge carriers formation with linear configuration; as a result conductivity changes substantially [40].

It should be noted that these values are comparable with the dimension of a PANI molecule either in the compact-coil or extended-coil conformation. So, one can expect that PANI chains fold around inorganic ions which serve as centers of the polymer chain coordination, thus leading to growth of grains [41].

Thus, the smallest HOMO-LUMO gap was observed for the secondary $KMnO_4$-doped sample, as shown in Figure 7, while the biggest energy gaps were obtained for EB, samples. Thus, this is correlated with the corresponding energy gap [42]. The orientation of structures and morphology of samples at the macroscopic level affects the mobility of charge carriers and, thus, influences conductivity. It seems that in addition to the size quantization, the doped PANI imparts symmetry to the valence and conduction bands and expanded the width of localized levels that reduced the band gaps [43, 44].
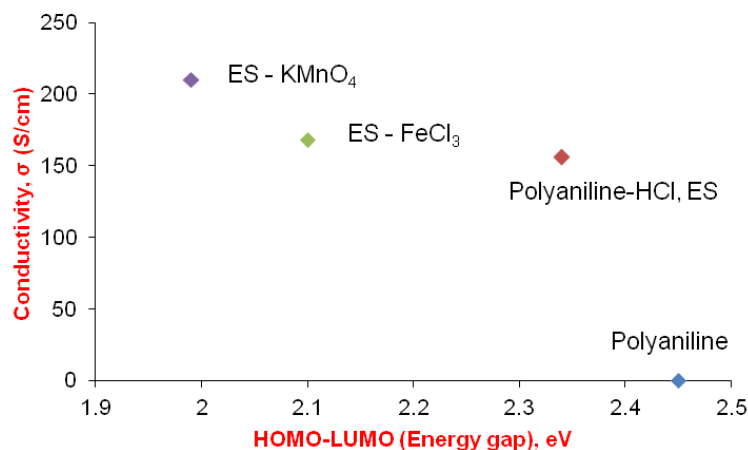
Figure **7** Conductivity versus HOMO-LUMO gap plot of the PANI-ES samples with different dopants.

Conclusion

The dramatically rise in conductivity was said to be induced from the secondary doping is attributed by structural rearrangement from a compact-coil form of PANI to a more expanded conformation. Therefore it is possible to conclude that secondary doping increased the π conjugation. The most direct proof should be the characteristic absorption peak of π conjugation bonds of the EB- of PANI after de-doping of both $FeCl_3$ and $KMnO_4$ secondary doped ES, so as to cancel the effect of different kinds of doping acids. It can be seen that absorption peak of conjugated structure of EB- of PANI chains becomes widened and red-shifted significantly. This fact directly demonstrates that secondary doping enhances the π conjugation structure of PANI in the composite.

Acknowledgement

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