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Optical properties for prepared polyaniline / Ferro fluid nano composites

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Abstract

Pure nano Ferro fluid was synthesized by chemical co-precipitation method. The composite of polyaniline with nano sized Ferro fluid was prepared by In-situ–chemical oxidation polymerization method with ammonium per sulphate as an oxidant in aqueous hydrochloric acid under constant stirring at room temperature. The optical properties, absorption, transmission, optical energy gap (E_g) and optical constant refractive index (n) have been investigated. The value of the E_g decreased with increasing Ferro fluid concentration.

Key words
Polyaniline, Ferro fluid, Nanocomposite, optical properties, UV-Vis spectrophotometer.

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الخواص البصرية للمركب النانوي المحضر بولي انلين \ المائع الحديدي

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الخلاصة

تم في هذا البحث تحضير المائع الحديدي (Ferro fluid) بطريقة الترسيب الكيميائي المشترك. المتراكب المتكون من البولي انلين مع المائع الحديدي بطريقة البلمرة الاكسدة الكيمائية للنظام مع الامونيوم- سلفيت كمادة مؤكسدة في محلول حامض الهيدروكلوريك وتحت تدوير ثابت ودرجة حرارة الغرفة. الخواص البصرية مثل الامتصاصية، فجوة الطاقة، معامل الانكسار تم دراستها. ولقد وجد ان قيم فجوة الطاقة تتناقص مع زيادة تركيز المائع الحديدي.

Introduction

In recent years the manufacture of devices using inorganic/organic hybrid materials has attracted much interest from both the scientific and the technological points of view, improvements in the electronic and the optical properties of these devices are closely related to surface effects. The grain boundaries (a double Schottky barrier could be formed at the grain boundaries) of polycrystalline materials play a significant role in their electrical properties and interfaces, which usually play important roles in device characteristics [1]. Magnetic fluids are stable colloidal dispersions of nanosized magnetic, particles in a liquid carrier. Although. The particles used in most commercial applications are iron oxides (magnetite, maguemite) because of their resistance to oxidation, transition metals have the benefit of higher saturation magnetisation. Magnetic fluids can be used in rotating shaft seals, exclusion seals, loudspeakers, dampers, in clinometers shock absorbers of DVD and CD actuators, medical applications, etc. [2]. Incorporation of a magnetic material, such as Fe_3O_4, into an organic material has attracted great attention due to the resulting electrical properties as well as the many different applications, such as: charge dissipation devices for computer hard disks, batteries, electrochemical display devices, molecular electronics, non-linear optics, sensors and microwave absorption materials [3]. Polyaniline (PANI) as the organic material has attracted much attention due to its characteristics, such as air stability and good solubility in several solvents, besides it shows several changes in its electronic structure depending on its oxidation level. Also, muli-functionality of the PANI micro-nanostructures combined with optical or magnetic function has also attracted interests in order to match the requirements of the technology applications [4]. PANI is usually considered as a *p*-type semiconductor [5], presence of reactive –NH– groups in the polymer chain which in parts chemical flexibility to the system and improves the processcibility to a large extent [6]. Electrical and optical properties can be changed by oxidation and/or by protonation. Several reports are dealing with the preparation of hybrid materials such as SnO_2/polyaniline [7] TiO_2/polyaniline [8], Fe_2O_3/polyaniline [9], and ZnO/Polyaniline [10]. PANI is widely used in the area of electrochemical materials.

Experimental work

This part presents raw materials and preparation method used to prepare polyaniline /Ferro fluid nano composites.

1. Raw materials

The raw material used to prepare the samples were: aniline hydrochloride(C_6H_5 NH_2.HCl) as a monomer, supplied by Hopkin and Williams company and purity 99 .999%, Ammonium persulphate $(NH_4)_2S_2O_4$ supplied by BDH company and purity 99.95%, Ferric chloride $FeCl_3$ and Ferrs chloride $FeCl_2$ supplied by Central Drug House CDH, and they have purity 95%, Amonia NH_3 supplied by BDH company and purity 99.5%,Olic acid $C_{17}H_{33}COOH$ supplied by Hopkin & William LTD and purity 99% Dimethyl sulfoxide $(CH_3)_2SO$ supplied by CDH- India and purity 99.96%**.**

2. Preparation of Ferro fluid

Measure 2gm of ferric chloride ($FeCl_3$) in to a Beaker, add 10ml of distilled water, stir the solution, measure 1gm of ferrous chloride ($FeCl_2$), add 10ml of distilled water, add drop wise HCL (1M) to melt the solution completely, add the solution to the beaker containing $FeCl_3$ and continue in stirring. Add a small piece of steel woo lcontinue in stirring until the solution has turned dark green. Filter with a coffee filter. While stirring, add 150 ml of house hold ammonia (NH_3), the solution color will change to Black. With the stirring, heat the solution to near boiling, add 5ml of olic acid, continue in stirring and heat near boiling until the smell of ammonia disappears, usually about an hour. Power of and collect the magnetic particles (the Black amount). The reaction for the prepared Ferro fluid is shown below:

$$2FeCl_3 + FeCl_2 + 8NH_3 + 4H_2O \rightarrow Fe_3O_4 + 8NH_4Cl \qquad (1)$$

3. Preparation of polyaniline\ ferro fluid nano composite

Polyaniline – Ferro fluid nanocomposites were prepared for different weight of (1, 1.5, and 2) g of Ferro fluid by in-situ oxidation polymerization method. Initially known weight of Ferro fluid (1g) was added to aniline prepared in aqueous hydrochloric acid (1M) and stirred for half an hour, then allow settling down for another half an hour. To this solution, ammonium persulphate as an oxidant prepared in aqueous hydrochloric acid (1M) was added drop-wise for half an hour under constant stirring at room temp. The monomer to oxidizing agent ratio was kept at 1: 2. Stirring was continue for two hours, the resulting dark green mixture was kept over night and then filter. The precipitated polymer was washed with300ml distilled water, then with 150 ml methanol to remove excess initiator, monomer and oligomer. Finally, the polymer was dried in air for about one hour and then in an oven at 80°C for 6 hours. Similarly nanocomposites for remaining weight of Ferro fluid were prepared.

4. sample preparation

Polyaniline /Ferro fluid nano composites powder of weight (0.05) g. was dissolved in 5 mL of Dimethyl sulfoxide (DMSO), then the solution was stirred by using electromagnetic stirrer for two hours to achieve a homogenous content. Because the Polyaniline was partially dissolved, the solution should be filtered, to remove any particles not solving. UV/160 Shimadzu spectrophotometer was used to measured transmission and absorption spectra of the prepared samples at wavelength range (200-800nm).The absorptions spectrum was used to determine the optical energy gap. Computer program is used and Tauc formula was employed in the program.

Result and discussion

1. Absorption

The absorption was determined for the PANI /Ferro fluid. The variation of the absorption versus the wavelength for different concentration of Ferro polyanyline is shown in Fig.1. From the figures, in general the absorption is high at UV region and decreasing in the optical region.

2. Optical energy gap

Tauc [11] put the empirical equation between the optical energy gap and energy of incident photon which is

$$\boldsymbol{\alpha h v = A\left(h v - E_g\right)^r} \qquad (\mathbf{2})$$

where A is a constant, hυ is the energy of incident photon, which can be calculated using the equation $hv = {}^{1240}/_{\lambda(nm)}$, and r is the order of the optical transition depending on the nature of electronic transition. The transition is called direct if the extremities of V.B. and C.B. lie at the same point in k – space, while the transition is called indirect if the transition is possible only with phonon assisted ($\Delta k \neq 0$) [12]. Thus the value of r may be 1/2, 2, 3/2 and 3 corresponding to the allowed direct, allowed indirect, forbidden direct and forbidden indirect transition respectively. The optical energy gap (E_g) for polyaniline has been determined. A plot of $(\alpha h\gamma)^2$ versus hν with different concentration of Ferro fluid (1,1.5, and 2 wt%) as shown in Fig. 2 the plot is linear indicating the direct band gap nature of the polymer. Extrapolation of the line to the hν axis gives the band gap to pure and doped samples therefore the optical energy gap is determined from this figure. The additive of Ferro decreases the optical band gap from 3eV to 2.4eV. The reduction in the optical band gap is probably due to the modification of the polymer structure [13].

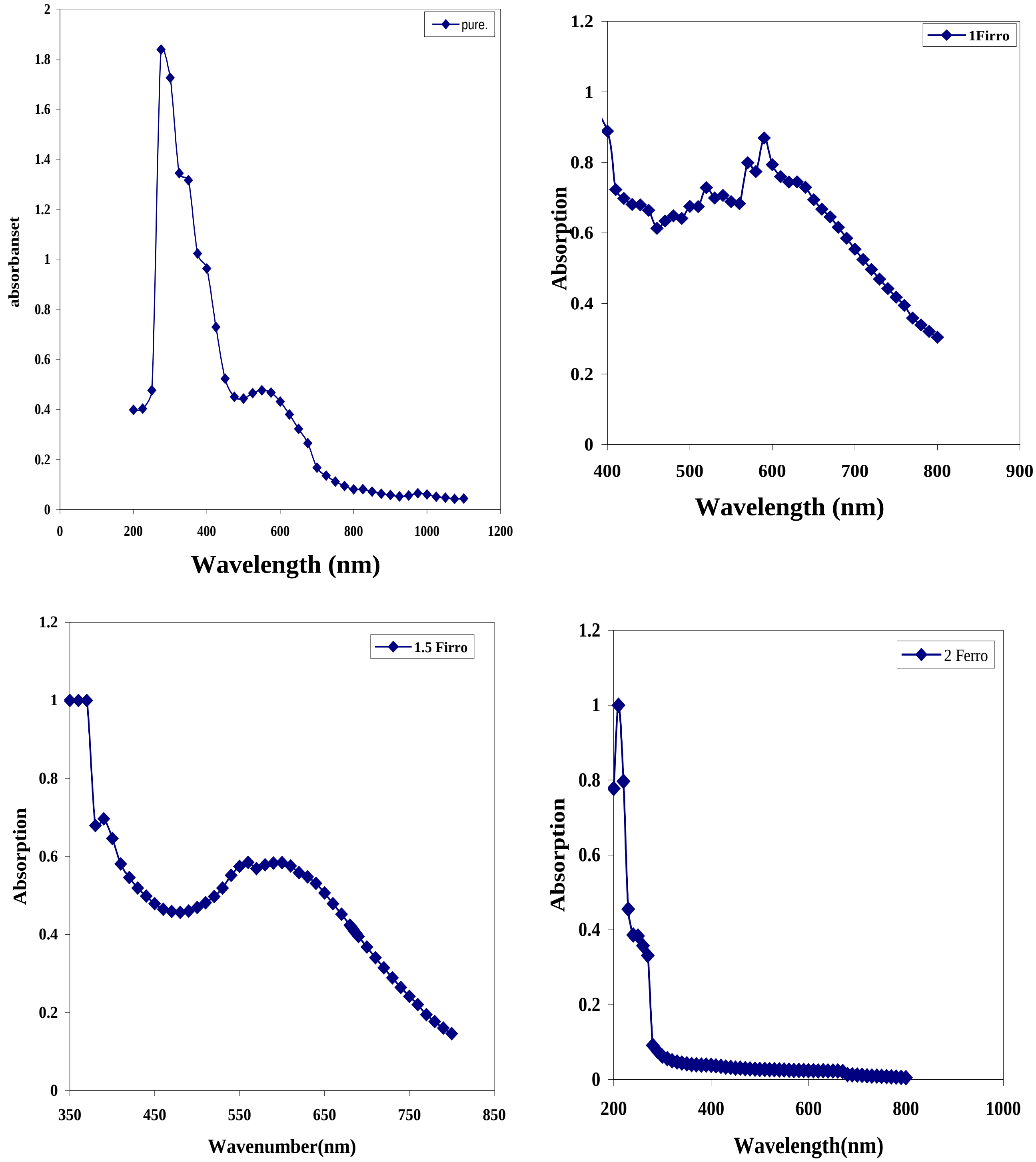

Fig. 1: The variation of absorption as a function of wavelength for PANI/Ferro fluids samples.

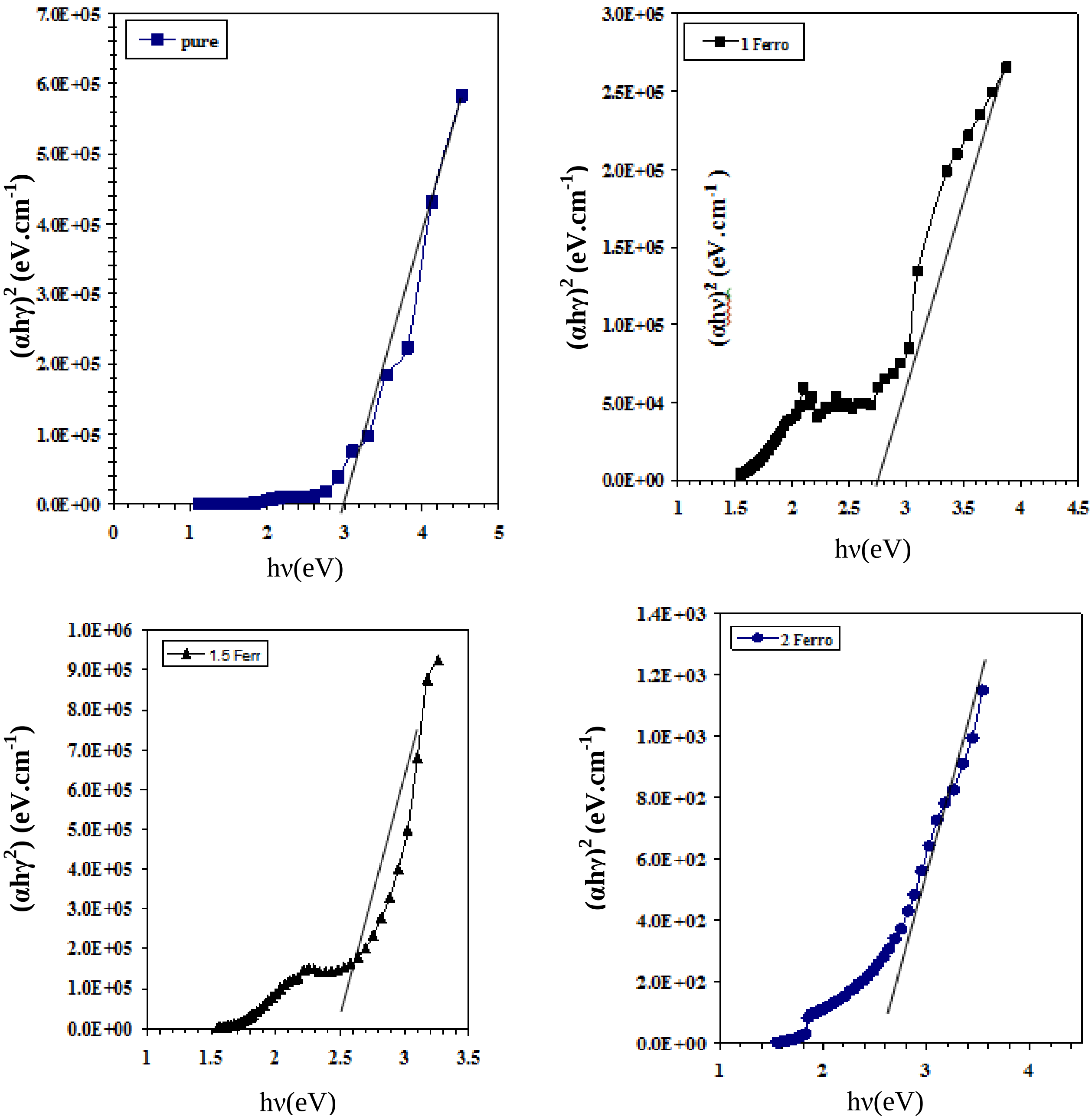

Fig.2: $(\alpha h\gamma)^2$ as a function of photon energy for Polyaniline /Ferro fluid at different wt.%.

Fig.3 shows the relation between the energy gap and the concentration percentage of Ferro fluid. It can be seen from this figure that all samples have one direct optical energy gap. We have found energy gap decreases with increasing the concentration percentage of Ferro of 1%, 1.5% while for sample with 2% wt. The increasing is very fast and this increasing in the optical energy gap can be explained as fallow: The addition of Ferro to Polyaniline above 1%, increases the degree of disorder then selective absorption of the photon energies of incident light that such energy is devoted to breaking up and hence deforming of partially crystalline structure of the polymer. Increasing the degree of disorder causes the band tail to increase which, according to the electronic structure of amorphous materials, will lead to the increasing of the estimated optical gap. Our results are in close agreement with the results of Sayed [14].

3. Refractive index

For normal incident of plane electromagnetic wave the reflectance is given by the equation (15)

$$R = \frac{(n+1)^2 + k^2}{(n-1)^2 + k^2} \qquad (3)$$

which leads to

$$n = \sqrt{\frac{4R}{(R-1)^2} - k^2} - \frac{R+1}{R-1} \qquad (4)$$

The variation of the refractive index as a function of the wavelength for Polyaniline at different Ferro fluid wt.% doping is shown in Fig. 4 which shows a variation of n at room temperature. It is observed that in general the refractive index decreases with the increase of wavelength. The dispersion curve of n(λ) is presented in figure for pure and doped PANI. The refractive index decreases in pure PANI but it has higher values compared with doped samples because the addition of Ferro, in general, the reflective index which increases by increasing the C – H bonds [16]. Fig. 5 shows the reflective index for pure PANI.

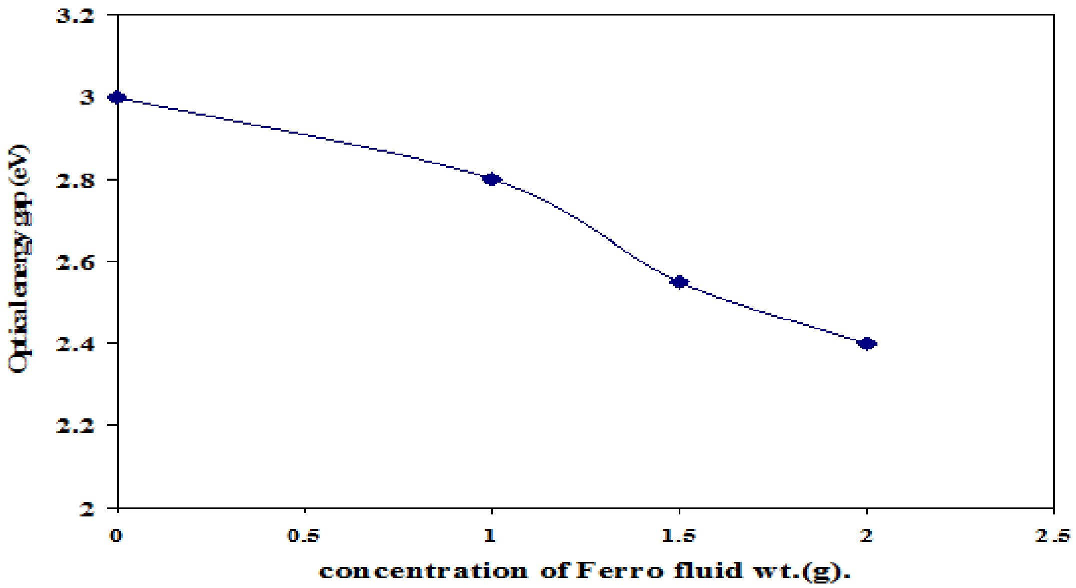

Fig.3: Optical energy gap at different Ferro fluid wt.

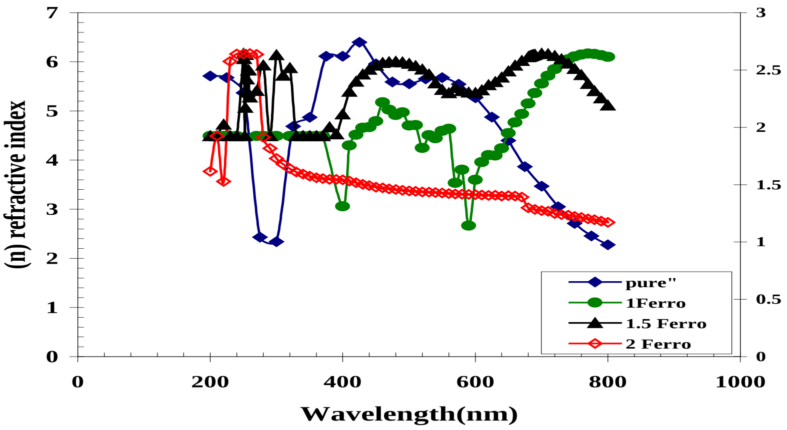

Fig. 4: Variation of refractive index as a function of wave length (nm) for different Ferro fluid wt. %.

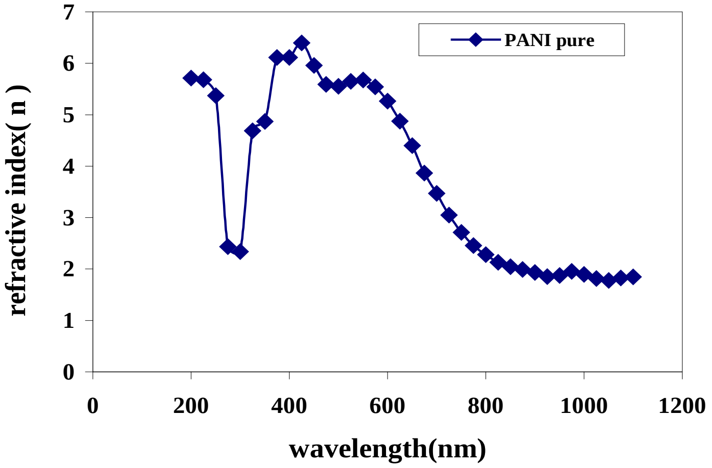

Fig.5: Variation of refractive index as a function of wave length (nm) for PANI pure.

Conclusions

Polyaniline polymer was prepared via the oxidation of aniline hydrochloride with ammonium peroxy disulfate in aqueous medium. The Ferro/fluid was prepared by co-precipitation method. The composite of polyaniline with nano sized Ferro fluid was prepared by In-situ – chemical oxidation polymerization method. It was found the optical energy gap was decreasing when increasing the concentration of Ferro fluid wt% from (3-2.4eV). was noticed that all samples have allowed direct optical energy gap.

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