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Research Article

Electrochemical synthesis and characterization of aniline by $K_2Cr_2O_7$ as an oxidant and H_2So_4 as a dopant.

V. B. Deshmukh[1] K. S. Paithankar[2], U. N. Shelke[2], V. K. Gade[3]

[1]Department of Physics, Hutatma Rajguru Mahavidyalaya, Rajgurunagar, Pune, Maharashtra, India.

[2]Department of Physics, Research Center, Ahmednagar College Ahmednagar, Maharashtra, India.

[3]Department of Physics, Shri Anand College, Pathardi, Maharashtra, India

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***Corresponding author E-mail address:** vbdeshmukhsir@gmail.com*

ABSTRACT
Electrochemically synthesized Polyaniline film using $K_2Cr_2O_7$ as an oxidant and H_2So_4 as a dopant is characterized by UV-visible spectroscopy, FTIR and Conductivity and also calculate band gap energy and results are analyzed. FTIR spectra recognized the existence of polarons and bipolarons in polymer samples. UV spectra showing the absorption peaks due to π-π* transition of polyaniline. The electrical conductivity of the synthesized film was measured by using four probe methods at room temperature. In this process the ITO coated glass plate would have to use as a working electrode, platinum foil as a counter electrode and Ag/AgCl as a reference electrode.

KEYWORDS
Polymer, Polyaniline, electrochemical polymerization, Conductivity.

1. INTRODUCTION

Researchers are developed a new area in Material Science i.e. synthesis of thin film by using conducting polymer and its application in various field such as solar cells, Capacitors, electrodes for rechargeable batteries, biosensors etc. Thin film is used in every field as a sensor system such as detection of pesticides and bio-components [1], the discovery of thin film microelectrode chips strongly support the interdisciplinary research and development of miniaturized biosensor. The conducting polymer such as polyaniline, polypyrrole, polythiophene and its derivatives are complex dynamic structures that are used in immobilization of different enzymes for sensor. Past few years various research groups worked out on this area for synthesis of thin film in 1988 Josowicz. M. and Janata worked on chemical sensor technology. Then in 2000 Baily, R.A. and Persaud K.C. in polymer sensor and actuators, in 2001 Barson N. and Weimar U. conduction model of metal oxide gas sensor. In recent Kareema M. Ziadan lcrabit, A. Haykaz and Ali Q. Abudalia (2012) some electrical properties of soluble conducting polymer prepared by electrochemical polymerization are studied. Conducting polymer has one large advantages of synthesis and their chemical structure to changes its physical properties. They exhibit an electrical conductivity and can exhibit metallic to insulator property (10^5-10^{-9} s/cm) 'Conducting polymer having lot of application such as biosensor, solar cell and rechargeable batteries [2]. In present work electrochemical synthesis and characterization of H_2SO_4 doped aniline is carried out with $K_2Cr_2O_7$ as an oxidant at 677mV. FTIR, UV, SEM, and conductivity, solubility, inhibition studies exposed the conducting nature of polyaniline [3].

2. MATERIALS AND METHODS

All chemicals were used in analytical grade. Aniline and indium tin oxide (ITO) sheet (resistance 50 Ω/cm) were purchased from Sigma-Aldrich. The ITO of 1 cm x 3 cm was used as a working electrode. An area of 3 cm^2 (1cm x 3 cm) from one end of the ITO was bare to the electrolyte and the upper area was used as a place for taking electrical contact to anode. Platinum foil was used as a counter electrode to cathode and the reference electrode was silver/silver chloride (Ag/AgCl). Potassium dichromate ($K_2Cr_2O_7$) was used as a dopant. We were freshly prepared 0.1N an aqueous solution PANI (99%) in double distilled water, Also we prepared an aqueous solution of 0.1N potassium dichromate ($K_2Cr_2O_7$) in double distilled water. The pH of mixture are maintain by using buffer solution. The electrochemical polymerization of PANI was carried out by galvanostatic method in one compartment electrochemical cell. All three electrodes were placed vertically in an electrochemical cell. Before film deposition, the ITO substrate was cleaned with detergent and diluted hydrochloric acid in an ultrasonic bath and was then rinsed with ethanol and distilled water. All solutions were prepared using distilled water. After film deposition potentials were referred to the Ag/AgCl electrode.

3. RESULTS AND DISCUSSION

Electrochemically synthesis of PANI recognized that using $K_2Cr_2O_7$ as supporting oxidants, the nature and concentration of synthesize a conducting polymer affect its morphology and some of its other properties. The previous reported work electrochemical synthesis of PANI on Indium Tin Oxide substrate [4-5]. However, once the PANI oxidation was initiated, this process is much

faster for increased polyelectrolyte concentration that was investigates the effects of various synthesis parameters such as electro-polymerization method, monomer concentration and electrolyte on electro-polymerization of PANI [6-7].

3.1. UV-Visible Spectroscopy

The optical absorption spectrum of synthesized PANI with oxidant $K_2Cr_2O_7$ films with optimized parameters are as shown in fig.1. It is recorded that the wavelength range is 350-800nm. For measurement of UV-visible Spectrophotoscopy of thin film Lab India spectrometer (V-2000) was used. All spectra were recorded in the wavelength range of 350-800 nm & the peak is appearing at 600, nm for PANI/$K_2Cr_2O_7$ film, It shows very good resemblance with earlier work.

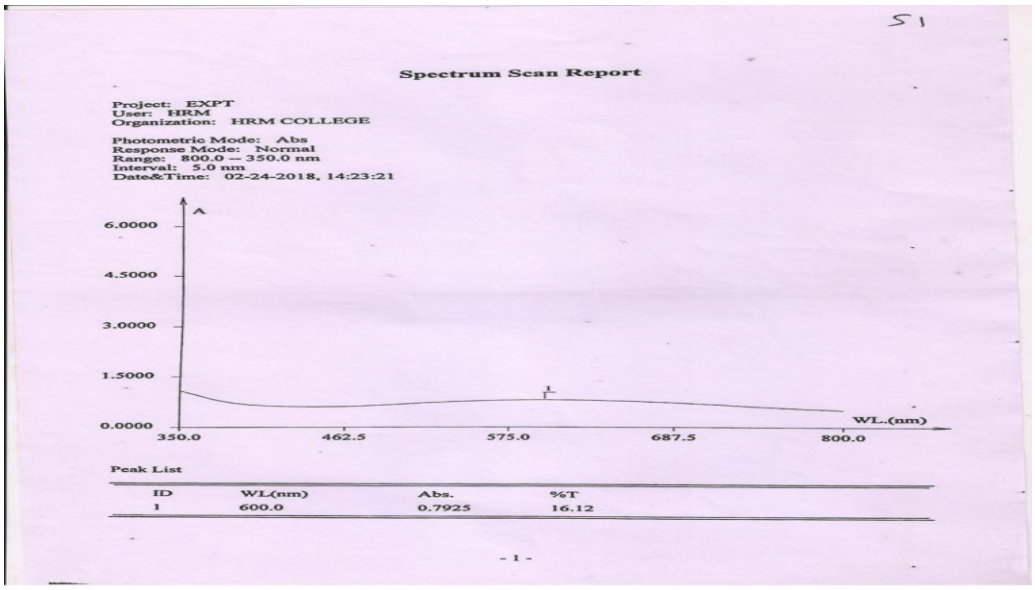

Figure 1. UV of PANI/ $K_2Cr_2O_7$ Thin film (Absorption)

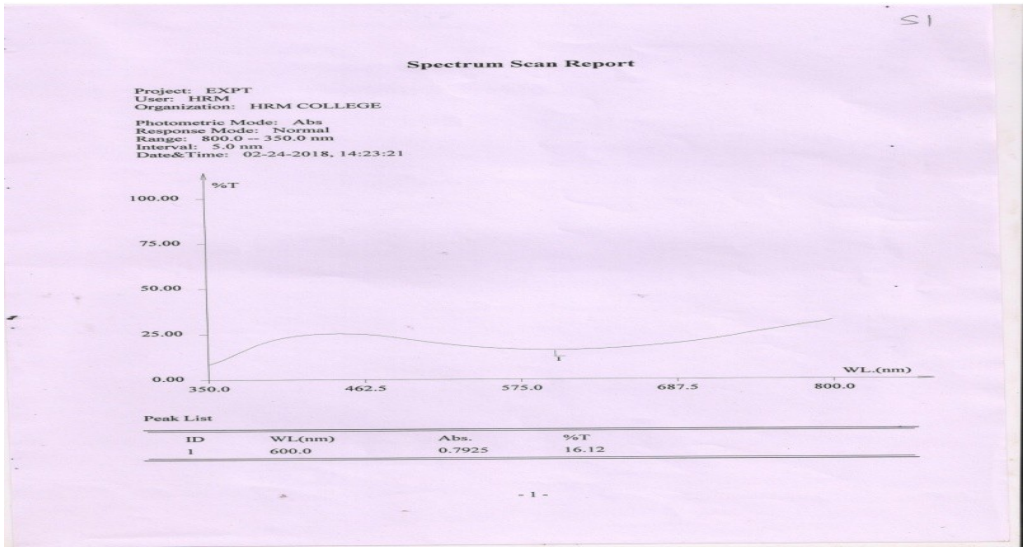

Figure 2. UV of PANI/ $K_2Cr_2O_7$ Thin film (Transmittance)

3.2. Fourier Transform Infrared

The FTIR spectroscopy is used for structural morphology of synthesized Poly- Aniline with supporting oxidants $K_2Cr_2O_7$ film with optimized parameters for as shown in fig.3, it was recorded that the wave number range is 400 to 4000 cm^{-1}on the Alpha Bruker.

Fig.3 shows FTIR spectrum of synthesized samples of PANI for H_2SO_4 dopants and its recorded range is 400 - 4000cm^{-1}. The bonds 1463 cm^{-1} and 1597 cm^{-1} corresponds to C=C stretching vibrations of the benzoid and quinoid rings respectively. The peak at 1259 cm^{-1} is the characteristic band of aromatic C-N stretching vibration and a weak peak at 3462 cm^{-1} is assigned to stretching mode of N-H. The absorption band appears at 1101 cm^{-1} has been explained as vibration band of Nitrogen quinine (N=Q=N). In addition the band at 860 cm^{-1} can be ascribed to C-H out of plane bending vibrations for the aromatic ring which clearly supports the formation of PANI. The polymer shows the absorption bands at 2968 are due to asymmetric C-H stretching and symmetric C-H stretching vibrations. These bands corresponds to the characteristics bands of Aniline, it shows Very good agreement. Thus the FTIR spectral lines results confirm the formation of Polyaniline [9].

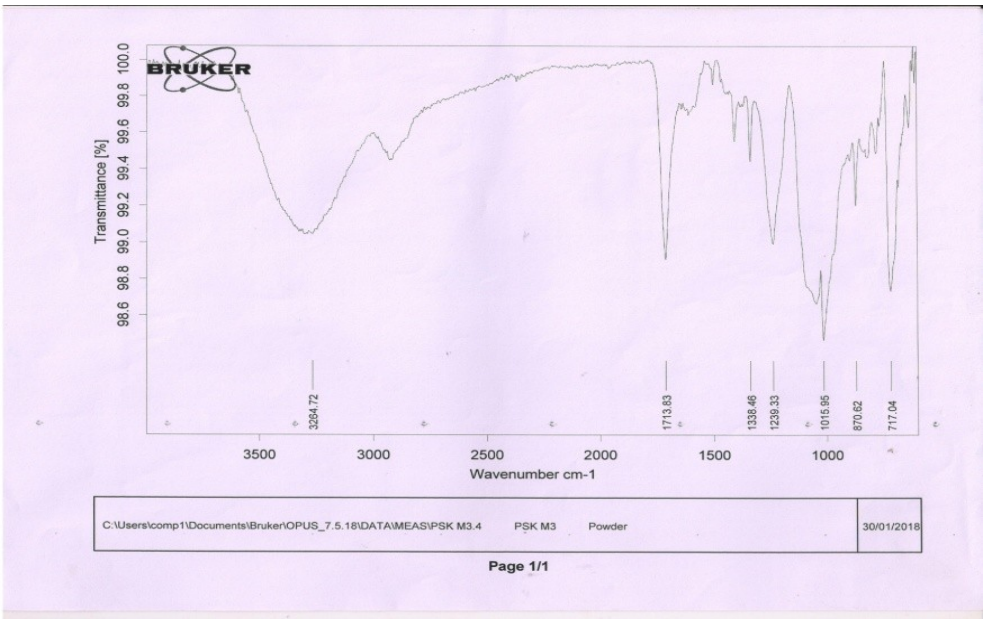

Figure 4. FTIR of PANI/ $K_2Cr_2O_7$ Thin film

3.3. Conductivity Measurement

The four-probe is used for the measurement of electrical conductivity of synthesized PANI films. The Four Probe Method is one of the standard and most widely used methods for the measurement of resistivity of semiconductors. In its useful form the probes are collinear the error due to contact resistance, which is especially serious in the electrical measurement on semiconductors, is avoided by the use of two extra contacts (probes) between the current contacts. In this arrangement the contact resistance may all be high compare to the sample resistance, but as long as the resistance of the sample and contact resistances are small compared with the effective resistance of the voltage measuring device (potentiometer, electrometer or

electronic voltmeter),the measured value will remain unaffected. Because of pressure contacts, the arrangement is also especially useful for quick measurement on different samples or sampling different parts of the same sample. Conductivity of PANI films with $K_2Cr_2O_7$oxidants is getting 1.63 S/cm at potential 670 mV for current density 0.5A/2cm^2 at pH 6.

3.4. Band Gap Energy

The energy spacing between the highest occupied and lowest uncoupled bands is called the band gap. The highest occupied band is called the valence band and lowest unoccupied band is the conduction band. The electrical properties of conventional materials depend on how the bands are filled. When the bands are filled or empty, no conduction occurs. If the band gap is narrow, at room temperature thermal excitation of electrons from the valence band to the conduction band gives rise to conductivity. This is what happens in classical semiconductors. When the band gap is too wide, thermal excitation at room temperature is insufficient to excite electrons across the gap and become an insulator. The high conductivity of metals is due to partially occupied bands, a partially filled conduction band, a partially empty valence band or a zero band gap. Conductive polymers are peculiar in that they conduct current without having a partially empty or partially filled band. Conductive polymers show enhanced electrical conductivity by several orders of magnitude of doping. Conductivity in conducting polymers is influenced by a variety of factors including polaron length, the conjugation length and overall chain length and by the charge transfer to adjacent molecules. These are explained by large number of models based on inter soliton hopping, hopping between localized states assisted by lattice vibrations, intra-chain hopping of bipolarons, variable range hopping in 3-dimensions and charging energy limited tunneling between conducting domains. To explain some of the electronic phenomena in these organic polymers, concepts from physics that are new for chemists, including solitons, polarons and bipolarons have been applied to conducting polymers since early 1980's. When an electron is removed from the top of the valence band of a conjugated polymer, such as polyacetylene or polypyrrole, a vacancy (hole or radical cation) is created that does not delocalize completely, as would be expected from classical band theory. Only partial delocalization occurs, extending over several monomeric units and causing them to deform structurally. Moreover, π-bonding, in which the carbon orbitals are in the sp^2pz configuration and in which the carbon orbitals of successive carbon atoms along the backbone overlap, leads to electron delocalization. This electronic delocalization provides the highway for charge mobility of the polymer chain. Therefore, the electronic structure in conducting polymers is determined by the chain symmetry i.e. the number and kind of atoms within the repeat unit with the result that such polymers can exhibit semi-conducting or even metallic properties. The energy level associated with this radical cation represents a destabilized bonding orbital and thus has a higher energy than the energies in the valence band.

In other words, its energy is in the band gap. This rise in energy is similar to the rise in energy that takes place after an electron is removed from a filled bonding molecular orbital. In solid-state physics, a radical cation i.e. partially delocalized over some polymer segment is called polaron. It stabilizes itself by polarizing the medium around it.

Band gap energy of polyaniline /Potassium dichromet film is 2.0706 eV, it shows film is conducting.

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