

Secondary electrochemical doping level effects on polaron and bipolaron bands evolution and interband transition energy from absorbance spectra of PEDOT: PSS thin films

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ARTICLE INFO

Article history:

Received 23 March 2016
Received in revised form 14 August 2016
Accepted 16 August 2016
Available online 24 August 2016

Keywords:

PEDOT:PSS
Polaron
Bipolaron
Transition energy
Doping
Midgap states

ABSTRACT

Doping induced effect on interband transition energy levels of PEDOT: PSS films deposited by spin coating have been studied experimentally by following changes in vibrational, optical and electrochemical properties. Absorbance spectra of films have been used as a tool to study formation of polaron/bipolaron bands, their energy shift and binding energies with change in doping concentration. Energy level structure evolving from optical spectra has been sketched and corresponding energies required for transition at different doping levels have been indicated. Electrochemical studies show redox peaks in agreement with spectroscopic results demonstrating storage of charge in sub-band states in the form of polarons/bipolarons. Increased absorption due to π - π^* transitions on secondary doping reveal non linear characteristic in the plot of hue vs.chroma traversing from faint blue to deep blue region in the chromaticity diagram.

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1. Introduction

Conducting Polymers (CP) like polyaniline, polypyrrole, polythiophene have been attracting widespread attention for a number of novel applications because of their innate properties [1,2]. Polyaniline and polypyrrole are conducting polymers with high conductivity but lack properties of solubility and processibility [3,4]. However, by controlling the pendant chain chemistry, Polythiophene, can be used to prepare new polymers with tunable properties. Polythiophene and its derivatives have been found to be stable both in their doped and undoped states. They also exhibit high stability of the optical spectrum and high conductivity retention at elevated temperatures for long intervals [5]. Poly(3,4-ethylenedioxythiophene): poly(styrenesulfonate) (PEDOT:PSS), a polythiophene derivative is one such CP with exceptional optical, conductive and solubility properties. It forms a dispersion of oxidatively doped cationic derivative PEDOT electrostatically bound to a polyanion PSS in water [6]. PSS also acts as a charge compensating counter-ion and stabilizes the p-doped PEDOT. The solution- processability of this aqueous colloidal dispersion can be used to achieve a thin, virtually transparent film

for use as a flexible electrode numerous electronics applications, as well as in anti-static coatings, supercapacitor materials, sensors, OLED applications, transparent electrodes, solar cells, organic transistors [7–13] etc. Doped PEDOT:PSS has been used widely for depositing thin, transparent films for use as an electrode in electronics applications [14]. Thin films of PEDOT:PSS show high conductivity of the order of several hundred S/cm. It is also a promising candidate for electrochromic device (ECD) like windows/displays due to its fast response time, small electronic bandgap, low redox potentials and facile fabrication [15,16]. PEDOT: PSS thin films can be easily deposited using different techniques like template synthesis, CVD, spin coating, inkjet printing, electro-polymerization and spraying [17,18].

PEDOT:PSS is a low bandgap p-type semiconducting material with its energy gap lying in the VIS-NIR range (1.6 eV for π - π^* transition) and shows an absorption maximum in the middle of the visible spectrum at 600 nm. Doped PEDOT:PSS is almost transparent in the visible region (with a light blue tint) and while neutral polymer possesses a blue-black color. In its pristine state, a film of PEDOT-PSS consists of a mixture of undoped and doped PEDOT units in the ratio 1:4, corresponding to an intermediate state between the fully doped (oxidized) and undoped (reduced) state. Electrochemical doping of PEDOT:PSS results in addition of mid-gap energy levels, producing absorptive transitions in the visible region that invoke an observable color change. This high-contrast

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electrochromic phenomenon associated with electrochemical doping and the corresponding changes in absorption spectrum are of particular interest to understand the charge storage mechanism during doping/deoping process. Whenever electrochemical doping takes place, ions are incorporated into or extracted from the PEDOT:PSS film. This incorporation of ions manifests itself in the form of increase in electrical conductivity. The conductivity increase in these materials arises from the introduction of polaronic and/or bipolaronic species on the polymer backbone [19], which are charge-compensated by a counter ion. The presence of these charged molecular defects introduces symmetric mid band gap energy states [20]. At higher doping levels, broad bipolaron bands develop, effectively minimizing the bandgap and moving the material into a quasi-metallic regime [21]. This electrochromic behavior brought about by electron transfer reaction that takes place during the electrochemical oxidation and reduction of the polymer makes PEDOT:PSS suitable as a cathodically coloring polymer in construction of ECDs [22,23]. Such an ECD has been studied in detail by several groups like Reynolds et al. [10,11], Delongchamp et al. [24], Cho et al. [25] etc. However, to date, to the best of our knowledge, there are no reports on studies of evolution of midband transitions on electrochemical doping due to polaron/bipolaron formation and the corresponding interband energy required for these transitions in PEDOT:PSS thin films. In this paper, we report the shift in energy level for interband transition with the change in doping concentration, corresponding emergence of polaron/bipolaron bands and intensity variations from the experimental data and correlate the observations to deduce the interband transition energies alongwith the energy level structure.

2. Experimental techniques

PEDOT:PSS was purchased from Sigma Aldrich and used as received as an aqueous dispersion. Prior to film deposition, ITO glasses were cleaned with double distilled water, acetone, ethanol, isopropyl alcohol and ultrasonic bath. These ITO substrates were kept in a vacuum oven for 10 min to dry. Aqueous dispersion of PEDOT:PSS was coated on to the precleaned substrate by spin coating technique using a programmable spin coater (APEX instrument, Kolkata) at a rotational speed of 2000 rpm for 30s. After that, the films were kept in vacuum oven for 15 min to allow the samples to dry completely. Films of different thickness were deposited by varying the number of deposition cycles. They were optimized for highest transparency and good electrochromic contrast. FT-Raman spectra of the films were recorded in the spectral range of 250–1000 cm^{-1} using FT-Raman spectrometer (Bruker MultiRAM, Germany) employing Nd:YAG laser source with an excitation wavelength 1064 nm and resolution 4 cm^{-1} . Optical characterisation was carried out using UV-Vis spectrophotometer (Shimadzu, model: UV-1800, Japan) in the wavelength range of $300 < \lambda < 1100$ nm to study spectral transmittance modulation with respect to the changes in the applied polarizing voltage. All electrochemical measurements were performed in 0.5 M LiClO_4 dissolved in a binary electrolyte comprising of Propylene Carbonate (PC) and Acetonitrile (ACN) using Electrochemical Analyzer (CH Instruments, CHI-400A USA). A conventional three electrode setup was employed for this purpose with saturated calomel electrode (SCE) serving as the reference electrode. Variations in diffusion current and current density were recorded using cyclic voltammetry in a potential window within predetermined safety limits. Colorimetric analysis was done with the help of Shimadzu make UV-Vis spectrophotometer equipped with color analysis software by analyzing transmittance spectra of films in colored/bleached state to evaluate $L^*a^*b^*$ and Y_{xy} values.

3. Results and Discussion

3.1. Raman studies

Raman characterisation can be used for probing the changes occurring at molecular level to gain insight into the vibrational modes of the material. Fig. 1 shows FT-Raman spectra of as deposited PEDOT:PSS films. A number of well defined bands assigned to PEDOT vibrations can be generally found in the region of 500–2000 cm^{-1} . The form of spectra and relative intensity of the peaks depend on the oxidation level of the film [26–28]. Raman mode frequencies and intensities for the PEDOT:PSS have been often associated with the optical and electronic structures of poly and oligothiophenes with structures containing π -conjugated backbone [29]. Fig. 1 shows six dominant principal peaks related to PEDOT polymer structure in PEDOT:PSS films of different thickness. The peak at 1521 cm^{-1} represents $C_\alpha = C_\beta$ asymmetric vibrations; 1407 cm^{-1} can be assigned to $C_\alpha = C_\beta$ symmetric vibrations, 1361 cm^{-1} to C–C stretching deformations, 1246 cm^{-1} to C–C in-plane symmetric stretching, 1149 cm^{-1} and 1097 cm^{-1} to C–C in-plane bending vibrations [30]. The peak at 1409 cm^{-1} is associated with the characteristic thiophene ring while the shoulder at 1361 cm^{-1} corresponds to the characteristic PEDOT vibrations. The form of Raman band associated with $C_\alpha = C_\beta$ symmetrical stretching at 1400–1500 cm^{-1} is used to distinguish between benzenoid and quinonoid form and find information about secondary doping [31].

Two extreme geometric structures are possible, an entirely benzenoid one, and an entirely quinonoid one, with the quinonoid structure generally possessing a slightly higher energy and thus being less favorable, than the benzenoid one. The benzenoid form may be the preferred structure for a coil conformation in the low conductivity phase while the quinonoid structure may be the favored form for a linear or expanded-coil structure in the high conductivity regime. The band located at 436 cm^{-1} was assigned to SO_2 bending from PSS. The peak positions and their assignment are in good agreement with reported literature data. As we proceed from sample P_1 to P_3 , with the increase in number of layers deposited from 10 to 30, there is an increase in intensity and sharpness in the band at 1409 cm^{-1} . The peak at 1246 cm^{-1} which is indiscernible for film with less thickness gets more prominent as the number of layers increase. This increase in relative intensity of

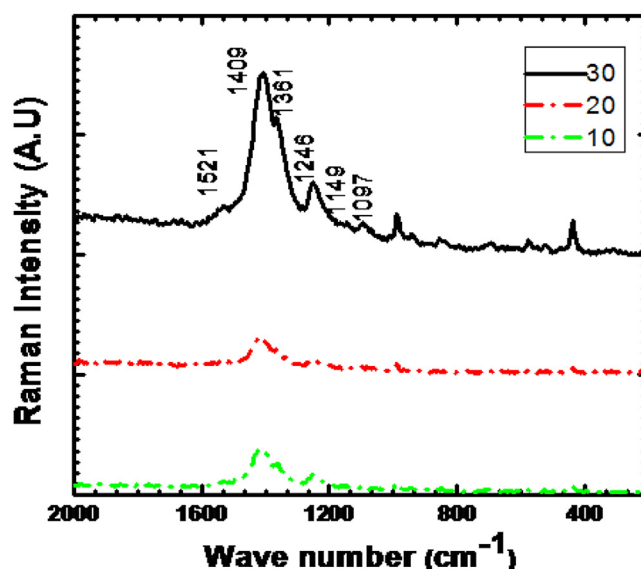


Fig. 1. Raman spectra of PEDOT:PSS samples with 10, 20 and 30 layers deposition.

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