



Quantum confinement effects in highly conducting, ultrathin polyaniline films pursued through spectroscopic investigations

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ABSTRACT

Polyaniline (PANI) is well-known for its remarkable electrical and optical properties which find immense applications in polymer optoelectronics. Though extensive work has been reported in polyaniline samples both in bulk and thin film forms, much attention has not been paid to investigate the quantum confinement effects in ultrathin polyaniline films. The present work is devoted to the search for quantum confinement effects in ultrathin polyaniline films having nanometer thickness, prepared from m-cresol, through conventional and less sophisticated spectroscopic techniques. Remarkable blue-shift has been observed in the absorption spectrum of these samples. Much intense photo-luminescent emission with considerable blue-shift observed in these ultrathin films is cited as the clear evidence for confinement effects.

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1. Introduction

Conducting polymers, otherwise called synthetic metals, have been the subject of intense study over the last few years owing to the ever increasing interest in their technological and industrial applications [1]. Polyaniline (PANI) is among the most stable conducting polymers ever studied. It is environmentally stable both in conducting (doped) and non-conducting (de-doped) forms. It occupies a unique position among the conducting polymers and is well known for the excellent electrical and optical properties [2]. PANI has its immense applications in the fields of polymer LEDs, photovoltaics, batteries, electrostatic charge dissipative coatings, electromagnetic shielding, and sensors [3–11]. One of the most important properties of PANI is its tunable electrical, optical, and structural properties. PANI has become one of the most technologically and industrially important conducting polymers owing to its unique processibility together with the availability of relatively inexpensive precursors and better yields of polymerization. Non-conducting polyaniline exhibits electrical conductivity of the order of 10^{-10} S/cm; but doping with an acid results in a considerable increase in its conductivity up to 10–12 orders of magnitude. The process of doping causes the delocalization of the charge and spin along the backbone of the polymer, there by enhancing the conductivity of the polymer [12]. The conducting mechanism of

PANI has been widely investigated [12–17]. The charge carriers travel inside the chains by intra-chain hopping and in between PANI molecular chains via inter-chain hopping. There is also a possibility of tunneling of charge carriers, from local crystalline (ordered) regions to nearby crystalline regions through amorphous regions inside the polymer network. Thus the effective conductivity is a sum of the contributions from inter-chain hopping, intra-chain hopping and tunneling of charge carriers within the polymer system [7,18].

Advances in conducting polymers over the past few years provide an opportunity for the fabrication of various structures and devices of nanometer dimensions. Major developments in conducting polymers during these years have almost reached the fundamental physical limits and the miniaturization threshold for electronic devices made of conventional semiconductors. This has accelerated the interest in nano-structured organic materials and devices which have the ability to control their properties on a molecular scale [19,20]. Conducting polymer nanostructures combine the advantages of organic conductors and low dimensional systems and as a result, exhibit many interesting physico-chemical properties for useful applications.

Conducting polymers can respond to various external stimuli and hence represent a new class of 'intelligent materials' [7,21]. The inherent stability of PANI and its tunable electrical and optical properties make it an ingenious element suited for various optoelectronic device applications [22]. The method adopted for polymerization and the reaction conditions strongly influence the morphology and, optical and electrical properties of PANI.

In the present work, acid doped PANI synthesized by chemical oxidative polymerization is cast as thin films from meta-cresol in

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nanometer and micrometer thickness scales and the quantum confinement effect is established in nanometer scale PANI through UV–vis–NIR absorption and photoluminescence (PL) studies. There are no reports on the quantum confinement effects in PANI films based on spectroscopic investigations. Spectroscopic investigations are widely known for identification of quantum confinement in semi-conducting materials. Probably there is only a single paper related to confinement effects in polyaniline film in which a polyaniline based quantum well structure has been fabricated and the investigations are mainly based on sophisticated techniques such as Scanning Tunneling Microscopy (STM) and Scanning Tunneling Spectroscopy (STS) [23]. The authors also suggest that quantum well behavior can be achieved in 40 nm sized, iodine doped PANI which is in the lower semi-conducting regime. The present work is significant since, conventional and cost effective spectroscopic techniques have been employed to confirm the quantum confinement effects in ultrathin PANI films. Blue emission in PANI films is not reported in detail elsewhere and the intense blue emission observed in ultrathin PANI films, in the present work, is novel in all respects.

2. Experimental

Aniline and other reagents were bought from SD fine chemicals, India. Meta-cresol and aniline were distilled separately under reduced pressure before use. Other reagents were used as purchased. Pre-distilled aniline was polymerized in 1 M HCl medium using 1 M ammonium peroxydisulphate as initiator via chemical oxidative polymerization [24,25]. The mixture was stirred for 5 h kept in a freezing mixture at -5°C . It was then thoroughly washed and filtered using acetone and distilled water. The sample was dried in dynamic vacuum for 24 h and ground to obtain PANI in its powder form. The obtained Emeraldine salt (ES) form of PANI was de-doped using 1 M ammonia solution to obtain the Emeraldine base (EB). The obtained EB form of PANI was then washed and filtered thoroughly using plenty of distilled water and dried under dynamic vacuum for 24 h. The EB powder was re-doped using 1 M camphor sulphonic acid (CSA) to obtain the soluble and conducting form of PANI. The powder form of conducting PANI was then dissolved in m-cresol to obtain a good solution [25]. Homogeneous and good quality thin films in nanometer and micrometer thickness scales were obtained by spin coating (SPS Spin wafer 150) the solution at different spin speeds in different durations on ultra-sonically cleaned glass substrates. The minimum thickness for PANI films spin coated on glass substrates was in the order of 50 nm and the maximum about 4 μm . The thickness of the films thus obtained was measured using Dektak 6M stylus profiler and films with thickness 50 nm (± 5 nm), 100 nm (± 5 nm), 150 nm (± 5 nm) and 4 μm (± 100 nm) were selected for the present studies. Although all micrometer thick samples (bulk) show the same properties (as it should be), we have selected the thickest sample prepared as a representative for the bulk film whose properties are already well investigated and characterized by many people. The film thickness could be precisely controlled by varying the viscosity of the PANI solution, spin speed and spinning time. Room temperature dc electrical conductivity of these PANI films was measured using standard 4-probe technique [26] employing Keithley 2400 Sourcemeter and Keithley 2001 Multimeter interfaced to a PC with a program developed in LabVIEW. These bulk films were found to be highly conducting with room temperature dc electrical conductivity of about 200 S/cm.

Fourier transform infrared spectra (FTIR) of PANI powder in the doped, de-doped and re-doped forms were obtained using Bruker-Tensor 27 FTIR spectrophotometer. The UV–vis–NIR absorption

studies of the samples were performed using Jasco V-500 UV–vis–NIR (Xenon lamp) spectrophotometer. The scan rate was fixed as 200 nm/min. The PL spectra of the PANI film samples were recorded using Fluoromax 3 fluorescence spectrophotometer.

3. Results and discussion:

FTIR spectra of PANI powder shown in Fig. 1 exhibit all the reported peaks which confirm the formation of PANI in CSA re-doped form. All major peaks are listed in Table 1 given below with respective vibrations [27–30].

3.1. UV–vis–NIR spectroscopic studies

Fig. 2(a) and (b) show the UV–vis–NIR absorption spectra of PANI films having thickness 4 μm and, 50 nm, 100 nm and 150 nm. From the figures, one can see that the major absorption peak at 390 nm corresponding to the π to π^* transition in the 4 μm thick PANI film has been blue-shifted to 294 nm in the case of ultrathin PANI films with thickness 50 nm, 100 nm and 150 nm. A free-carrier absorption tail extending to the NIR region can also be seen in the absorption spectra of the 4 μm PANI thin film sample which indicates the metallic nature and the corresponding higher electrical conductivity of this sample [25]. However, such a free-carrier absorption tail is absent in the ultrathin PANI films. The blue shift of about 100 nm observed in the optical absorption spectrum of ultrathin PANI films compared

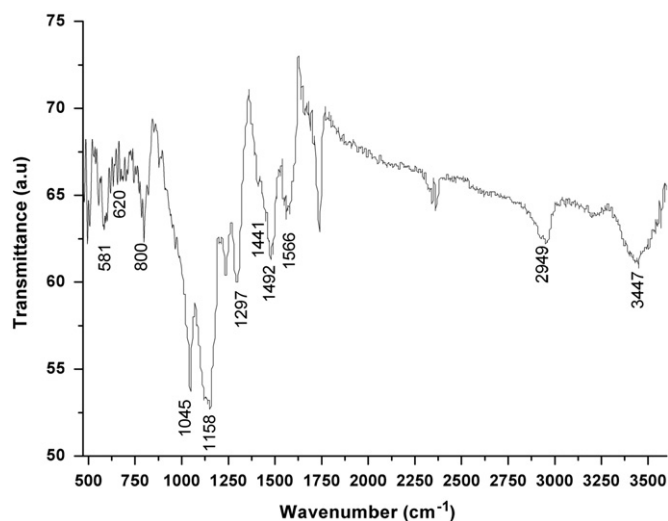


Fig. 1. FTIR spectra of CSA re-doped PANI.

Table 1
FTIR of CSA re-doped PANI.

Wavenumber (cm^{-1})	Assignment
581	S=O stretching mode [27]
800	aromatic C–H out of plane bending [27]
1045	$\text{NH}^+ \dots \text{SO}_3^-$ interaction [28]
1158	Vibrational mode of $-\text{NH}^+$ structure which occurs due to protonation of PANI [29]
1297	C–N ⁺ stretching vibration in the polaron structure (characteristic of conducting protonated form [27])
1441	C=C benzenoid ring vibration [28]
1492	Vibrational stretching of N-benzenoid ring [27]
1566	Vibrational stretching of N-quinoid ring [27]
3447	N–H stretching [30]

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