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Citation: AIP Conference Proceedings **1953**, 100070 (2018); doi: 10.1063/1.5033006
View online: https://doi.org/10.1063/1.5033006
View Table of Contents: http://aip.scitation.org/toc/apc/1953/1
Published by the American Institute of Physics

Spectroscopic Investigations Upon 100MeV Oxygen Ions Irradiation On Polyaniline And Poly-o-toluidine

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Abstract. Conducting polymers are the materials been extensively studied in the field of organic devise applications. The extended π-orbital which enables electron to move from one to another end of polymer made it flexible in tailoring different properties and therefore are known to be the considerably attractive materials. Here in this report Polyaniline (PANI) and Poly-o-toluidine (PoT) the derivative of PANI where one hydrogen atom of main polymer chain is substituted with the methyl group are studied upon irradiation with 100MeV oxygen ions irradiation at different fluences. PANI and PoT consist of interesting properties viz. electrochemical and optical properties, moderate conductivity, as well as environmental stability, may be applicable to the chemical sensing applications. Swift Heavy Ions (SHI) irradiation is the exclusively applied tool in detrimental modifications of solid materials. The effects of SHI irradiation on PANI and PoT were studied using UV – Vis spectroscopy and Raman spectroscopy. The band gap studies were done with Tauc plot calculations.

INTRODUCTION

Organic conducting polymers (OCPs) are extensively studied due to their wide range of applicability in various areas viz. energy storage, electrochemical devices, memory devices, chemical sensors, electrocatalysts etc.[1-6]. The applicability of OCPs have grabbed more attention since are having interesting characteristic properties viz. environmental stability, low cost, considerable flexibility in chemical structures that can be modified & resultantly could achieve the desired electrical conductivity, etc.[7]. Swift heavy ions (SHI) irradiation is well accepted technique in tuning various physicochemical properties of conducting polymers which is ultimately been applied in many application areas viz. chemical sensors etc.[8-10].When highly charged particles pass through the materials, the interaction of ions with solids results in energy loss to both atomic nuclei and electrons in the solid. Energy transfer to the electronic & atomic structures, and corresponding response of materials depend on the energy dissociated. For high energy ions having energy more than 1 MeV per nucleon (MeV/u), particularly for swift heavy ions (E > 50 MeV), electronic energy loss dominates, leading to intense local ionization that can cause damage production, track formation, or damage recovery and the formation of long, straight ion tracks with nanometer diameters by swift heavy ions [11]. Polyaniline (PANI) is the most interesting and well-studied amongst all OCPs, the SHI irradiation is also been explored enormously with different ions, fluences and energies. Subhash Chandra et al. has investigated that the changes induced in PANI after energy 80 MeV, O^{+7} ions irradiation are due to cross linking and formation of single and multiple helices creation of polaron and defect sites in the polymers[12]. A. Kumar et al. and Jayanta Hazarika et al. has reported nanofibers of PANI explored for 90 MeV O^{7+} ion and 160MeV Ni^{12+} ions irradiation induced variations in the vibrational spectra and structure of PANI nanofibers and concluded that there is increase in optical band-gap, crystalline domain size decreases, transformation from the benzenoid to quinoid structures as increasing irradiation fluence [13,14]. Here in this report, we investigate the effects of 100MeV O^{+7} ions irradiation on PANI and

2nd International Conference on Condensed Matter and Applied Physics (ICC 2017)
AIP Conf. Proc. 1953, 100070-1–100070-4; https://doi.org/10.1063/1.5033006
Published by AIP Publishing. 978-0-7354-1648-2/$30.00

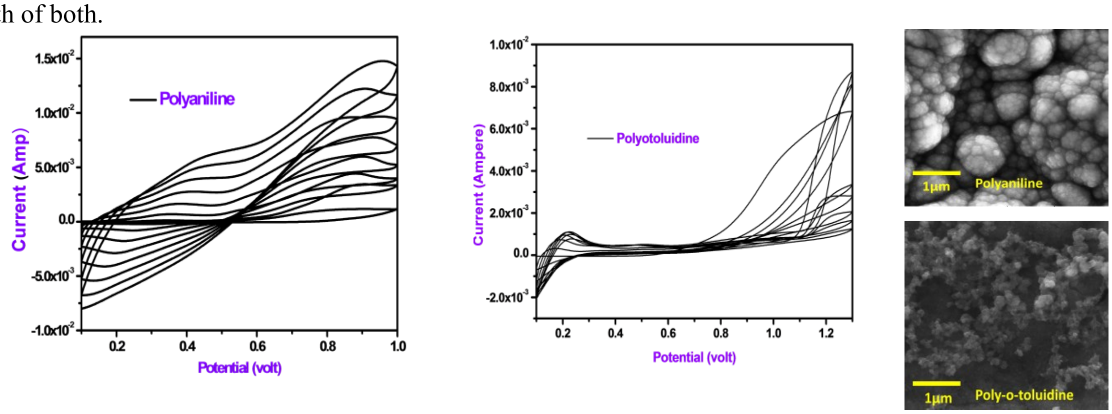
its derivative poly-o-toluidine (PoT). The investigations are carried out through spectroscopic techniques such as UV – Vis spectroscopy and Raman spectroscopy.

EXPERIMENTAL DETAILS

Synthesis of PANI and PoT was done through electrochemical route using cyclic voltammetry (CV) in single compartment assembly of three electrodes. Indium tin oxide (ITO) as working electrode, platinum as counter and saturated Ag/AgCl as reference electrode, were used in electrochemical cell. CH Instruments CH660C electrochemical workstation was used for electrochemical deposition. UV-Vis spectra were recorded using Hitachi U - 3300 spectrophotometer. Raman spectra were obtained by Seki Technotonics of make STR 150 Raman spectrometer. FE-SEM images were recorded by TESCAN, MIRA II LMH CS. The monomers aniline, o-toluidine and dopant Sulfuric acid (H_2SO_4) were purchased of reagent grade of Molychem. Monomers were distilled prior to use. All measurements were done in normal room temperature. The 15UD palletron facility available at Inter University Accelerator Centre, New Delhi (India) was used for SHI irradiation.

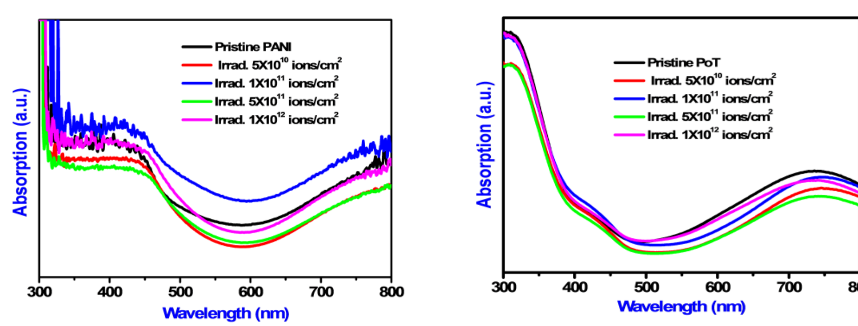
RESULTS AND DISCUSSIONS

For the deposition of PANI the dynamic potential window in CV was kept between 0.1volt-1.0volt and 0.1volt - 1.3volt for the PoT on ITO substrate. Figure 1 (a) and (b) shows the cyclic voltammogram of both PANI and PANI SWNTs. The successive cycles one after another has shown the increase in current density and simultaneously the growth on ITO substrate revealing the successful deposition of said OCPs respectively. As micrograph analysis is helpful tool in determination of morphological investigations of materials, fig. 1 (c) shows FESEM images of both PANI and PoT. Both OCPs shows well distinguished morphologies, and are also in well agreement with the successful growth of both.



(a) (b) (c)

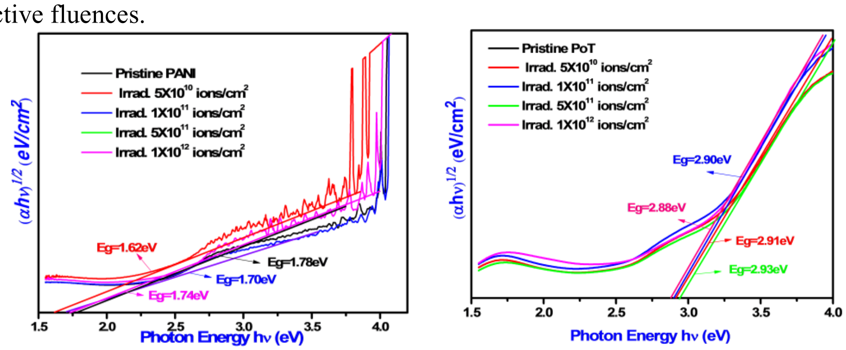
FIGURE 1 Cyclic Voltammogram for (a) PANI and (b) PoT



(a) (b)

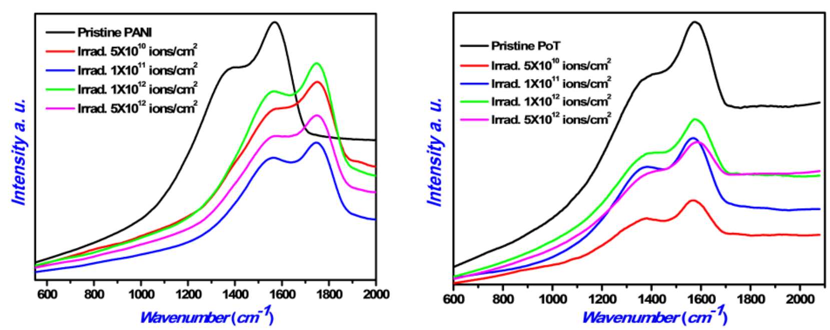
FIGURE 2 UV-Vis Absorption spectra of (a) PANI and (b) PoT before and after irradiation

The PANI and PoT were exposed for oxygen ions irradiation of 100MeV energy at four different fluences 5×10^{10} ions/cm^2, 1×10^{11} ions/cm^2, 5×10^{11} ions/cm^2 and 1×10^{12}ions/cm^2 respectively. Figure 2 (a) & (b) shows the UV-Vis absorption spectra of PANI and PoT before and after irradiation in spectral range 300nm to 800nm. The UV-Vis spectra of PANI shown in fig. 2 (a) shows the absorption peaks at ~ 320nm which is assigned to $\pi - \pi^*$ transition in the benzoid structure and increase in absorption from ~ 610 nm is attributed to exciton formation in the quinoid rings[15]. The UV-Vis spectra of PoT shown in fig. 2 (b) shows absorption peaks at ~310 nm, ~420nm, ~750nm assigned to $\pi - \pi^*$ transition of the benzenoid rings, polaron–π^* transition and π – polaron transition, respectively. The irradiation has influenced on the intensity of absorption, shows the average increase in the intensity and is the indication of decrease in band gap and results are inline calculated form Tauc relation ($\alpha h\nu = B\,(h\nu - E_g)^n$. The calculation of indirect transition energy gap, the plot of $(\alpha h\nu)^{1/2}$ as a function of photon energy versus $h\nu$ for PANI and PoT is as shown if fig. 3 (a) & (b).The optical indirect transition energies were found to be equal to 1.78eV & 1.62eV, 1.70eV, 1.71eV, 1.62eV for PANI and 2.91eV & 2.91eV, 2.90eV, 2.93eV, 2.88eV for PoT calculated for pristine and respective fluences.



(a) (b)

FIGURE 3 Variation of $(\alpha h\nu)^{1/2}$ versus $h\nu$ for (a) PANI and (b) PoT before and after irradiation



(a) (b)

FIGURE 4 Raman spectra for PANI (a) & PoT (b) before and after irradiation

The Raman spectrum shown in fig. 4 recorded for PANI and PoT before and after irradiation shows significant changes in respective spectra. The measurement was carried out in the range 600cm^{-1} to 2000 cm^{-1}. The shift observed in the band position may be caused by the mode of excitation of laser, observed in case of pristine PANI. In case of PANI there is shift in the Raman peaks after irradiation and that may be due to the breaking of the bonds and the formation of new bonds at different sites due the formation of free radicals, cations and anions after ion irradiation [16].The Raman band observed ~1600 cm^{-1} correspond to C-H in-plane [13]. It is observed that after irradiation there is decrease in the Raman bands in case of both PANI and PoT which reveals the amorphization of both.

CONCLUSIONS

The present investigation reports the electrochemical modification of ITO electrode with PANI & PoT and irradiation of 100MeV oxygen ions with four different fluences. CV during synthesis of both showed the electroactive nature of both OCPs. FESEM micrograph has illustrated the deposition of PANI and PoT. The UV – Vis absorption spectra shows the decrease in intensity and remarkably noted that there is decrease in band gap values upon irradiation of oxygen ions. The results from Raman analysis shown the amporphus nature of PANI and PoT after irradiation. It can be stated that there are notable modifications upon irradiation on OCPs and can be utilized in application areas, where the crosslinking of polymer chains and creation of defect sites make remarkable differences viz. electrochemical sensors. Modified

ACKNOWLEDGMENTS

Authors extend their sincere thanks to Inter University Accelerator Center (IUAC), New Delhi, India (UFR no. 55305) and DST - SERB, New Delhi (Project no.: SB/ EMEQ-042/2013), Rashtria Uchachatar Shiksha Abhiyan (RUSA), Government of Maharashtra, UGC – DAE – CSR - RRCAT Indore (Project no.: CSR-IC-BL66/CRS-183/2016-17/847) for providing financial support under.

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