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Dimethylglyoxime Modified Swift Heavy Oxygen Ions Irradiated Polyaniline/ Single Walled Carbon Nanotubes Composite Electrode for Detection of Cobalt Ions

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Abstract: Present communication deals with study of effect of SHI irradiation of 100MeV oxygen ions on the electrochemically synthesised polyaniline (PANI)/ single walled carbon nanotube (SWNTs) composite electrode. PANI/SWNTs composite was used for the modification of stainless steel electrode. The composite was irradiated with fluences $1x10^{10}$ ions/cm^2, $1x10^{11}$ ions/cm^2 and $1x10^{12}$ ions/cm^2 of oxygen ions having energy 100 MeV. Electrochemical techniques viz. cyclic voltammetry (CV) and electrochemical impedance spectroscopy (EIS) were used to study the electroactive nature of composite before and after irradiation. Morphological study was carried out using Field Electron Scanning Electron Microscopy (FESEM) and Transmission Electron Microscopy (TEM). Composite matrix irradiated with fluence $1x10^{10}$ ions/cm^2 had shown good electroactive nature and therefore was used for analytical application viz. electrochemical detection of divalent cobalt ions. The irradiated PANI/SWNTs composite was modified by chelating ligand viz. dimethylglyoxime (DMG) to ensure the selectivity of metal ion viz. Co(II). The electrode (DMG modified SHI irradiated PANI/SWNTs composite) could detect the lowest concentrations to 0.355 μML^{-1}or 0.1 mgL^{-1} which is equal to Maximum Contaminant Level (MCL) of cobalt ions proposed by U.S. EPA. The analytical behaviour of electrode has proved the SHI irradiation as suitable tool for modification of organic conducting polymers (OCP)/ SWNTs composite.

Keywords: Polyaniline, SWNTs, electrochemical synthesis and characterization, SHI irradiation, detection of divalent cobalt ions.

1. Introduction:

Composites are to entangle the superlative properties of two materials such that the combination of both can perform relatively comprehensive. Organic conducting polymers (OCPs) are well investigated materials since they possess extraordinary properties such as ease in synthesis and the modulation of conductivity from conducting to insulating regime. Moreover, the properties viz. environmental stability, ease of processability, etc. made OCPs much popular materials for various applications. However, charge carrier mobility in OCPs is not encouraging and therefore need to be improved such that it can be employed for the efficient devices [1, 2]. Carbon nanotubes (CNTs) are being exposed to reinforce the OCPs matrix, since it possesses high flexibility, low mass density, large aspect ratio, a unique combination of mechanical, electrical, and thermal properties. Many theoretical and experimental results confirm that SWNTs are excellent materials for various applications [3]. In the progressive improvement of OCPs, SWNTs can play a vital role as a backbone for transduction mechanism. The OCPs can be used for non-covalent functionalization of SWNTs which involves the physical adsorption and/or wrapping of polymers on to the surface of the SWNTs. On one hand, the graphitic sidewalls of SWNTs provide the possibility for π-stacking interactions with conjugated polymers. On the other hand, grafting of polymer chains to the SWNTs, which resultantly gives the relatively low reactivity and high steric hindrance of macromolecules [4]. In approach to develop chemical sensor based on OCPs, the non – covalent modification of SWNTs can perform better [5]. Many researchers have reported composites of CNTs and OCPs for the detection of metals ions, showing the improved sensitivity upon inculcation of CNTs [6,7,8,9,10]. In present investigation, the composite of PANI/ SWNTs was synthesised electrochemically and was

used as a electrochemical sensor for detection of heavy metal ions viz. divalent cobalt ions up to its lower detection limit. Improvement in selectivity and sensitivity of the electrode was the main emphasis of the present investigation.

Swift heavy ions (SHI) irradiation is most acceptable tool in modification of physical and chemical properties of conducting polymers. For the ions of energy $E < 0.5$ MeV where the energy is transferred to the atomic nuclei which causes the nuclear energy loss through elastic scattering collisions between atomic nuclei in ballistic collision cascades. In case of SHI $E > 50$ MeV, electronic energy loss dominates, leading to intense local ionization that can cause track formation and the formation of long, straight ion tracks with nanometer diameters [11]. In modification of different physical and chemical properties of PANI many researchers have suggested SHI as effective tool for tuning various properties. A. M. P. Hussain et al have irradiated the 160MeV Ni^{12+} [12] and 120MeV Si^{9+} [13] ion beam on electrochemically synthesised PANI, and observed cross linking of polymer chains, bond breaking and creation of defects sites, increase in crystallinity, conductivity. They have claimed that irradiation plays important role in tuning the charge – discharge characteristics of polymer giving rise to *enhanced stability of the supercapcitors*. Somik Banerjee et al. have reported the effects of 90 MeV O^{7+} ions on nanofibres of PANI for optical [14] and structural [15] studies which revealed that there is transition of benzenoid to quinoid states of polymer chains which is attributed to the decrease in the degree of conjugation and the reduction in the fibre diameters. The dielectric properties of polyaniline nanotubes were studied upon irradiation of 160 MeV Ni^{12+} [16] and observed significant changes in dielectric and electrical properties with *the increase in carrier concentration* and structural modifications in the polymer films. A. Kumar et al have investigated the antioxidant activity and biocompatibility of irradiated PANI nanofibers and ultimately claimed that SHI irradiation is *useful technique in modification of nanostructured forms of polymers* [17, 18].

In summary SHI irradiation is one of the effective tool for tailoring the properties of the material of desired application. The analytical determination of metal ions has been an important task in order to measure the concentration levels. The metal ions such as iron, cobalt, zinc, copper, manganese, etc. are essentially required for the living organisms; in the biological functioning of cells such as transportation and cell signalling at optimum concentration level and can cause the threats to life if exceeded above threshold level. The threshold levels of toxicity of the metal ions is being regulated by worldwide regulating authorities viz. World Health Organization (WHO), Environmental Protection Agency (EPA) [19]. There are some conventional approaches in determination of cobalt ions such as voltammetric approach employing adsorptive stripping techniques using the mercury film electrodes [20]. Different extraction and pre-concentration materials have been explored viz. biosorbent based on the modification of miswak fibers by NaOH [21] to develop the simple, rapid, inexpensive method. However Baban Kumar Bansod et al has reviewed that the electrochemical detection techniques for heavy metal ions are user friendly, low cost, provides on-site and real time monitoring as compared to any other spectroscopic and optical techniques [22].

The present investigation has demonstrated the wrapping of PANI onto the surface of SWNTs called PANI/SWNTs composite. The composite was irradiated with 100 MeV O^{7+} ion beam at fluences $1x10^{10}$ ions/cm^2, $1x10^{11}$ ions/cm^2 and $1x10^{12}$ ions/cm^2. The influence of SHI irradiation was studied with electrochemical, optical and morphological characteristics. The fluence $1x10^{10}$ ions/cm^2 has shown remarkable electrochemical characteristics and therefore the sensing characteristics of same electrode were studied in detection of Co(II) ions.

2. Experimental:

2.1 Reagents

Monomer aniline was purchased from Fisher Scientific. Dopant sulphuric acid (H_2SO_4) sodium hydroxide (NaOH), dimethylglyoxime (DMG) and cobalt (II) sulphate (heptahydrate) were purchased from Molychem. Single Walled Carbon Nanotubes (functionalised with COOH group) were purchased from Nanoshel LLC-Wilmington, DE, USA. Surfactant dodecyl benezene sulphonic acid sodium salt (DBSA) of laboratory grade was purchased from Kemphasol. Stainless steel (SS 304) was purchased from Jindal stainless steel, India. The solution of divalent cobalt ions was prepared by dissolving 1gm of cobalt (II) sulphate into buffer solution having pH equal to 7 – called stock solution. For electrochemical characterizations viz. cyclic voltammetry (CV) and electrochemical impedance spectroscopy (EIS) 0.5 M H_2SO_4 was used as supporting electrolyte.

2.2 Instruments

Electrochemical synthesis and characterizations were done using electrochemical workstation CH Instruments CH660C (CHI, USA). A single compartment three electrode cell assembly was used; platinum, stainless steel and saturated Ag/AgCl electrodes were used as counter, working and reference electrode. Micrographs of composite were recorded before and after irradiation using field emission scanning electron microscope TESCAN, MIRA II LMH CS. Raman spectra were obtained by STR 150 Raman spectrometer (Seki Technotonics). Swift heavy ions irradiation was done using 15UD palletron facility available at Inter University Accelerator Centre, New Delhi (India). Oxygen ions 100MeV beam having charge state +7, and beam current 0.5pnA were kept while irradiation. At three fluence rates viz. $1x10^{10}$ ions/cm^2, $1x10^{11}$ ions/cm^2 and $1x10^{12}$ ions/cm^2. composite was irradiated.

2.3 Electrolyte Preparation

Monomer aniline with 0.5 M and dopant with 1 M H_2SO_4 in DI water was used for electrolyte solution. The suspension of SWNTs was prepared in 1 ml DBSA solution. The proportion of SWNTs & DBSA was 1:10 and proportion of SWNTs decided w. r. t. wt% of monomer and is taken of 10 wt%. The suspension was kept for 4hrs ultra-sonication and then poured into the electrolyte solution and kept for continuous stirring for 20 min.

2.4 SHI Irradiated Composite Electrode Modification

Dimethylglyoxime (DMG) was used for the modification of SHI irradiated PANI/SWNTs composite. DMG solution was prepared in distilled water having 0.1 M NaOH and 0.2 M DMG, with continuous stirring. The irradiated composite electrode was kept in DMG solution for four hours with constant stirring rate (350 rpm). After dipping of four hours electrodes were rinsed with distilled water and kept for air drying at normal room temperature.

3. Results and Discussions:

3.1 Electrochemical synthesis and analysis of PANI/SWNTs composite

3.1.1 Synthesis

In the synthesis of PANI/SWNTs composite electrochemical cyclic voltammetry technique was used. The synthesis was performed at normal room temperature. The dynamic potential window was swept between 0.1 volt to 1.0 volt with scan rate 0.1 volt/sec *vs.* saturated silver/silver chloride reference electrode (Ag/AgCl). The preferred numbers of cycles were equal to 15, over each cycle a change in colour was observed while deposition on the working electrode SS green to its dark shade. After each successive cycle, an increase in current density was observed (fig. 1) revealing the electroactive nature of synthesized

composite PANI/SWNTs. Reduction and oxidation potentials were observed to be at 0.4 volt, 0.3 volt and 0.55 volt respectively.

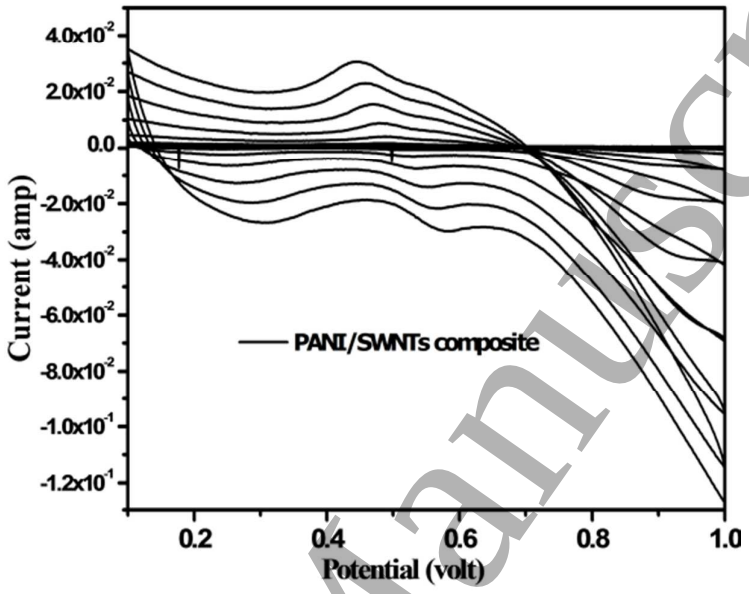

Figure 1. Electrochemical synthesis of PANI/SWNTs composite

3.1.2 Cyclic Voltammetry

In the electrochemical analysis, redox states of PANI/SWNTs are typically studied using CV technique [23]. Figure 2 shows the voltammograms of pristine and irradiated composites at different fluences. The measurements were taken in electrochemical cell containing 0.5 M H_2SO_4 as supporting electrolyte with potential window from 0.1 volt to 1.0 volt with scan rate 0.1 volt/sec, potentials applied were against saturated Ag/AgCl reference electrode. The clear oxidation peak observed at 0.24 volt and reduction at 0.55 volt, the peak oxidation & reduction current was significantly increased after irradiation. Regarding increase in current density after irradiation, fluence $1x10^{10}$ ions/cm^2 has more current density than other two fluences viz. $1x10^{11}$ ions/cm^2 and $1x10^{12}$ ions/cm^2. This revealed that there is improvement in the electroactive nature of composite after irradiation of 100 MeV oxygen

ion. The electrochemical behaviour of materials is dependent on many parameters including the applied potential, the choice of material and the surface area of the electrodes, composition of the electrolyte, and temperature [24]. In spite of having similar experimental conditions for pristine and irradiated sample, we could observe improved electroactive nature in case of irradiated samples.

In case of conducting polymers the inter-chain electron hopping is responsible for conduction between chains of polymer molecules which is reduced due to cross linking of polymer chains upon SHI irradiation. Defect sites induced due to irradiation in the molecular structure of the polymer chains may lead to the higher conductivity as charge accumulation occurs at defected sites. The increase in current density observed after SHI irradiation for fluence 1x 10^{10} ions/cm^2 may be resulted due to maximum accumulation of charges at the defect sites producing charge carriers polarons than any other fluences studied herein.
This indicates that SHI irradiation was responsible for having improvement in the conductivity of the PANI/SWNTs composite. Amongst all fluences 1x10^{10} ions/cm^2 has shown maximum current density of the composite and therefore can be considered as most electroactive electrode.

3.1.3 Electrochemical Impedance Spectroscopy

Electrochemical impedance spectroscopy (EIS) is an effective tool to investigate the interfacial properties of electrode and electrolyte. EIS plays very important role in the characterization of sensors. Many fundamental characteristics can be stated viz. adsorption/film formation, rate of charge transfer, ion exchange, diffusion, etc which occur at the electrode–electrolyte interface [25]. Figure 3 shows the Nyquist plots of pristine and irradiated PANI/SWNTs composite. A semicircle gives the information about the charge-

transfer-controlled process; the appearance of semicircle is ascribed to the fact to the charge transfer [26].

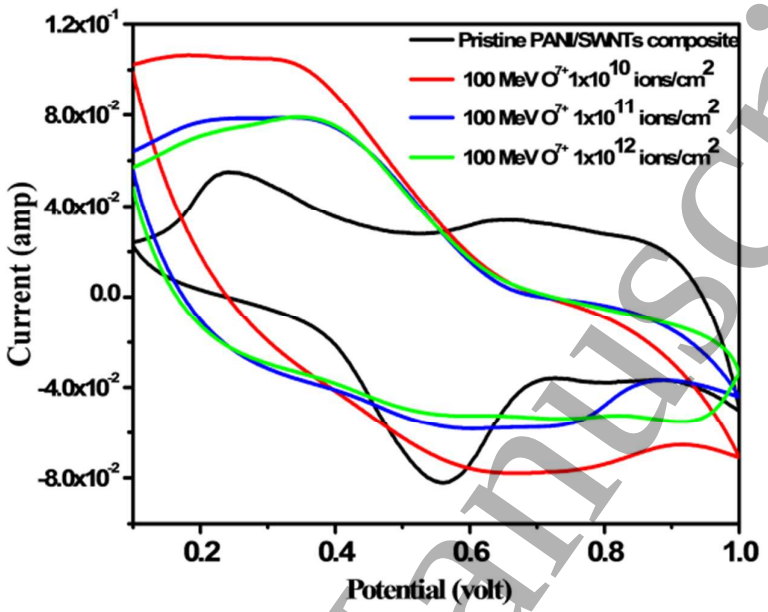

Figure 2. Cyclic voltammogram for PANI/SWNTs composite before and after irradiation

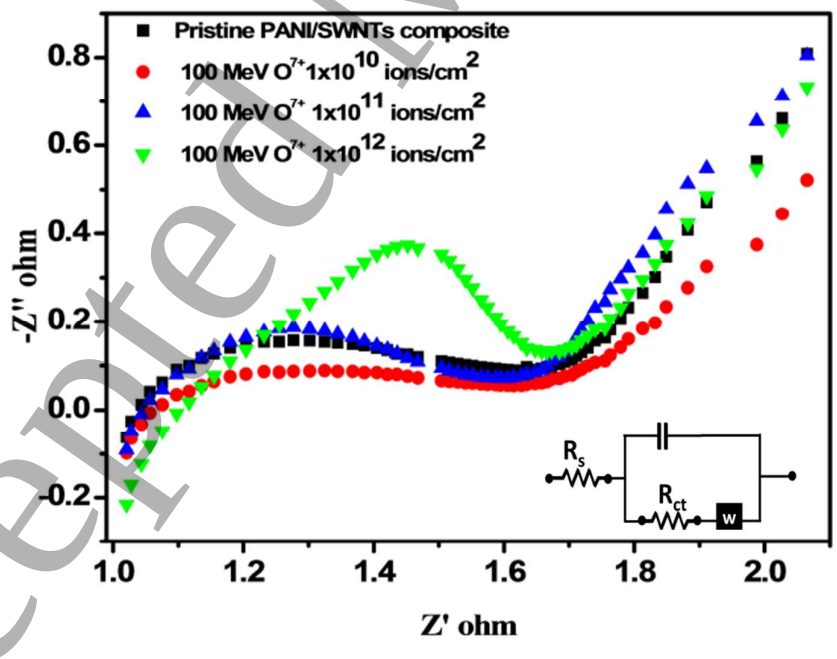

Figure 3. Electrochemical impedance spectra of PANI/SWNTs composite before and after irradiation

The inset displayed in fig 3 shows Randles equivalent circuit used to fit Nyquist diagrams. It comprises solution resistance (R_s), constant phase element (Q), charge transfer resistance (R_{ct}) and Warburgh impedance (Z_w) respectively. The R_{ct} value was found to be lower for $1x10^{10}$ ions/cm^2 (0.42 Ω) in comparison with pristine PANI/SWNTs composite (0.61 Ω) and other two fluences $1x10^{11}$ ions/cm^2 (0.76 Ω) and $1x10^{12}$ ions/cm^2 (0.88 Ω). The lowest R_{ct} value obtained for oxygen ion irradiated ($1x10^{10}$ ions/cm^2) composite is related to the fact that SHI irradiation has resultantly enabled the high interfacial electron transfer ability to the composite.

3.2 Structural and morphological studies of pristine and irradiated PANI/SWNTs composite

3.2.1 Raman Spectroscopy

The structural characteristics of PANI/SWNTs composite before and after irradiation were studied using Raman spectroscopy. Figure 4 shows the Raman spectra recorded in range 500 cm^{-1} - 3000 cm^{-1}, broadly it can be stated that the intensity of peaks got decreased upon irradiation. Somik Banergy et al. reported that the conformational modifications in the OCP matrix can be drawn from the changes observed at the low wave numbers. We could observe decreased intensity in case of irradiated composite, especially at low wave number ~500 cm^{-1} to ~700 cm^{-1}, this indicates the changes in crystallinity arrangements and resultantly there is increase of the torsion angles of the C_{ring}–N–C_{ring} segments. This is due to the loss of π-staking of the polymer chain which leads to the amorphization of the matrix. This means that the energetic ions irradiated onto the composite had the great impact through electronic interaction with C-N site of PANI. The peak 1353 cm^{-1} indicated C-N$^+$ stretching modes of the delocalized polaronic charge carrier and 1609 cm^{-1} shows symmetric C-C stretching [15].

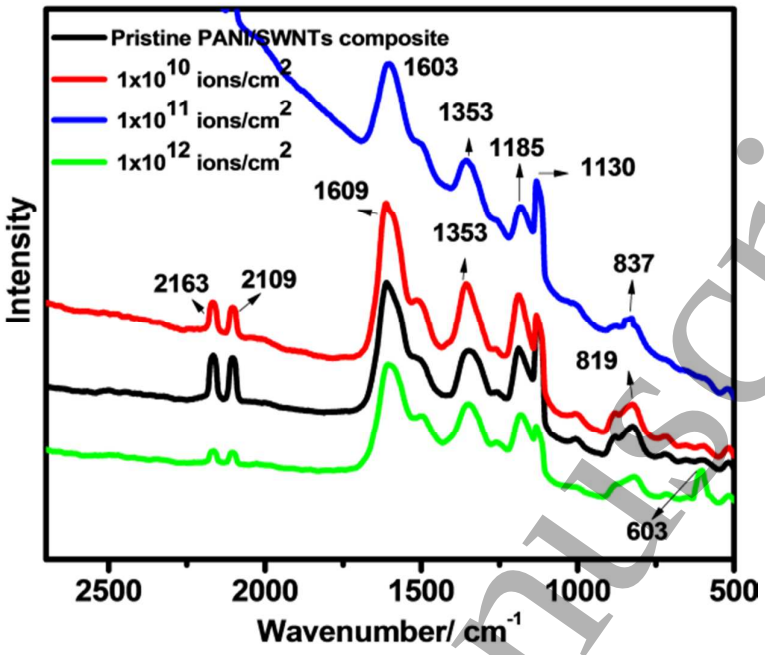

Figure 4. Raman spectra of PANI/SWNTs composite

3.2.2 Field Electron Scanning Electron Microscopy (FE-SEM) and Transmission Electron Microscopy (TEM)

Figure 5 shows the morphological characterizations, FE-SEM (a, b, c, d), TEM (a_1, b_1, c_1, d_1) and SAED (Selected Area Electron Diffraction) pattern (a_2, b_2, c_2, d_2) of pristine PANI/SWNTs composite and irradiated with 100 MeV oxygen ions with fluences $1x10^{10}$ ions/cm^2, $1x10^{11}$ ions/cm^2 and $1x10^{12}$ ions/cm^2. A. Kumar [17] reported that as conducting polymers are semiconducting, the Coulomb explosion model (the intense ionization and excitation along the ion path leads to an unstable zone in which atoms are ejected into the non-excited part of the solid by Coulomb repulsion) is more appropriate to describe the generation of strains in the PANI nanofibers grains upon SHI irradiation.

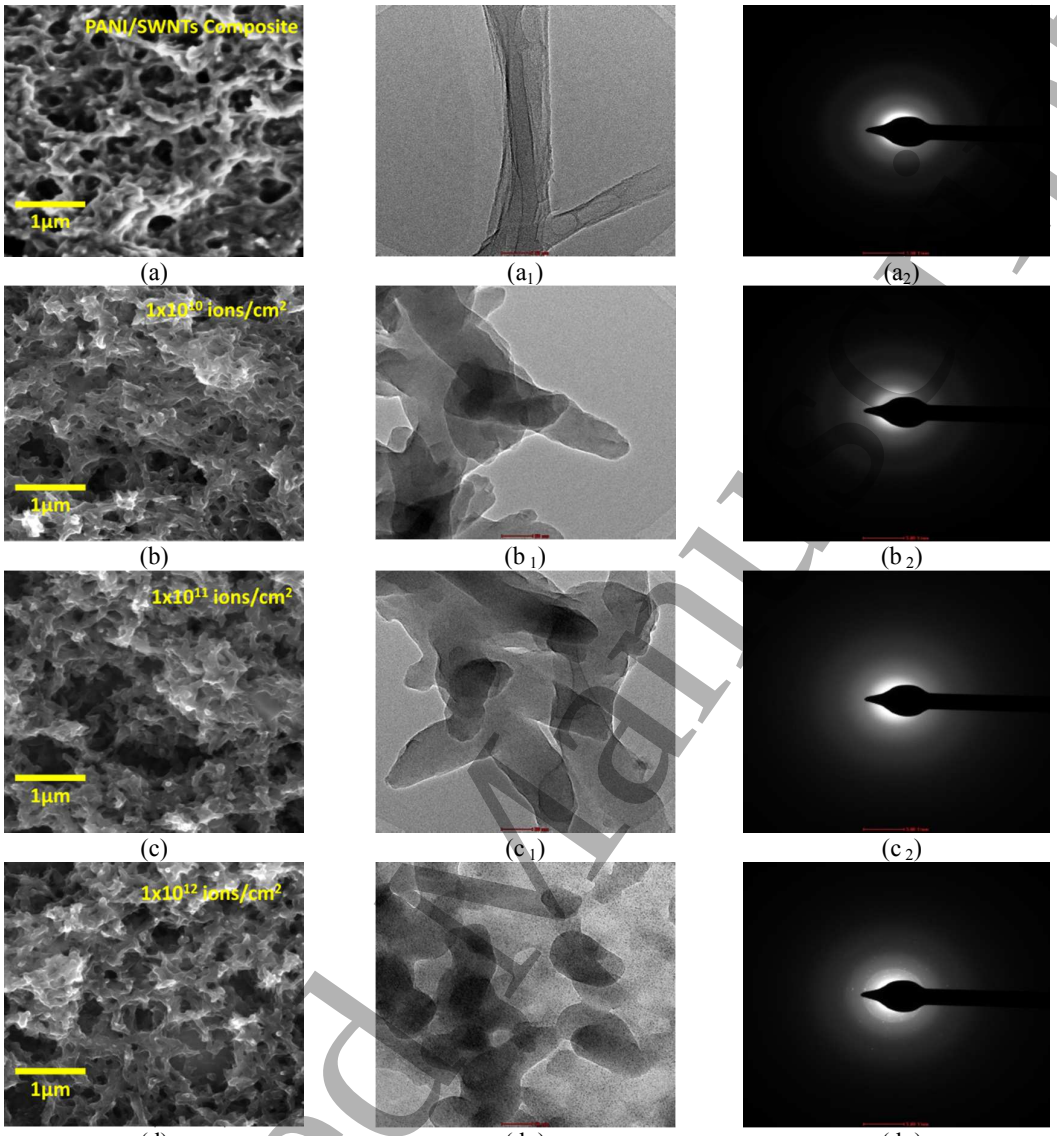

Figure 5. Effects of 100 MeV oxygen ions irradiation on PANI/SWNTs composite pristine and with fluences 1x10^{10} ions/cm^2, 1x10^{11}ions/cm^2 and 1x10^{12} ions/cm^2 FESEM (a,b, c, d) TEM (a_1, b_1, c_1, d_1) SAED pattern (a_2,b_2, c_2, d_2) respectively

When the fluence of ions irradiation was increased the dense micrographs were observed (fig. 5 a, b, c, d). The fragmentation of composite could be well elaborated through the TEM (fig. 5 a_1, b_1, c_1, d_1) images. The corresponding SAED pattern (fig. 5 a_2, b_2, c_2, d_2) shows the appearance of only two low intensity diffused rings which suggests that the composites are in amorphous phase. In summary, it can be concluded that the irradiation has

introduced fragmentation and the increase in the fluence has impact on the length of the composite.

3.3 Detection of Co(II) ions on DMG modified Oxygen ions irradiated PANI/SWNTs Composite electrode

In the process of electrochemical detection of heavy metal ions anodic stripping voltammetry (ASV), cathodic stripping voltammetry (CSV) and adsorptive stripping voltammetry (AdSV) are the techniques which are involved very conventionally having rest step, deposition step and then stripping step. The stripping step can be opted from linear, staircase, squarewave, or pulse voltammetry. Herein, we report the detection of Co(II) ions with differential pulse voltammetry (DPV) technique. Different parameters such as potential range (V) = -1.48 to -1.2, amplitude (V) = 0.05, pulse width (sec) = 0.05, sensitivity (A/V) = 0.01, respectively with sensitivity 10mA/V were applied while measurements.

The modification of oxygen ions irradiated PANI/SWNTs composite with DMG has allowed selective accumulation of ions onto the surface of composite electrode, which can be directly analysed, neglecting the rest and deposition steps from conventional methods of electrochemical detections of heavy metal ions. PANI/SWNTs composite irradiated with fluence $1x10^{10}$ ions/cm^2; from CV and EIS it has been found more electroactive and therefore was involved for detection of divalent cobalt ions. Figure 6 (A) indicated the suitable composite electrode which is irradiated with fluence $1x10^{10}$ ions/cm^2 and modified with DMG; which has demonstrated the good sensitivity for the Co(II) at concentration 0.355 μML^{-1}.

Figure 6 (B) shows the DPV response of electrode with different concentrations to (b) 1 gm/10000 lit (0.355 μML^{-1}), (c) 1 gm/5000 lit (0.711 μML^{-1}), (d) 1 gm/1000 lit (3.5 μML^{-1}), (e) 1 gm/100 lit (35 μML^{-1}). The lowest detection limit achieved by the

electrode was 0.36 μM/L^{-1}. The U.S. EPA (United States Environmental Protection Agency) has given maximum contamination limit for it is 0.1 mg/lit (0.355 μM/L^{-1}). This lower detection limit was achieved through the DMG modified oxygen ions irradiated PANI/SWNTs composite, since irradiation facilitated high surface defects and better electron transfer rate.

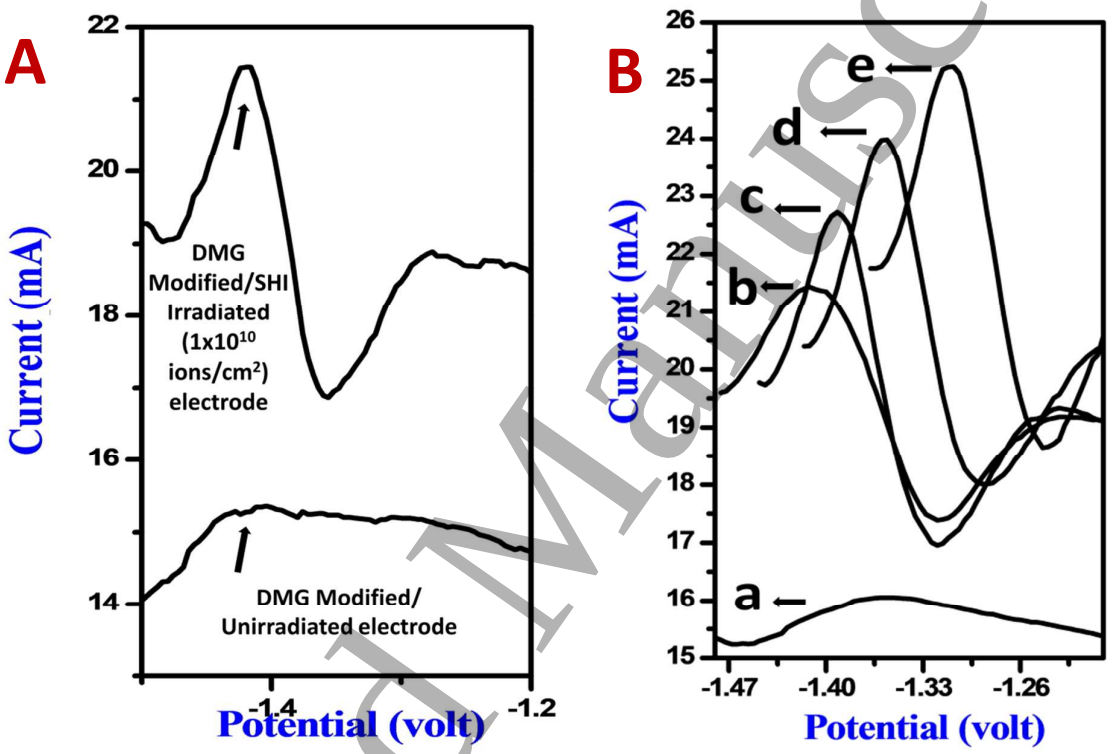

Figure 6. (A) DPV response of DMG modified/ unirradiated composite electrode and DMG modified/ SHI irradiated with fluence 1x10^{10} ions/cm^2 *composite electrode of PANI/SWNTs with the concentration of Co(II) ions 0.355 μML^{-1} (B) DPV response of DMG modified/ SHI irradiation with fluence* 1x10^{10} ions/cm^2 composite electrode *before accumulation of Co(II) ions(a) and for different concentrations viz. 0.355 μML^{-1} (b), 0.711 μML^{-1}(c), 3.5 μML^{-1} (d), 35 μML^{-1}(e)*

4. Conclusions:

The electrochemical synthesis of PANI/SWNTs was successfully carried out. The composite was irradiated with oxygen ions of energy 100 MeV. There were significant SHI irradiation assisted changes on electrochemical and morphological characteristics of the

PANI/SWNTs composites. The electrochemical studies revealed that fluence $1x10^{10}$ ions/cm^2 is optimum for composite electrode and is more suitable for the electrochemical detection of Co (II). The SHI irradiated composite was further modified by DMG. The DMG modified PANI/SWNTs electrode exhibits excellent sensing for detection of Co (II) ions. The lowest detection limit of the sensor was found equal to 0.355 μML^{-1}.

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