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# Preparation and characterization of prospective disulfide based electrode materials for lithium batteries

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**Abstract:** Organic disulfide compounds are having higher theoretical capacity than the conventional cathode material and are considered as the important storage material. Here, we are reporting the preparation of poly (2,2'-dithiodianiline) PDDA/multiwall carbon nanotubes, (MWCNTs) composites under different experimental conditions. Amine functionalized and unfunctionalized MWCNTs were independently used for the preparation of composites. Composites were prepared in the presence of cetyl trimethyl bromide (CTAB), a cationic surfactant, and also in the absence of CTAB. A physical mixture of PDTDA and MWCNTs was formed with unfunctionalized MWCNTs. Grafting of PDDA onto MWCNTs was performed by chemical oxidative polymerization of 2, 2'-dithiodianiline in the presence of amine functionalized MWCNTs. The composites of MWCNTs and PDTDA were characterized for structure, morphology and thermal properties through Fourier transform infrared spectroscopy, Fourier transform Raman spectroscopy, scanning electron microscopy and UV-visible spectroscopy. The composite materials prepared by this method are expected to find applications as electrode materials for lithium batteries.

**Key words:** 2,2'-dithiodianiline, chemical oxidative polymerization, cathode materials

## 1. Introduction

The development of low-cost, solid-state rechargeable batteries is attracting technological importance. A key development in this stride is to develop material that would give high energy density as electrodes in electrochemical storage devices. In this consideration, the use of organic materials having high theoretical energy storage capacity, low weight and good mechanical strength has attracted attentions. Disulfide compounds have been introduced as a new organic/polymer cathode material in lithium batteries.[1-4] A series of compounds having –SH groups within the molecules are being considered as energy storage materials. The energy exchange occurs through cleavage and recombination of S–S bonds. The kinetics of the process is slow.

To promote the rate of cleavage-recombination process, two approaches are generally considered. In the first approach, a suitable catalyst is used to enhance the redox of disulfides at an ambient temperature. In this regards electropolymerized polyaniline (PANI) has been used as an efficient electrocatalyst to accelerate the relatively slow redox properties of

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2,5-dimercapt-1,3,4-thiadiazole, DMCT.[5-7] In the second approach, higher energy density was obtained by using polysulfide.[8] The S linkage recombination efficiency can be improved when the material has a confined polymer structure or conformation interconnected with S–S bonds.

Poly(2,2’-dithiodianiline) (PDTDA), a substituted PANI having interconnected S-S bonds, has been synthesized by Naoi *et al.*[9] Several reports are available on the synthesis of poly(2,2’-dithiodianiline) and its copolymers.[9-13] PDTDA can be synthesized as an electro-active thin film by cycling the potential during electropolymerization. The discharge capacity and the energy density of the unit cell using the PDTDA as an active material of cathode were 270 Ah/kg and 675 Wh/kg, respectively.[14] Reports on the preparation of nanostructures of PDTDA are scarce.

Carbon nanotubes (CNTs), one of fundamental block in nanotechnology, have a novel structure, a narrow distribution of size, high surface area, low resistivity, high stability.[15] Based on the unique and excellent physical properties of CNTs, many structural and smart applications of them have been proposed.[16] Polymer/carbon nanotube have attracted much attention, since they were introduced by pioneers like Ajayan *et al.*[17] The polymer/CNTs nanocomposites are finding several applications. However, the challenges for developing high performance CNTs/polymer nanocomposites are: (i) homogeneous dispersion of CNTs in the matrix and (ii) strong interfacial interactions so as to effect efficient load transfer from the polymer matrix to the CNTs. In the past decade, there has been an increasing interest in the studies of polymer/CNTs nanocomposites due to the unique combination of promising properties and construction of multifunctional structures of each component.[18-23]

Poly(2,2’-dithiodianiline) (PDTDA), a substituted PANI having interconnected S-S bonds, has been used as a cathode material in lithium batteries. Exploiting the unique and excellent physical properties of CNTs, many functional materials in the form of polymer/carbon nanotubes have been prepared. We are reporting few synthetic strategies to prepare CNT-PDTDA in the process of improving the performance characteristics of PDTDA. To the best our knowledge, this is the first attempt to make nanocomposites based on PDTDA. We believe that the present study would open-up methodologies to prepare functional materials for using as cathode in lithium batteries.

In the present study, we are reporting few synthetic strategies to prepare carbon nanotube/PTDA composites. While chemical oxidative polymerization was used for the preparation of composites, synthetic strategies were evolved by using unfunc- tionalized MWCNTs and amine functionalized MWCNTs. Also, polymerization conditions were used involving a surfactant. Thus, MWCNTs/PDTDA composites were prepared by performing chemical oxidative polymerization with unfunctionalized/amine functionalized MWCNTs in the presence/absence of cetyl trimethyl ammonium bromide (CTAB) as the surfactant. The morphological and structural properties of the MWCNTs/PDTDA composites prepared under these conditions are compared.

## 2. Experimental

### 2.1. Chemicals

2,2’-dithiodianiine (DTDA), MWCNTs-DBSA, ammonium persulfate, cetyl trimethyl ammonium bromide (CTAB) and hydrochloric acid were analytical grade samples and used as received.

### 2.2. Synthesis of MWCNT/PDTDA composites

Composites of MWCNTs and PDTDA were prepared with $-NH_2$ functionalized/unfunctionalized MWCNTs in the presence/absence of CTAB.

#### 2.2.1. Preparation of MWCNT/PDTDA composites with unfunctionalized MWCNTs:

MWCNTs/PDTDA composites were prepared in the presence/absence of CTAB medium. A typical procedure for the preparation of composite in the presence of CTAB is outlined. A 5 % solution of DTDA was prepared in 1M HCl (aqueous) by heating to 80 °C. 20 mg of un-functionalized MWCNTs were added to an aqueous solution of 0.01M CTAB and the solution was sonicated for 30 min. The two solutions were mixed and stirred well. Ammonium peroxydisulfate (APS) was used as the oxidant. The oxidant solution was slowly added to the reactant mixture with vigorous stirring. Then, the reaction mixture was agitated continuously for 12 h at 70 °C. The precipitate was collected and dried at vacuum oven. MWCNTs/PDTDA composites were also prepared in the absence of CTAB by using a solution of unfunctionalized MWCNTs in the second stage of solution preparation.

### 2.2.2. Preparation of MWCNT/PDTDA composites with –$NH_2$ functionalized MWCNTs:

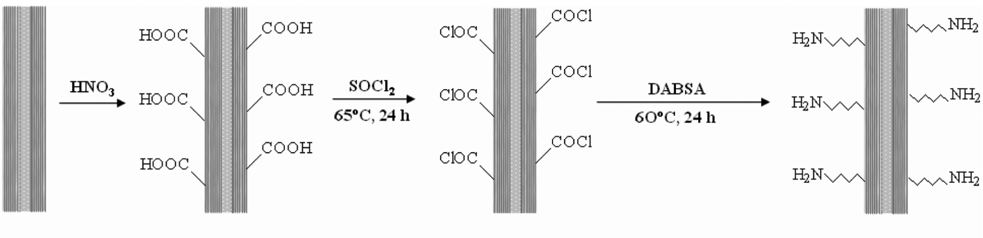
Here again, MWCNTs/PDTDA composites were prepared in the presence/absence of CTAB medium. A similar procedure as described for the unfunctionalized MWCNTs was used instead of the use of –$NH_2$ functionalized MWCNTs .

## 3. Results and Discussion

### 3.1. Formation of MWCNT/PDTDA composite:

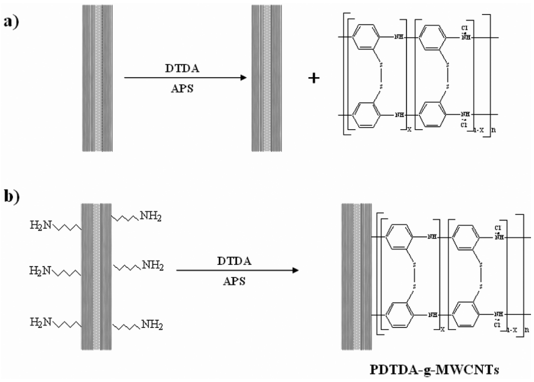
Composites of PDTDA and MWCNTs were prepared by chemical oxidative polymerization with pristine MWCNTs and amine functionalized MWCNTs, independently. And, preparation of the composites was done in the presence of CTAB. Amine functionalized MWCNTs (MWCNTs-$NH_2$) was prepared using sequential steps as listed in *Scheme* 1. The steps involvedin the formation –COOH and –COCl functionalization of MWCNTs are presonted (*Scheme* 1). There are structural variations in the MWCNT/PDTDA composites prepared with the above conditions. Our main objective of the present investigation is to identify the differences in structural and morphological properties between the composites prepared in the above mentioned conditions.

Firstly, let us analyze the formation mechanism of the PDTDA composites with amine functionalized and unfunctionalized MWCNTs. During oxidative polymerization of DTDA, upon addition of APS, dithiodianiline cation radicals are expected to be formed which may be transformed into PDTDA through dimerization and subsequent polymerization reactions.[9,10] However, in the presence of unfunctionalized MWCNTs, the PDTDA may be intermixed with MWCNTs to results physical blend of MWCNTs and PDTDA (*Scheme* 2). In the case of polymerization of DTDA with the presence of amine functionalized MWCNTs, a different type of composite is expected to be formed. In the initial stages of oxidation, simultaneous oxidation of amine sites at MWCNTs-$NH_2$ and amine units in DTDA is possible. The cation radicals thus generated from MWCNTs-$NH_2$ and DTDA can interact to nucleate grafting of PANI chains onto MWCNTs (*Scheme* 2). We anticipate that simultaneous oxidation of amine units in MWCNTs-$NH_2$ and DTDA could happen in our system. This could cause a cross-reaction between oxidized amine groups in MWCNTs-$NH_2$ and cation radicals form DTDA. As a result, the formation of PDTDA grafted MWCNT composite is expected. The formation of MWCNTs/PDTDA composites in the presence of pristine and amine functionalized MWCNTs is schematically presented [*Scheme* 2].

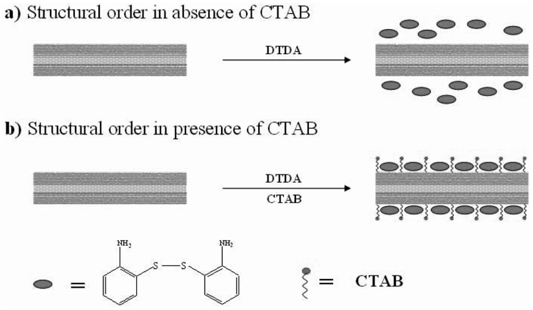


DABSA = Diamino benzene sulphonic acid

*Scheme* 1: Amine Functionalization of MWNTs.



*Scheme* 2. Formation of different types of composites between PDTDA and MWCNTs in the presence of a) unfunctionalized MWCNTs and b) amine functionalized MWCNTs.



*Scheme* 3. Formation of structural order in DTDA in the presence of CTAB.

We have also prepared the MWCNTs/PDTDA composites in the presence of CTAB. The surfactant CTAB is expected to play an important role in the synthetic pathway. CTAB has two important roles in the preparation of the composites. CTAB initially debundles the CNTs into individual tubes during sonication process before the oxidative polymerization. Secondly, CTAB is adsorbed onto backbone of CNTs backbone and arranged at the surface in the regular pattern [*Scheme* 3]. DTDA in HCl forms DTDA-hydrochloride (HCl) and adsorbed at the surface of CNTs and arranged with CTAB in an ordered structure [*Scheme* 3]. DTDA-HCl molecules may also exist in solution before polymerization. Upon addition of APS, a precipitate is formed (CTAB-$S_2O_8^{2-}$ complex) due to electrical neutralization between quaternary ammonium cation of CTAB and peroxy disulphate anions ($S_2O_8^{2-}$). Hence, the adsorbed CTAB onto MWCNTs is deactivated and the oxidized amine sites in DTDA that is present on the surface of CNTs could have possibilities to interact with DTDA molecules in solution. Thus, the formation mechanism of MWCNTs/PDTDA in the presence and absence of CTAB would be entirely different.

In the case of MWCNTs/PDTDA composites formation with unfunctionalized MWCNTs, the oxidized DTDA molecules at the surface of CNTs and in solution could undergo polymerization reaction to results a physical mixture of MWCNTs and PDTDA. However, the physical mixture of MWCNTs and PDTDA formed in the presence of CTAB may have a different morphology in comparison to physical mixture of MWCNTs and PDTDA formed in the absence of CTAB. In the case of MWCNTs/PDTDA, physical mixture formation with CTAB in the medium, and debuilding of CNTs into individual nanotube and preferential adsorption of DTDA-HCl molecule onto the surface of CNTs occur prior to polymerization. As a result, an intimately mixed composite of PDTDA and MWCNTs is expected in the presence of CTAB.

Turning back to the formation of MWCNTs/PDTDA composites with amine functionalized MWCNTs in the presence of CTAB, it is to be noted that adsorbed DTDA-HCl molecules on the surface of MWCNTs would have closer proximity for reaction with the amine sites adsorbed onto the surface of MWCNTs-$NH_2$. Hence, grafting of PDTDA onto the surface of MWCNTs would be more facile in comparison to the reaction in the absence CTAB. The probable morphology of MWCNTs/PDTDA found in the presence of CTAB is detailed in *Scheme* 3.

From the forgoing discussion, it is clear that the MWCNTs/PDTDA composites formed in the presence/absence of CTAB would have different morphological and structural features. The ensuing discussion details the morphological, structural and electronic properties of MWCNTs/PDTDA composites formed in the presence/absence of CTAB with -$NH_2$ functionalized/unfunctionalized MWCNTs.

### 3.2. Morphology

From the above discussion, it is clear that surface

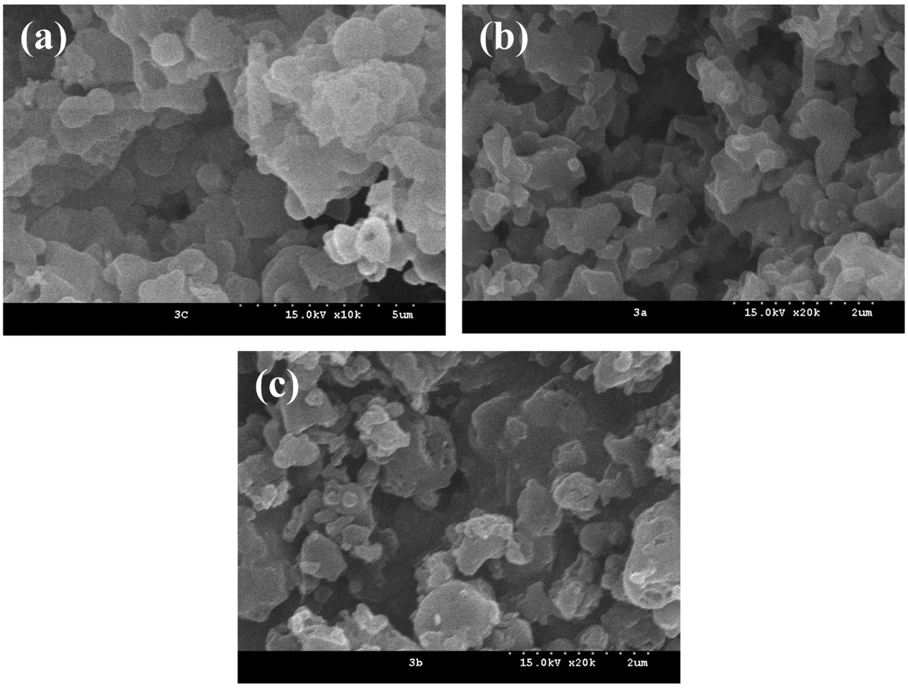


*Fig.* 1. SEM images of (a) pristine PDTDA and MWCNTs/PDTDA composites prepared with b) functionalized MWCNTs (c) unfunctionalized MWCNTs. Polymerization was carried out in the presence of CTAB.

morphology of the MWCNTs/PDTDA prepared under different conditions is influenced by the polymerization conditions. Two different types of condition are utilized i) surfactant induced intimate mixture (physical) of MWCNT and PDTDA and ii) CNTs surface linked PDTDA formation (chemical grafting). SEM was used to inform the morphological differences between the MWCNTs/PDTDA composites.

*Fig.* 1 presents the SEM photographs of pristine PDTDA, physical mixture of MWCNTs and PDTDA and PDTDA grafted MWCNTs prepared in the presence and absence of surfactant. *Fig.* 2 gives the SEM pictures of pristine PDTDA, pphysical blend MWCNT and PDTDA and PDTDA grafted MWCNT prepared in the presence of CTAB. Pristine PDTDA formed in the absence (*Fig.* 1a) and presences of CTAB are having porous morphology. The particles sizes of PDTDA are larger in the case of PDTDA formed in the absence of CTAB. Also, there are surface cracks in the particles in both cases. However, the cracks are minimum in PDTDA prepared in the presence of CTAB. We envisage that formation of PDTDA involves grafting of chain utilizing two amino groups. This may generate branched structure for PDTDA. The cracks in SEM pictures signify such a branched structure. The minimum cracking in the case PDTDA prepared with CTAB may be due to the ordering of PDTDA molecules with CTAB prior to polymerization. MWCNT/PDTDA composites prepared with MWCNT-$NH_2$ structure have a more compact morphology (*Fig.* 1b) in comparison to the one prepared with functionalized MWCNT. This feature is noticeable for the composites prepared in the presence/absence of CTAB (*Fig.* 2a and 2b).

### 3.3. FTIR spectroscopy

*Fig.* 3 represents FTIR spectrum of PDTDA and MWCNT/PDTDA composites prepared with $-NH_2$ functionalized/unfunctionalized MWCNT in the presence/absence of CTAB. The band assignments are made based on available literature.[12,13,24,25] The strong absorption band around 3450 $cm^{-1}$ corresponds to -NH stretching mode of secondary amine. Bands around 1500 $cm^{-1}$ and 1600 $cm^{-1}$ are assigned to the

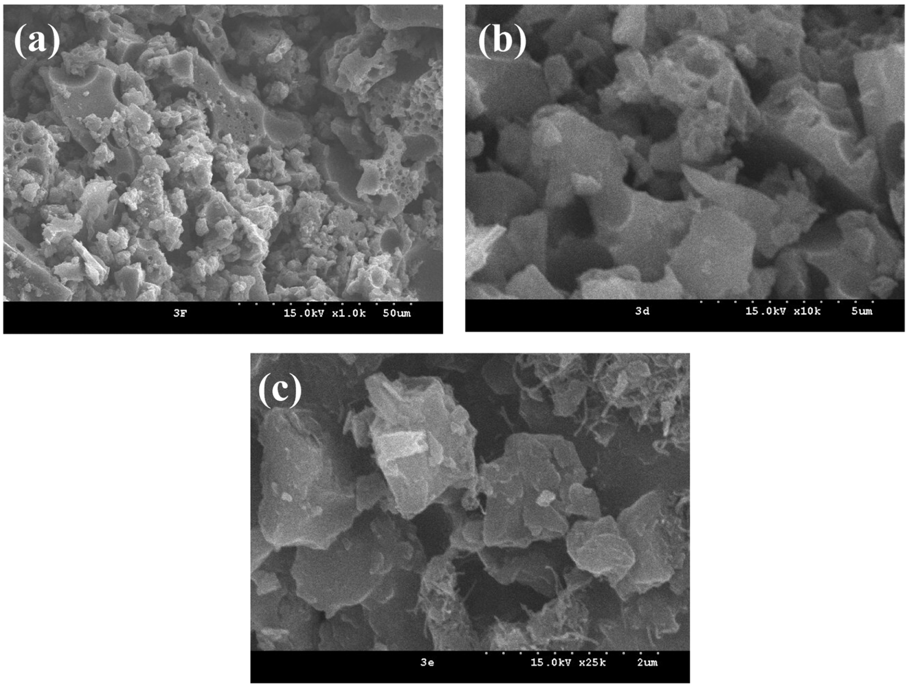


*Fig.* 2. SEM images of (a) pristine PDTDA and MWCNTs/PDTDA composites prepared with b) functionalized MWCNTs (c) unfunctionalized MWCNTs.

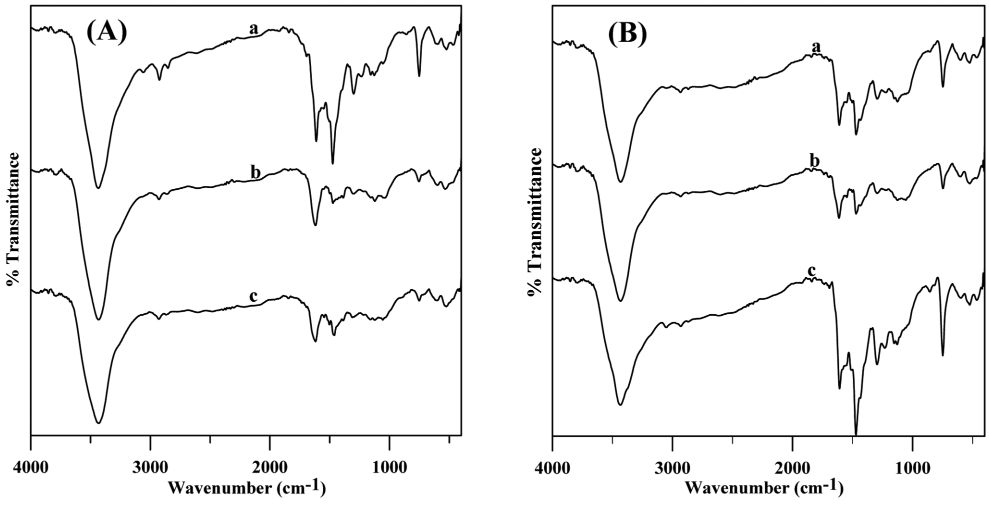


*Fig.* 3. FTIR spectra of (a) pristine PDTDA and MWCNTs/PDTDA composites prepared with b) functionalized MWCNTs (c) unfunctionalized MWCNTs. (A) Polymerization was carried out in the presence of CTAB and (B) in the absence of CTAB.

non symmetric $C_6$ aromatic ring stretching modes. The higher frequency vibration band arises from quiniod rings whilst the lower frequency band from benzeniod rings. Interestingly, there are relative variations in the intensities of these two bands between the composites. A close comparison of these relative intensities of the band at 1600 cm$^{-1}$ ($I_{1600}$) to band at 1500 cm$^{-1}$ ($I_{1500}$) informs the following. The variations in $I_{1600}/I_{1500}$ indicate that there can be different proportions of amine and imine units[26] in the backbone of PDTDA of the composites. The $I_{1600}/I_{1500}$ is low for pristine PDTDA (*Fig.* 3c) prepared without CTAB as compared to PDTDA prepared in the presence of CTAB. This indicates that PDTDA formed in the presence of CTAB is more doped and hence contain more quinoid units. DTDA molecules might be arranged in order in the presence of CTAB during polymerization and interactions of amine units with $S_2O_8^{2-}$ would be more probable to generate quinoid units. A comparison of $I_{1600}/I_{1500}$ between PDTDA/MWCNTs composite (physical mixture) (prepared with unfunctionalized MWCNTs) and PDTDA-g-MWCNTs is made. $I_{1600}/I_{1500}$ is relatively higher for the physical mixture as compared to PDTDA grafted MWCNT. This may be attributed to the possible difference in the conversion of bezeniod to quinoid units when PDTDA is chemically linked to MWCNT. The PDTDA and MWCNT/PDTDA composites have a band around 750 cm$^{-1}$ characteristic of C-S stretch[8] The weak band around 850 cm$^{-1}$ corresponds to *para* linked 1,2,4 trisubstituted phenyl rings.

### 3.4. Raman spectroscopy

*Fig.* 4 displays the Raman spectra of pristine PDTDA, pristine MWCNTs and PDTDA/MWCNTs composites prepared with –$NH_2$ functionalized/unfunctionalized MWCNT in the presence and absence of CTAB. The band around 1580 cm$^{-1}$ corresponds to G line representing in plane stretching of $E_{2g}$ mode and the shoulder around 1600 cm$^{-1}$ is assigned for D line (disorder line).[27] It is to be noted the intensities of characteristic band of MWCNTs are significantly suppressed in the MWCNTs/PDTDA composites. The probable reason may be the submerging of MWCNTs within the bulk PDTDA. This type of behavior has earlier been noticed in polymer/CNTs nanocables.[28] The peak around 1400 cm$^{-1}$ signifies the presence of PDTDA and this band is present for pristine PDTDA and PDTDA/MWCNTs composites. Raman spectra of the composites and PDTDA show a band around 1500 cm$^{-1}$ characteristic C=C stretching of the benzeniod ring of aniline units.[29] A very weak band was observed around 1600 cm$^{-1}$. The band around 1600 cm$^{-1}$ may be due to C=N stretching of quiniod units or the intensities suppressed G-band of CNT. For the composites prepared with amine functionalized CNTs, a band around 1330 cm$^{-1}$ that corresponds to C-N$^+$ stretching is additionally observed. This band is absent for the composites prepared with unfunctionalized CNTs. This band signifies that MWCNTs-g-PDTDA composites are more doped probably due to the liking in the CNTs.

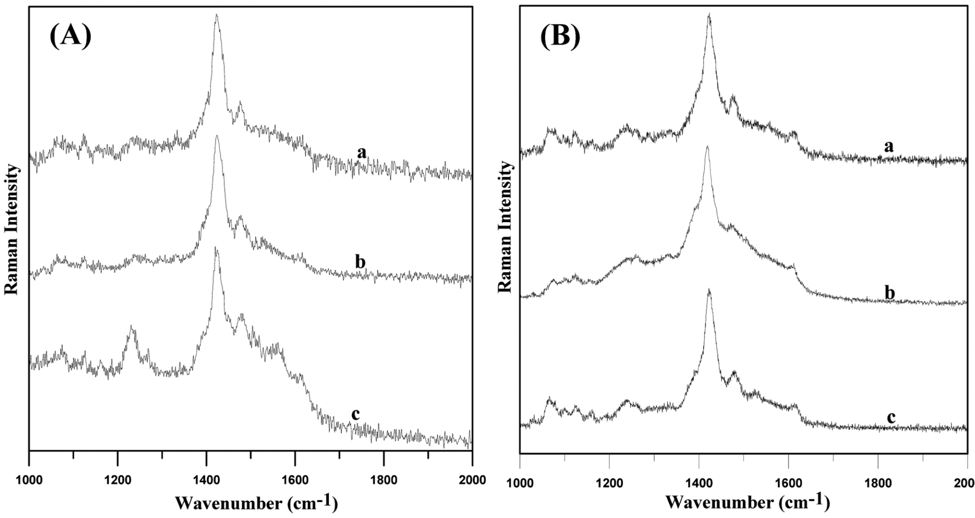


*Fig.* 4. Raman spectra of (a) pristine PDTDA and MWCNTs/PDTDA composites prepared with b) functionalized MWCNTs (c) unfunctionalized MWCNTs. (A) Polymerization was carried out in the presence of CTAB and (B) in the absence of CTAB.

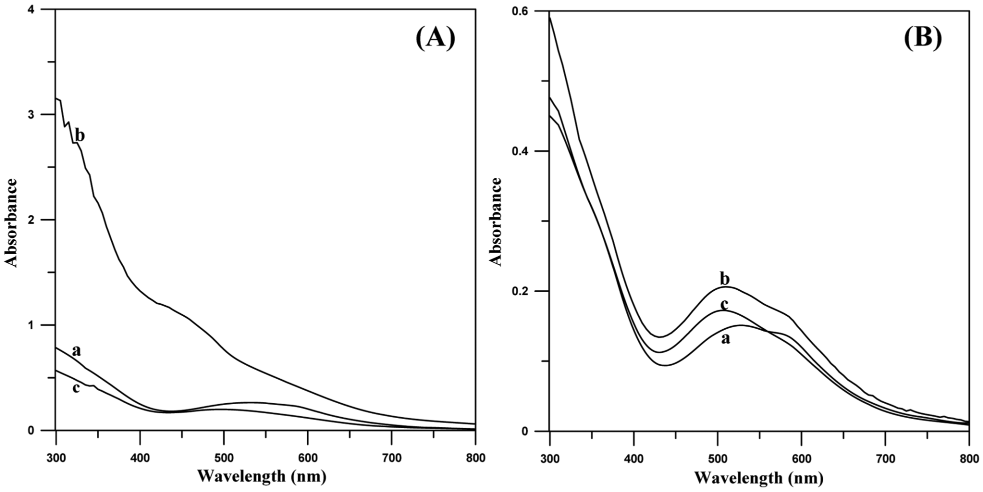


*Fig.* 5. Raman spectra of (a) pristine PDTDA and MWCNTs/PDTDA composites prepared with b) functionalized MWCNTs (c) unfunctionalized MWCNTs. (A) Polymerization was carried out in the presence of CTAB and (B) in the absence of CTAB.

### 3.5. UV-Visible spectroscopy

*Fig.* 5 shows UV-visible spectra of pristine PDTDA and composites of PDTDA with MWCNTs prepared with $-NH_2$ functionalized/unfunctionalized MWCNT in the presence and absence of CTAB. The spectral characteristics of PDTDA and the composites show differences in the electronic features between the materials prepared in the presence and absence of CTAB. PDTDA prepared with CTAB, exhibits two bands around 340 nm and two broad bands between (520-580 nm). The band around 340 nm is attributed to $\pi$-$\pi^*$ transition of aniline unit of emaraldine type. The band around 520-580 nm arises due to excitonic transition in the quinine amine units.[12,30] Generally, for polyaniline, the excitonic quinoid peak appears around 800 nm.[31] However, when aniline units in PANI backbones are substituted, the excitonic peak blue shifts down to 600 nm. In the present study, the appearance of peak around 550-580 nm for PDTDA is consistent with the substituent effect. The appearance of quinoid peak at lower wavelength is resulted from the substitution in the aromatic units of PDTDA and also due to shorter conjugation length than the unsubstituted PANI case.

In the case of MWCNTs/PDTDA composites prepared with $-NH_2$ functionalized MWCNT in CTAB, the UV-visible spectrum (*Fig.* 5a) shows an additional band around 450 nm that is characteristic of polaronic form of aniline type units in PDTDA. The existence of polaronic band for MWCNTs-g-PDTDA composites informs that aniline type units in PDTDA are more doped. This result is consistent with the observation from FTIR spectroscopy (*Fig.* 3) and Raman spectroscopy (*Fig.* 4). It is also to noted that such a polaronic band is less significant in the case of PDTDA-g-MWCNTs prepared in the absence of CTAB. Thus, it is evident that CTAB plays an important role in anchoring PDTDA units onto the surface of MWCNTs in the presence of $-NH_2$ functionalized MWCNTs.

## 4. Conclusion

Composites of S-S links containing polyaniline derivative and MWCNTs were prepared as a physical mixture as well as the chemically linked grafted structure. The surfactant used during the preparation plays an important role in the morphology and properties of the composites. The S-S links containing polyaniline is in more doped state when it is grafted to MWCNTs. The results are encouraging to prepare the MWCNTs grafted material to utilize for energy storage applications.

## Acknowledgement

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