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Polyaniline / carbon nanotube composites: starting with phenylamino functionalized carbon nanotubes

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Summary

Composites of carbon a nanotube with polymers are a developing and interesting area of research. The dispersion of the nanotube in polymer matrices is an important factor while making its nanocomposites. Even though in-situ polymerization approach offers a better approach for synthesizing homogeneous polymer nanotube composites, the dispersion of the nanotubes in the monomer solution is a problem. In this article we report a new chemical method for dispersing nanotubes in monomer and the preparation of uniform tubular composite of polyaniline (PANI) and multiwalled carbon nanotube (MWNT). For this the oxidized multiwalled nanotube (*o*-MWNT) was functionalized with *p*-phenylenediamine, which gave phenylamine functional groups on the surface. This functionalization helped to disperse the nanotubes in acidic solution. The *in-situ* polymerization of aniline in the presence of these well dispersed nanotubes gave a new tubular composite of carbon nanotube having an ordered uniform encapsulation of doped polyaniline. The phenylamine functional groups on the surface were grown into polyaniline chain so that the composite contains polyaniline functionalized CNT and they were no more an “impurity” in the final nanocomposite. The microscopic and structural properties of this composite were compared with that of a composite prepared under identical condition using *o*-MWNT.

Introduction

Carbon nanotubes, the smart hollow tubular carbon architecture of nano range, are attractive candidates for use as nano materials and nano devices on account of their structural characteristics and promising electronic and mechanical properties. Embedding of carbon nanotubes in conducting polymeric matrices like polythiophene, polyaniline, PPV etc for various nanocomposites material is now a popular area of research especially in organic electronics [1-5]. The combination of CNT with conducting polymers offers an attractive route to reinforce polymer as well as introducing electronic properties based on morphological modification or electronic interaction between two components. The chemical tailoring of CNT surface with polymeric architectures and construction of complex nano structured composite materials in bulk broadened the applicability of these materials. The quality of nanocomposites depends on the dispersion of carbon nanotube in the polymer matrix or homogeneity of the material. In the case of nanotube their insolubility and poor compatibility with the polymer make the uniform dispersion of carbon nanotubes in the polymer matrix very difficult, and the resulting inhomogeneous nanocomposites often have unsatisfying properties.

Currently different methods are used to incorporate nanotubes into polymer matrix. The common methods are:

i) Direct mixing: carbon nanotubes are dispersed into a low-viscosity thermosetting resin followed by curing [6] ii) Solution mixing: carbon nanotubes are dispersed in a solution of thermoplastic polymer followed by removal of the solvent or precipitation of the polymer. Some times the carbon nanotubes are chemically attached to the matrix polymer [7-9]. iii) Melt mixing: carbon nanotubes are mechanically dispersed into a polymer melt (prepared by heating) using a mixer or a compounder. The composite is processed using processing techniques such extrusion, injection molding and compression molding [10, 11]. iv) In –situ polymerization: This is a good approach for synthesizing homogeneous polymer nanotube composites where the matrix polymer is formed in the presence of nanotube [12-14]. In some in-situ polymerizations the surface of the nanotubes are grafted with polymer [15]. Generally in this method the carbon nanotubes are dispersed in a solution of monomer of the matrix polymer followed by the addition of the polymerization initiator. So the polymer is formed in the presence of the carbon nanotube and a composite is formed in a single step. This method usually leads to a firm wrapping of polymer on nanotubes. In such a method the homogeneity of the composite can again be affected by the dispersion of the nanotubes in the monomer solution. The more it is dispersed the higher will be the homogeneity of the composite.

In this work we used polyaniline, the conducting polymer which is a promising candidate for the synthesis of nanocomposites due to its ease of synthesis, electrical conductivity and environmental stability. Many groups have reported on the synthesis and properties of polyaniline/ carbon nanotube composites [16-18]. Cochet *et al.* reported that the *in-situ* chemical oxidative polymerization of PANI in the presence of CNT led to the formation of true composite material with enhanced electronic properties. In that composite effective site-selective interactions between the quinoid ring of the PANI and the MWNTs facilitated charge-transfer processes between the two components [19]. In such composites, CNT can improve the polymer properties by *(i) inducing additional structural ordering of the polymer (ii) improve the compactness and conjugation or chain length (iii) higher delocalization of charges in composite (iii) thermal stability (iv) charge carrier mobility* [17].

In this work we report a new approach for the preparation of homogeneous nanocomposite of polyaniline and MWNT by the *in-situ* polymerization. For this we covalently functionalized the multiwalled nanotubes with *para*-phenylene diamine expecting that,

i) the phenylamino groups on the surface helps to disperse them well in the dopant acid solution
ii) the phenylamine functional part will no longer be an ‘impurity’ in the composite since it can also be converted to polyaniline during polymerization.

For comparison we also prepared a composite in the same way in which CNT is not functionalized with *para*-phenylene diamine.

Experimental

Materials and methods

Aniline and ammonium persulphate (APS) were purchased from Sigma-Aldrich. CNTs were synthesized by the decomposition of acetylene gas by microwave chemical vapor deposition at 600 C with fine iron (III) nitrate as a catalyst. This method is based on the pyrolysis of acetylene by microwave heating on nanosized catalyst particles embedded in magnesium carbonate, which serves as a catalytic support. This method is capable of producing raw nanotubes of about 60–80% in purity. The average diameter of these multiwalled CNTs ranges from 10 to 15 nm.

UV-Visible spectra were taken using an Agilent 8453 spectrophotometer. X-ray powder diffraction studies were carried out with a Scintag diffractometer (DMC 105) using Cu Kα radiation (λ=1.5418Å). Microscopic images were taken using a Hitachi 3000N scanning electron microscope (SEM) and a Philips 420T transmission electron microscope (TEM). SEM observation was done directly by spreading a small amount of sample on a double sided carbon tape sticked on a sample mount. Due to the conducting property of carbon nanotubes, no gold coating is necessary for SEM imaging. For TEM a small amount of nanotubes was ultrasonically dispersed in acetone for about 20 min and a drop of the dispersion was spread on a 300 mesh copper grid (from Electron Microscopy Sciences). Fourier transform infrared (FTIR) spectra were recorded with a Digilab model FTS60 spectrometer using KBr pellets. The conductivity was measured using a Magnetron, Model M-700 four-probe instrument.

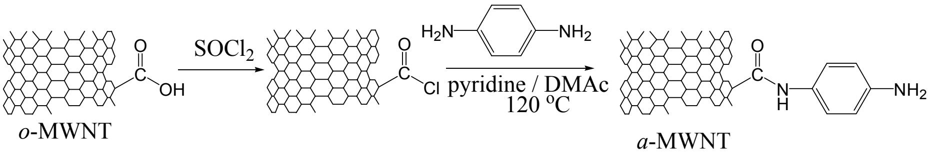
Oxidation of nanotubes

The nanotubes were oxidized using potassium permanganate with the help of phase transfer catalyst [20]. Purified nanotubes (0.12 g) and dichloromethane (25 ml) were added to a 100 ml flask and the suspension was vibrated ultrasonically for 0.5 h. Phase transfer agent (1.0 g, Aliquat 336, from Aldrich) was added, followed by powdered potassium permanganate (5 g) in small portions over a period of 2 h. Acetic acid (5 ml) was also added. The mixture was then stirred vigorously overnight at room temperature. It was then filtered, washed with conc. HCl and water and dried to get oxidized MWNT (*o*-MWNT)

Preparation of Composites

a. Composite with of para-phenylenediamine functionalized carbon nanotubes ***(C1)***

Oxidized carbon nanotubes (*o*-MWCT) (100 mg) were refluxed with thionyl chloride (5ml, excess) for 24 hours. Excess thionyl chloride was removed by distillation. The residue is dispersed well in N,N-dimethylacetamide (20ml), added of *para*-phenylenediamine (150mg) and few drops of pyridine (0.5 ml). The mixture is stirred at 120 ^{o}C for 3 days in a nitrogen atmosphere. The resulting product *p*-phenylenediamine functionalized MWNT or amino functionalized MWNT (*a*-MWCT) is separated by centrifugation and washed well with methanol and dried in vacuum. (Scheme **1**)



Scheme **1**. Conversion of *o*-MWNT to *a*-MWNT

The *a*-MWNT (100 mg) was dispersed in 10 ml 1M HCl and ultrasonicated for 30 minutes to disperse the nanotube. Then aniline (0.5 ml) is added and sonication was continued. Then ammonium perdisulphate (1.14 g in 10 ml water) was added to this dispersion slowly under stirring. The reaction was continued at room temperature for 5 hours. The dark green product was filtered after washing with HCl to remove unreacted oxidant and monomer. It is then washed with water and acetone and dried to get the composite **C1**.

*b. Composite with oxidized carbon nanotubes (**C2**)*

For the preparation of **C2** the above method for the preparation of C1 was used, starting with oxidized carbon nanotubes (*o*-MWCT).

Results and discussion

Preparation of composites

The surface functionalization of carbon nanotube is usually done by using the carboxylic acid moieties along the surface. The carboxylic acid groups were generated on the surface by oxidation using potassium permanganate in the presence of a phase transfer reagent. The carboxylic acid groups were confirmed by the peaks 1730 cm^{-1} (C=O stretch) and 1260 cm^{-1} (C-O stretch) The acid groups were converted to acyl chloride, by treatment with thionyl chloride, which are susceptible to react with molecules having amino functional groups [21]. The acid chloride functionalized nanotube was then treated with para-phenylene diamine. An excess of para-phenylene diamine was used to avoid the crosslinking between the nanotubes. The functionalization was confirmed by the IR spectra of this material. Absence of strong bands around 1730 cm^{-1} and 1260 cm^{-1} showed that the carboxylic acid groups were completely reacted and the new peaks around 1670 cm^{-1} (amide I band, C=O stretch), 1610 cm^{-1} (amide II band, N-H bending) and 1200 cm^{-1} (C-N stretch, amine). A dispersion of para-phenylene diamine functionalized nanotubes (*a*-MWCT) in HCl was found to be very stable and uniform than that of o-MWNT due to the presence of the NH_2 functional groups along the walls of nanotube (Figure-**1**). In acid solution the NH_2 groups get protonated and became NH_3^+. Thus the surface of the nanotubes become positively charged and easily dispersed due to repulsion.

Aniline was added to this dispersion followed by the slow addition of ammonium per sulfate oxidant, in 1 M HCl, to get a dark green composite, **C1**. **C2** was prepared under identical conditions using o-MWNT dispersed in HCl solution. In the UV-Visible spectra both the composite showed peaks around 450 nm and 800 nm due to the $\pi \rightarrow \pi^*$ transitions in the benzenoid and quinoid segments of doped polyaniline. The IR spectrum of the composites showed peaks around 1490 cm^{-1} and 1590 cm^{-1} due to benzenoid and quinoid ring vibrations.

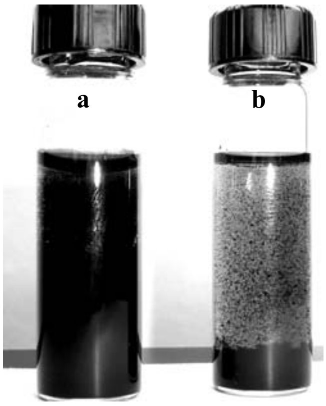


Figure **1**. Photograph showing the stability of CNT dispersions in HCl solution after ultrasonication **a**) *a*-MWNT **b**) o-MWNT

Microscopic, XRD and conductivity studies

A detailed morphology and size of the composites were analyzed by microscopic studies, SEM and TEM. The microscopic studies showed the tubular morphology of the composite which has a core shell structure, the carbon nanotubes as core encapsulated by the polyaniline shell. Compared to the carbon nanotube diameter, the diameters of the tubular composite are large. The SEM images of the nano composites are shown in the figure **2**. The diameters of MWNT are in the range of 10-15 nm (**2a and 2b**). From figure **2d** in the composite C1 the tubes are almost of uniform diameters in the range of 90-105 nm. For **C2**, figure **2f** the diameters are in the range of 60-90 nm and are not uniform. Thus in the composite with functionalized nanotubes, the nanotubes are uniformly and thickly coated with polyaniline than with the unfunctionalized. Figures **2c and 2e** shows that **C1** is more compact and only the tubes coated with polyaniline were seen. But in the images of **C2** granular polyaniline can also be seen. For a closer view of polyaniline wrapping over CNT the composites were analyzed by TEM imaging. Figure **3a** shows the TEM image of oxidized CNT. The thickness and uniformity of polyaniline coating can also be compared using figures **3b** and **3c** in which single tubes are visible. In **C1** the nanotubes are uniformly coated with polyaniline and the diameter of the tubes are in the range of 100nm where for C2 the diameter is around 80 nm. Also with TEM analysis less coated or uncoated nanotubes were also found in the composite **C2**, (see figure 3**d).**

In XRD diffractogram (figure **4**) polyaniline showed an intense broad peak at $2\theta = 21^{o}$ with a shoulder at 26^{o}. This diffractogram is similar to the HCl-emeraldine salt of polyaniline with doping level between 0 and 0.1 [22]. This polyaniline is almost amorphous. XRD studies of PANI showed that as the doping level is increased, the amorphous peak disappears. Instead new peak appears at 15^{o} and peak intensity at 10^{o} and 26^{o} increases [22]. MWNT showed characteristic peaks, the intense one around $2\theta = 26.5^{o}$ and some low intense peaks around 45^{o}.

The diffractogram of the composite showed a different pattern from PANI as well as MWNT. There is no broad amorphous peak of PANI. **C1** showed peaks at $2\theta = 10^{o}$ (weak), 15^{o} (weak), 21.5^{o} (low intense) and 26^{o}. **C2** showed peaks at 10^{o} (weak) and 26^{o}. Some authors reported that in tubular composites of polyaniline with carbon

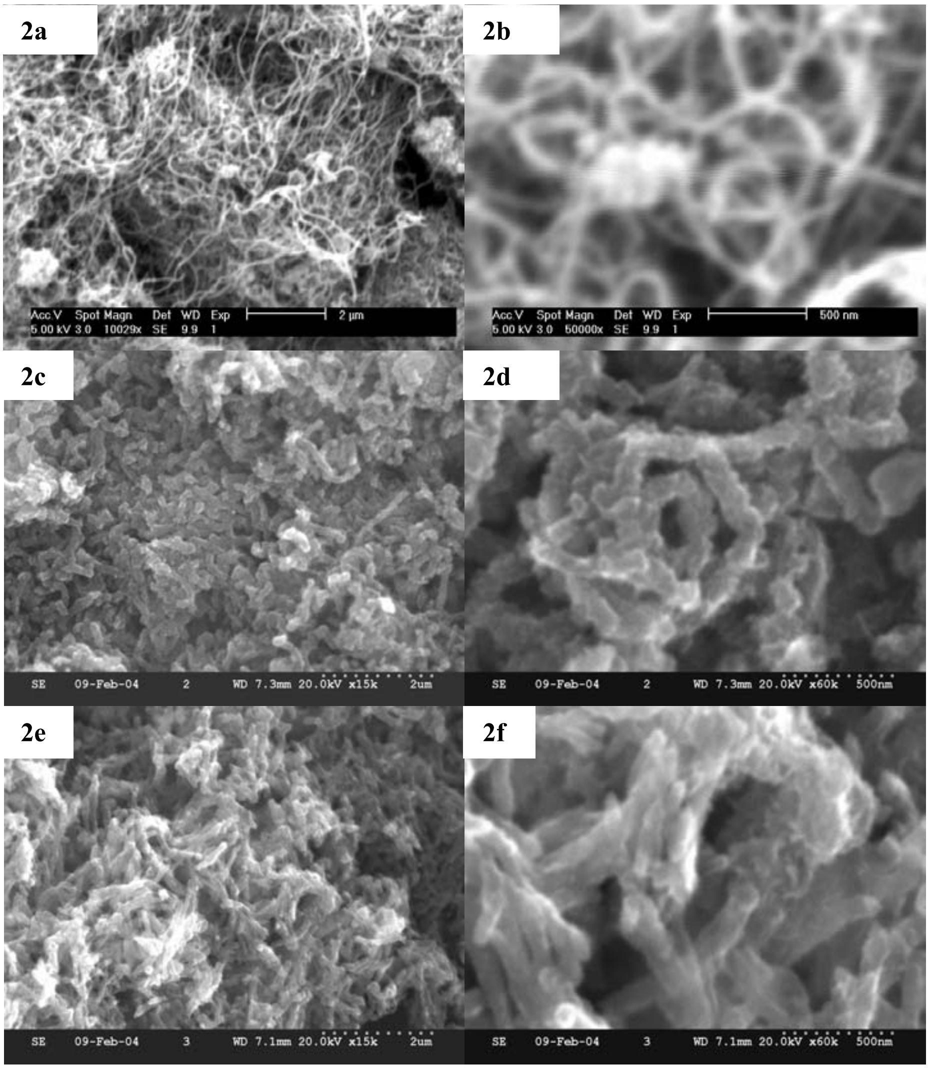


Figure **2**. SEM images of oxidized carbon nanotubes (**2a** and **2b**), composite C1 (**2c** and **2d**) and C2 (**2e** and **2f**)

nanotubes, due to small mass fraction of carbon nanotubes, the graphite like diffraction peak of MWNT at $2\theta = 26^o$ can hardly be detected [23]. Thus the peak around 26^o in these composites came from the PANI coating. Thus in the composites the intensity of peaks at 10^o and 26^o is higher than that of PANI prepared under same condition. This can be due to two reasons

(i) increase in doping level due to the presence of carbon nanotubes because it was also reported that the carbon nanotubes can induce a dopant effect on polyaniline and increase effective delocalization on polymer chains [16]. The diffractogram of the composite **C1** showed more similarity to the polyaniline with doping level slightly higher than 0.1

(ii) due to ordering of polyaniline macromolecule along CNT axis [23].

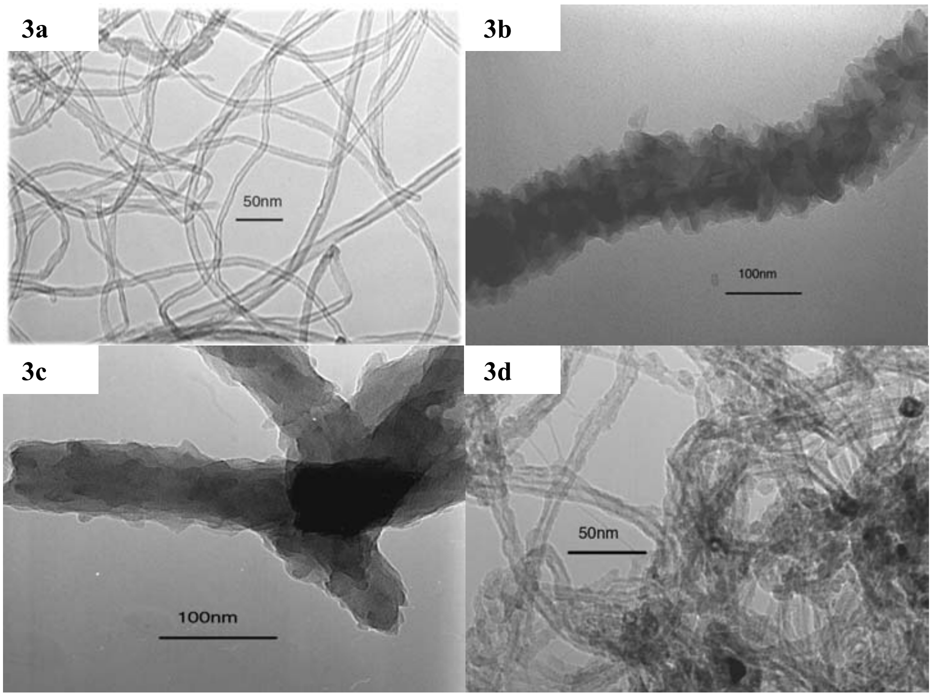


Figure **3**. TEM images of oxidized carbon nanotubes (**3a**), composite **C1** (**3b**) and **C2** (**3c** and **3d)**

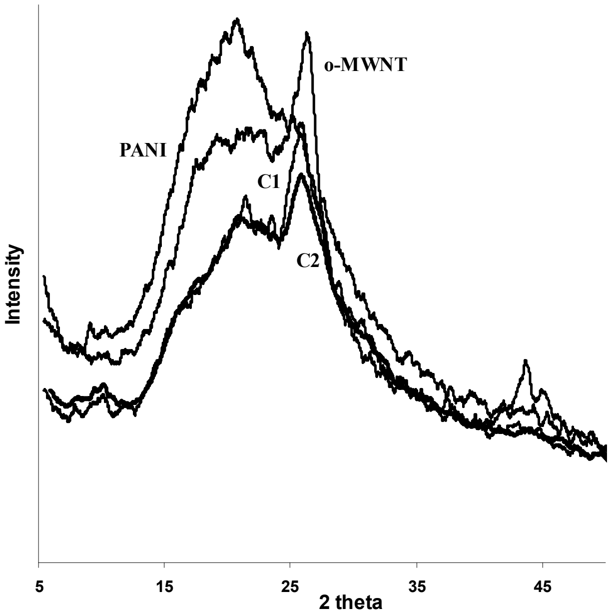


Figure **4**. X-ray diffractograms of PANI, MWNT, **C1** and **C2**

Since the intensity of the peak is higher for **C1**, the dopant effect of carbon nanotube and the ordering of polymer chain along nanotubes are high in **C1** than in **C2**.

The conductivities (measured by a four probe method) of the PANI, **C1** and **C2** are 8.2×10^{-3} Scm^{-1}, 6.5×10^{-2} Scm^{-1} and 2×10^{-2} Scm^{-1}. The composites showed a higher conductivity than PANI. This may be attributed to presence of nanotubes in the composites which increased the charge delocalization by doping effect and also provided an efficient matrix for charge transport. Among the composites conductivity of **C1** is higher than that of **C2**. This can be due to the higher homogeneity in the composite **C1** [24] which also enhanced the effective delocalization on polymer chains in **C1** than in **C2**.

Mechanism of composite formation

A general mechanism of polyaniline formation is reported elsewhere [25]. The formation of the composites can be explained as follows. When carbon nanotubes are dispersed in aniline / HCl solution, aniline hydrochloride ions get adsorbed on the nanotube surface. On addition of the oxidant (APS) the adsorbed species get oxidized and form cation radicals which initiates polymerization on the surface. The reaction takes place faster on the surface of carbon nanotube than in the bulk due to low activation energy (based on the principles of heterogeneous catalysis). This leads to the formation of the polyaniline shell over CNT. Thus the nanotubes act as template for the formation of tubular composites. In a well dispersed solution of carbon nanotube the adsorption of aniline hydrochloride will be high and uniform, which can lead to the formation of a *thicker uniform coating* of polyaniline. This is what happened in the formation of **C1**. Since *a*-MWNTs were well dispersed in the solution than *o*-MWNTs a *thicker uniform coating* of polyaniline was formed on it surface.

In order to check whether the phenylamino group on *a*-MWNT surface initiated polymerization during the formation of the composite **C1**, a small portion of **C1** was dedoped using aqueous ammonia (0.1 N). On dedoping the green composite became dark blue due to the conversion of emeraldine salt of polyaniline to the emeraldine base (*eb*) form. This was then treated with DMF to remove the base. The washing was continued until the DMF became colorless. This material was then washed with acetone and dried. This material is designated as **C3**. **C2** was also dedoped and washed with DMF exactly in the same way as did for **C1.** The final material is **C4**.

The TEM images of **C3** and **C4** are given in figure **5**. In the case of **C4** the coating can be hardly seen after dedoping and washing (figures **5 a** and **b**). In the case of **C3** (figures **5 c** and **d**) no continuous or uniform coating of polyaniline can be seen instead there are heaps of polyaniline (marked by arrows in the figure) in some areas along sides of the tube and a high concentration at the tube ends. The formation of these polyaniline heaps can be explained as follows; during the purification and oxidation of carbon nanotubes the tube ends are largely decorated with carboxy groups. These groups also appear at the defective sites along the sidewalls [21]. Thus during the covalent functionalization of the nanotube through the carboxy groups, the functionalization takes place more at the tube ends and defective sites along the surface. The presence of such heaps at the tube ends and sidewalls showed the presence of covalently functionalized polyaniline on nanotubes in **C3**.

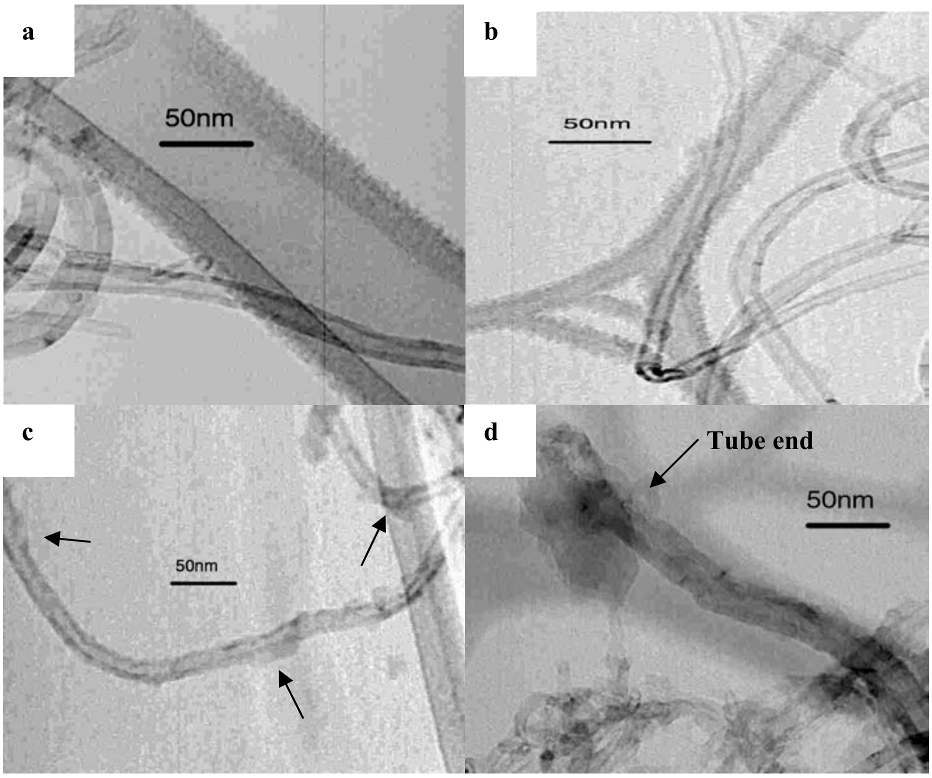
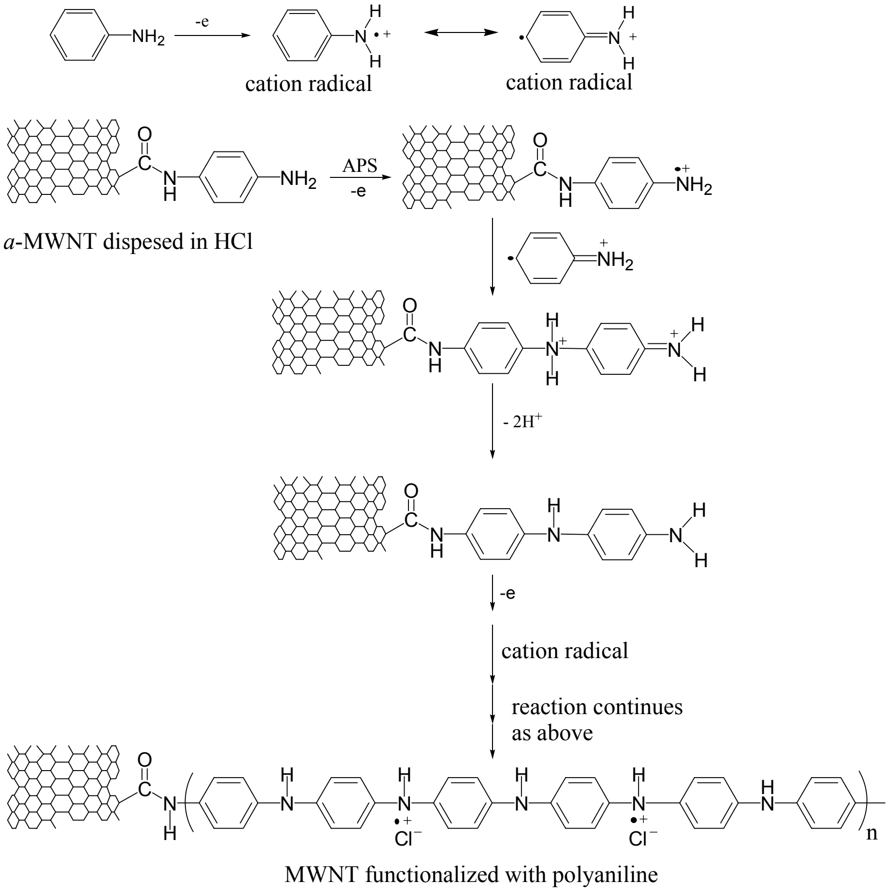


Figure **5**. TEM images of **C4** (**a** and **b**) and **C3** (**c** and **d**)

Since **C3** is formed from **C1**, the nanotube surface in **C1** contains *covalently functionalized* and *non-covalently functionalized* polyaniline. The phenylamino groups on the *a*-MWNT surface initiated polymerization during the formation of the composite **C1**. The phenylamino groups on oxidation gives cation radicals and react with the cation radicals on the surface or in solution (see scheme **2**). Since in *a*-MWNT, the phenyl amino groups can also initiate polymerization, the concentration of the monomeric species is high on the *a*-MWNT surface than in *o*-MWNT. This also explains the formation of thicker coating on the surface as observed in the case of thin films of polyaniline grown on primed substrates [26]. The formation of **C1** and **C2** are compared in figure **6**.



Scheme **2**. Conversion of the phenylamino groups on CNT surface to polyaniline

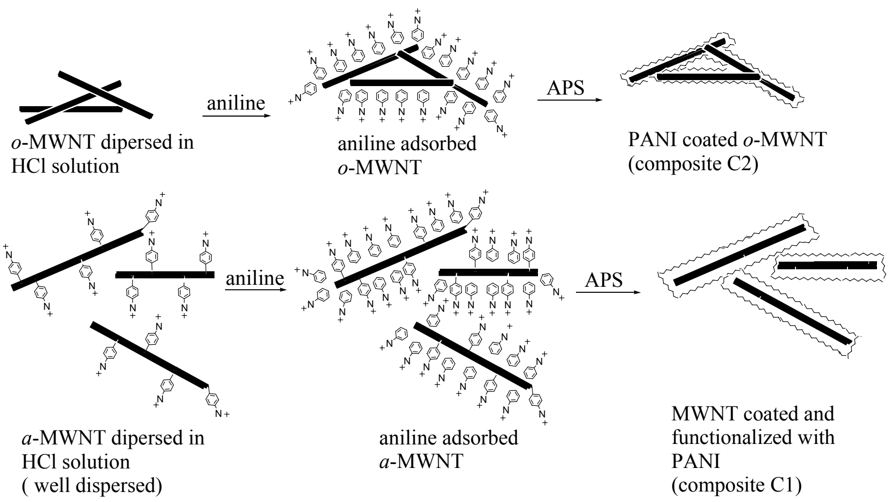


Figure **6**. Formation of **C1** and **C2**

Conclusions

Carbon nanotubes, which are insoluble and bundled, make their homogeneous dispersion in a reaction medium a significant challenge. The functionalization of carbon nanotube with polymer is a good approach to disperse or solubalize them. But the species used for functionalization will become an “impurity” in the final nanocomposite. Such problems can be overcome by using the side wall chemistry of nanotubes in the proper way. In our work we functionalized CNT with p-phenylene diamine so that phenylamino groups are formed on the surface. The composite prepared using this functionalized nanotubes was compared to that prepared from unfunctionalized carbon nanotube. The comparison between the composites showed that the phenylamino fuctionalization helped to disperse carbon nanotubes homogeneously in the reaction medium and due to this dispersion, a tubular composite with an ordered polyaniline shell of uniform thickness was obtained. Also the phenylamino groups were no longer impurities in the composite since they were also converted to the polyaniline during the composite formation. Since in the composite the MWNT is covalently functionalized with the polyaniline, it can ensure the compatibility of carbon nanotube in the polyaniline matrix which can avoid potential microscopic phase separation in the nanocomposite.

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