New strategy for chemically attachment of Schiff base complexes on Multiwalled Carbon Nanotubes surfaces

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C H R O N I C L E	A B S T R A C T
	Chemically attachment of Schiff base complexes on multiwalled carbon nanotubes (MWCNTs) surfaces through a convenient and simple method was studied. In the first step of this method, we present a new method for preparation of aminated MWCNTs in order to attachment of (new) chlorinated salen Schiff bases. Amination of multiwalled carbon nanotubes performed under microwave (MW) irradiation through a one pot two step reaction. The chemically attachment of salen Schiff bases on functionalized MWCNTs (salen@MWCNTs) performed under a facile simple nucleophilic substitution reaction and complexation of attached salen Schiff bases (salen complex@MWCNTs) in last step, have been occurred with reaction of transition metal salts and salen@MWCNTs. The obtained products were characterized in detail, using FTIR, XRD, UV-Vis absorption, SEM and EDX methods.

1. Introduction

Until the 1980s, the carbon universe was built on the well-known modifications, graphite and diamond. This perspective totally changed with the discovery of the carbon allotropes such as fullerenes, carbon nanotubes[1] (CNTs), carbon nanohorns, and carbon onions. Because of so many outstanding performances, CNTs exhibit great promise for potential applications in many technological fields such as hydrogen storage[2-4], catalyst supports[5,6], chemical sensors[7,8] and nanoelectronic devices[9]. One of the most powerful approaches to improve CNT handling is the covalent functionalization of their side walls and tips[10-13]. A wide variety of reactions has been described for functionalization of CNTs. Because amine groups are versatile and undergo a variety of reactions, particular interest in functionalization processes is the attachment of amino groups (-NHR or NH_2 groups) on CNT surfaces. In fact, the aminated MWCNTs have some advantageous for several applications, such as the attachment of nanoparticles to single and multiwalled carbon nanotubes[14-16], the attachment of DNA to SWCNTs[17,18] and carbon nanofibers[19,20] and also

immobilization of Schiff base complexes[21] on CNT surfaces. The Schiff bases and their metallic complexes have catalytic properties and can be used as homogen and heterogeneous catalysts in wide variety of chemical reactions[22-26]. The homogeneous catalysts, have some drawbacks such as difficulties in the catalyst recovery and product separation in contrast to heterogeneous catalysts, that have many advantages such as easy separation and facile recovery of the solid catalyst from the reaction mixture. In recent years, the interest of many researchers has been focused on heterogenizing of homogeneous catalysts, and there are a number of successful demonstrations of immobilized homogeneous complexes on supports. Heterogenization of homogeneous catalysts with similar activities affords an appealing methodology to expand the industrial application of homogeneous catalysts; for this purpose, immobilization of metal Schiff base complexes on organic or inorganic supports had been widely reported[27-29]. Immobilization via covalent bond on the support is more advantageous and improving the long-term stability of the solid catalyst.

Here we report a simple convenient method for chemically attachment of salen Schiff bases and Schiff base complexes to MWCNTs surfaces. In the first step of this method, we try to aminated of MWCNTs through a new one pot reaction and in second step, attachment of synthetic chlorinated Schiff bases (on CNT surfaces) performed under a nucleophilic substitution reaction. Complexation of attached salen Schiff base on MWCNTs (Salen complex@MWCNTs) has been occurred through the reaction of transition metal salts and salen@MWCNTs.

2. Results and discussion

The present method is containing to several steps: 1. amination of MWCNTs, 2. synthesis of chlorinated Schiff bases, 3. chemically attachment of Schiff bases to functionalized MWCNTs and 4. complexation of attached Schiff bases on MWCNTs.
The products of every step have been characterized with FTIR, UV-Vis absorption, XRD, SEM and EDX methods. In continue, we discuss about the obtained results.

3. Conclusion

Here we present a new method for chemically attachment of salen complexes to MWCNTS surfaces through a clean, convenient and fast method. Functionalization of MWCNTs with amino groups in first step, provide a useful material for attachment of chlromethylated salen Schiff bases via a nucleophilic substitution reaction. Analysis results show that CNTs were functionalized in a high concentration. After the immobilizing the Schiff bases to CNT surfaces, reaction of them with Cu and Ni salts, leads to Salen complex@MWCNTs.

Our method in functionalization of CNT surfaces has some advantages in compare with other reported results [6, 21], because of; here we don't use acids and hazardous reagents in procedure of the attachment of Schiff bases on CNT surfaces. Also aminated CNTs were prepared in fast and clean conditions. In fact, this new procedure provides functionalized CNTs (salen@MWCNTs and Salen complex@MWCNTs) with high concentration of functional groups. The final reaction products can be used as heterogeneous catalysts in chemical reactions. The process has proved to be very effective, safe and easy to operate and also the scale up of this method is easy.

Aknowledgment

4. Experimental

4.1. Materials

Multiwalled carbon nanotubes were obtained from Shenzhen Nanotechnology Co., Ltd. (China) The Purity of the CNTs was about 90-95%, with their diameters and lengths ranging between 20-40 nm and 5-15 μm, respectively. The other reagents and solvents were purchased from Merck Company.

4.2. Apparatus

FT-IR spectra were recorded on a Bruker ISS-88 spectrophotometer in KBr pellets. ^{1}H NMR (400 MHz) spectra were measured in CDCl$_3$ solvent and referenced to the solvent signals by Bruker Avance DPX instrument. The spectra in the UV–Vis range were taken using Cary 100 varian el 12092335 UV–Vis scanning spectrometer. ASTRA 3D Bath sonicator was applied for debundeling of MWCNTs also XRD instrument model Philips Analytical PC-APD was used for characterization of the reaction products. Cambridge 360 scanning electron microscope (SEM) with energy dispersive X-ray spectroscopy (EDX) analysis was used for surface image measurements and chemical characterization of Cu and Ni salencomplex@MWCNTs.

4.3. General procedure for amination of MWCNTs

180 mg of AlCl$_3$ mixed with 10 mg MWCNTs and grind for 5 minutes and then added to 50 ml CH$_2$Cl$_2$. The mixture was sonicated for 10 minutes in bath sonicator. After that, the homogen mixture was irradiated in a microwave oven for 10 minutes with power of 900 watt. After this time, 200 mg of ammonium benzoate (as ammonia source) was added to the mixture and the reaction continues for 10 minutes under microwave irradiation with power of 900 watt. After this time, the mixture cool to room temperature and filtered. Then 50 ml warm ethanol were added and sonicated for 10 min to remove remained unreacted compounds, and then the mixture was filtered and the resulting products were dried at 80°C for 10 hours (Scheme 1).

4.4. Chloromethylation of Salicylaldehyde

17.5 g (160 mmol) salicylaldehyde, 24 ml formaldehyde, 1.2 g ZnCl$_2$ and 100 ml of concentrate HCl were poured in a 250 ml flask and stirred for 24 hours at room temperature (under N$_2$ atmosphere). After this time, a white solid was formed .To isolate the product, [5-chloro-methyl-2-hydroxy-Benzaldehyde (**1**)], the solids dissolved in diethyl ether, and the organic phase was washed by saturated sodium bicarbonate. For removal of water from organic phase, a small amount of magnesium sulfate was added and crystallization was performed in petroleum ether [30] (Scheme 2).

4.5. General procedure for synthesis of Schiff Bases

3.41 g (20 mmol) of 5-chloro-methyl-2-hydroxy-Benzaldehyde (**1**) was dissolved in a minimum of dichloromethane. Then, according to the stoichiometry of 1 to 2 of diamine to **1**, the amounts of diamines was mesured and dissolved in minimum volume of dichloromethane and were added to **1**. The mixture was stirred in room temperature for 1 to 3 hours (the completion of reaction monitored by TLC). After this time, the solution was filtered and the obtained precipitate was washed with dichloromethane and dried in 70°C for 6 hours (Scheme 2).

4.6. General procedure for synthesis of salen @MWCNTs

50 mg of aminated MWCNTs were added to 8 ml of methanol containing 100 mg of Schiff base and refluxed for 24 hours at 70°C. After this time, the reaction mixture was filtered and washed with methanol and finally was dried at 70°C in oven (Scheme 3).

4.7. General procedure for synthesis of salen complex@MWCNTs

0.5 g of transition metal salts were dissolved in 20 ml of methanol and 1 g of salen @MWCNTs (from previous step), was added and refluxed in $40^{\circ}C$ for about 4 hours. After that, the mixture was cooled to room temperature and filtered and finally, the reaction product washed with MeOH and dried (Scheme 4).

4.8. Characterization of aminated MWCNTs

4.8.1. FTIR

The high symmetry presented on raw CNTs generates very weak infrared signals due to the weak difference of charge state between carbon atoms. The weak difference of charge state leads to very small induced electric dipole, providing a silent spectrum. In FTIR spectrum of raw and aminated MWCNTs (Fig. 1), several peaks are exist.
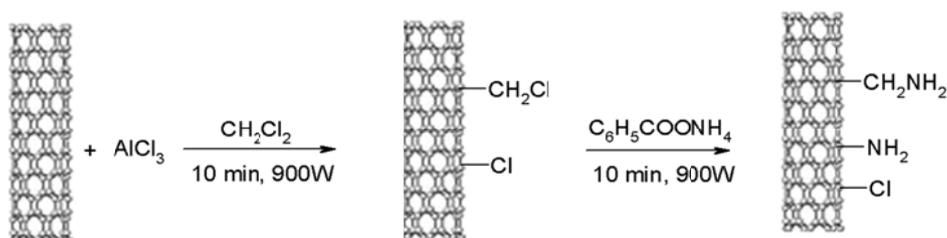
**Scheme 1.** The procedure used for functionalization of MWCNTs

The peak related to C=C bond at approximately 1600 cm^{-1} is not seen clearly in the spectrum of pristine CNTs. This effect can be explained by the very low formation of electric dipoles. The functionalization breaks the symmetry of nanotubes structures, which enhances the generation of induced electric dipoles and signs as detected. Peaks at 3500 and about 2900 cm^{-1} (Fig. 1) are the characteristic stretching vibrations of N–H and C-H bonds. Aminated CNTs, also show the appearance of a peak approximately at 1050 cm^{-1}, which corresponds to the C-N stretching indicating the attachment of NH_2 groups due to surface modification.
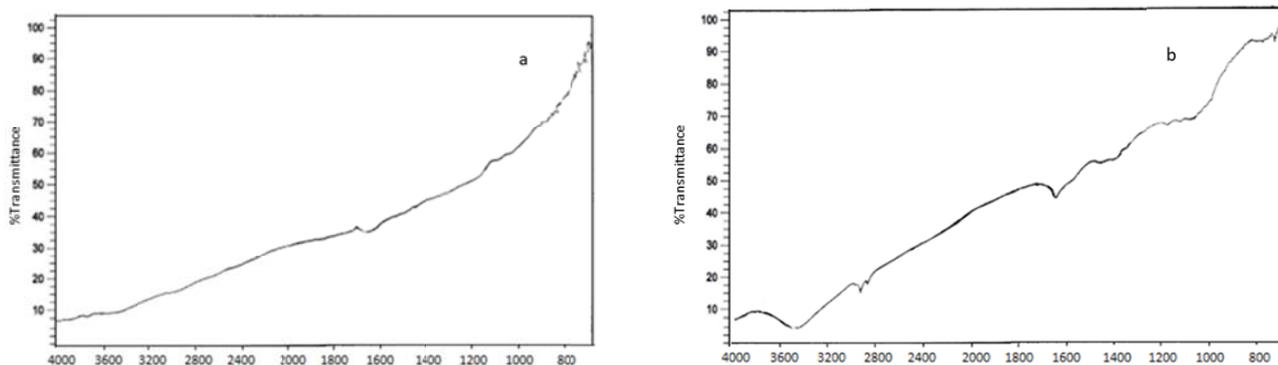
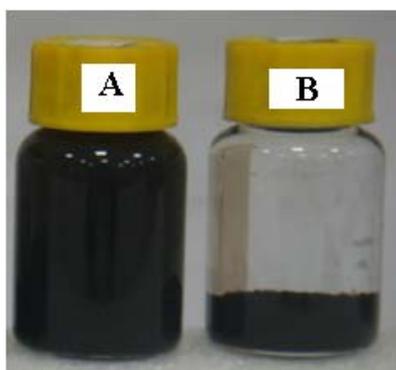**Fig. 1.** FTIR spectra of raw (a) and aminated (b) of MWCNTs

4.8.2. XRD

Fig. 2 exhibits the XRD patterns of pristine and modified MWCNTs. XRD patterns show that MWCNTs have similar cylinder wall structures before and after the modification. In addition, inter-planner spacing of functionalized materials remained the same. These results demonstrate that the functionalization would not change the structure of MWCNTs.
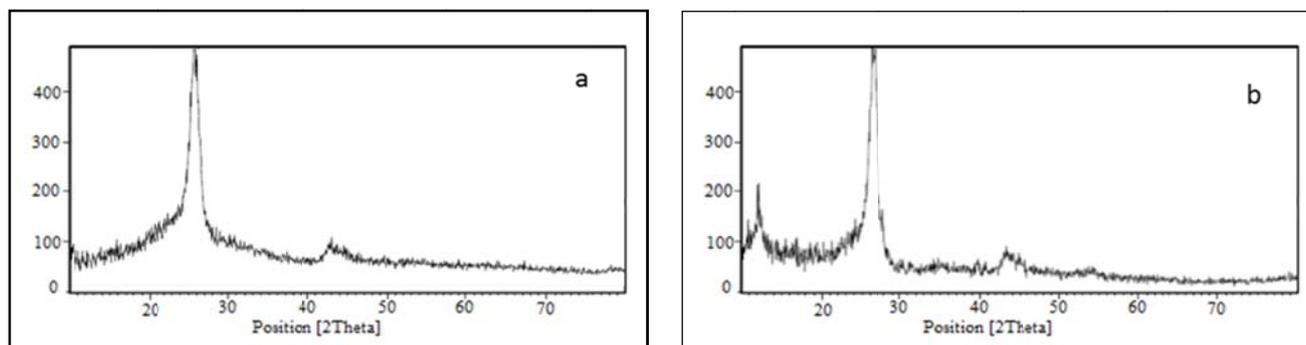
Fig. 2. XRD patterns of Raw (a) and Functionalized MWCNTs (b)

4.8.3. Settling behavior

To estimate the dispersibility of raw and modified MWCNTs, a sedimentation test was performed. Aminated MWCNTs (1mg) were ultrasonically dispersed in ethanol for 5 min. It was observed that aminated MWCNTs could be easily dispersed in ethanol due to hydrogen bonds, that could be formed between aminated MWCNTs and polar solvent molecules. Modified MWCNTs could be dispersed when hydrogen bonds overcome the van der waals interactions among MWCNTs. Fig 3. shows the stability of dispersion after 3 weeks.

Fig. 3. Photographs of dispersion stability of: functionalized (A) and raw MWCNTs (B)
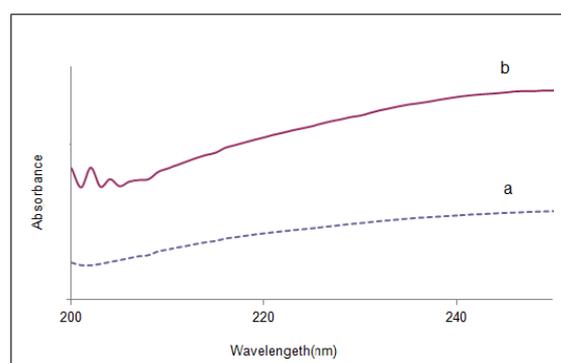
Fig. 4. UV-Vis absorbtion spectra of raw (a) and aminated MWCNTs (b)

4.8.4. UV-Vis absorption

UV-visible absorption spectrum can also verify the functionalization of carbon nanotubes. UV-Vis absorption spectra of raw and aminated nanotubes (in ethanol) have been shown in Fig. 4. Pristine MWCNTs (dispersed in ethanol) do not show any optical absorption at room temperature. However, after functionalization with $-NH_2$ groups, optical absorption peak below 210 nm is observed. These bands are due to n$\rightarrow$ σ* transition electrons of amino groups.

4.9. Characterization of synthetic Schiff bases

For synthesis of chlorinated Schiff bases, 5-chloromethyl-2-hydroxy benzaldehyde (1)were prepared from salycil aldehyde, through an electerophilic substitution reaction (Scheme 2). The reaction product was characterized by FTIR and ^{1}H NMR techniques.
IR (KBr, cm^{-1}), 3200 (-OH), 2900 (-CH$_2$), 1650 (C=O), 1490-1500 (aromatic C=C), 1260 (-CH$_2$), 720 (C-Cl).

^{1}H NMR (CDCl$_3$, δ ppm), 11.08 (s, 1H), 9.91 (s, 1H), 7.0–7.6 (m, 3H), 4.6 (s, 2H).

Chlorinated Schiff Bases, [N,Ń-bis (3-chloro methyl salysilidine) 1,4-butanediamine (salen **2**) and N,Ń-bis (3-chloro methyl salysilidine) 1,8-octanediamine (salen **3**)], were synthesized by the reaction of diamines (1,4- diamino butane and 1,8 diamino octane) with **1**, respectively (scheme 2).
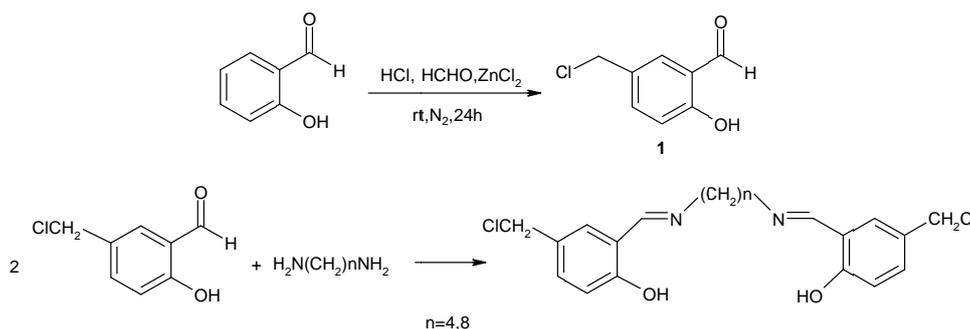

Scheme 2. The procedure of preparation of chlorinated salen Schiff bases

4.9.1. FTIR

The structure of the chlorinated Schiff bases were confirmed by the presence of several bands in their FTIR spectra. A broad absorption band is related to O–H stretching vibrations in the region 3300–3600 cm^{-1}, aromatic C-H stretching vibration in 300-3100 cm^{-1}, aliphatic C-H vibration at 2850 and 2960 cm^{-1}, strong C=N and C=C absorption bands respectively at 1620 and 1500-1520 cm^{-1} and C-Cl band at about 750 cm^{-1} confirm the structure of the products (Fig. 5).
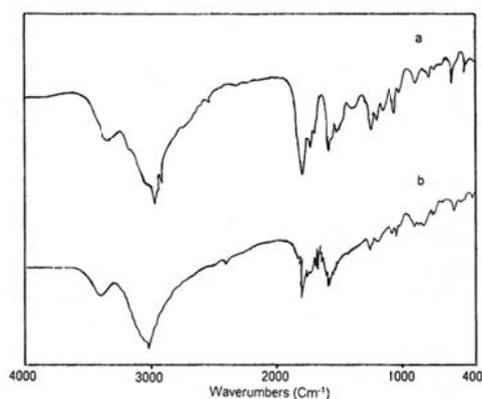
Fig. 5. FTIR spectra of salen **2** (a) and **3**(b)
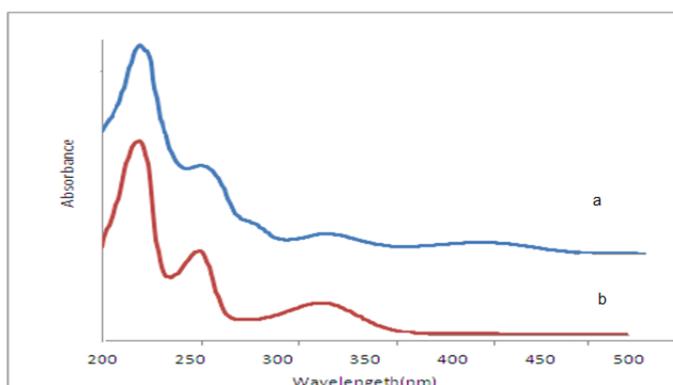
**Fig. 6.** UV-Vis spectra of salen **2** (a) and **3** (b)

4.9.2. UV-Vis absorption

In UV-Vis absorption spectra of Schiff bases (Fig. 6), the compounds exhibit intense bands in the 200–400 nm regions. These absorption bands may be assigned to n→π* and π→π* transitions. The 210–300 nm bands are due to the π→π* transitions of the aromatic rings and the bands at the 300–350 nm range, involve π→π* transitions of the C=N group in salen Schiff base **2** and **3**.

4.10. Characterization of salen @MWCNTs

4.10.1. FTIR

Salen Schiff bases were chemically attached to aminated MWCNTs through a simple nucleophilic substituted reaction (Scheme 3). The reactions products were characterized by FTIR, UV-Vis and SEM techniques.
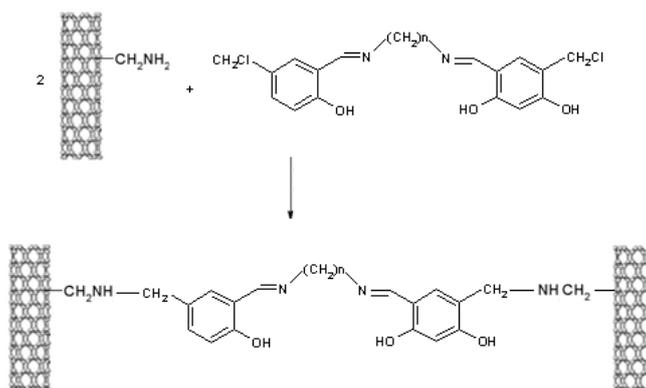
**Scheme 3.** Procedure of preparation of salen @MWCNTs

The FTIR spectra of functionalized MWCNTs are shown in Figs. 7. The IR spectra of functionalized MWCNTs contain several bands due to Schiff base structures. A broad band at about 3450 cm^{-1} is related to the bending mode of O-H groups. Peaks at about 2800 and 2920 cm^{-1} are due to C–H stretching modes of the CH_2 groups. The stretching band of the C=N groups appears at around 1600 cm^{-1}. C=C and C–N vibrations appear in 1420-1550 and 1050 cm^{-1} respectively. These results indicate that salen Schiff bases attachment to the MWCNTs surfaces performed successfully.
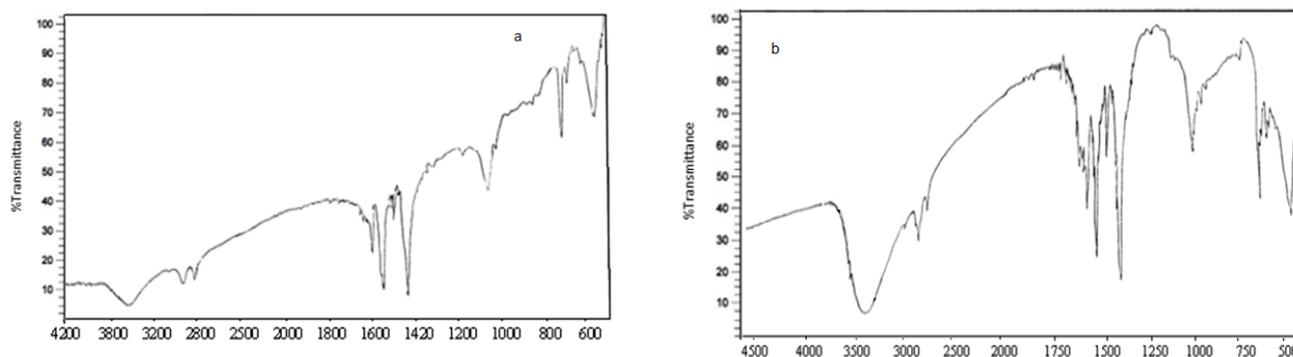
Fig. 7. FTIR spectra of salen **2**@MWCNTs (a), Salen **3**@MWCNTs (b)

4.10.2. UV-Vis absorption

From comparison of adsorption spectra of salen Schiff bases (Fig. 6) and salen@MWCNTs (Fig.8), it clearly can be recognized, that the Schiff bases were chemically attached to the surfaces of functionalized CNTs.
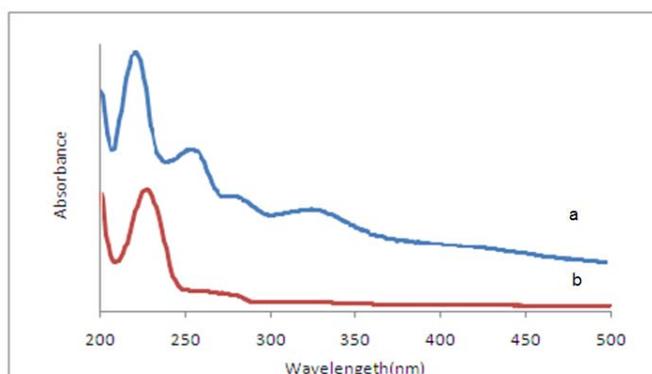
Fig. 8. Uv-Vis spectra of salen **2**@MWCNTs (a) and salen **3**@MWCNTs (b)

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4.10.3. SEM

Fig. 9 exhibits a comparison of the SEM images of raw and salen @MWCNTs. importantly, the MWCNTs have found to be remained to their length. In fact, cutting of nanotubes has not occurred during the reaction procedure. These images also reveal that the nanotube diameters become thicker after functionalization and also the endcaps of CNTs were opened.

Fig. 9. SEM images of raw MWCNTs (A), salen**2**@MWCNTs (B) and salen**3**@MWCNTs (C)

4.11. Characterization of salen complex @MWCNTs

Conversion of Schiff base @MWCNTs to their complex moieties can be occurred through the reaction of transition metal salts with Schiff base @MWCNTs (Scheme 4). Here we prepare Cu and Ni complexes @MWCNTs.
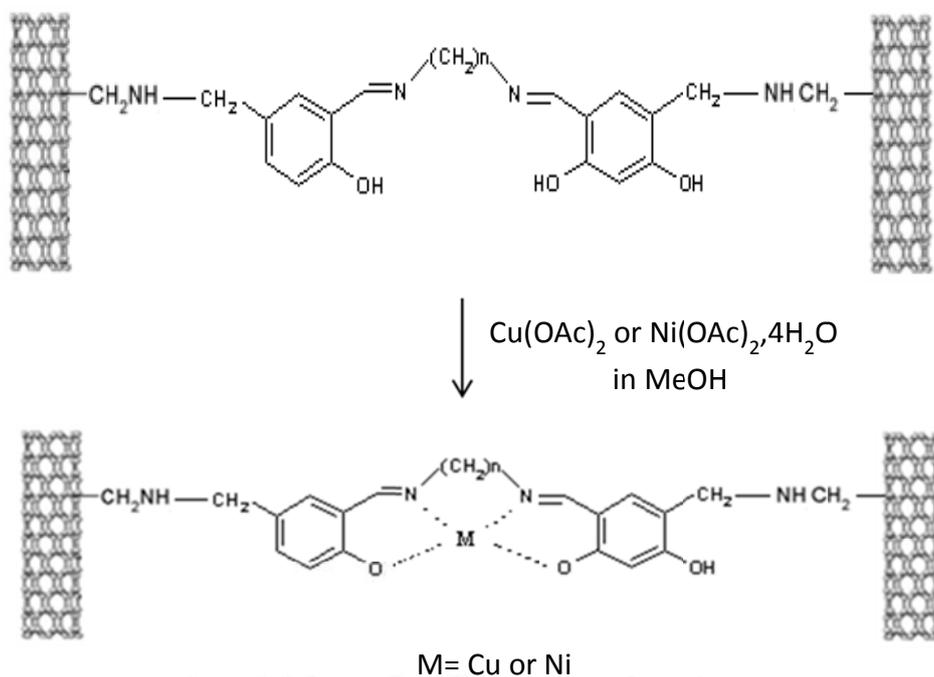
Scheme 4. Preparation of salen complex@MWCNTs

4.11.1. XRD

The attachment of salen complexes on MWCNTs can be supported by XRD analysis. Fig. 10 shows XRD patterns of salen complexes@ MWCNTs. Pristine MWCNTs, has peaks at 25.95^o and 43.38^o (Fig. 2). The patterns of Cu and Ni complexes @MWCNTs differ from those of raw MWCNTs due to transition metal chelation to salen@MWCNTs. According to the FTIR and UV-Vis results, it is believed that metal supported catalyst on MWCNTs is indeed obtained.
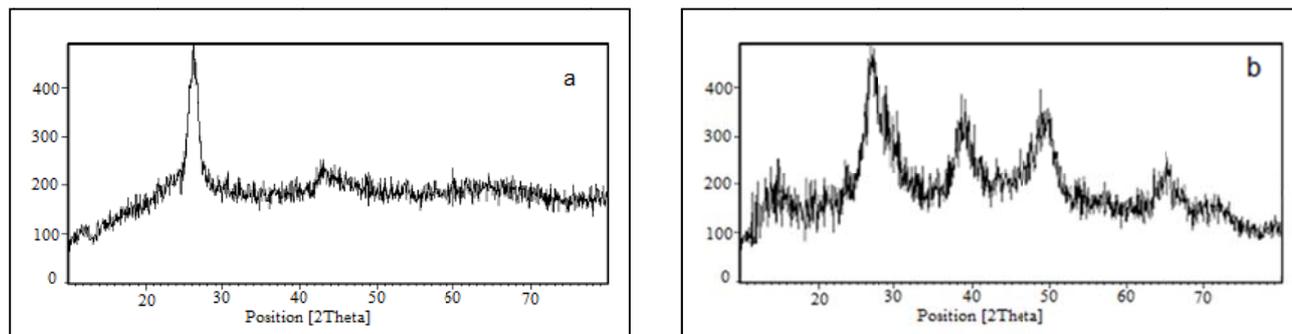
Fig.10. XRD patterns of: (a) Cu complex@MWCNTs and (b) Ni Complex@MWCNTs (from 2@MWCNTs)

4.11.2. EDX analysis

Fig. 11 give the EDX distribution of elements for the Cu and Ni complexe@MWCNTs. The existence of C, O, Cu and Ni in the functionalized CNTs was confirmed by the XRD results and show that the metal complexes were successfully attached on the CNT surfaces.
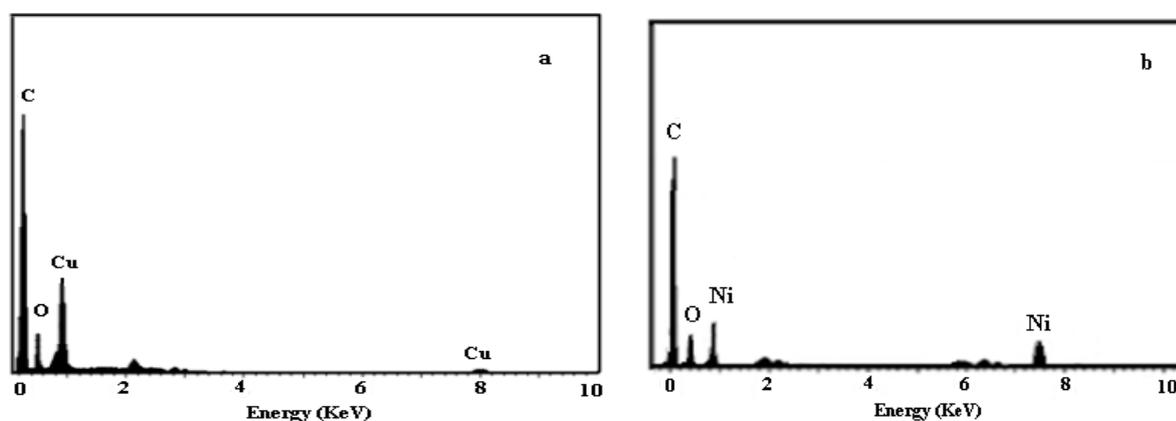

Fig.11. EDX of Cu (a) and Ni (b) complex@MWCNT

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