

Reaction of Azo Dyes with Amino functionalized Multi walled carbon Nano Tubes.

Nasim Khoshlahjeh Motamed

Department of Chemistry, Tehran North Branch, Islamic Azad University, Tehran, Iran

Abstract— In this paper the synthesis of functionalized MWCNT Solution of multi-step reactions have been reported during carbonylated nanotubes is obtained with the desired amines. After purification of MWCNT oxidation with nitric acid and the formation of nanotubes carboxylated MWCNTS - CoCl obtained. The reaction product of aromatic amines and aliphatic several factors such as 1,4 phenylene diamine, 4-hydroxy- 1,3 phenylene diamine, 4-methyl -1,3 phenylene diamine, 1,3 phenylene diamine, 1,8 diamino-3,6 dioxo octane derivatives. Significant operating and nanotubes MWCNTS-CO-NH-R-NH₂ Was changed. Because of this structure, solubility in organic solvents can react with various functional groups and heavy metals ions in water is used. Each product at each stage of spectroscopic methods IR, RAMAN, ¹H NMR, ¹³ C NMR, SEM, TGA, were identified and analyzed. Then we make the dye, the dye composition of amino nano tubes and then deposited obtained by spectroscopic methods such as IR/TGA analysis was identified.

Keywords—Nano Tube, Azo Dyes, Amines.

I. INTRODUCTION

The carbon nanotubes are one of the most important structural blocks. The high power and the electrical conductivity of these materials are not comparable to the carbon nanotubes. The carbon nanotubes contain the thin cylindrical layers of graphite. Their electrical conductivity is similar to copper, but, they have the ability to transfer the higher currents. Generally, the carbon nanotubes are divided into two groups of the single-walled carbon nanotubes and the multi-walled carbon nanotubes [1,2]. The carbon nanotubes have a widespread application in the production of composite fibers. These fibers have a potential for use in the safety equipment, the anti-explosion coatings, and the protective shields of electromagnetic fields. Meanwhile, the buckypaper nano-sheets are more solid than the steel and harder than diamonds which can be used in the structures of automobiles and aircraft. The buckypaper is a very thin sheet which is made of a mass of carbon nanotubes [3]. The electrical conductivity of these materials is similar to copper or silicon and they transfer the heat very well like steel or brass. In fact, these nanotubes are the strongest

and most stiffness known fibers and also they are called the most conductive fiber which can also be used as the semiconductors. This material can be used as a wonderful material for manufacturing the aircraft and automobiles based on the unique properties [4].

In other words, the solar cells are photovoltaic systems which supply their photons from the sunlight. The solar cells can be divided into three generations. The first generation is mainly made of the single-junction silicon parts (p-n junction) with the very high purity. The second generation of solar cells uses the inorganic semiconductors which require the less preparation processes. These semiconductors usually are used as the crystalline films and the efficiency of these cells is much lower than the first generation. The third generation of solar cells consists of organic molecules. The cost of making these cells is lower than the other two generations. The methods of making them are simpler. However, the efficiency of these cells is still not acceptable and the efforts are continuing to increase it. The third generation consists of the dye-sensitized solar cell (DSSC), the polymer cells, and the small cells [4,5]. Generally, an organic pigment-sensitized semiconductor material is used as an optical electrode for the cells in this type of photochemical cells. The light radiation with the suitable wavelengths to the electrode causes the light to be absorbed by the pigment and consequently, the molecule is stimulated by the light. The electron-hole pair is separated from each other at the interface of the semiconductor pigment and the electron enters the external orbit through the semiconductor conduction level and leads to create a current. In this case, the organic pigment is reduced by the intermediate sample in the electrolyte of solar cells and the intermediate sample oxidized in the opposite electrode is reduced by the electrons passing through the external orbit. There are different methods for the preparation of azo dyes; but, generally, they are produced by the coupling reaction of the diazonium materials. These materials are produced from the diazotization reaction of the first-order aromatic amines. The diazotization reaction was discovered in 1862 by Grill and it caused a change in the painting industries [5]. Phenol, naphthol, and arylamines are used as a coupling agent in these reactions.

The carbon nanotubes are useful for making the non-organic moulds and preparing the modern hybrids. The carbon nanotube structure-based hybrids are used in the catalysis with the biosensors, the hydrogen storage, the drug delivery, the biomaterials, and the nanoelectronics fields. The challenge here is that use of nanotubes requires a functionalized surface to spread their dispersion and the ability to participate in the physical and chemical reactions. Many strategies have been used to functionalize the nanotubes, such as the oxidation of the strong acids, the covalent conversion with the organic molecules and the polymers. Other methods based on the functionalization of the nanotube have developed such as modulating and facilitating by benzyl mercaptan, the cationic polymers, and the polyelectrolyte surfactants [6,7]. The non-covalent functionalization may maintain the electronic structure as well as sp^2 and produced the metal particle hybrids of the carbon nanotubes under the gentle conditions and the evolution. The non-covalent functionalization of the nanotubes with biomolecules like DNA and proteins is an additional potential strategy to prepare the new bio-electronics nanomaterials [8,10]. It can benefit from the advantage of the recognized molecular properties in the biomolecules bond. For example, Bill et al. reported an easy strategy to modify and modulate the multi-walled nanotubes by poly-L-lysine, albumin bovine serum, bean-shaped seeds of Glycine max L. oxidase, and α^1 -acid glycoprotein [11-13]. They found that the absorbed proteins can be controlled the growth of nanoparticles of supported silver on multi-walled nanotubes. In this research, proteins should be selected which can directly modify and modulate the single-walled nanotubes through non-agricultural methods. The supported silver metallic nanoparticles were not synthesized in a gentle condition. The sub-products of the supported silver metallic nanoparticles with the hybrids of supported silver metallic nanoparticles of the multi-walled carbon nanotubes were together in the same conditions [14-16].

At the same time, Corpa et al. also found that the hydrophobic protein called HFB $^{\pm}$ can be used to control the non-covalent functionalization of the single-walled nanotubes and yet, it can also be planned to control the aggregation of the gold nanoparticles after the bond formation of these particles on the proteins [17-18]. Initially, they chose a specific protein to do the purpose, but, this protein was not readily available and their method can't be used which directly applied to the majority of proteins for the use of their attitude [19-20].

II. EXPERIMENTAL

Step 1

In the two neck round bottom flask pour 80mgr of nanotube carboxilate and 25cc of DMF was add, 30 min. over ultrasonic. After 30 min, put the mixture in the ice bath, containing acetone the 10mm of oxalic choloride, was added slowly, this reaction protected under nitrogen (atm) with stirring. Durring time temperature was under controlled.

The reaction minture was about $-13^{\circ}c$ with adding acetone with ice, then reaction mixture was kept for further 2hr at $0^{\circ}c$. left it for overnight at room tempereture for more drying, put it on the heater until temperature rise to $70^{\circ}c$

Step 2

7.5 gr (0.04 mol) of (b4) –phenylendiamine dissolved in 15cc of DMF was added in 0/5 gr of previous product (1 step) at 30 min. under ultrasonic. The mixture put in the microwave. (T. $110^{\circ}c$, P.70) for 2hr, evaporated solvent the residue was collected. This compound was reacted with 8gr of 4-hydroxy- 1,3 phenylene diamonium dichloride, 5 gr of 4-metyl 1,3- phenylene diamine, 4.5 gr of 1,3-phenylene diamine and 5 gr of 1,8 diamine – 3,6 – dioxaoctane respectively some of five drivatives added THF and then for 30 min. kept under ultrasonic. The percipitation was happened after 2 days and then 50ml of THF was added and seperated the residue by filtration and dry it. All product were confirme by IR / RAMAN / HNMR / $^{13}CNMR$ / and SEM, TGA spectroscopic

Preparation of DSSC

0.3 gr of each drivatives of nanotubes containing amines pour in the beaker and then some ice added, stirred slowly until nanotube desolved completely. 4cc Hydrogen choloride (5N) was added in the above beaker and reaction mixture was reached to ($0^{\circ}c$). In the other hand desolved onegr of Sodium Nitrite in 25cc of water and in an other beaker (0.4gr) blue azo dyes desolved in 10 ml of mixture of water and etanol, and then mixed the two beakers solution in the previous mixture, after filtration, purification, checked the product by IR / TGA respectively

III. RESULT AND DISCUSION

Derivative 1: 1,4 Phenylene diamine

IR (KBr, cm^{-1}) ν_{max} : 3400-3800 (OH), 3300-3500 (NH), 3000-3100 (CH, Ar), 2773-2973 (CH, Al), 1660-1760 (C=O), 1630-1690 (N-C=O), 1030-1230 (C-N), 548 (C-Cl) RAMAN: 3200-3600 (OH), 2500-3000(CH₃, CH₂, CH) (C=C), 1600-2000 (C=O, CoOH), 1600-1800 (C=C) 1Hnmr (DmSO, 300 MHZ) 8 ppm 3.3-4.5 (S, 1H), 3.5 (S, 2H, NH₂), 4.5-6.5 (S, 1H) 6.5-8 (m, 4H, Ar), 9.1 (1H, S, NH) $^{13}CNMR$ (DmSO, 300 MHZ) 8 ppm 200.0, 160.2,

135.1, 122.2, 420.1, 119.8, 118.2, 80.2, 65.4, 57.1, 40.5, 30.2

Derivative 2: 1.3 Phenylendiamonioum dicholoride

IR (KBr, cm^{-1}) ν_{max} : 3400-3800 (OH), 3500-3300 (NH), 3000-3100 (CH, Ar), 2773-2973 (CH, Al), 1660-1760 (C=O), 1630-1690 (N-C=O), 1030-1230 (CN), 548 (C-Cl) RAMAN: 1600-2000 (C=O, CoOH), 1600-1800 (C=C), 1200-1400 (CH, Ar) $^1\text{Hnmr}$ (DmSO, 300 MHZ) 8 ppm 3.3-4.5 (S, 1H), 6.5-8 (2Hm, Ar), 7.5 (S, 2H, NH₂), 9.1 (1H, S, NH), 10-12 (OH), $^{13}\text{CNMR}$ (DmSO, 300 MHZ) 8 ppm 160.2, 152.8, 125.2, 122.7, 120.1, 119.8, 118.2, 70.2, 55.1, 47.8, 40.5, 30.2

Derivative 3: 4 metyl – 1.3 Phenylendiamin

IR (KBr, cm^{-1}) ν_{max} : 3300-3500 (NH), 3421 (OH), 3000-3100 (CH-Ar), 2773-2972 (CH, Al), 1660-1760 (C=O), 1630-1690 (N-C=O), 1030-1230 (C-N), 548 (C-Cl) RAMAN: 1600-2000 (C=O, CoOH), 1600-1800 (C=C), 1200-1400 (CH, Ar) $^1\text{Hnmr}$ (DmSO, 300 MHZ) 8 ppm. 1.3-2.5 (3H, S, Ar), 3.3-4.5 (S, 1H), 4.5-5 (S, 2H, NH₂), 9.1 (1H, S, N), $^{13}\text{CNMR}$ (DMSO, 300 MHZ) 8 ppm 160.2, 135.2, 55.1, 47.8, 40.5, 30.2, 20.3

Derivative 4: 1.3 Phenylendiamine

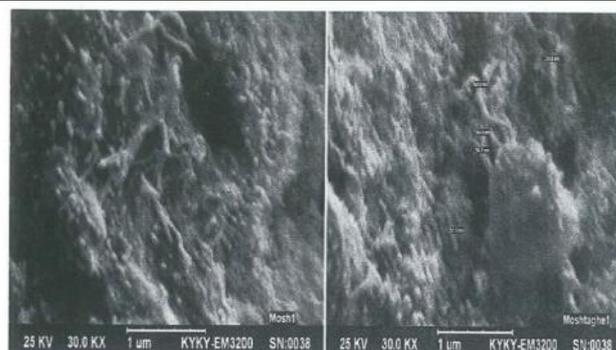
IR (KBr, cm^{-1}) ν_{max} : 3400-3800 (OH), 3300-3500 (NH), 3000-3100 (CH, Ar), 2773-2972 (CH, Al), 1660-1760 (C=O), 1630-1690 (N-C=O), 1030-1230 (C-N), 548 (C-Cl) RAMAN: 1600-2000 (C=O, CoOH), 1600-1800 (C=C), 1200-1400 (CH, Ar) $^1\text{Hnmr}$ (DMSO, 300 MHZ) 8 ppm 2.2 (S, 2H, NH₂), 2.82 (1H, S, Ar), 3.3-4.5 (S, 1, N), 4.5-6.5 (2H, S), 6.5-8 (4H, m, Ar), 9.1 (1H, S, NH) $^{13}\text{CNMR}$ (DMSO, 300 MHZ) 8 ppm 160.2, 135.2, 55.1, 47.8, 40.5, 30.2, 20.3

Derivative 5: 1.8 diamino, 3.6- dioxuocan

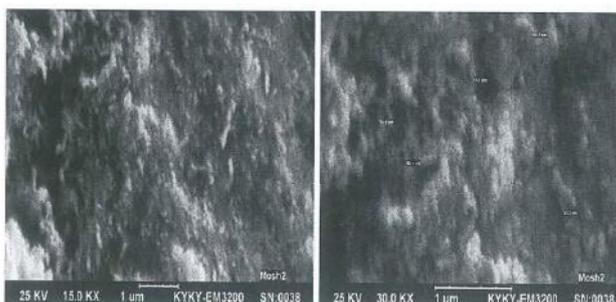
IR (KBr, cm^{-1}) ν_{max} : 3300-3500 (NH), 3421 (OH), 3000-3100 (CH, Ar), 2773-2972 (CH, Al), 1660-1760 (C=O), 1630-1690 (O=C-NH), 1030-1230 (C-N), 548 (C-Cl) RAMAN: 3200-3600 (OH), 2500-3000 (CH₃, CH₂, CH), 1600-2000 (C=O, CoOH), 1600-1800 (C=C), 400-700 (Cl) $^1\text{Hnmr}$ (DMSO, 300 MHZ) 8 ppm 2.83 (C=C-H), 4.26 (S, 1H), 4.94 (S, 1H), 5-7 (4H, m, C-C=H), 8.13 (1H, S), 4.1 (5CH₂ (10H, S)) $^{13}\text{CNMR}$ (DMSO, 300 MHZ) 8 ppm 160.2, 160.1, 158.7, 70.2, 65.2, 63.2, 62.1, 40.2, 40.1

SEM Spectroscopy:

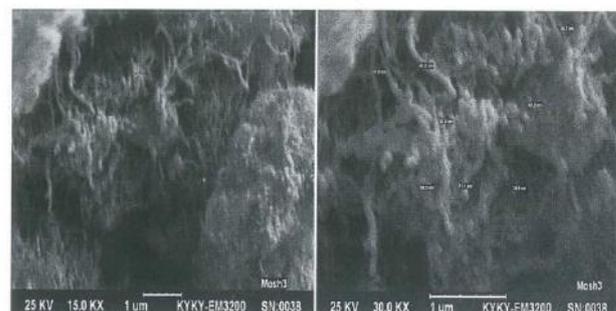
The same images of Carbon nanotubes Carboxilate are shown nanotubes groups are lied as in dependence chain beside of each other



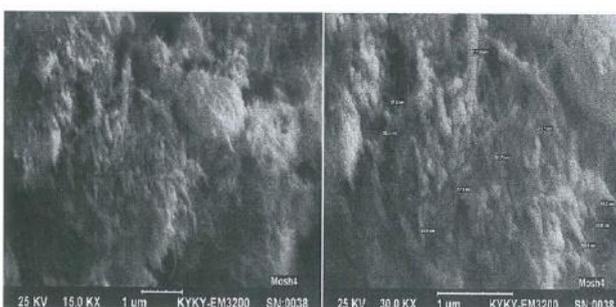
derivative 1



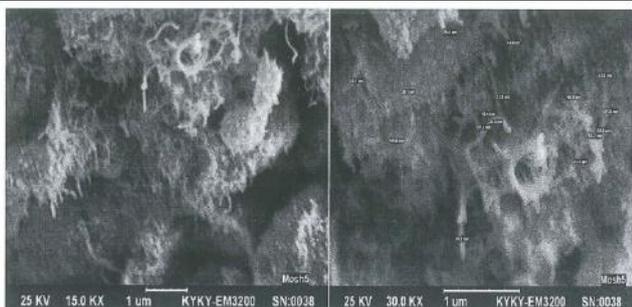
derivative 2



derivative 3



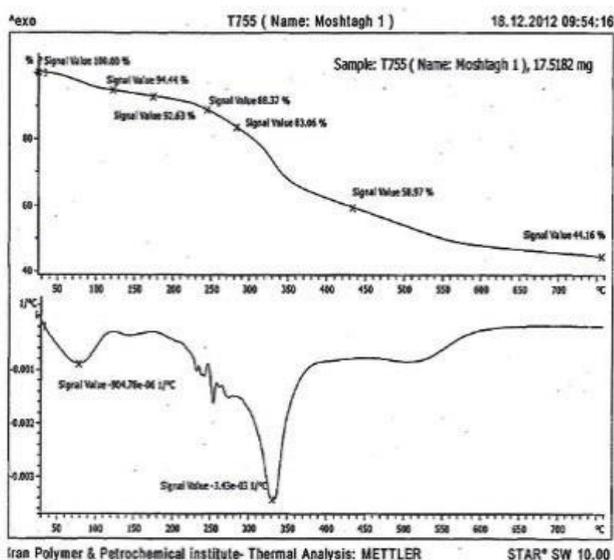
derivative 4



derivative 5

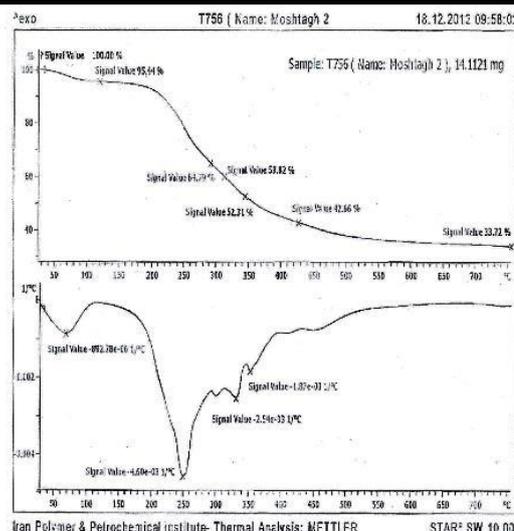
TGA Spectroscopy: (derivative 1) In above structure was shown decrease and increase of weight in 100^oc because the sample was observe some water .

In continue the Carboxile groups were destroyed in 170^oc and maximom decrease of weight appear at 330^oc and rised to 480^oc for completing. Next peaks appear at 550^oc that means the Oxidation of Carbon nanotubes was happened. The reason of Oxidation due of Carboxilic destruction which freedom Oxygen in TGA condition.



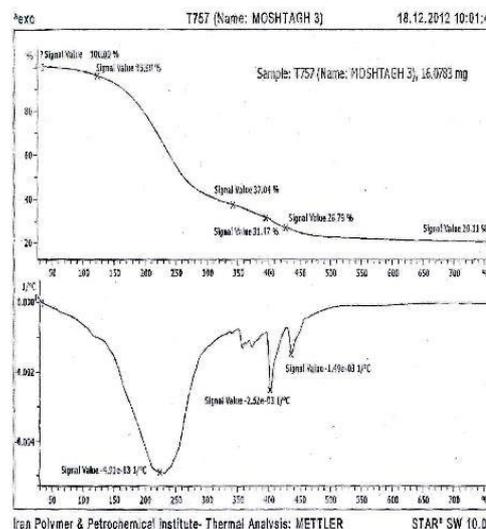
TGA Spectroscopy: (derivative 2)

In above structure was shown decrease and increase of weight in 70^oc because the sampl was observe some water. In continue the Carboxile groups were destroyed in 170^oc and maximom decrease of weight appear at 250^oc and rised to 430^oc for completing. Next peaks appear at 480^oc that means the Oxidation of Carbon nanotubes was happened. The reason of Oxidation due of Carboxilic destruction which freedom Oxygen in TGA condition.



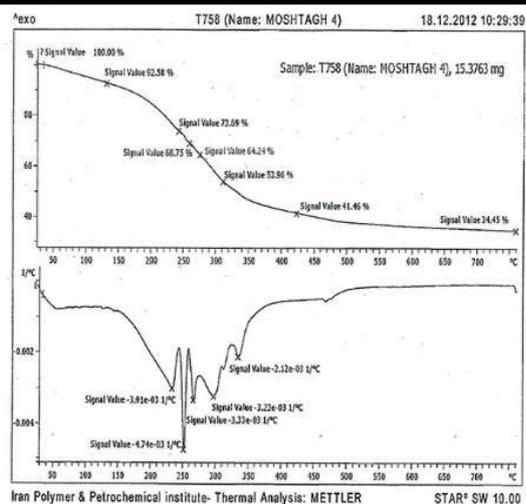
TGA Spectroscopy: (derivative3)

In above structure was shown decrease and increase of weight in 130^oc because the sample was observe some water. In continue the Carboxile groups were destroyed in 150^oc and maximom decrease of weight appear at 350^oc and rised to 430^oc for completing. Next peaks appear at 480^oc that means the Oxidation of Carbon nanotubes was happened. The reason of Oxidation due of Carboxilic destruction which freedom Oxygen in TGA condition.



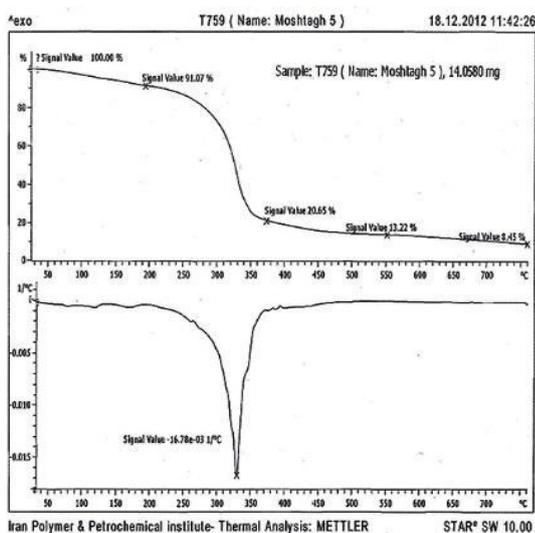
TGA Spectroscopy: (derivative 4)

In above structure was shown decrease and increase of weight in 130^oc because the sample was observe some water. In continue the Carboxile groups were destroyed in 150^oc and maximom decrease of weight appear at 250^oc and rised to 480^oc for completing. Next peaks appear at 530^oc that means the Oxidation of Carbon nanotubes was happened. The reason of Oxidation due of Carboxilic destruction which freedom Oxygen in TGA condition.



TGA Spectroscopy: (derivative 5)

In above structure was shown decrease and increase of weight in 200°C because the sample was observe some water. In continue the Carboxile groups were destroyed in 250°C and maximom decrease of weight appear at 380°C and rised to 350°C for completing. Next peaks appear at 400°C that means the Oxidation of Carbon nanotubes was happened. The reason of Oxidation due of Carboxilic destruction which freedom Oxygen in TGA condition.



IV. CONCLUSION

In this research we have done several steps as below, Carboxilated, Colorination, Amination, Purification, and then run IR / RAMAN / ¹HNMR / ¹³CNMR / SEM / TGA. All structure established by spectroscopic method as above. In final decision we would say functionalized these nanotubes Carbon by several of functional groups and then we can prepare several products of these functionalized nanotubes with respect of their properties which can be used in new solar cells and precipitate them very simply.

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