

available online *www.pccc.icrc.ac.ir* Prog. Color Colorants Coat. 10 (2017), 217-224



Synthesis of Some New Disperse Dyes-multi Walled Carbon Nanotubes Adducts and Impact Analysis of Substituents

R. Amiri^{*1}, F. Afshar Taromi², H. Cheghini¹, Y. Tishbi¹, N. Rezaee¹

¹ Department of Chemistry, Central Tehran Branch, Islamic Azad University, P.O. Box: 1465613111, Tehran, Iran.

^{2.} Faculty of Polymer and Color Engineering, Amirkabir University of Technology, P.O.Box: 15875-4413, Tehran, Iran.

ARTICLE INFO

Article history: Received: 07 Jun 2017 Final Revised: 26 Sept 2017 Accepted: 2 Oct 2017 Available online: 9 Oct 2017 Keywords: Anthraquinone Azo Chromophore Dye multi-walled carbon nanotube.

ABSTRACT

e have reported here a simple, low cost preparation of four new adducts from some anthraquinone disperse dyes with functionalized multi-walled carbon nanotubes in the presence of azochromophore. The structural differences between the final products are evaluated by visual dispersion test, UV-Vis Spectroscopy, Fourier transforms infrared, Raman, nuclear magnetic resonance and thermal gravimetric analysis. The morphology of themis detected using scanning electron microscopy. It has been shown that various substituents on the backbone of anthraquinone can affect the features of the adducts. *Prog. Color Colorants Coat. 10 (2017), 217-224*© *Institute for Color Science and Technology*.

1. Introduction

Anthraquinone disperse dyes are the second most important class of dyes. They are used in different fields such as textile, printing, plastic industries and solar cell [1-4]. Also, carbon nanotubes (CNTs) have attracted great interest in multi-disciplinary owing to their remarkable physical and chemical properties [5-12]. Since, the pure carbon nanotubes have their own restrictions such as the low solubility or dispersibility in common organic materials, the functionalization of CNTs has been widely developed. In this regard, various organic and inorganic materials have been used on the surface of CNTs. Covalent or non-covalent modification of nanotubes have also been explored in order to control the chemistry of CNTs [13, 14]. Among these, modification with anthraquinone groups has found interest for several applications specially electrochemical capacitors [15]. However, less attention has been paid to the effects of different groups in the sidewalls attachments. So, in this research, we show that chemical substituents have noticeable impact on the functionalized carbon nanotube network. We bonded anthraquinone disperse dyes to the functionalized multi-walled carbon nanotubes in the presence of azochromophore. It was reported that the aryl diazonium functional groups can be chemically grafted into the surface of CNTs by using reducing agents or elevated temperature [16, 17].

The present work introduce a simple coupling reaction between the functionalized-MWCNTs and the diazonium salts of anthraquinone dyes. For the first time, we analyzed the influence of different groups in anthraquinone moiety on the structure and chemical properties of the final adducts. On the other hand, we showed that the covalent attachment of CNTs to a dye not only can add the properties of nano-tubes to dye, but its color can also be greatly preserved. Therefore, this approach can be applied to adjust the product properties according to the specific applications.

2. Experimental

2.1. Materials and Instrumentation

Purified (purity>95%) multi-walled carbon nanotubes (average outer diameter: 15 nm, length: up to 50 μ m) were supplied from Nanocyl S.A. (Sambreville, Belgium). Thionylchloride (SOCl₂), 4-aminophenol, 1amino-2-phenoxy-4-hydroxy-anthraquinone (1), 1, 2diaminoanthraquinone (2), 1, 5-dihydroxy-4, 8-diamino-2-Bromoanthraquinone (3), 2, 6-diaminoanthraquinine (4) and the other reagents were obtained from Merck.

The resulting mixtures were sonicated in OS ultrasonic bath. Fourier transform infrared spectroscopy (in KBr pellets) was recorded on Perkin-Elmer 1605 FT-IR spectrometer. Thermal studies were carried out on a Perkin-Elmer AST-2 Diamond TG/DTG analyzer. The spectra in the UV-Vis range of 200 nm to 700 nm were taken using spectrophotometer V570 Jasco. Scanning electron microscopy (SEM) was performed on XL-30 Philips instrument. Hydrogen nuclear magnetic resonance (NMR) spectroscopy was carried out on a Bruker AVANCE 500 MHz using DMSO as the solvent and TMS as the internal reference. Raman spectra were acquired on a Renishaw Raman System 3000 equipped with a CCD detector and an Olympus microscope (BTH2) that allows a rapid accumulation of Raman spectra with a resolution of about 1 µm (micro-Raman technique).

2.2. Oxidation process

Crude MWCNTs were added to a mixture containing concentrated sulfuric acid and nitric acid at the rate of 3:1 by volume. The suspension was sonicated in an ultrasonic bath for 30 min and heated up to 90°C for 3 h. After centrifuging and washing with hot distillated water, the suspension was stirred in sodium hydrogen carbonate solution overnight and washed again [18]. The oxidized MWCNTs were dried in vacuum.

2.3. Acylation of MWCNTs

MWCNTs-COOH (125 mg) was synthesized as described above and was then reacted with 100 mL of

 $SOCl_2$ at 70 °C for 24 h under reflux to convert the surface-bound carboxylic acid into acyl chloride group. The solids that were subsequently obtained were filtered and washed with anhydrous THF. The filtrate was dried under vacuum at room temperature for 4 h to give acyl chloride–functionalized MWCNTs (MWCNTs-COCl, 100 mg) [19].

2.4. Modification of MWCNTs with 4-aminophenol

4-aminophenol (100 mg) was added to a suspension of MWCNTs-COCl (100 mg) in DMF (50 mL). The mixture was vigorously stirred at 120 °C for 72 h. After cooling the mixture, the black solid were collected by filtration and then was washed thoroughly with DMF and dried under vacuum for 24 h (MWCNTs-CONH-4- C_6H_4OH , 76 mg) [18].

2.5. Preparation of f-MWCNTs/diazo compound (1-4)

The resulting MWCNTs-CONH-4- C_6H_4OH was sonicated for 30 min with DMF (50 mL) to get a visually homogeneous suspension. Fine powdered NaNO₂ (1 mmol) was added slowly with stirring to the mixture containing anthraquinone dyes (1 mmol), HCl (0.3 mL) and H₂O (3 mL). Temperature must be kept below 5 °C. The solution was then added drop wise to the primary suspension of MWCNTs-CONH-4- C_6H_4OH and Na₂CO₃ (1.2 mmol) in H₂O (5 mL). After stirring for 1 h, the nano-azo products (1-4) were filtered and washed with H₂O until the filtrate became colorless. The products were then dried in vacuum for 36 h before characterization.

3. Results and Discussion

In this work, anthraquinone disperse dyes with different substituents (especially amino groups) have been bonded to the functionalized MWCNTs through azochromophore (products **1-4**, Scheme 1).

3.1. Structural Characterization of compounds 1-4

Fourier transform infrared study of products **1-4** confirms the presence of -OH (3056-3452 cm⁻¹). C=O (1650-1730 cm⁻¹), C-N (1380-1465 cm⁻¹) and C-O (1020-1296 cm⁻¹) functional groups. The absorption of N=N should be at about 1450 cm⁻¹ in the FT-IR spectra

of products **1-4**, but it may overlap with other stretching peaks and hence making the visualization of the individual peak impossible (Figure 1).

The chemical structures of compounds **1-4** were investigated by ¹H-NMR analysis. ¹H-NMR spectra of these compounds in DMSO-d₆ is shown in Figure 2. The aromatic protons have appeared between δ =6.23-8.39 ppm in¹H-NMR of the products **1-3**. However, the number of peaks has decreased for compound **4** (two singlet at 7.91 and 8.45 ppm). The most important characteristic signals of this ¹H-NMR are the allylic protons connecting to the nanotubes (around 2-3 ppm) [20]. Also, the protons of –CONH and OH groups have not been appeared in the spectra. The hydrogen atoms can form hydrogen bonds and they can undergo molecular exchanges. Therefore, the intra- and intermolecular exchanges may lead to both signals broadening and disappearing.



Scheme 1: The schematic view of the reaction for preparation of the products 1-4.



Figure 1: FT-IR spectra of the products 1-4.

Figure 2: ¹HNMR spectra of the products **1-4**.

0



Figure 3: Visual dispersion of the products 1-4.

3.2. Visual dispersion test

Surprisingly, the products 1-4 can be dispersed in organic solvents such as hexane, CH_2Cl_2 , DMF, DMSO and even in H_2O to produce color. This process may be qualitatively monitored by visual observation of their solution. The dispersibility of the adducts 1-4 in DMSO are comparatively exhibited in Figure 3. The vials contained the same amount of 1mg/mL for each

of them in DMSO. The photographs were taken after vigorous shaking and they remained unchanged for several days. As can be observed, the solubility of products **3** and **4** are less than that of products **1** and **2**. These observations show that dual attachment of the functionalized MWCNTs to the disperse dyes could decrease the dispersibility of the final adducts. Also, the existence of more auxochromes in dyes moieties **1** and **3** can lead to different colors.

3.3. UV-Vis spectra analysis

UV-Vis absorption spectra of products 1-4 (1mg/mL) in DMSO are shown in Figure 4. As can be seen in this figure, UV-Vis spectra of products 1 and 2 are not the same. The existence of additional substituents in 1 leads to the appearance of characteristic absorptions for this compound. The higher absorption of this compound could be attributed to the π - π * transition of trans-azo benzene. In addition, it has a maximum absorption of about 300 nm corresponding to the $n \rightarrow \pi^*$ transition of phenoxyl and hydroxyl groups. The UV-Vis spectra of products 3 and 4 are more analogous. Apparently, increasing the carbon nanotubes content in products 3 and 4 has led to a reduction in their solubility. So, the absorption picks do not appear clearly in their UV-Vis spectra. Also, this phenomenon can be related to the light scattering of the suspended carbon particles [21].

3.4. Raman analysis

Raman spectra are obtained by the focused 663 nm laser in order to monitor the change of the vibrational stability of MWCNTs. The most important band in Raman spectra of the products 1-4 are a G band (1457-1581 cm⁻¹) which can be ascribed to the splitting of the E₂g stretching mode of graphitic pattern and a D band (1264-1346 cm⁻¹) which is related to scattering from the structural defects present in MWCNTs. D band is caused by the covalent functionalization process (Figure 5). The primary disperse dyes are completely dominated by the MWCNTs in products 1-4, and therefore low intensity bands of their functional groups are observed in other regions. The relative intensity of D-band to G-band (I_D/I_G) is also increased for products 1-4. This observation is ascribed to an enhanced degree of functionalization in these products, which lead to a greater number of sp³-hybridized carbons [22].



Figure 4: UV-Vis spectra of the products 1-4.



Figure 5. Raman spectra of the products 1-4.

3.5. TGA analysis

Figure 6 displays the non-isothermal gravimetric analysis of the products 1-4. The TGA curves of the samples 1 and 2 differ from that of samples 3 and 4. Upon increasing the temperature, the rate of mass loss for compounds 1 and 2 has become much greater than compounds 3 and 4. Such a large mass loss is probably a result of the easier removal of a dye molecule from MWCNTs. Heating to 600 °C in nitrogen atmosphere left a residue of about 62 wt% for sample 1 in comparison with 68 wt% for 2. However, the residues of sample 3 and 4 were above 80 wt% and 75 wt%, respectively.

Therefore, the amount of MWCNTs in the products **3** and **4** is more than the others which is in agreement with the aforementioned results. Also, TGA analysis showed that the main degradation of the products **1** and **3** has started at about 300 $^{\circ}$ C, while this point for

compounds **2** and **4** is at about 200 °C. So, the thermal resistance of f-MWCNTs/disperse-dyes with additional substituents (**1** and **3**) is more than the adducts without them [23].

3.6. SEM images

The morphology study of f–MWCNTs/dye adducts 1-4 have been performed using scanning electron microscopy (Figure 7). According to the SEM images of product 1, azo dyes clusters have attached to nanotube surface. Also, the product 3 such as 1 seems to be still nanotube like, only with cross–linking between them. The samples 2 and 4 are more similar to each other. The submerged carbon nanotube can be seen in the recent images. It might be related to more accumulation of dye molecules. This phenomenon can be due to the lower distances between them because of the absence of additional substituents.



Figure 6: TGA spectra of the products 1-4.



Figure 7: SEM images of the products 1-4.

4. Conclusion

In this work, modification of MWCNTs using disperse dyes has significantly improved the dispersibility of carbon nanotubes in organic solvents. The presence of additional chromophores and auxochromes in disperse dyes moieties of the products **1** and **3** leads to the considerable absorption in the visible region. Consequently, the final adducts **1** and **3** have yielded different colors. Furthermore, according to the SEM images, the structure of the carbon nanotubes is better

5. References

- X. Chen, H. Wang, H. Yi, X. Wang, Anthraquinone on porous carbon nanotubes with improved supercapactior performance, *J. Phys. Chem.*, 118(2014), 8262-8270.
- 2. M. Ghanem, I. kocak, A. Al Ayouf, Ph. N. Bartlett, Solid phase modification of carbon nanotubes with anthraquinon and nitrobenzene functional groups,

preserved in these adducts. Also, products 1 and 3 have higher thermal resistance. So, the knowledge gained from this study will help to design a product with the desired characteristics.

Acknowledgement(s)

This work has been supported by the Iranian nanotechnology initiative council. We would also like to thank Central Tehran Branch of Islamic Azad University for the use of equipment research laboratory.

Electrochem. Commun., 34(2013), 258-262.

- 3. W. Zhang, S. Ravi, P. Silva, The effects of phenolic hydrogens and methyl substitute groups in organic dyes on their dispersion of multiple-walled carbon nanotubes, *Carbon.*, 48(2010), 2063-207.
- 4. H. Nikoofard, A. Omrani, M. Meftah Niaki, Preparation and characterization of poly(1-amino-

9,10-anthraquinone)/multiwalled carbon nanotube nanocomposite, *Monatsh. Chem.*, 145(2013), 267-273.

- K. T. Demble, R, Nechache, L. Nikolova, A. Vomiero, C. Santato, S. Licoccia, F. Rosei, Effect of multiwalled carbon nanotubes on the stability of dye sensitized solar cells, *J. Power. Sources*, 223(2013), 93-97.
- 6. Y. M. Dai, W. J. Liu, T. C. Pan, J. M. Jheng, Surface activation on multi-wall carbon nanotube for electrochemical capacitor applications, *Appl. Surf. Sci.*, 258(2012), 3027-3032.
- X. Ren, C. Chen, M. Nagastsu, X. Wang, Carbon nanotubes as adsorbents in environmental pollution management, *Chem. Eng. J.*, 170(2011), 395 – 410.
- D. Zhao, W. Zhang, C. Chen, X. Weng, Adsorption of methyl orange dye onto multi walled carbon nanotubes, *Procedia. Environ. Sci.*, 18(2013), 890 – 895.
- J. Zhao, J. Ma, X. Nan, B. Tang, Application of noncovalent functionalized carbon nanotubes for the counter electrode of dye-sensitized solar cells, *Org. Electron.*, 30(2016), 52-59.
- 10. B. C. Nathb, B. Gogoia, M. Boruah, S. Sharma, M. Khannama, G. A. Ahmed, SK. Dolui, High performance polyvinyl alcohol/multi walled carbon nanotube/polyaniline hydrogel (PVA/MWCNT/PAni) based dye sensitized solar cells, *Elrctrochim. Acta.*, 146(2014), 106-111.
- J. Chen, B. Li, J. Zheng, J. Zhao, Zh. Zhu, Role of carbon Nanotubes in Dye-Sentesitized TiO₂-Based Solar Cells, *Phys. Chem.*, 116(2012), 14848-14856.
- 12. Sh. Tangestaninejad, M. Moghadam, V. Mirkhani, I. Mohammadpoor-Baltork, MS. Saeedi, Efficient epoxidation of alkenes with sodium periodute catalyzed by reusable manganese (III) salophen on multi-wall carbon nanotubes, *Appl. Catal. A.*, 381(2010), 233-241.
- 13. W. Zhang, S. R. P. Silva, Reversible functionalization of multi walled carbon nanotubes with organic dyes, *Scripta. Mater.*, 63(2010), 645 648.
- J. Liu, M. R. Zubiri, B. Vigolo, M, Dossot, Y. Fort, J. J. Ehrhardt, E. Mcrae, Efficient microwave-assisted

radical functionalization of single-wall carbon nanotubes, *Carbon.*, 45(2007),885-891.

- 15. K. Kalinathan, D. P. Desroches, X. Liu, P. G. Pickup, Anthraquinone modified carbon fabric supercapacitors with improved energy and power densities. *J. Power. Sources*, 181(2008) 182-185.
- 16. P. Abiman, G.G. Wildgoose, R.G. Compton, Investigating the mechanism for the covalent chemical modification of multiwalled carbon nanotubes using aryl diazonium salts. *Int. J. Electrochem. Sci.*, 3(2008) 104-117.
- C.G.R. Heald, G.G. Wildgoose, L. Jiang, T.G.J. Jones, R.G. Compton, Chemical derivatisation of multiwalled carbon nanotubes using diazonium salts. *Chem. Phys. Chem.*, 5(2004) 1794-1799.
- 18. B. Kim, W.M. Sigmund, Functionalized multi-wall carbon nanotube/gold nanoparticle composite, *Langmuir*, 20(2004), 8239-8242.
- 19. K.R. Reddy, B.C. Sin, K.S. Ryu, J.C. Kim, H. Chung, Y. Lee, Conducting polymer functionalized multi-walled carbon nanotubes with Nobel metal nanoparticles: synthesis, morphological characteristics and electrical properties. *Synth. Met.*, 159(2009), 595-603.
- 20. R. Amiri, S. Rasouli, A. Ghasemi, B. Eghbali, S. Mohammadi, Structrural dependence of the multi-walled carbon nanotubes to the substituents on the grafted diazo compounds, *J. Nanopart. Res.*, 16(2014), 2388, DOI:10.1007/s1105/014-2388-0.
- 21. G.M. Do Nascimento, R.C. De Oliveira, N.A. Pradie, P.R. Gessolo Lins, P.R. Worfel, G.R. Martinez, P. Di Mascio, M.S. Dresselhaus, P. Corio, J. Photochem. Photobiol. A: Chem., 211(2010) 99-107.
- 22. U. Ritter, P. Scharff, C. Siegmund, O.P. Dmytrenko, N.P. Kulish, Y.I. Prylutskyy, Radiation damage to multi-walled carbon nanotubes and their Raman vibrational modes, *Carbon.*, 44(2006), 2694-2700.
- 23. L. Stobinski, P. Tomasik, C.Y. Lii, H.H. Chan, H.M. Lin, H.L. Liu, Single-walled carbon nanotubeamylopectin complexes. *Carbohydr. Poly.*, 51(2003) 311-316.

How to cite this article:

R. Amiri, F. Afshar Taromi, H. Cheghini, Y. Tishbi, N. Rezaee, Synthesis of some new disperse dyes-multi walled carbon nanotubes adducts and impact analysis of substituents. Prog. Color Colorants Coat., 10 (2017), 217-224.

