REGULARITIES OF FUNCTIONALIZATION MULTILAYER CARBON NANOTUBES IN INTARACTION WITH AROMATIC DIAZOCOMPOUNDS

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Abstract

Studied the effect of conditions on degree of functionalization in interaction multi-walled with aromatic diazo compounds. On the basis of experimental data and computer simulations are made conclusions about the mechanism of the process.

Keywords: Multi-walled carbon nanotubes, diazocompound, structure, properties

INTRODUCTION

Carbon nanotubes (CNT) - commonly known today class of nano-objects, which have a whole set of properties and have found various areas of application. However, the lack of solubility and difficulties manipulation in any solvents impose significant limitations on their use. This is due to the complexity of the uniform distribution in a variety environments. Chemical modification of the carbon nanotubes by forming on the surface organic heteroatomic functional groups is a method of controlled adjustment of their structure, variation of the physical and physicochemical properties. Unsaturated chemical bonds CNT system allows direct introduce bulky organic moieties in the structure of nano-objects without breaks the carbon skeleton.

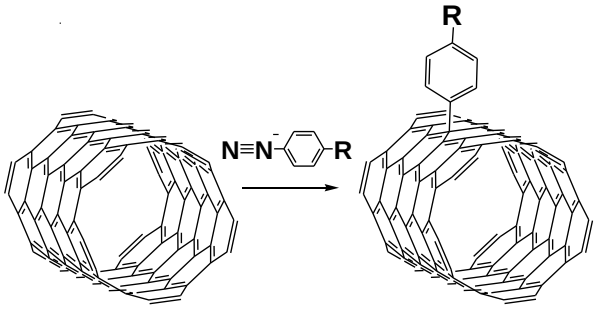
Promising variants of functionalization is the reaction of diazo compounds with carbon nano-objects, having a system of unsaturated bonds. Data for such process in conditions of the electrochemical reduction of diazo compounds, leading to the formation on the surface of graphite aromatic fragments are described in [1]. The authors assumed that the functionalization of the carbon surface flows through the formation of the corresponding aryl radicals. In [2], the above process is implemented for single-walled CNTs.

Later it was found that unsaturated chemical bonds system allows directly enter volumetric structure in the surface of single-wall and multiwall CNTs via diazo not only in conditions of the electrochemical reduction [3-7]. It was concluded about mechanism of the process. The authors suggested that at the stage of interaction CNT surface with a diazo compound the electron is transferred from the carbon nanostructures on organic product. This leads to elimination the nitrogen and formation of highly reactive aryl radical. Its accession leads to the formation of C-C bond. The radical nature of the process indicates the influence of the addition of a radical initiator [8].

It should be noted that different samples of CNTs are very different on the possibilities of forming an organic periphery. We have investigated the chemical behavior of multi-walled coaxial tapered according to the method of packing of graphene layers CNTs in reactions with aromatic diazo compounds. Effect of conditions realization of the process on the degree of functionalization of the resulting objects, features of their structure and spatial organization considered.

1. EXPERIMENTAL

Introduction of the functional groups of aromatic nature carried out by reacting the aromatic diazo compounds (produced in situ in a medium of sulfuric, hydrochloric and acetic acids from the corresponding substituted anilines) with the unsaturated bonds in CNT.



R = H, NO_2, CH_3

Fig. 1

The process was carried out by reacting aryl diazonium cation, prepared by diazotizing the corresponding aniline with carbon nanotubes. Aromatic components was dissolved in 10-40% sulfuric acid solution and cooled to 5-10 °C. Then sodium nitrite solution cooled to the same temperature was added. After 20 minutes with constant stirring diazotization products are transferred into three necked flask and the suspension of carbon nanotubes in N,N-DMFA added. The mixture was heated to 60 °C and after the process, cooling, separated by filtration under vacuum, washing first with distilled water and then with ethanol, before discoloration washing water.

Control of structure and elemental content of MWCNT were performed by using a scanning electron microscope (Carl Zeiss Supra 40)/

As a method of analysis is used IR spectroscopy as an effective method for identifying functional groups. Getting the vibrational spectra was carried out in vaseline oil on a spectrometer PerkinElmer Spectrum 60.

Quantum chemical calculations were performed by means software package MOPAC 2012, using a semi-empirical method RM7.

2. RESULTS AND DISCUSSION

Studied the effect process conditions on the degree of functionalization when used *para*-nitroaniline. In all cases process flow observed. On the IR spectrum of the reaction product for R = NO_2 seen the emergence of bands typical for the *para*-substituted nitroarenes: absorption bands in the 1342, 1554, 1602, 1627 cm^{-1}. Also noted the content of O and N on the surface of CNTs. The degree of functionalization was evaluated by the mass change sample CNT imposed and recovered from the reaction mixture, and elemental content (Table 1).

As varied parameters were used time of the process (Table. 1) and the ratio of CNTs: *para* -nitroaniline.

Table 1 Effect of time interaction MWCNTs with hydrosulphate *para* -nitrobenzenediazonium on the degree of functionalization (weight of the starting non-functionalized MWCNTs 0.1 g, *para*-nitroaniline - 3 g)

Reaction time (h).	**10**	**20**	**35**	**50**
Mass of the resulting product (r)	0,135	0,147	0,140	0,140
Elemental content N/O, %	2/9	2/12	2/8	2/8

Varying ratios MWNT: *para* -nitroaniline by weight in the range of 1/5 - 1/30 (at the time of the process 50 hours) did not produce a significant variation in weight of the resulting product, and by its elemental content.

The data presented in Table 1 show maximum yields of functionalized MWNTs at 20 hours of the process, then it decreases. The content of nitrogen at the surface of the tube substantially constant, oxygen - passes through a maximum. Furthermore, samples for 10 and 20 hours showed signs of sulfur. This suggests that the following reactions are realized. Together with the nitrophenyl radical, counter-ion of an organic component diazo compound (hydrosulfate) attached to the surface of MWCNTs. Later, in the conditions of continuing process, it decomposes with elimination of sulfur-containing component. Evaluation of elemental balance in the implementation of such process gives a similar relationship with the experiment.

Use as an environment of acetic acid and hydrochloric acid gaves similar results, however, was a lower intensity of the diazotization reaction and lower degree functionalization of nanotubes.

In the investigation of the morphology of the obtained functionalized MWCNTs was found that their structure and organization differ significantly from the single-walled nanotubes. In [4, 8] is indicated on the destruction of dense associates of single-walled CNTs after functionalization by diazonium salts.

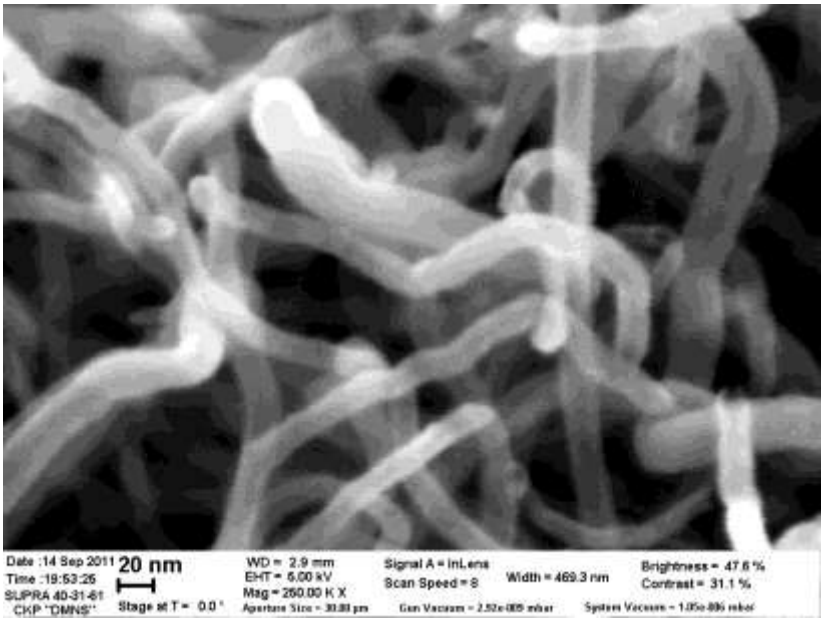


Fig.2 Non-functionalized MWCNTs

Comparison of morphological features of the original and modified MWCNTs by scanning electron microscopy (Carl Zeiss Supra 40) (see Fig. 2, 3) showed that after the introduction of the nitrophenyl fragments, tubes collected in bundles significantly larger diameter than the non-functionalized single objects.

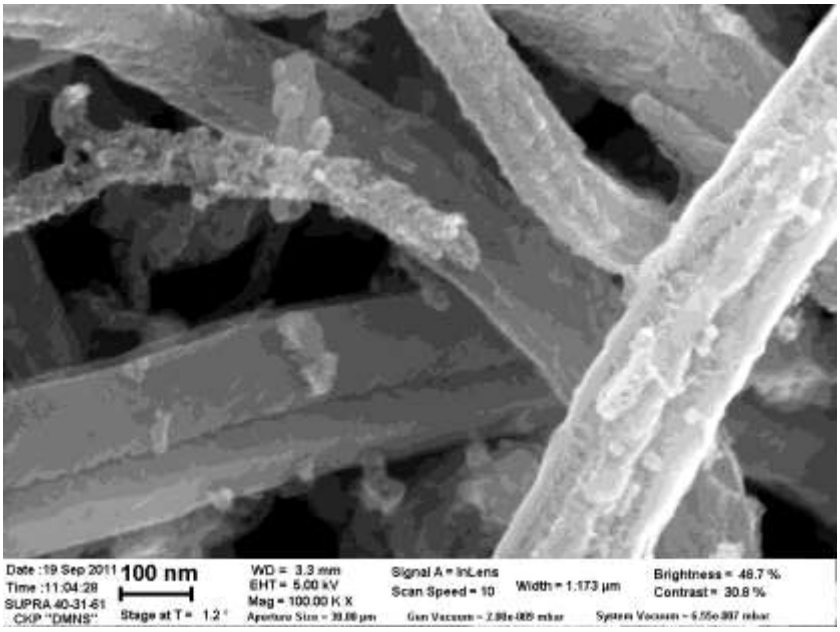


Fig.3 MWCNTs after the introduction of the nitrophenyl fragments

The reason for this can be increased interaction multiwalled CNTs after the introduction of the periphery of aromatic nature. It is often observed for the non-covalent modification of CNTs by carbo- and heteroarenes.

The structure of the organic groups of the functionalized MWCNTs and evaluation of their interaction was investigated by quantum-chemical modeling. The examined object and the data on its structure are presented in Figure 4.

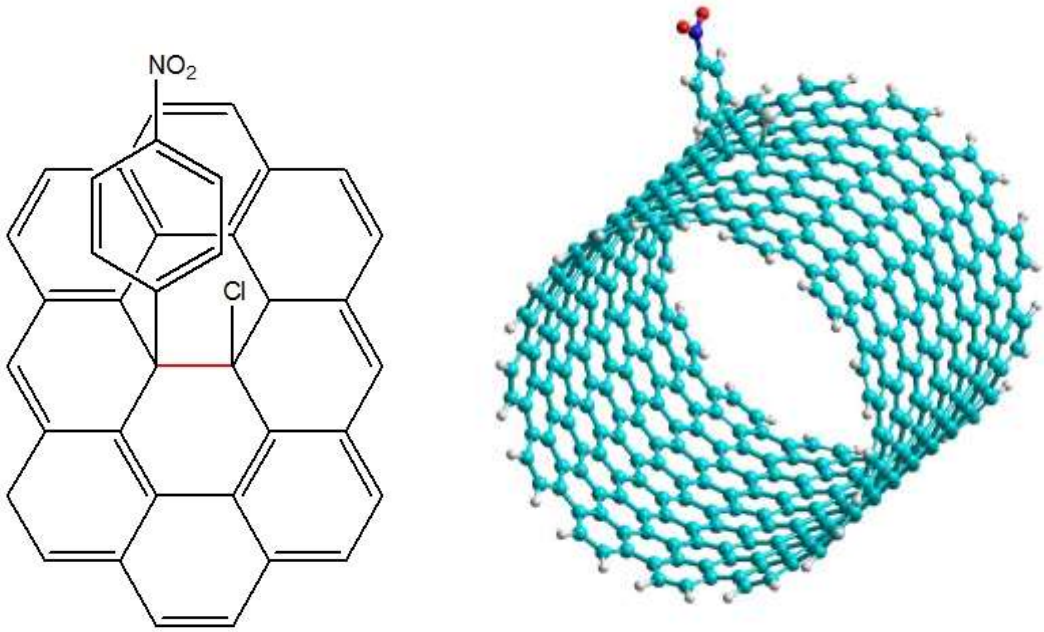


Fig.4 The structure of the functionalized nanotubes

Assessing the interaction of heteroatomic fragments of two functionalized CNTs showed the value of 45 kJ / mol. At largely functionalization can offer a sufficiently high energy association CNTs, which leads to the observed effects.

3. CONCLUSION

Studied the effect of conditions on degree of functionalization in interaction multi-walled with aromatic diazo compounds. On the basis of experimental data are made hypothesis about the mechanism of the process., is found that the modification of the surface of MWCNTs by nitrophenyl fragments allows controlled adjustment of properties of nano-objects. We observed an ordered association of multiwalled CNTs after the introduction of peripheral functional groups of aromatic nature.

ACKNOWLEDGEMENTS

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