Identification of Endohedral Metallofullerenes by Method of UV-VIS Spectroscopy

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ABSTRACT

The endofullerenes attract a close attention of theorists and practicians and especially after appearance of possibility to produce them in macroscopic amounts. This has allowed the investigation of their atomic-molecular architecture, electron structure, the determination of levels for their possible applications. The search for the optimum composition of metal-carbon composites has been done. Analytical control over the EMF content in soot has been performed according to the specially developed procedure. At first the products of arc synthesis have been extracted from fullerene-containing soot by toluene using fractional extraction. After complete extraction of hollow fullerenes, extraction from "poor" soot has been continued in dimethylformamide at the boiling point. identification The fullerenes identification in the extracts has been preformed by the method of UV-VIS spectroscopy.

Keywords: endohedral metallofullerene, soot, arc synthesis, evaporation, absorption, spectroscopy

1 INTRODUCTION

As the class of new synthesized compounds endofullerenes attract a close attention of theorists and practicians and especially after appearance of possibility to produce them in macroscopic amounts. This has allowed the investigation of their atomic-molecular architecture, electron structure, the determination of levels for their possible applications.

2 EXPERIMENTAL

The simplest method of producing endohedral metallofullerenes (EMF) is the electric arc method. Although there exist many theoretical works focused on the formation of fullerenes in carbon-containing plasma, the mechanism of EMF formation in the arc discharge plasma is still unclear [1]. Therefore the search for optimum parameters of arc EMF synthesis is a topical problem. Efficiency of the arc method for EMF producing depends on the technological parameters of synthesis, the composition of metal-carbon composites, the preliminary treatment of graphite anodes and a number of other reasons.

The search for the optimum composition (that increases EMF yield) of metal-carbon composites has been done in the present work. Analytical control over the EMF content in soot has been performed according to the specially developed procedure. At first the products of arc synthesis have been extracted from fullerene-containing soot by toluene using fractional extraction. After complete extraction of hollow fullerenes, extraction from "poor" soot has been continued in dimethylformamide at the boiling point. Identification of fullerenes in the extracts has been preformed by the method of UV-VIS spectroscopy.

3 RESULTS AND DISCUSSION

Fig.1 shows UV-VIS spectra measured in dimethylformamide extracts from the "poor" soot produced in arc evaporation of metal-carbon composites for five different compositions. We believe that the spectra are absorption spectra of EMF. The form of the spectra confirms this supposition. As a rule, absorption spectra of EMF have a long "tail" directed to the long wave region [2, 3]. The maximums in characteristic absorption bands for EMF are usually observed in the range of 500-1000 nm. Fig.2 shows UV-VIS-NIR spectra recorded in the present work and taken from [4].

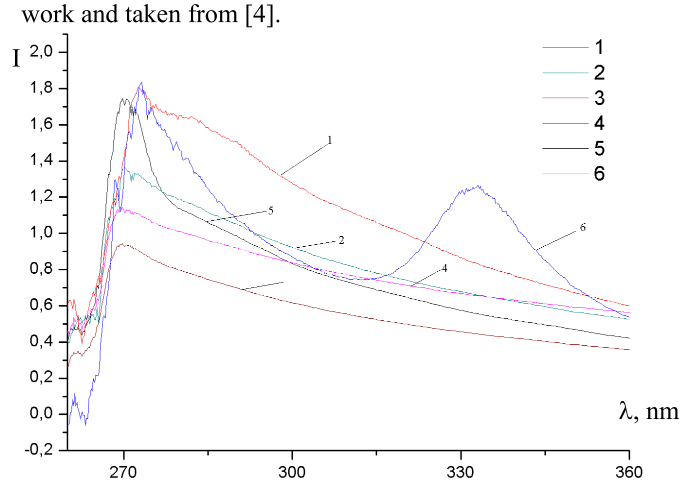

Figure 1: UV-VIS spectra of M@C_n measured in dimethylformamide extracts: spectrum 1 – (M=Ni, treatment 1), spectrum 2 – (M=Ni, treatment 2), spectrum 3 – (M=Y), spectrum 4 – (M=Cu), spectrum 5 – (M=Co), spectrum 6 – C_{60} and C_{70} mixture in dimethylformamide solution.

As Fig. 2 shows, the positions of maximums in absorption bands in the spectra of EMF that contain different metal coincide practically. The observed identity of the spectra is within the framework of the empiric rule that concerns the relation between absorption characteristics and the isomer structure of EMF. UV-VIS-NIR spectra of one metal are analogous to those of the other

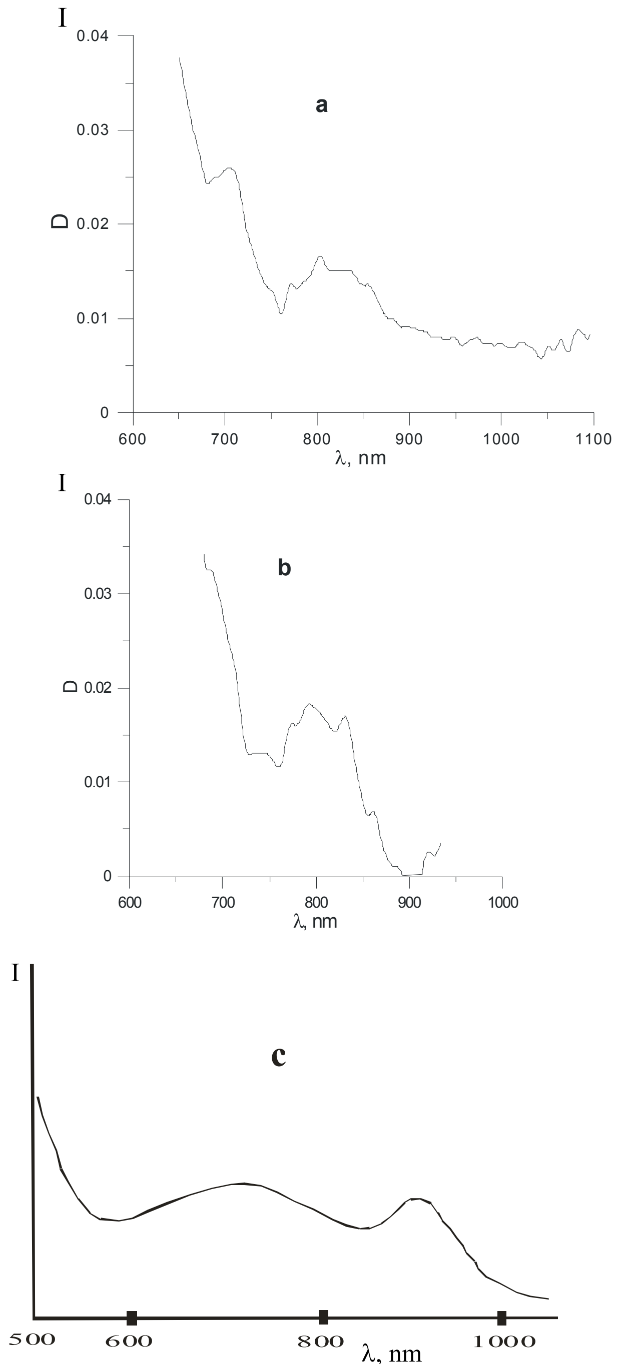

Figure 2: UV-VIS spectra: a) spectrum for $Y_2@C_{82}$ in toluene, b) spectrum for $Ni_2@C_{82}$ in toluene, c) spectrum for $Y_2@C_{82}$ in CS_2 [3].

metal independently on the type of an encapsulated atom when the cage structure and the charge of atoms are identical [2, 3]. When we proceed from the opposite, EMF prepared in this work (their spectra are given in Fig.2, a, b) have $Y_2 @ C_{82}$ and $Ni_2 @ C_{82}$ formulae, respectively. In spectrum 6 (Fig.1) measured in the dimethylformamide solution of C_{60} and C_{70} fullerenes mixture the absorption band with the maximum at 335 nm is characteristic of C_{60} and C_{70} fullerenes. The absence of this absorption band in spectra 1-5 indicates that dimethylformamide extracts contain only EMF. Hence we can judge about the quantitative content of EMF in the extract and consequently in soot by the value of optical density of the EMF spectrum at the chosen wavelength. Based on the comparison of intensities of absorption spectra given in Fig.1, we can conclude that the largest EMF yield has been achieved during evaporation of modified anode 1 (Fig.1, spectrum 1).

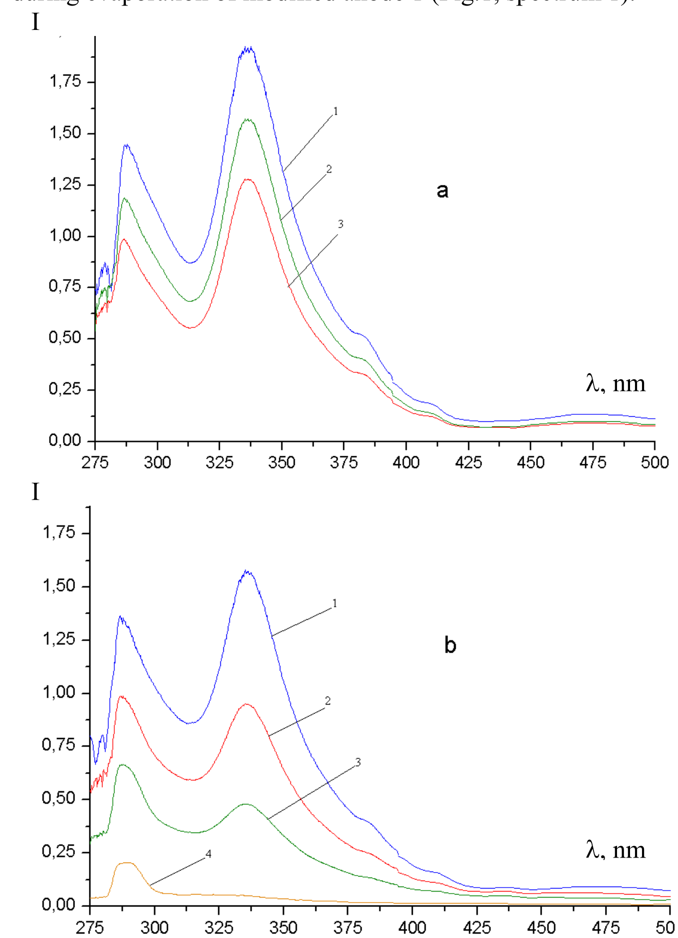

Figure 3: a) UV-VIS spectrum 1, 2, 3 measured in fractions 1, 2, 3, respectively, of toluene extraction from the soot containing only “hollow” fullerenes; b) UV-VIS spectra 1, 2, 3, 4 measured in fractions 1, 2, 3 and in the last fraction of toluene extraction from the soot containing C_{60}, C_{70} and $Ni@C_n$, respectively.

Fig.3 shows the spectra measured in toluene extracts of the products of arc synthesis. The soot has formed during arc evaporation of a graphite anode (Fig.3a). Fig.3b shows spectra for the soot containing EMF. Intensity of spectra (Fig.3a) in each subsequent fraction decreases. In this case the value of A_1/A_2 ratio remains constant (A_1 and A_2 – optical densities at 335 and 287 nm, respectively) (Fig.4, curve 2). The value of the ratio in spectra (Fig.3b) decreases (Fig.4, curve 2).

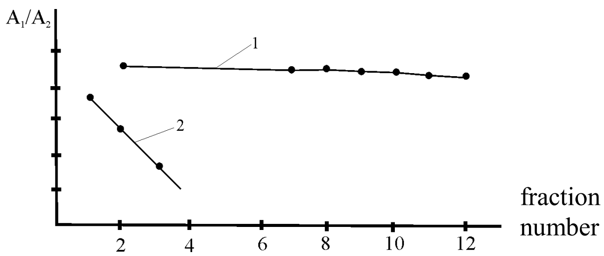

Figure 4: Curves 1 and 2 illustrate how the values of A_1/A_2 ratio change in UV-VIS spectra given in Fig.3a and 3b, respectively.

The decrease in the value of the A_1/A_2 ratio occurs due to the decrease in the concentration of hollow fullerenes in each subsequent fraction of the extract. Intensity of the band at 287 nm decreases slower than that at 335 nm.

4 CONCLUSIONS

In parallel with C_{60} and C_{70}, EMF is also washed out with toluene, and EMF absorption intensity is very high in the UV region. Hence we can conclude about the presence or the absence of EMF in the soot produced by the spectra for only toluene fractions.

REFERENCES

[1] A.S. Fedorov, P.V. Novikov and G.N. Churilov, “Influence of electron concentration and temperature on endohedral metallofullerene $Me@C_{84}$ formation in a carbon plasma”, Chemical Physics, V. 293, N 2, 253-261, 2003.

[2] H. Shinohara, “Endohedral metallofullerenes”, Rep. Prog. Phys., V. 63, 843-892, 2000.

[3] T. Inoue, T. Tomiyama, T. Sugai and H.Shinohara, “Spectroscopic and structural study of Y_2C_2 carbide encapsulating endohedral metallofullerene: $(Y_2C_2)@C_{82}$”, Chem. Phys. Letters, V. 382, N3-4, 226-231, 2003.

[4] T. Inoue, T. Tomiyama, T. Sugai, et.al., “Trapping a C_2 radical in endohedral metallofullerenes: synthesis and structures of $(Y_2C_2)@C_{82}$ (isomers I, II and III)”, J. Phys. Chem. B, V. 108, N 23, 7573-7579, 2004.