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ATOMIC CLASTERS

Yttrium-Containing Endohedral Metallofullerenes: Synthesis and Extraction

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Abstract—Yttrium-containing endohedral metallofullerenes are synthesized in an RF arc discharge in the helium flow with embedded Y_2O_3. It is shown that the formation of the metallofullerenes depends on the helium pressure in a chamber; however, this dependence cannot be explained using the model of formation of conventional fullerenes without a guest atom in a molecule. The results of extraction of $Y@C_{82}$ by pyridine and carbon disulfide are reported. The pressure corresponding to the maximum yttrium-containing endohedral metallofullerene content is shown to be 60 kPa; under this pressure, extraction by carbon disulfide allows obtaining 27.1 wt % of the endohedral metallofullerene, while extraction by pyridine yields its amount of 17.3 wt %.

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1. INTRODUCTION

It has been shown experimentally and theoretically that the helium pressure of fullerene synthesis is the main parameter affecting both the amount of forming fullerenes and the qualitative composition of a fullerene mixture [1, 2]. Thus, the effect of pressure on the quantitative yield of fullerenes and qualitative composition of the fullerene mixture is well-explained using the model of formation of conventional fullerenes, which takes into account the effect of electron density and annealing of carbon clusters [3]. In the synthesis of endohedral metallofullerenes (EMFs), the helium pressure in a chamber also remains an important factor. However, this effect has still been unexplained. The experimental data accumulated by now have still been insufficient to develop a concept of the EMF formation. This is due to the fact that the properties of various EMFs strongly differ [4]. In particular, the EMF extraction using different solvents yields different quantitative results. The cluster nature of solvability also complicates the fractionation. In view of the aforementioned, one cannot avoid the loss to transformation of a substance from the solution in one solvent to the solution in another solvent and its partial irreversible sorption on a sorbent. Fullerenes are usually dissolved in toluene, the solvents are chromatographically separated, and the extracted fractions are analyzed. This method complicates adequate estimation of the effect of synthesis parameters on the EMF formation. We managed to avoid these difficulties and investigated the effect of pressure on the Y-containing EMF synthesis in an RF arc plasma.

In this work, we used the complex of mass spectral analysis, X-ray photoelectron spectroscopy (XPS), high-performance liquid chromatography, and atomic emission spectroscopy, which allowed us to unambiguously establish the EMF content in carbon condensates (CCs) obtained under different pressures. In addition, we report the results that evidence for the high efficiency of fullerene extraction from the CCs obtained by embedding Y_2O_3 using pyridine and carbon disulfide by the Soxhlet technique.

2. EXPERIMENTAL

The CCs containing fullerenes and EMFs were synthesized in an ac arc discharge with a frequency of 60 kHz on a setup described by us in [5]. The use of ac current prevents formation of a cathode deposit; therefore, the electrode material is completely (by almost 100%) converted to the fullerene-containing CCs. The RF current arc is characterized by the absence of fast running of cathode spots in one large spot. Therefore, the electrode material is uniformly evaporated even at large arc currents and high pressures and does not crumble at large temperature gradients [5].

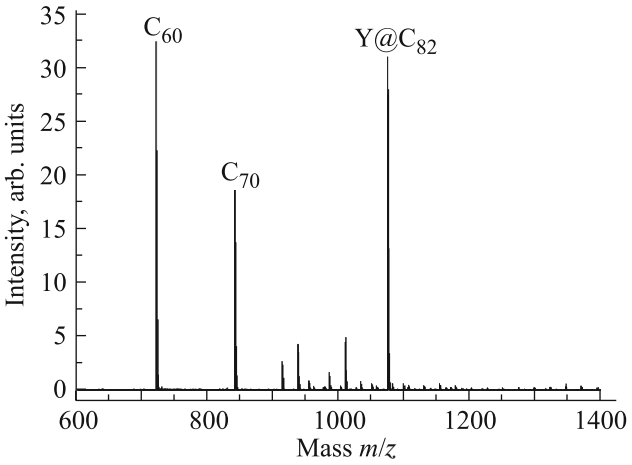

Fig. 1. MALDI-TOF Bruker BIFLEX TM III mass spectrum of the fullerenes extracted by pyridine with adding Y_2O_3 under a pressure of 360 kPa (positive mode).

The carbon condensate was formed by sputtering rods for atomic emission analysis (TU 3497-001-51046676-2008) with axial holes with a diameter of 3 mm and a length of 85 mm. The axial holes were filled with a mixture of graphite powder and Y_2O_3 (OST 48-208-81) in a mass ratio of 1 : 1. The rods were annealed in vacuum at a temperature of 1800°C and fixed in water-cooled holders located in a water-cooled sealed chamber. The synthesis was performed under helium pressures of 33–360 kPa. The rods were continuously supplied during their burning-off so that the arc current remained constant. A helium flow rate of ~4 L/min was kept and the pressure variation in the chamber was no more than (2–3)% of the specified value. The obtained CC was divided in two equal parts. The EMFs were extracted from the CC in a Soxhlet apparatus. One part was extracted by pyridine and the other, by carbon disulfide. Based on the results obtained, we calculated the EMF amount using the technique developed by us in [6].

3. RESULTS AND DISCUSSION

According to the literature data, extraction of each type of EMFs requires a certain solvent [7]. Carbon disulfide can be considered as the most universal one, but it can insert sulfur impurities in the fullerene extract, which is undesirable for further investigations. Nevertheless, the metallofullerenes containing more than one guest atom in the carbon framework can be extracted the most effectively by this very solvent. The EMFs extracted by pyridine are poorly redissolved in toluene and leave an undissolved precipitate enriched with the EMFs [8]. We showed that during the fullerene synthesis with adding Gd_2O_3 at a pressure of 98 kPa and a current of 190 A the $Gd@C_{82}$ content in the pyridine extract was 2.9 wt %, while, upon redissolving in toluene, we found only 1.0 wt %; the precipitate undissolved in toluene contained 7.1 wt % [9].

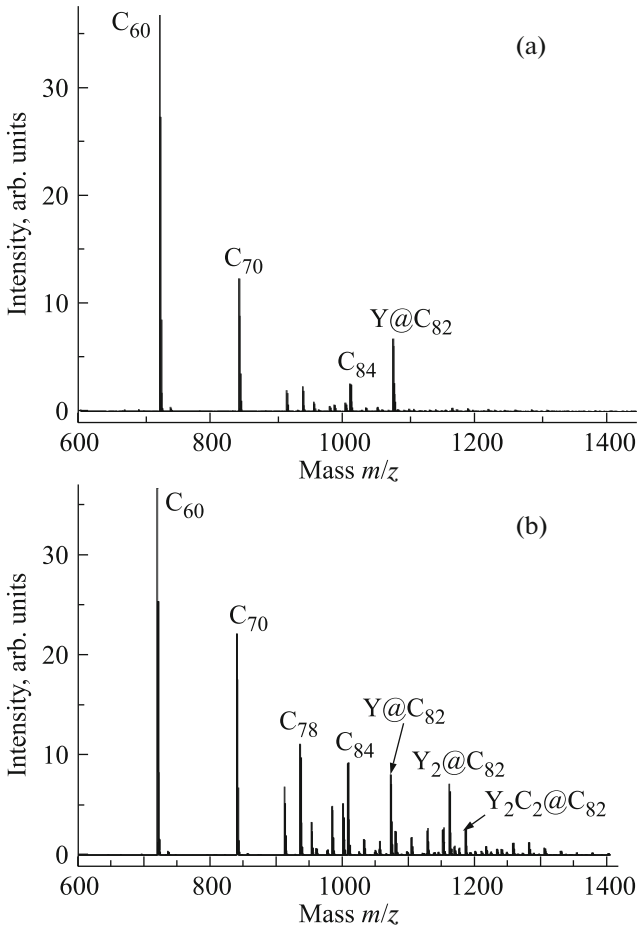

Fig. 2. Mass spectra of the fullerene extracted from the CC obtained by embedding Y_2O_3 under a pressure of 60 kPa using (a) pyridine (positive mode) and (b) carbon disulfide (positive mode).

It was established that the EMFs with one guest atom in a molecule are better extracted by pyridine (Fig. 1) and those containing more than one guest atom, by carbon disulfide. In particular, extraction by pyridine from one part of the CC allowed us to extract well only the EMF with one metal atom, i.e., $Y@C_{82}$ (Fig. 2a). Extraction by carbon disulfide from the other part of this CC yields an EMF series containing $Y@C_{82}$, $Y_2@C_{82}$, and $Y_2C_2@C_{82}$ (Fig. 2b).

Since drying with the subsequent repeated dissolving leads to the EMF loss, to quantitatively estimate the effect of synthesis parameters on the efficiency of fullerene formation we studied the fullerene extracts without repeated dissolution. Using atomic emission spectroscopy [7], we analyzed the fullerene extract (Fig. 2b) and established that the Y content in it was 4.5 wt %. XPS analysis of the sample on a

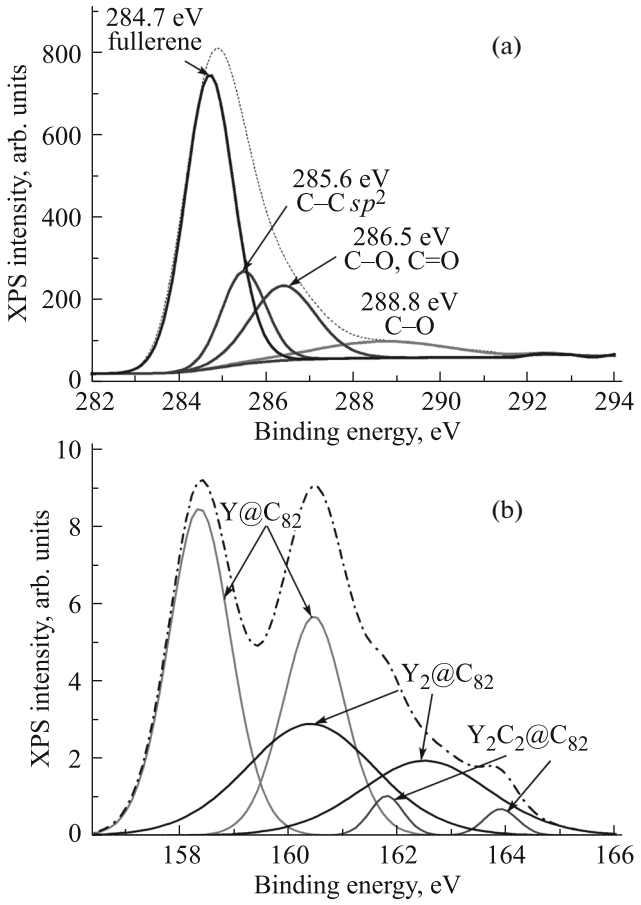

Fig. 3. XPS spectrum of the fullerene extract obtained by embedding Y_2O_3 under a pressure of 60 kPa by carbon disulfide. (a) C 1*s* line and (b) Y 3*d* line.

UNI-SPECS spectrometer revealed an Y content of 4.1 wt % in the sample.

In the photoelectron spectrum of the fullerene extract obtained with adding Y_2O_3 under a pressure of 60 kPa using carbon disulfide, the Gaussian/Lorentzian decomposition of the C 1*s* line (Fig. 3a) yielded the components corresponding to binding energies of $E_b = 284.7$ eV (fullerene), $E_b = 285.6$ eV (C sp^2 hybridization, 56.4 and 16.1% of the C 1*s* line area, respectively), $E_b = 286.5$ eV (C–O– and C=O, 19% of the C 1*s* line area), and $E_b = 288.8$ eV (C–O, 8.5% of the C 1*s* line area). First, we found that Y bound with the fullerene is in the three states characterized by three doublets obtained by the Gaussian/Lorentzian decomposition of the Y 3*d* line (Fig. 3b). After Ar ion etching for 3 min (1 kV, 10 μA), we observed only one doublet corresponding to $Y@C_{82}$. Thus, the $Y@C_{82}$ compound is the most stable against external factors. The extracted components of the Y $3d_{5/2}$ line [10] correspond to $E_b = 158.3$ eV ($Y@C_{82}$, 56% of the Y $3d_{5/2}$ line area), $E_b = 160.4$ eV ($Y_2@C_{82}$, 40% of the Y $3d_{5/2}$ line area), and $E_b = 161.8$ eV ($Y_2C_2@C_{82}$, 4% of the Y $3d_{5/2}$ line area) and confirm the results of mass spectroscopy study (Fig. 3b). According to [11], the presence of the Y_2 dimer inside a molecule can lead to the significant strain of the C_{82} atomic framework.

If the mass spectroscopy investigations show that the metal is located only in the EMF structure, then, using the XSP technique, we unambiguously determine the content of formed EMFs at the specified synthesis parameters from the binding energies. In addition, based on mass spectroscopy study and the determined quantitative content of the metal in the fullerene extract, we can qualitatively estimate the synthesis efficiency. In particular, the yttrium contents in the fullerene extract calculated on the basis of the above investigations were found to be 4.4 wt % at a helium pressure in the chamber of 360 kPa, 5.5 wt % at 230 kPa, 6.9 wt % at 120 kPa, 11.4 wt % at 60 kPa, and 11.3 wt % at 30 kPa.

4. CONCLUSIONS

Thus, the content of yttrium-containing EMFs in the CCs formed in the RF arc discharge significantly decreases with increasing helium pressure in the chamber. The increase in the amount of forming higher fullerenes and the decrease in the content of EMFs with increasing pressure are indicative of different mechanisms of their formation. The optimal pressure ensuring the maximum yttrium-containing EMF yield is 60 kPa.

It was shown that the use of pyridine is reasonable at the extraction of EMFs with one atom inside a molecule. The use of carbon disulfide makes it possible to extract with the maximum efficiency the EMFs containing more than one guest atoms in the carbon framework. In our investigations, in the case of yttrium-containing EMFs, carbon disulfide allowed extracting $Y@C_{82}$, $Y_2@C_{82}$, and $Y_2C_2@C_{82}$. According to the XPS data, $Y@C_{82}$ is the most stable against external factors.

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