Preparation and Charecterization of Bromofullerenes in New Stoichiometry

Reema Mehrotra, Darshan Lal, V. S. Tripathi♣ and G. N. Mathur

Defence Material and Stores, Research and Developement Establishment, Kanpur-208013

♣e-mail: *dmsrde@sancharnet.in*

Abstract

It is well established that halogenated fullerene derivatives act as synthetic intermediates for further substitution via replacement with nucleophlies. In the present work, systematic studies were carried out on the synthesis of bromofullerenes under different experimental conditions. The effect of reaction time on the product formed was observed. We observed the formation of new compound of bromofullerenes in a different stoichiometric ratio i.e., $C_{60}Br_{14}$; in addition to previous reported bromofullerenes in the stoichiometric ratio of $C_{60}Br_6$, $C_{60}Br_8$, and $C_{60}Br_{24}$. The new derivative of bromofullerene was isolated and well characterized by various analytical techniques like FT-IR, TGA, DSC, and elemental analysis. In this paper, detail of the synthesis and characterization of the bromofullerene prepared are described. The yields obtained were better than those reported previously.

Keywords : *Fullerenes, bromination, bromofullerenes, thermal analysis, and stoichiometry*

1. Introduction

Halogenation of [60]fullerene has been carried out by various research groups and halogenated fullerenes was among the first derivatives prepared which opened a new field with the reactivity of nucleophiles. Halofullerenes have been intensively studied as versatile synthetic intermediates in fullerene chemistry. Fluorination was attempted first on [60]fullerene. Fluorination is usually carried out by the elemental fluorine or with transition metals fluoride salts [1, 2]. Fluorofullerenes are more stable in comparison to bromides and chlorides of fullerene, which are easily characterized by mass spectrometry and ^{19}F NMR.

Chlorination of [60]fullerene has also been successfully performed. Poly-chlorofullerenes in the ratios $C_{60}Cl_6$, $C_{60}Cl_{10}$ and $C_{60}Cl_{24}$ have been isolated and characterized [3, 4]. Chlorination of [60]fullerene in carbon tetrachloride by chlorine gas, for one hour gave a crystalline yellow product that gave the elemental analysis corresponding to $C_{60}Cl_{40}$ [5].

Bromination of [60]fullerene by neat bromine at 20~50ºC was reported earlier with two or four bromines attached based on weight uptake were confirmed [6]. Similarly Tebbe and coworkers [7] have shown that bromination of [60]fullerene with neat bromine gives yellow-orange microcrystalline bromo derivatives of composition $C_{60}Br_{24}$. They prepared bromo-fullerene having the lower composition of bromine i.e. hexa and octa bromofullerenes ($C_{60}Br_6$, and $C_{60}Br_8$), and obtained the single crystal of the compound $C_{60}Br_{24}$ [7].

The immense importance of these halofullerenes in organic synthesis of fullerene chemistry is they act as the precursor material for further derivatization. Substitution of the halo-fullerenes can be performed to give the required functional group incorporated in the fullerene structure. Bromofullerenes being thermally labile and the ease at which the bromine is lost at low temperature without effecting the fullerene structure is of particular interest as they can be substituted to the desired moiety. In addition, according to a recent report, bromofullerenes act as the precursor for the preparation of fullerene dimmer ($C_{120}O$), by heating $C_{60}Br_{24}$ in a controlled atmosphere leads to the formation of $C_{120}O$, which otherwise requires a tedious process [9].

Systematic studies on bromination of [60]fullerene were carried out under different experimental conditions, to obtain different possible derivatives of halofullerenes in different stoichiometry. We studied the effect of reaction parameters like the reaction time on the product formed, as well as the solvent effect on the reaction was worked out. Our findings and results indicate the formation of a new stoichiometric ratio of fullerene and bromine compound that is $C_{60}Br_{14}$. The formation of bromofullerenes i.e., $C_{60}Br_6$, $C_{60}Br_8$, and $C_{60}Br_{24}$ is also described. The method of synthesis of bromofuller-enes and yield of the fullerene bromides, which we obtained, are better than reported previously. Details of the synthesis, and characterizations of various bromofullerenes are described in this paper.

2. Experimental

2.1. Materials

[60]fullerene (purity > 99.95%,) was obtained from MER Corporation. The purity of the fullerene sample was evaluated by FT-IR and UV-Vis, and was used without further purification. [60]fullerene was subjected to slow progressive heating up to 200ºC in vacuum for two-four hours to remove all occluded solvent and O_2 before the experiment. Molecular bromine (Extra pure Merck) and solvents carbon disulphide and benzene were of analytical grade from RANBAXY. Moisture free solvents and reagent purity are an important factor for the synthesis of any fullerene derivatives. Pure anhydrous solvent was assured by distillation and used them by drying over molecular sieves or a dehydrating agent to remove traces of moisture adsorbed in the solvent.

2.2. Synthesis and Characterization

2.2.1. Synthesis of bromofullerene in neat fullerene.

In the first experiment, bromine and [60]fullerene were reacted in absence of any solvent i.e. in neat bromine. 50 mg of [60]fullerene was taken in the reaction flask and 8 to 10 ml of bromine was added to it. The resultant solution was kept without stirring at room temperature in an inert atmosphere. On observing a precipitate, in the solution, the precipitate was isolated, excess unreacted bromine was removed under reduced pressure.

The compound formed was dried under vacuum till complete dryness. Deep orange to light brown micro crystals of regular shape were isolated.

2.2.2. Synthesis of bromofullerene in solvent

Reaction of bromine and [60]fullerene was carried out in two different solvents, benzene and carbon disulphide. The yields obtained were higher in carbon disulphide (CS_2) and therefore subsequent experiments were conducted in CS_2. Results described in this paper pertain to experiments conducted in CS_2 solvent. A saturated solution of [60]fullerene was prepared and used in different batch reaction.

Measured quantity of bromine was added to the saturated fullerene solution. The reaction mixture was stirred and kept under observation for two to twelve days till a precipitate was observed. Products formed were analyzed gravimetrically as well as by using different analytical techniques as mentioned below.

2.2.3. Characterization

FT-IR (KBr pellet) spectra were recorded on Nicolet − 750 spectrometer. We have used transmission FT-IR as the initial tool to monitor the structural changes taking place during the reaction. The characteristic absorption of the C-Br bond was observed at 500~700 cm^{-1}, whether the reaction has occurred and bromine has attached to the fullerene cage through

covalent bond can be easily monitored through FT-IR. Comparative study was made with the FT-IR of pure fullerene with that of bromofullerenes.

Thermal stability of bromofullerenes was studied by *themogravimetry (TGA)-MS* analysis with heating rate of 10ºC per minute, in nitrogen flow 60 ml/min by TG Instrument − 2950.

Percentage composition of elements was assessed by the *Elemental analyzer* by CHSN elemental Vario EL Fabri − NR 11961010.

DSC (*Differential Scanning Calorimetry*) studies of the samples were carried out by TA instrument − 2910 with heating rate of 10ºC per minute, in nitrogen flow of 100 ml/min.

Bromofullerenes are insoluble in most of the organic solvents like benzene and toluene, but soluble in bromine. Due to lack of solubility of bromofullerenes in most of the organic solvent ^{13}C NMR spectra in solution did not indicate discernible absorptions.

Mass spectrometry (FAB-Mass spectrum) showed no peak corresponding to bromofullerenes, due to decomposition of the compound.

3. Results and Discussion

Occurrence of the reaction was monitored by FT-IR analysis. The number of bromine atoms attached to the fullerene cage was determined gravimetrically, and by the weight loss observed thermo-gravimetrically was in agreement with the calculated value from gravimetric calculations. Also the stability of the bromofullerenes with temperature can be drawn from the TGA graphs. DSC studies clearly indicated the purity of the bromocompounds as well as presence of occluded bromine or solvent. Loss of solvated bromine as well as decomposition of bromocompounds was monitored by DSC.

Bromofullerenes were formed both in solvent as well as in the absence of solvent, though there is lot of difference in the reaction time in both cases. It was observed that the reaction time between bromine and fullerene was the impotent factor for the stoichiometric composition of the bromofullerenes when the experiments were performed in neat bromine. On the contrary, reaction time was not the criteria for the product to be formed in the case when solvent was used in the experiment. It is usually observed that long reaction time (six to twelve days) was required for the bromocompounds to be formed when solvent is used in the experiment.

For the bromination in neat bromine, the reaction time was varied from ten minutes to six days; Periodically after a fixed interval of time, reaction mixture was taken out, consecutively unreacted bromine was removed under reduced pressure, and characterized by FT-IR. Product formed was collected in the intervals of five minutes to one hour for
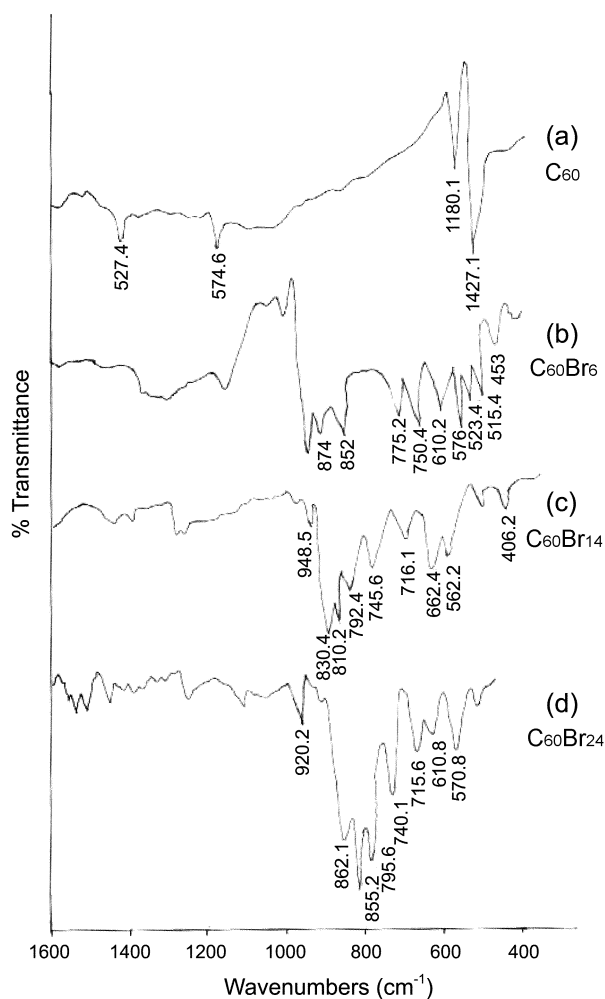
Fig. 1. FT-IR spectra of various bromofullerenes.

characterization; progress of the reaction was accessed by the disappearance of the typical fullerene peaks with the reappearance of new ones.

No changes were seen in FT-IR in five minutes (Fig. 1a). No other absorption peaks other than that of fullerene was observed, indicating that no chemical reaction had occurred. The four prominent peaks of pure fullerene cage i.e. at 525, 574, 1180, 1427 cm^{-1} were evident indicating no chemical change.

It was observed that reaction in neat bromine occurred after ten to fifteen minutes. The first bromo derivative was obtained after fifteen minutes, as indicated in the FT-IR spectrum (Fig. 1b). The appearance of absorption lines at 600~850 cm^{-1} appears corresponding to brominated fullerene for octa-bromofullerenes. The prominent peaks are 453, 515, 523, 562, 576, 610, 750, 775, 820, 840, 852, 890 cm^{-1}. These peaks are in accordance with the reported in the literature for octa-bromofullerenes [11, 12]. Yield (70%), elemental analysis (C- 46%, Br- 49%).

We also isolated bromofullerenes with the stoichiometric

composition $C_{60}Br_{10}$, and $C_{60}Br_{12}$, but since it had the spectra identical to $C_{60}Br_8$, the compound corresponds to bromofullerene complex having one and two occluded bromine molecules i.e. $C_{60}Br_8 * Br2$ and $C_{60}Br_8 * 2Br2$ respectively. The loss of occluded bromine was clear from the TGA as well as DSC studies.

On keeping the reaction mixture for twenty-five minutes to half hour (30 min.) a different product in different stoichiometric ratio was observed. The new compound was formed which indicated the stoichiometry of $C_{60}Br_{14}$, based on the weight uptake (gravimetrically), which was not reported previously. The FT-IR of this compound was different from those reported previously and did not match with hexa, octa or twenty-four bromofullerenes. The TGA pattern of this compound was also different from rest of the fullerene bromides prepared so far. This $C_{60}Br_{14}$ is a new compound not reported previously (Fig. 1c). Important absorption peaks of FT-IR at 810, 842, 858, 920 cm^{-1} were seen. Yield (72%), elemental analysis (C- 35%, Br- 65%).

In confirmation of the synthesis of this new product of bromofullerenes i.e. $C_{60}Br_{14}$, similar results has recently been reported by Troshin *et al.* where they also have observed $C_{60}Br_{14}$ [10].

The compound prepared in stoichiometric ratio $C_{60}Br_{14}$ was not very stable, since after few hours (eight to ten hours) it was converted to $C_{60}Br_{24}$, when it was left in the bromine solution. $C_{60}Br_{14}$ slowly decomposed to $C_{60}Br_8$ after ten to fifteen minutes. From the various experiments performed, we could conclude that the formation of $C_{60}Br_{14}$ is the possibly intermediate step in the process of formation of $C_{60}Br_8$ to $C_{60}Br_{24}$.

After one hour the reaction had proceeded, the FT-IR of the product formed indicates the appearance of peaks corresponding to twenty-four bromine atoms attached on the fullerene surface. Major absorption peaks lie at 715, 740, 750, 773, 815, 842, 858, 920 cm^{-1} (Fig. 1d). These peaks corresponding to the formation of $C_{60}Br_{24}$ are in accordance with the reported literature [7, 11]. Yield (74%), elemental analysis (C- 26%, Br- 74%).

Another important notable feature observed when bromination was carried out in neat bromine was that the formation of the compound $C_{60}Br_6$ was not observed.

The result of TGA-MS showed that the intensity of the process of thermal degradation depends largely on the content of bromine atoms attached in the fullerene molecule. TGA of the compound is shown in (Fig. 2a), two peaks appear, in the region 60°C to 70°C, and in the region 150°C to 210°C. A clear desorption of the physically adhered bromine molecule in the lattice of fullerene moiety at temperature 60°C to 70°C, is detected. Loss in weight is due to elimination of occluded bromine adhered at the surface, with a total loss of four percent. It was then followed by strong, sharp, thermal evolution of bromine molecule at an onset temperature of 150°C that reached a maximum at
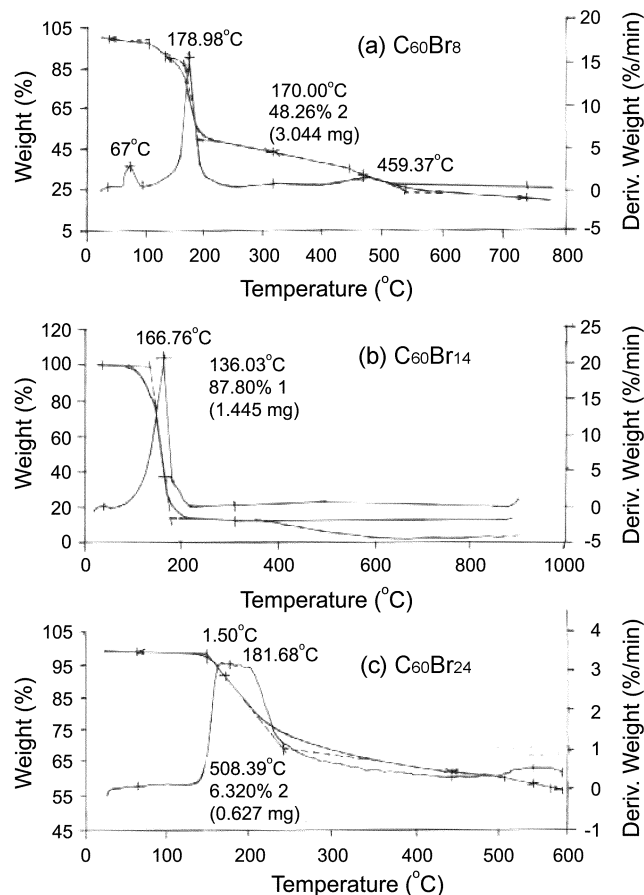
Fig. 2. TGA thermograms of various bromofullerenes.

Fig. 3. DSC thermograms of various bromofullerenes.

210°C. This is the due to thermal cleavage of the C-Br chemical bond of the compound. In the region, 150°C~210°C the region where thermal degradation takes place fastest, and comprises of about forty eight percent weight loss which corresponds to loss of eight bromine atoms which further confirms the structure for $C_{60}Br_8*2Br$.

DSC of the compound (Fig. 3a), showed loss of occluded bromine from the compound, since no other impurity (solvent) was used during the reaction, loss at 132°C is due to the decomposition of C-Br bond, in confirmation with TGA results.

Similar pattern of the result of TGA-MS (Fig. 2b), are observed in the case of $C_{60}Br_8$. It showed no decomposition of occluded bromine, only one step loss in weight is observed at the region 150°C to 200°C. Decomposition of bromofullerenes was observed at temperature of 150°C that reached a maximum at 200°C. Maximum loss occurring at temperature 166°C, the loss is due to dissociation or the cleavage of the C-Br chemical bond as described in detail above.

DSC of $C_{60}Br_8$ is shown in Fig. 3b; it indicated single step loss at temperature 125°C, indicating no occluded bromine.

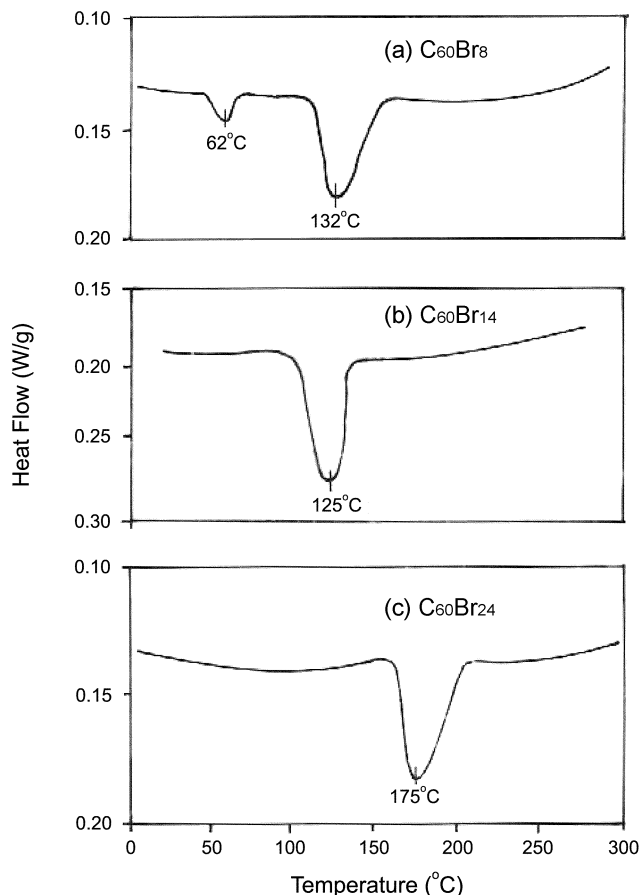TGA of the compound is shown in (Fig. 2c); it shows the

purity of the compound, which has no occlusion of bromine. On set temperature begins at 150°C as observed above, but in contrary it is more stable as compared to previous ones, it is stable up to 260°C and loss occurs gradually. The maximum temperature reached in this case is at 182°C where as in other two cases it was at 175°C and 166°C respectively.

DSC of the compound is shown in Fig. 3c; here single step loss occurs at temperature 175°C, indicating the absence of occluded bromine or solvent.

In the experiments carried out in solvent CS_2, different results are observed in comparison to those in neat bromine. Firstly all the compounds prepared in solvent contained occluded solvent or bromine molecule in the lattice of fullerene. This was confirmed by the presence of FT-IR peak at 1502 cm^{-1} for CS_2. It was difficult to obtain bromofullerenes without having occluded solvent.

It was also noted that bromination in solvent was not time sensitive as compared to bromination in neat bromine. Time required often took more than eight to ten days for a precipitate to be formed. Long duration was required for the bromofullerenes to be formed. Most important observation was the formation of $C_{60}Br_6$, which was not observed in experiments carried out in neat bromine.

The FT-IR graph of $C_{60}Br_6$ showed prominent peaks at 508, 512, 518, 520, 523, 545, 572, 612, 712, 752, 775, 820, 845, 840, 890, 960 cm^{-1} etc. Elemental analysis (C 58%, Br-35%). TGA- same stability and decomposition pattern (100-160°C) were observed as of other bromofullerenes.

Based on the TGA pattern we could conclude the following decomposition pattern for different fullerene bromides prepared, i.e. (140~160°C) for $C_{60}Br_6$, (100~160°C) for $C_{60}Br_8$, (150~170°C) for $C_{60}Br_{14}$ and (160~220°C) for $C_{60}Br_{24}$. The stability of bromofullerenes increases in the similar pattern, thus $C_{60}Br_{24}$ is the most stable.

4. Conclusion

Bromine being a diatomic molecule in a volatile liquid state and the intermolecular forces are *Vander Waals* force, which is weak in comparison to other bonds. Thus under mild conditions bromine is converted into free radicals. Bromination of fullerene being a radical process consists of several sequential reactions. The first stage of the process for bromination is breaking of molecular bromine in to the radical form i.e.

Br$_2$ → Br• + Br•

The next step of the process includes attacking of the bromine radicals to the double bonds on the fullerene surface. No bromine radical attached to fullerene is adjacent due to the steric repulsion.

Bromofullerenes of different stoichiometric ratios were prepared and well characterized. Maximum of twenty-four bromines attach to the cage through covalent bonding. More than twenty-four bromine cannot be attached to the cage in symmetrical way since [60]fullerene has only thirty double bonds distributed on the curved surface. On attachment of more than twenty-four bromine atoms to the fullerene cage produces strain in the fullerene structure due to steric repulsion. It is also not favored steriochemically, on placing more the bromine would be placed in the pentagons, which in turn destabilizes the structure. Thus, suggests that the bromofullerenes with more than $C_{60}Br_{24}$, is not possible.

Reaction time taken in solvent was much more as compared to that in without solvent. Reaction time for bromination in neat bromine was less usually varied from ten minutes to one hour, for the product to be formed. For bromination in solvent, the product is formed after six to ten days. Hexa-bromofullerenes was not supported in bromination in neat bromine; even if it is formed it immediately converts into octa-bromofullerenes. Hexa-bromofullerenes is usually formed in bromination in solvent.

Bromine attached to the fullerene surface being thermally labile and the ease at which these bromofullerenes lose bromine (150~250°C) is of particular interest, as they can be used in the synthesis of desired polyadducts by replacement of the bromine under ordinary conditions. The cage structure of fullerene was intact and no loss in material was observed. From the different experiments conducted on bromination of [60]fullerene in neat as well as in solvents we could conclude that bromination of [60]fullerene occurred at ease, bromocompounds of fullerene could be prepared at room temperature under simple conditions.

References

[1] Selig, H.; Lifshitz, C.; Peres, T.; Fisher, J. E.; McGhie, A. R.; Romanov, W. J.; Mc Cauley, J. P.; Ross, M. S.; Calahan, J. h.; *J. Am. Chem. Soc.* **1991**, 5475.

[2] Holloway, J. H.; Hope, E. G.; Taylor, R.; Langlay, G. L.; Avent, A. G.; Denis, T. J.; Hare, J. P.; Kroto, H. W.; Walton, D. R. M. *J. Chem. Soc., Chem. Commun.* **1991**, 966.

[3] Birkett, P. R.; Avent, A. G.; Darwish, A. D.; Kroto, H. W.; Taylor, R.; Walton, D. R. M. *J. Chem. Soc. Chem. Commun.* **1993**, 1230.

[4] Birkett, P. R.; Avent, A. G.; Darwish, A. D.; Kroto, H. W.; Taylor, R.; Walton, D. R. M. *J. Chem. Soc. Chem. Commun.* **1995**, 683.

[5] Taylor, R. *J. Chem. Soc. Perkin Trans 2* **1993**, 813.

[6] Olah, G. A.; Brusci, I.; Lambert, C.; Aniszfeld, R.; Trivedi, N. J.; Sensharma, D. K.; Prakash, G. K. S.; Adcock, L. *J. Am. Chem. Soc.* **1991**, *113*, 1385.

[7] Birkett, P. R.; Hitchcock, P. B.; Kroto, H. W.; Taylor, R.; Walton, D. R. M. *Nature* **1992**, *357*, 479.

[8] Tebbe, F. N.; Harlow, R. L.; Chase, D. B.; Thorn, D. L.; Campbell, G. C.; Calabrese, J. J. C.; Norman, H.; Young, R. J.; Wasserman Jr., E. *Science* **1992**, *256*, 822.

[9] Resmi, M. R.; Ma, Shuguang; Caprioli, R.; Pradeep, T.; *Chem. Phy. Lett.* **2001**, *333*, 515.

[10] Troshin, P. A.; Kolesnikov, D.; Burtsev, A. V.; Lubovskaya; Denisenko, N. I.; Popov, A. A.; Troyanov, S. I.; Boltalina, O. V. *Full. Nanotubes Carbon Nanostr.* **2003**, *11*, 61.

[11] Djordjevic, A.; Vojinovic-Miloradov, M.; Petranovic, N.; Devecerski, A.; Lazar, D.; Ribar, B. *Fullerene Science and Technology* **1998**, *6*(4), 689.