

Green Chemistry of Carbon Nanomaterials

E. V. Basiuk (Golovataya-Dzhymbeeva)* and V. A. Basiuk**

* Centro de Ciencias Aplicadas y Desarrollo Tecnológico, Universidad Nacional Autónoma de México (UNAM), Circuito Exterior C.U., 04510 México, D.F., Mexico, elbg1111@gmail.com

** Instituto de Ciencias Nucleares, UNAM, Circuito Exterior C.U., 04510 México, D.F., Mexico, basiuk@nucleares.unam.mx

ABSTRACT

We summarize the results obtained up to now on solvent-free techniques for the functionalization of fullerene C_{60} , single-walled and multi-walled carbon nanotubes (SWNTs and MWNTs, respectively), as well as nanodiamond (ND). We designed a series of simple and fast functionalization protocols based on thermally activated reactions with chemical compounds stable and volatile at 150-200 °C under reduced pressure, when not only the reactions take place at a high rate, but also excess reagents are spontaneously removed from the functionalized material, thus making unnecessary its purification. The main two classes of reagents are organic amines and thiols, which can be used in conjunction with different forms of nanocarbons. The resulting chemical processes comprise nucleophilic addition of amines and thiols to fullerene C_{60} and to defect sites of pristine MWNTs, as well as direct amidation of carboxylic groups of oxidized nanotubes (mainly SWNTs) and ND.

Keywords: fullerene C_{60} , carbon nanotubes, nanodiamond, functionalization, solvent-free

1 INTRODUCTION

The global trend of searching for ecologically friendly, 'green' chemical processes manifested itself in the chemistry of carbon nanomaterials (CNMs), in particular, in the development of techniques for their chemical (both covalent and noncovalent) modification. A number of chemical reactions taking place under solvent-free conditions have been designed in other research laboratories, but mainly for the covalent chemical modification (or functionalization) of carbon nanotubes (CNTs). They can be exemplified by fluorination, additions of aryl diazonium and other radical species, noncovalent deposition of inorganic nanoparticles, which can be initiated by temperature, plasma or mechanochemical treatment. Equally to the conventional liquid-phase reactions, the solvent-free techniques allow for the introduction of organic addends into the nanotube ends and sidewalls. They yield CNT materials with improved solubility/dispersibility in organic and aqueous solvents, as well as enhanced reactivity required for further chemical derivatization. One should note that, while the use of

solvents is greatly reduced, in some instances the term 'solvent-free' refers to the reaction conditions only, but does not eliminate the need of further auxiliary purification steps, which do consume organic solvents along with additional time and labor.

Our effort was focused on two aspects: (i) the development of totally solvent-free (mainly covalent) functionalization techniques; (ii) an attempt to apply our solvent-free approach not only to CNTs but to other CNMs.

2 FULLERENES

In our first attempt of the solvent-free functionalization of fullerene C_{60} [1], the latter was first impregnated from solution onto the surface of silica gel in order to disperse it on an inert solid surface, and then treated under reduced pressure with vaporous nonylamine (NA) at 150 °C. The reaction produced a complex mixture of isomeric addition products. According to elemental analysis, the number of NA molecules attached to fullerene was three on average. At the same time, mass spectrometric study revealed the presence of adducts with up to six NA moieties attached to C_{60} . DFT quantum chemical calculations suggested that the addition most likely takes place across the 6,6 bonds of pyracylene units. DFT calculations were also undertaken to address the regioselectivity of amine polyaddition: that is, to what C atoms of fullerene cage the second, third, fourth, etc., amine molecules will be added [2]. By comparing the energies of formation of different possible isomeric adducts of methylamine, we found that the thermodynamically favorable additions are always observed on the 6,6 C=C bonds, and that a preferable polyaddition pattern is the one where NHCH₃ and H addends form an aligned chain, with the C atoms to which they are attached alternating in a zigzag order. We also approached the problem of regioselectivity in terms of general-purpose reactivity indicators [3].

Further studies dealt with the addition of more complex amines, including aliphatic and aromatic mono and diamines, onto C_{60} bulk material and thin films. For example, we applied the solvent-free functionalization of C_{60} with 1,8-diaminooctane (1,8-DAO) at 150-170°C, to prepare cross-linked fullerene thin films capable of binding silver nanoparticles [4]. The functionalization reduced dramatically C_{60} solubility in toluene, indicating the transformation of pristine C_{60} into a solid phase with cross-linked fullerene molecules. At the second step, Ag

nanoparticles (AgNPs) were deposited onto 1,8-DAO-functionalized fullerene films through the coordination bonding between metal atoms and N donor atoms of the attached diamine. As shows the comparison of high-resolution transmission electron microscopy images (HRTEM) of AgNPs deposited onto pristine and 1,8-DAO-functionalized C₆₀, the particles of ca. 5-nm diameter were typically observed on the functionalized films, whereas they had much more variable sizes as well as exhibited twinning when deposited onto pristine fullerene.

The gas-phase treatment with 1,5-diaminonaphthalene (DAN) was proposed as an efficient way of covalent functionalization of fullerene films in order to modify their electronic properties [5]. A temperature of about 190 °C and reaction time of 4 h were found to be optimal reaction conditions. Similarly to the functionalization with 1,8-DAO, two amino groups of DAN were expected to cross-link fullerene molecules. The resulting oligomeric and/or polymeric adducts had lower solubility in toluene as compared to pristine films, and a lower surface roughness according to AFM. DAN molecules were able to penetrate throughout the entire fullerene phase to provide an efficient and uniform functionalization.

The detailed chemical mechanisms of C₆₀ cross-linking with 1,8-DAO and DAN were addressed in [6], by using both DFT and different experimental techniques. We analyzed two alternative mechanisms of the amination reaction via polyaddition and cross-linking of fullerene with diamines. In terms of the relative energies of formation calculated by DFT, the cross-linking mechanism turned to be more thermodynamically preferred than that the diaddition pathway. Laser desorption/ionization time-of-flight mass spectrometry (LDI-TOF MS) confirmed both mechanisms in the case of DAN, whereas the polyaddition turned to be more likely in the case of 1,8-DAO.

Despite of SH groups are less active nucleophiles as compared to NH₂ groups, thiols were found to add onto fullerene cage similarly to amines. This reaction was exemplified by the solvent-free functionalization C₆₀ thin films with 1,8-octanedithiol (1,8-ODT) at ca. 140 °C, which were further used as supports for deposition of gold nanoparticles [7].

3 CARBON NANOTUBES

3.1 Nanotube Sidewalls

Some complex macrocyclic compounds, exemplified by synthetic porphyrins and phthalocyanines, being non-volatile at room temperature, can sublime without decomposition in vacuum at elevated temperatures. One of such compounds is nickel(II) complex of 5,7,12,14-tetramethyldibenzo-1,4,8,11-tetraazacyclotetradeca-3,5,7,10,12,14-hexaene (or simply NiTMTAA). Recently [8] we attempted the noncovalent functionalization of open-end SWNTs and pristine MWNTs with NiTMTAA in the gas phase at two selected temperatures of 220 and 270 °C. The

nanohybrids obtained were characterized by means of a number of electron microscopic and spectroscopic techniques, as well as TGA. SWNTs and MWNTs functionalized exhibited very similar features in the SEM and TEM images. At the same time, TGA found interesting differences in their composition, which were interpreted as the possibility of NiTMTAA adsorption both on the external sidewalls and inside SWNTs, whereas pristine MWNTs had closed ends with no access for adsorbates into their inner cavities.

In a more general sense, the term ‘solvent-free’ functionalization may be applied not to a process where the liquid phase is totally absent, but to that where no *organic* solvent is employed, that is, the functionalization carried out in aqueous media can be qualified as solvent-free. Such conditions are particularly common in the case of noncovalent functionalization of CNTs with biomolecules, especially proteins. CNTs with strongly adsorbed protein molecules can further serve as templates for the deposition of metal NPs. This was demonstrated by us for human serum albumin adsorbed on MWNTs, which was further used for the decoration with AgNPs generated by reduction of silver nitrate with citric acid [9]. The nanoparticles deposited onto albumin-functionalized MWNTs had a controlled diameter of ca. 2 nm and a narrow size distribution.

3.2 Oxidized Carbon Nanotubes

The very first implementation of solvent-free gas-phase covalent functionalization of CNTs was the direct amidation of oxidized SWNT defects [10,11]. Usually, we carry out the amidation reaction at at 150-170 °C for 1-2 h. Apparently, the reaction temperature can be even lower, e.g. 110 °C, but then the reaction time should be substantially increased. Amide-derivatized SWNTs exhibited an enhanced solubility/dispersibility in many organic solvents. The strongest effect was found for ODA [11], although the derivatization with NA gave good results as well [10].

If the amine employed for amide derivatization is bifunctional, the second NH₂ group can remain dangling and thus available for another derivatization step. We demonstrated this possibility by using 1,8-DAO-amide functionalized SWNTs for the second amidation with *L*-alanine and ϵ -caprolactam [12]. While the volatility of ϵ -caprolactam is relatively high, and the derivatization can be performed in a sealed vial at about 160 °C, the reaction with zwitterionic *L*-alanine needs constant evacuation and higher temperatures of 160-200 °C. In the case of ϵ -caprolactam, we found clear indications of its polymerization into nylon 6 initiated by the amino groups of 1,8-DAO attached to the nanotubes. In particular, SEM images showed dramatic changes in the SWNT bundle structure: while all other SWNT samples exhibited a typical fluffy morphology with numerous nanotubes and thin bundles coming out of the sample, the polymeric phase

formed in the ϵ -caprolactam-treated nanotubes 'glued' them together and made the samples look much more compact. This type of covalent bond generation might be useful for improving mechanical properties of CNT-polymer composites.

3.3 Pristine Multi-Walled Carbon Nanotubes

Pristine MWNTs have pentagonal and other defects, which are responsible for the spherical curvature of the closed ends, as well as for the nanotube kinking, when they are present in the sidewalls. We expected that the nucleophilic addition of primary and secondary amines known for spherical fullerenes can take place in a similar way at the closed ends of pristine MWNTs. Furthermore, we expected that the solvent-free conditions of fullerene functionalization with amines (Section 3.1) can be applied equally successfully to the closed-end nanotubes.

This was initially tested with octadecylamine (ODA) [13]. ODA-MWNTs formed stable solutions/dispersions in isopropanol under sonication, which did not exhibit visible changes for more than one month. TEM observations showed that the closed nanotube ends in ODA-MWNTs were covered with about 2-nm amorphous layer, which apparently originated from electron beam burning of ODA covalently bonded to the pentagonal (and/or other) defects. In addition to that, TEM imaging of the sidewalls revealed similar amorphous formations located at the sites with well-pronounced curvature. On the contrary, almost ideal nanotube sidewalls did not contain any additional material. Other monofunctional amines successfully tested for the functionalization of pristine MWNTs were NA, dodecylamine and 4-phenyl-butylamine [14].

The further effort was focused on the use of bifunctional and polyfunctional amine reagents, including polyethylene glycol diamine (PEGDA) and polyethylenimine (PEI) [15,16]. However, since nonvolatile polymeric reagents cannot be used for the gas-phase functionalization, we treated nanotubes with molten PEGDA and PEI at selected temperatures of 170 °C and 190 °C for 8 and 12 h, respectively. The unreacted excess of polymeric amines cannot be removed by heating and pumping out: instead, MWNTs functionalized were purified by repeated washing in water, centrifugation/decantation cycles, and drying in vacuum. Thus, no organic solvents were used even though the auxiliary steps were necessary.

CNT functionalization with diamines is of interest from different points of view. For example, it can facilitate a number of biomedical applications, since strong electrostatic interactions between amine groups and biological components can provide reliable immobilization of biological compounds onto the nanotube surface. The chemical functionalization using bifunctional molecules can enable the cross-linking of CNTs to form complex networks for nanoscale electronic circuits. Also, covalent cross-linking can dramatically enhance mechanical strength of CNT-polymer composites. These considerations

motivated us to undertake a deeper search for cross-linking effects in MWNTs covalently functionalized by the solvent-free technique with 1,8-DAO, 1,10-diaminododecane (1,10-DAD), 1,12-diaminododecane (1,12-DAD) and DAN [17]. As a result, we found different manifestations of such effects. In particular, the diamine functionalization made MWNTs totally insoluble in isopropanol in the case of 1,8-DAO, 1,10-DAD and 1,12-DAD, and dramatically reduced solubility/dispersibility in the case of DAN. Striking changes in the morphology of MWNT aggregates were observed by TEM and AFM, where the diamine-functionalized MWNTs appeared as very dense yarn-like structures, in which nanotubes exhibited a high degree of ordering. High-resolution TEM imaging showed the presence of amorphous matter at the sites of close contact between MWNTs, interpreted as cross-linking molecules.

Another reason of our interest toward the solvent-free functionalization of pristine MWNTs with diamines is the possibility of further derivatization of the dangling NH_2 groups [12]. Similarly to 1,8-DAO-amide functionalized SWNTs (Section 3.2), 1,8-DAO-MWNTs were subjected to the second amidation reaction with *L*-alanine and ϵ -caprolactam. In a later report [18] we found a minimum temperature for an efficient ϵ -caprolactam polymerization, along with the optimal weight ratio of 1,8-DAO-MWNTs to ϵ -caprolactam and reaction time.

Amines are not the only nucleophilic reagents which can be employed for the functionalization of defect sites of pristine MWNTs. We also successfully tested the one-step solvent-free addition of bifunctional aliphatic thiols [19,20]. The reaction conditions were very similar, since the reagents selected (1,4-butanedithiol, 1,6-hexanedithiol, 1,8-octanedithiol, and 2-aminoethanethiol) are volatile under reduced pressure and elevated temperature. The dithiol-functionalized MWNTs were shown to bind Zn^{2+} cations [19] and AuNPs [20].

4 NANODIAMOND

In terms of reactivity, ND is similar to oxidized SWNTs due to the presence of oxygen-containing functionalities, including COOH groups, on its surface. The one-step solvent-free amidation originally designed for derivatization of oxidized SWNTs (Section 3.2) proved to be a very efficient approach to changing the chemical nature of ND surface. A number of amines was tested for the temperature-activated amidation of COOH groups of pristine ND, which include 1,8-DAO, 1,10-DAD, 1,12-DAD, DAN, PEGDA, and PEI [17,21]. The functionalization with aliphatic diamines 1,8-DAO, 1,10-DAD and 1,12-DAD reduced solubility/dispersibility of ND due to the cross-linking effects, observed by different microscopic techniques.

5 CONCLUSIONS AND FURTHER PROSPECT

We designed a series of simple and fast functionalization protocols based on thermally activated reactions with compounds stable and volatile at 150-200 °C under normal or reduced pressure. In most of these protocols not only the reactions take place at a high rate, but also excess reagents are spontaneously removed from the functionalized material, therefore making unnecessary its purification. The main classes of reagents are amines and thiols (including diamines and dithiols), which can be used in conjunction with different CNMs, resulting in the following combinations:

- nucleophilic addition of amines to fullerene C₆₀;
- nucleophilic addition of thiols to C₆₀;
- direct amidation of carboxylic groups of oxidized CNTs (mainly SWNTs);
- nucleophilic addition of amines to defect sites of pristine MWNTs;
- nucleophilic addition of thiols to defect sites of pristine MWNTs;
- direct amidation of carboxylic groups of ND.

In the case of diamines and dithiols, reactions of the second functional group can give rise to cross-linking effects, or be employed for further derivatization steps (e.g., deposition of metal nanoparticles).

The possibility of applying the solvent-free strategy to nonoxidized graphene is deemed rather problematic. The reason is that the highly exfoliated state of graphene requires the use of a dispersing solvent. The exception is single graphene sheets deposited from solution/dispersion or CVD-grown on solid supports: in this case the solvent-free technique is definitely applicable. On the other hand, the resulting tiny samples can hardly be characterized by most spectral techniques, which is indispensable to prove successful functionalization. Another possibility is the functionalization of graphene oxide, which is common in powder form, similarly to fullerenes, CNTs and ND.

6 ACKNOWLEDGEMENTS

We are indebted for financial support from the National Council of Science and Technology of Mexico (grant CONACYT-127299) and from UNAM (grant DGAPA-IN100112).

REFERENCES

- [1] E. V. Basiuk (Golovataya-Dzhymbeeva), V. A. Basiuk, V. P. Shabel'nikov, V. G. Golovaty, J. O. Flores, and J. M. Saniger, *Carbon* 41, 2339, 2003.
- [2] O. Amelines-Sarria and V. A. Basiuk, *J. Comput. Theor. Nanosci.* 6, 73, 2009.
- [3] F. F. Contreras-Torres, V. A. Basiuk, and E. V. Basiuk, *J. Phys. Chem. A* 112, 8154, 2008.
- [4] V. Meza-Laguna, E.V. Basiuk (Golovataya-Dzhymbeeva), E. Alvarez-Zauco, D. Acosta-Najarro and V.A. Basiuk, *J. Nanosci. Nanotechnol.* 7, 3563, 2007.
- [5] E. Martínez-Loran, E. Alvarez-Zauco, V. A. Basiuk, E. V. Basiuk and M. Bizarro, *J. Nanosci. Nanotechnol.* 11, 5569, 2011.
- [6] F. F. Contreras-Torres, E. V. Basiuk, V. A. Basiuk, V. Meza-Laguna and T. Yu. Gromovoy, *J. Phys. Chem. A* 116, 1663, 2012.
- [7] V. Meza-Laguna, E.V. Basiuk (Golovataya-Dzhymbeeva), E. Alvarez-Zauco, T.Yu. Gromovoy, O. Amelines-Sarria, M. Bassiouk, I. Puente-Lee and V.A. Basiuk, *J. Nanosci. Nanotechnol.* 8, 3828, 2008.
- [8] V. A. Basiuk, L. V. Henao-Holguín, E. Álvarez-Zauco, M. Bassiouk, and E. V. Basiuk, *Appl. Surf. Sci.* 270, 634, 2013.
- [9] A. Rodríguez-Galván, F. F. Contreras-Torres, E. V. Basiuk, A. Heredia, and V. A. Basiuk, *Can. J. Chem. Eng.* 91, 264, 2013.
- [10] E. V. Basiuk, V. A. Basiuk, J. G. Bañuelos, J.-M. Saniger-Blesa, V. A. Pokrovskiy, T. Yu. Gromovoy, A. V. Mischanchuk and B. G. Mischanchuk, *J. Phys. Chem. B* 106, 1588, 2002.
- [11] V. A. Basiuk, K. Kobayashi, T. Kaneko, Y. Negishi, E. V. Basiuk and J.-M. Saniger-Blesa, *Nano Lett.* 2, 789, 2002.
- [12] V. A. Basiuk, C. Salvador-Morales, E. V. Basiuk, R. M. J. Jacobs, M. Ward, B. T. Chu, R. B. Sim, and M. L. H. Green, *J. Mater. Chem.* 16, 4420, 2006.
- [13] E. V. Basiuk, M. Monroy-Peláez, I. Puente-Lee and V. A. Basiuk, *Nano Lett.* 4, 863, 2004.
- [14] E. V. Basiuk, T. Yu. Gromovoy, A. Datsyuk, B. B. Palyanytsya, V. A. Pokrovskiy, and V. A. Basiuk, *J. Nanosci. Nanotechnol.* 5, 984, 2005.
- [15] E. V. Basiuk (Golovataya-Dzhymbeeva), O. Ochoa-Olmos, F. F. Contreras-Torres, V. Meza-Laguna, E. Alvarez-Zauco, I. Puente-Lee and V. A. Basiuk, *J. Nanosci. Nanotechnol.* 11, 5546, 2011.
- [16] F. F. Contreras-Torres, O. E. Ochoa-Olmos, and E. V. Basiuk, *J. Scanning Probe Microsc.* 4, 100, 2009.
- [17] E. V. Basiuk, V. A. Basiuk, V. Meza-Laguna, F. F. Contreras-Torres, M. Martínez, A. Rojas-Aguilar, M. Salerno, G. Zavala, A. Falqui, and R. Brescia, *Appl. Surf. Sci.* 259, 465, 2012.
- [18] E. V. Basiuk, O. A. Solis-González, E. Alvarez-Zauco, I. Puente-Lee, and V. A. Basiuk, *J. Nanosci. Nanotechnol.* 9, 3313, 2009.
- [19] E. V. Basiuk, I. Puente-Lee, J.-L. Claudio-Sánchez and V. A. Basiuk, *Mater. Lett.* 60, 3741, 2006.
- [20] R. Zanella, E. V. Basiuk, P. Santiago, V. A. Basiuk, E. Mireles, I. Puente-Lee and J. M. Saniger, *J. Phys. Chem. B* 109, 16290, 2005.
- [21] E. V. Basiuk, A. Santamaría-Bonfil, V. Meza-Laguna, T. Yu. Gromovoy, E. Alvarez-Zauco, F. F. Contreras-Torres, J. Rizo, G. Zavala and V. A. Basiuk, *Appl. Surf. Sci.* 275, 324, 2013.