Solvent-Free Functionalization of Carbon Nanomaterials : Fullerene C60 and Multiwalled Carbon Nanotubes with Aromatic Amines

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Carbon nanomaterials such as fullerene (C60) and carbon nanotubes (CNTs) have gained much attention due to their unique properties and broad applications in such diverse areas as physics, chemistry, materials science, etc. The chemical functionalization of carbon nanomaterials is considered as a crucial step toward their biomedical applications, where carbon nanomateriales covalently functionalized with amines is particularly attractive, since the amine groups can participate in strong electrostatic interactions with biological components, and immobilize the latter securely onto the surface of nanoparticles. In the present study, we employed an ecologically friendly technique of one-step solvent-free functionalization in gas phase for the fullerene (C_{60}) and multi-walled carbon nanotubes (MWNTs), with three different aromatic amines: 1,5-diaminonaphthalene, 1-aminopyrene, 2-aminofluorene. This technique relies upon the direct amination of C_{60} and MWNTs with amines, through thermal instead of chemical activation. Despite of seeming dissimilarity of these two types of carbon nanomaterials, they do have in common one important feature: the chemical reactivity of fullerene cages toward nucleophiles such as amines is due to the presence of pentagonal rings, and pristine MWNTs are believed to have numerous (apparently isolated) pentagonal rings at their closed ends and as sidewall defects, as well. The applying of aromatic amines for covalent functionalization is expected to modify the electronic structure of pristine carbon nanomaterials.

The nanostructures obtained were characterized by infrared and Raman spectroscopy, as well as thermogravimetric analysis and temperature-programmed desorption—mass spectrometry. XPS and RMN analysis confirmed the successful covalent functionalization of carbon nanomaterials by amine groups. The morphology of the nanostructures was characterized by scanning probe microscopy, scanning and transmission electron microscopy. The electrical properties of functionalized with aromatic amines carbon nanomaterials were studied in comparison to pristine nanomaterials.

The possibility of development of functional devices such as specific sensors and membranes through the chemical modification of carbon nanomaterials by amines is discussed. The results obtained might be useful to open a new route to amino-functionalized carbon nanomaterials-based conductive lightweight materials.

Acknowledgements. Financial support from the grant DGAPA-IN100112 is greatly appreciated. I.J.R.C. thanks CONACYT for a fellowship.

REFERENCES

1. E. V. Basiuk (Golovataya-Dzhymbeeva), V. A. Basiuk, V. P. Shabel'nikov, V. G. Golovatyi, J. O. Flores, and J. M. Saniger, *Carbon*, **41**, 2339 (2003).
2. E.V. Basiuk, M. Monroy-Peláez, I. Puente-Lee and V.A. Basiuk. *Nano Lett.*, **4 (5)**, 863 (2004).
3. E. Martínez-Lorán, E. Alvarez-Zauco, V. A. Basiuk, E. V. Basiuk, and M. Bizarro, *J. Nanosci. Nanotech.*, **11**, 5569 (2011).
4. E. V. Basiuk, T. Yu. Gromovoy, A. M. Datsyuk, B. B. Palyanytsya, V. A. Pokrovskiy, and V.A. Basiuk, *J. Nanosci. Nanotech.*, **5**, 984 (2005).
5. F. F. Contreras-Torres, O. E. Ochoa-Olmos, and E. V. Basiuk, *J. Scanning Probe Microsc.*, **4**, 100 (2009).