ChemComm

COMMUNICATION

Preparation and characterization of soluble carbon nano-onions by covalent functionalization, employing a Na–K alloy†

Agustín Molina-Ontoria,[a] Manuel N. Chaur,[b] Marta E. Plonska-Brzezinska[c] and Luis Echegoyen*[a]

Herein we report the preparation of truly soluble CNOs by covalent functionalization with hexadecyl chains. These compounds are prepared in two steps: first, reduction of CNOs with a Na–K alloy in 1,2-DME under vacuum, followed by nucleophilic substitution employing 1-bromohexadecane.

Since the discovery of carbon nano-onions (CNOs) in 1992 by Ugarte,[1] these quasi-spherical, concentric graphitic shells (also known as multilayer fullerenes) have not received as much attention as carbon nanotubes (CNTs), although both exhibit similar interesting properties, chemical and physical, such as large surface area to volume ratio, low densities, and a graphitic multilayer morphology. These properties make them excellent candidates for different applications, for instance, in heterogeneous catalysis,[2] for field emission,[3] in fuel cells,[4] for optical limiting,[5] for electromagnetic shielding,[6] for gas and energy storage,[7] in tribology,[8] in therapy for cancer tumors[9] and more recently as supercapacitators[10] or bioimaging agents.[11]

Like CNTs, CNOs exhibit poor solubility or dispersity in most organic and/or inorganic solvents, and for this reason their use has been limited. Surface modification of CNOs allows their segregation, and improves their solubility or dispersity. Chemical functionalization of CNOs is strongly correlated with the size of the multilayer fullerenes; small CNOs (5 nm) possess significant curvature, and thus higher reactivity than larger-sized ones.[12] There are several methodologies for covalent functionalization of CNOs, for instance, esterification or amidation[13] reactions following oxidative treatment with nitric acid or a mixture of sulfuric and nitric acids. Outer shell functionalization *via* 1,3-dipolar cycloaddition of azomethine ylides,[14] [2+1] Bingel–Hirsch cyclopropanation,[12] [2+1] cycloaddition of nitrenes,[15] treatment with diazonium-based

compounds,[16] radical addition[12,17] and direct fluorination with elemental fluorine[18] have also been reported.

Billups *et al.*[19] reported the reductive alkylation of SWCNTs *via* Birch reduction, using lithium in liquid ammonia, and subsequently Tour *et al.*[20] employed the same methodology with MWCNTs using different electrophiles. Recently, Hirsch *et al.* reported the functionalization of SWCNTs using carbonyl compounds[21] and polycarboxylation,[22] employing carbon dioxide *via* reductive sidewall reactions. Similar reductive procedures have been reported for the functionalization of graphene *via* Na–K alloy treatment followed by reaction with diazonium salts and alkyliodides.[23] These reductive protocols represent a very convenient way for bulk functionalization of CNTs and one of the strongest and most effective methodologies available, and this is why they were selected for the present study. Here we present for *the first time* the alkylation of CNOs, employing a similar reductive methodology. As a result of the functionalization, soluble CNOs have been obtained. To our knowledge, no truly soluble CNOs have ever been described, only those that very well dispersed in some solvents. The resulting products were characterized by HR-TEM, Raman, NMR, FTIR, UV-vis spectroscopy and by TGA.

1,2-Dimethoxyethane (1,2-DME) was vapor transferred into a three necked flask containing 0.1 mL of a Na–K alloy and the solution was vigorously stirred until a deep blue color was obtained (see ESI,† Fig. S1). At this point, CNOs obtained by annealing (1650 °C) ultradispersed nanodiamond particles (ND) (5 nm size) under an inert atmosphere were added and the solution was stirred for 3 days, after which brownish CNO dispersions were formed due to the reductive treatment. The negative charges generated on the outer shells of the CNOs were trapped by adding an excess of the electrophile (1-bromohexadecane) to the solution, while stirring for 3 additional days (Scheme 1). The solution was washed with hexane, ethanol, THF and water. The sample was dried in a vacuum oven at 45 °C overnight, resulting in 38 mg of functionalized CNOs.

The first evidence for the covalent functionalization was provided by thermogravimetric analysis measurements (TGA). In order to determine the degree of functionalization of the functionalized-CNOs-C_{16}, TGA studies were conducted under a N_2 atmosphere from 30 °C until 1000 °C using a heating

[a] *Department of Chemistry, University of Texas at El Paso, El Paso, TX 79968-0519, USA. E-mail: echegoyen@utep.edu*
[b] *Departamento de Química, Universidad del Valle, Cali, Colombia. E-mail: manuel.chaur@correounivalle.edu.co*
[c] *Institute of Chemistry, University of Bialystok, Hurtowa 1, 15-399 Bialystok, Poland. E-mail: mplonska@uwb.edu.pl; Fax: +48 85-747-0113*
† Electronic supplementary information (ESI) available. See DOI: 10.1039/c3cc39077b
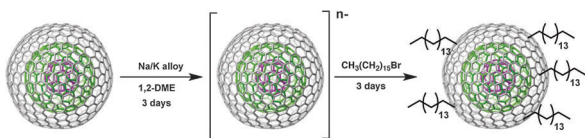
Scheme 1 Reductive treatment of CNOs by a Na–K alloy in 1,2-DME and subsequent alkylation using 1-bromohexadecane.

rate of 10 °C min^{-1}. Pristine CNOs were used as reference under the same conditions (Fig. 1a).

The TGA curve of the functionalized CNOs exhibits three different thermal stages for a total mass loss of 32%, at 215 °C (−4.0%), probably corresponding to the loss of physisorbed solvent, at 375 °C (−28.0%), corresponding to the removal of the alkyl chains form the surface of the CNOs and final decomposition of the CNOs at 420 °C. Pristine CNOs remain stable at that temperature, so the lower thermal stability of the functionalized CNOs is probably due to the insertion of ''structural defects'' upon functionalization, as observed for carbon nanotubes.[24]

Raman spectroscopy is one of the most powerful methods for the characterization of CNOs, providing unambiguous information about the size and the degree of functionalization of the CNOs by comparison of the relative intensities of the defective bands. The D-band is related to defects in the CNOs lattice (sp^3-hybridized carbon) and the G-band is due to the vibrations of the sp^2-hybridized framework. The Raman spectrum of the pristine CNOs exhibits a varying ratio of $I(D)/I(G)$, depending on the size of the CNOs. For CNOs prepared by arc discharge of graphite under water (20–30 shells) the $I(D)/I(G) = 0.8$, but CNOs obtained by annealing of ND particles (1650 °C) under an inert atmosphere lead to the formation of small CNOs (6–12 shells) with an $I(D)/I(G)$ ratio of 1.4, depending on the crystal size of the carbon nanodiamond. Therefore, dispersions of pristine CNOs and functionalized CNO-C$_{16}$ in DMF were deposited onto silicon wafers covered with a 300 nm SiO$_2$ thick layer by drop casting.

The Raman spectrum of the small pristine CNOs after excitation at 532 nm (Fig. 1b) shows the typical peaks, namely, the D-band at 1335 cm^{-1} and the G-band at 1577 cm^{-1}. In contrast, the D and G bands for the CNOs-C$_{16}$ are shifted to 1340 and 1585 cm^{-1}, respectively. The $I(D)/I(G)$ ratio for the functionalized CNOs is 1.64, indicating an increase in the number of defects (sp^3-hybridized) as a result of bulk functionalization.
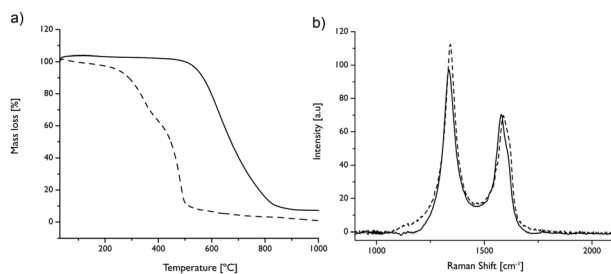

Fig. 1 (a) TGA of pristine CNOs (solid line) and functionalized CNOs-C$_{16}$ (dotted line) under a N$_2$ atmosphere and 10 °C min^{-1} of heating rate. (b) Raman spectrum (λ_{exc} = 532 nm) of pristine CNOs (solid line) and functionalized CNOs-C$_{16}$ (dotted line).

Thermal annealing of the functionalized CNOs-C$_{16}$ was carried out to determine the reversibility of the reaction. For this purpose, the functionalized CNOs-C$_{16}$ were annealed at 415 °C to remove the –C$_{16}$ addends and then Raman spectroscopy was performed, clearly showing the complete defunctionalization of the CNOs (Fig. S2, ESI†).

Since CNOs-C$_{16}$ exhibited relatively good dispersity in common organic solvents, NMR spectroscopy studies were employed to confirm the chemical functionalization of CNOs-C$_{16}$. Fig. S3 (ESI†) shows the spectrum of CNOs-C$_{16}$, before and after filtration through polyvinylidene fluoride (PVDF) filters of 0.2 μm porosity; however, when filtered, most of the functionalized onions remain in the filters. A sample of CNOs-C$_{16}$ was sonicated in CDCl$_3$ and its ^{1}H NMR spectrum was recorded using a 600 MHz JEOL spectrometer. The spectrum displays signals at 1.29 (–CH$_2$–) and 0.89 ppm (–CH$_3$), attributed to the hexadecyl chains. The signals from the aliphatic chains remained unchanged after the dispersion was filtered. The ^{1}H NMR spectrum of 1-bromohexadecane was recorded to compare with the CNOs-C$_{16}$ (Fig. S4, ESI†). It is important to note that the protons in the α and the β-position (a triplet at 3.4 and a quintuplet at 1.7 ppm) to the bromine disappear completely in the case of CNO-C$_{16}$, indicating a successful functionalization of CNOs.

To elucidate the effect of the functionalization, SEM and HR-TEM studies were performed. SEM images of a Au foil covered with non-modified CNOs and of CNOs functionalized with 1-bromohexadecane are shown in Fig. 2a and b. Non-modified CNOs tend to aggregate, because of strong van der Waals interactions between them (Fig. 2a). After functionalization of the CNOs with 1-bromohexadecane, the structures exhibit better dispersity and a more porous morphology, with many channels and outcroppings (Fig. 2b).

Fig. 2c and d show the low and high resolution TEM images of CNOs-C$_{16}$. N-Methyl-2-pyrrolidone (NMP) affords CNOs-C$_{16}$ solutions that go through the filters more efficiently than using other solvents (130 mg L^{-1} in NMP versus 60 mg L^{-1} in CHCl$_3$), probably due to strong interactions between the solvent and the outer shells of the CNOs (Fig. S8, ESI†). Solubility was determined by filtering sonicated solution, following the same procedure used for MWCNTs.[20] Similar observations have been reported for CNTs and graphene in NMP.[25] Therefore, the functionalized CNOs-C$_{16}$ were dissolved in NMP, sonicated and filtered through PVDF filters of 0.1 μm porosity. This resulted in a more homogenous distribution of CNOs with smaller average size domains (Fig. S5, ESI†). Statistical analyses were conducted over 250 HRTEM pictures in order to determine the average size of the CNO-C$_{16}$ before and after filtration. The filtered solutions appear to contain more homogeneously sized CNOs possessing smaller sizes than the pristine CNOs, with an average size of 5 nm with 5–7 graphitic shells and an interlayer distance of approximately 3.3 Å.

Additional studies were conducted to corroborate the covalent attachment of the hexadecyl groups on the outer sphere of the CNOs. FTIR studies reveal the appearance of two bands at 2915 and 2845 cm^{-1} corresponding to the C–H stretching of the hexadecyl chains, considerably stronger than those corresponding to the CNO framework (Fig. S6, ESI†). There are slight shifts of the C–H stretching bands of the CNO-C$_{16}$ compared
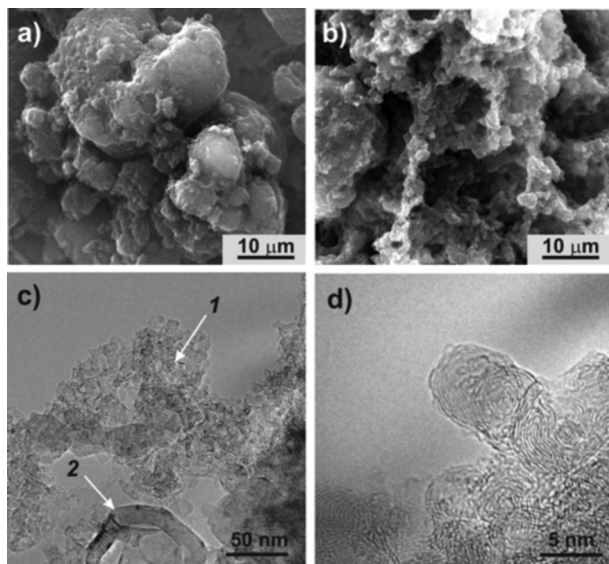
Fig. 2 SEM images of the Au foil covered with (a) pristine CNOs, and (b) CNOs-C_{16}. TEM images of the Cu holey carbon covered with (c) CNOs-C_{16}; (d) 1st structure of CNOs-C_{16}.

with those corresponding to the 1-bromohexadecane (2921 and 2852 cm^{-1}).

UV-Vis absorption studies were performed in different solvents. Noteworthily, the CNOs-C_{16} are very well dispersed in solvents such as $CHCl_3$, toluene, NMP, DME, THF and DMAC, among others, at a 0.1 mg mL^{-1} concentration (Fig. S7, ESI†). The UV-vis spectrum of the functionalized CNOs exhibits an absorption peak at 274 nm, which is not significantly affected by changing the nature of the solvent (Fig. S9, ESI†).

In summary, the reduction of CNOs using a Na–K alloy is a convenient method for the chemical functionalization of CNOs, which can be extended, in principle, to a variety of electrophiles. Additionally, the covalent functionalization reported here resulted in truly soluble CNOs which can be filtered through a 0.2 µm and 0.1 µm PVDF filter, resulting in a smaller and more homogeneous distribution of CNOs. This opens a wide range of potential applications, such as photovoltaics or molecular electronics, due to the processability of the CNOs.

Notes and references

1 D. Ugarte, *Nature*, 1992, **359**, 707.
2 N. Keller, N. I. Maksimova, V. V. Roddatis, M. Schur, G. Mestl, Y. V. Butenko, V. L. Kuznetsov and R. Schlogl, *Angew. Chem., Int. Ed.*, 2002, **41**, 1885.
3 M. Choi, I. S. Altman, Y. J. Kim, P. V. Pikhitsa, S. Lee, G. S. Park, T. Jeong and J. B. Yoo, *Adv. Mater.*, 2004, **16**, 1721.
4 (a) B. Xu, X. Yang, X. Wang, J. Guo and X. Liu, *J. Power Sources*, 2006, **162**, 160; (b) J. Guo, X. Yang, Y. Yao, X. Wang, X. Liu and B. Xu, *Rare Met.*, 2006, **25**, 305.
5 E. Koudoumas, O. Kokkinaki, M. Konstantaki, S. Couris, S. Korovin, P. Detkov, V. Kuznetsov, S. Pimenov and V. Pustovoi, *Chem. Phys. Lett.*, 2002, **357**, 336.
6 O. Shenderova, V. Grishko, G. Cunningham, S. Moseenkov, G. McGuire and V. Kuznetsov, *Diamond Relat. Mater.*, 2008, **17**, 462.
7 N. Sano, H. Wang, I. Alexandrou, M. Chhowalla, K. B. K. Teo, G. A. J. Amaratunga and K. Iimura, *J. Appl. Phys.*, 2002, **92**, 2783.
8 (a) Y. Hirata and N. Mataga, *J. Phys. Chem.*, 1984, **88**, 3091; (b) L. Joly-Pottuz, B. Vacher, N. Ohmae, J. M. Martin and T. Epicier, *Tribol. Lett.*, 2008, **30**, 69; (c) L. Joly-Pottuz, E. W. Bucholz, N. Matsumoto, S. R. Phillpot, S. B. Sinnott, N. Ohmae and J. M. Martin, *Tribol. Lett.*, 2009, **37**, 75.
9 L. Ding, J. Stilwell, T. Zhang, O. Elboudwarej, H. Jiang, J. P. Selegue, P. A. Cooke, J. W. Gray and F. F. Chen, *Nano Lett.*, 2005, **5**, 2448.
10 D. Pech, M. Brunet, H. Durou, P. Huang, V. Mochalin, Y. Gogotsi, P.-L. Taberna and P. Simon, *Nat. Nanotechnol.*, 2010, **5**, 651.
11 (a) S. K. Sonkar, M. Ghosh, M. Roy, A. Begum and S. Sarkar, *Mater. Express*, 2012, **2**, 105; (b) M. Ghosh, S. K. Sonkar, M. Saxena and S. Sarkar, *Small*, 2011, **7**, 3170.
12 A. Palkar, F. Melin, C. M. Cardona, B. Elliott, A. K. Naskar, D. D. Edie, A. Kumbhar and L. Echegoyen, *Chem.–Asian J.*, 2007, **2**, 625.
13 (a) A. S. Rettenbacher, B. Elliott, J. S. Hudson, A. Amirkhanian and L. Echegoyen, *Chem.–Eur. J.*, 2006, **12**, 376; (b) A. Palkar, A. Kumbhar, A. J. Athans and L. Echegoyen, *Chem. Mater.*, 2008, **20**, 1685.
14 (a) V. Georgakilas, D. M. Guldi, R. Signorini, R. Bozio and M. Prato, *J. Am. Chem. Soc.*, 2003, **125**, 14268; (b) C. T. Cioffi, A. Palkar, F. Melin, A. Kumbhar, L. Echegoyen, M. Melle-Franco, F. Zerbetto, G. M. A. Rahman, C. Ehli, V. Sgobba, D. M. Guldi and M. Prato, *Chem.–Eur. J.*, 2009, **15**, 4419.
15 L. Zhou, C. Gao, D. Zhu, W. Xu, F. F. Chen, A. Palkar, L. Echegoyen and E. S.-W. Kong, *Chem.–Eur. J.*, 2009, **15**, 1389.
16 K. Flavin, M. N. Chaur, L. Echegoyen and S. Giordani, *Org. Lett.*, 2010, **12**, 840.
17 A. S. Rettenbacher, M. W. Perpall, L. Echegoyen, J. Hudson and D. W. J. Smith, *Chem. Mater.*, 2007, **19**, 1411.
18 Y. Liu, R. L. Vander Wal and V. N. Khabashesku, *Chem. Mater.*, 2007, **19**, 778.
19 F. Liang, A. K. Sadana, A. Peera, J. Chattopadhyay, Z. Gu, R. H. Hauge and W. E. Billups, *Nano Lett.*, 2004, **4**, 1257.
20 J. J. Stephenson, A. K. Sadana, A. L. Higginbotham and J. M. Tour, *Chem. Mater.*, 2006, **18**, 4658.
21 B. Gebhardt, Z. Syrgiannis, C. Backes, R. Graupner, F. Hauke and A. Hirsch, *J. Am. Chem. Soc.*, 2011, **133**, 7985.
22 B. Gebhardt, F. Hof, C. Backes, M. Müller, T. Plocke, J. Maultzsch, C. Thomsen, F. Hauke and A. Hirsch, *J. Am. Chem. Soc.*, 2011, **133**, 19459.
23 (a) J. M. Englert, C. Dotzer, G. Yang, M. Schmid, C. Papp, J. M. Gottfried, H.-P. Steinrück, E. Spiecker, F. Hauke and A. Hirsch, *Nat. Chem.*, 2011, **3**, 279; (b) J. M. Englert, K. C. Knirsch, C. Dotzer, B. Butz, F. Hauke, E. Spiecker and A. Hirsch, *Chem. Commun.*, 2012, **48**, 5025.
24 S. Campidelli, C. Sooambar, E. Lozano Diz, C. Ehli, D. M. Guldi and M. Prato, *J. Am. Chem. Soc.*, 2006, **128**, 12544.
25 (a) Y. Hernandez, V. Nicolosi, M. Lotya, F. M. Blighe, Z. Sun, S. De, I. T. McGovern, B. Holland, M. Byrne, Y. K. Gun'Ko, J. J. Boland, P. Niraj, G. Duesberg, S. Krishnamurthy, R. Goodhue, J. Hutchison, V. Scardaci, A. C. Ferrari and J. N. Coleman, *Nat. Nanotechnol.*, 2008, **3**, 563; (b) C. A. Furtado, U. J. Kim, H. R. Gutierrez, L. Pan, E. C. Dickey and P. C. Eklund, *J. Am. Chem. Soc.*, 2004, **126**, 6095; (c) S. Giordani, S. D. Bergin, V. Nicolosi, S. Lebedkin, M. M. Kappes, W. J. Blau and J. N. Coleman, *J. Phys. Chem. B*, 2006, **110**, 15708; (d) B. J. Landi, H. J. Ruf, J. J. Worman and R. P. Raffaelle, *J. Phys. Chem. B*, 2004, **108**, 17089; (e) T. Hasan, V. Scardaci, P. H. Tan, A. G. Rozhin, W. I. Milne and A. C. Ferrari, *J. Phys. Chem. C*, 2007, **111**, 12594; (f) S. D. Bergin, V. Nicolosi, S. Giordani, A. de Gromard, L. Carpenter, W. J. Blau and J. N. Coleman, *Nanotechnology*, 2007, **18**, 455705.