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A soluble hybrid material combining carbon nanohorns and C_{60} †

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A soluble hybrid nanomaterial that combines fullerenes and carbon nanohorns (CNHs) has been prepared and fully characterized. Electrochemical investigations revealed that the CNHs modify the electron accepting ability of C_{60} in the hybrid material.

Owing to their remarkable electronic, thermal and mechanical properties, carbon nanostructures such as fullerenes, carbon nanotubes (CNTs) and graphene are extremely promising candidates for the preparation of new advanced materials for a large number of applications.¹ In recent years, hybrid structures combining two different forms of carbon nanostructures have been prepared with the aim to generate multifunctional nanomaterials with enhanced properties.² Examples include CNTs filled with fullerenes, *i.e.* nanopeapods³ and supramolecular ensembles in which fullerene derivatives are assembled around the external surface of CNTs.⁴ A few derivatives in which the fullerenes are covalently bonded to the outer surface of the CNTs have been also reported.⁵ However, in most of the cases, the resulting materials are completely insoluble thus making their characterization difficult and limiting in-depth investigations of their electronic properties. As part of this research, we now report the synthesis and the characterization of a soluble hybrid material that combines fullerenes and carbon nanohorns (CNHs) into a single structure in which fullerene derivatives have been covalently grafted to the outer surface of modified CNHs under the coppercatalyzed alkyne-azide cycloaddition (CuAAC) conditions. Owing to its good solubility, the electrochemical properties of the C₆₀-CNH conjugate could be investigated thus revealing

the existence of electronic communications between both kinds of carbon nanostructures in the hybrid material.

The synthesis of the C_{60} -CNH hybrid 8 is depicted in Scheme 1. Treatment of diol 2 with carboxylic acid 1 and N,N'-dicyclohexylcarbodiimide (DCC) in the presence of 4-dimethylaminopyridine (DMAP) and 1-hydroxybenzotriazole (HOBt) gave bis-malonate 3 in 81% yield. A double Bingel cyclopropanation was used to prepare fullerene bis-adduct derivative 4.6 Reaction of 3 with C₆₀, I₂, and 1,8-diazabicyclo[5.4.0]undec-7-ene (DBU) in toluene afforded **4** in 42% yield. Reaction of *pristine* CNHs with 5^7 in the presence of isoamyl nitrite in N-methyl-2-pyrrolidone (NMP) gave functionalized CNHs 6. Subsequent treatment with tetra-n-butylammonium fluoride (TBAF) gave the CNHs derivative 7 bearing terminal alkyne subunits. Reaction of 7 with azide 4 in NMP under the conditions optimized for fullerene-containing azides⁸ (CuSO₄. 5H2O and sodium ascorbate) afforded the targeted CNH-fullerene hybrid material 8. Owing to the four long alkyl chains per fullerene subunit, compound 8 is soluble in chlorinated solvents (up to 0.5 mg mL^{-1} in CH₂Cl₂) (see ESI⁺, Fig. S1).

As shown in Fig. 1, the morphology of the newly prepared CNH-fullerene **8** was observed with high resolution transmission electron microscopy (HR-TEM, TOPCON 002B) at 120 kV.

The spherical form of the CNH aggregates was not destroyed by the functionalization (Fig. 1), and C_{60} -like spherical molecules attached to the CNH surfaces were often found (Fig. 1, insets).

Raman spectroscopy provided important information on the covalent modification.⁹ It is known that the Raman vibrational spectrum of the CNTs family members, such as CNHs, has two prominent bands, assigned as the disorder-induced mode (D-band) and the tangential mode (G-band), centered at 1350 and 1590 cm⁻¹, respectively. The G band is associated with the vibrations of sp²-hybridized carbon atoms, whereas the D band is attributed to the sp³ carbon atoms existing within CNHs aggregates and corresponds to the CNH core as well as to the defect sites of the nanostructures. The Raman spectra ($\lambda_{exc} = 532$ nm) of *pristine* CNHs and modified CNHs **6** and **8** are shown in Fig. 2 (see also ESI†, Fig. S2).

In the case of the modified CNHs **6** and **8**, the intensity of the D-band is enhanced with respect to pristine CNHs as a result of the transformation of sp² hybridized C atoms of the CNH framework into sp³ ones.¹⁰ Specifically, after the first covalent functionalization of CNHs, the I_D/I_G ratio increased from 1.07 for *pristine* CNHs to 1.18 for **6**, indicating a clear

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Scheme 1 Synthesis of CNH-fullerene 8. *Reagents and conditions*: (i) DCC, DMAP, HOBt, CH₂Cl₂, 0 °C to rt, 60 h, 81%; (ii) C₆₀, DBU, I₂, PhMe, rt, 12 h, 42%; (iii) isoamyl nitrite, NMP, 70 °C, 24 h; (iv) TBAF, THF, NMP, rt, 1 h; (v) CuSO₄·5H₂O, sodium ascorbate, NMP, 70 °C, 48 h.



Fig. 1 HR-TEM images of modified CNHs 8. Insets show tips of SWNHs to which C_{60} -like molecules (black arrows) are attached.

enhancement of the disruption of the skeleton of CNHs, thus providing a first evidence for the covalent modification of the surface of CNHs. At this point, it is also worth noticing that D-band intensity for 8 is similar to that of 6 (Fig. 2), proving that the CNH framework is unaffected by the reaction



Fig. 2 Comparative Raman spectra ($\lambda_{exe} = 532$ nm) of *pristine* CNHs (black) and modified CNHs **6** (red) and **8** (blue), illustrating D and G bands. The spectra are normalized to the peak intensity of the *G* band.

conditions used for the grafting of the fullerene subunits onto the modified CNHs **6**. The reaction of azide **4** must therefore effectively occur on the alkyne subunits of **6** thus leading to the formation of triazole rings.¹¹

X-Ray photoelectron spectroscopy was used to determine the nature and the relative amount of functional groups present on the CNHs surface.¹² The survey spectra of CNHfullerene 8 and fullerene derivative 4 (see ESI⁺, Fig. S3) show the photoelectrons collected from C1s, N1s and O1s core-levels (together with the OKLL Auger emission). High resolution spectra were then recorded and the corresponding binding energy values are collected in Table S1 (see ESI[†]). All peaks were decomposed into several symmetrical components (*i.e.*, five or six for C1s; two for O1s and one or two for N1s) (see ESI[†], Fig. S3). The C1s peak of 8 was satisfactorily fitted to six components according to the peak assignment used by Stankovich et al.¹³ The most intense peak at 284.8 eV is due to sp² C–C bonds of graphitic carbon whereas the component at 285.4 eV is originated from sp3 C-C bonds.14 The next three components at 286.3, 287.6 and 289.3 eV have been often assigned to C-O, C=O and COO groups^{12,15} present on the surface of CNHs. In addition, CNH-fullerene 8 displays a weak component at around 291.4 eV corresponding to $\pi - \pi^*$ transition of carbon atoms in graphene structures,^{10,16} but is absent in fullerene derivative 4. Finally, a weak C-N* component should be expected somewhere around 286.3 eV, however it is overshadowed by the strongest C-O line and therefore it could not be resolved.

For simplicity and sake of easy understanding the O1s spectrum of **8** has been curve-resolved with only two components (see ESI[†], Table S1). A minor component at 531.7 eV corresponds to O=C surface groups and major one at 533.1 eV is likely associated with O-C bonds,^{10,11} demonstrating the existence of oxygen functional groups on the CNHs surface. The same components are observed for fullerene derivative **4** although both appear somewhat shifted toward higher binding energies. The high-resolution N1s spectrum (Fig. S3, ESI[†]) of **8** displays two components, a major one at a binding energy of



Fig. 3 DPV (reduction run) of pristine C_{60} (black), fullerene derivative **4** (magenta) and CNH-fullerene **8** (blue).

400.4 eV, belonging to two N-atoms bound to C-atoms as nearest neighbours,¹⁷ and a minor one 399.2 eV originating from the other remaining N-atom.¹¹ In contrast, fullerene derivative **4** bearing an azide group displays a single N1s component at 401.0 eV. These observations unambiguously confirm that the azide residue of fullerene building block **4** is not anymore present upon covalent incorporation into the CNHs and clearly supports the formation of triazole rings. This is also in perfect agreement with the IR spectrum of **8** showing that no azide (2092 cm⁻¹) residues remain in the final product (see ESI[†], Fig. S4). The incorporation of the fullerene moiety in the CNH framework through the formation of triazole rings was further confirmed by thermogravimetric analysis (TGA, see ESI[†]).

Owing to the solubility of hybrid compound 8, its electrochemical properties could be investigated by differential pulsed voltammetry (DPV) (Fig. 3). The electrochemical studies were performed at room temperature in o-dichlorobenzene/acetonitrile 4:1 containing tetra-*n*-butylammonium hexafluorophosphate (TBAPF₆) (0.1 M). The two characteristic reductions of C_{60} bis-adducts are observed for 8 (at -0.98 mV and -1.36 mV). Interestingly, comparison of the redox potential for the first reduction of 8 with that of its fullerene 4 revealed a cathodic shift of 80 mV. Indeed, the redox potential of the fullerene molety in **8** is similar to that of pristine C_{60} ($E_{red}^1 = -0.99$ mV) measured under the same conditions. This shift may be attributed to the existence of electronic interactions between the CNHs and the fullerene cages. It is however worth noting that molecular mechanic calculations show a distance of ca. 12 Å between the CNH surface and the C_{60} subunit. A similar shift has been recently observed in endohedral C₆₀@SWCNT,¹⁸ although in this case, the distance between is much shorter, around 3.4 Å. In our case, it is also likely that the observed potential shift may result from the specific nanoenvironment of the fullerene moieties grafted on the CNHs.

In summary, a soluble hybrid C_{60} -CNH has been synthesized under CuAAC conditions and fully characterized. Importantly, the developed synthetic route can be easily applied for the preparation of related hybrid systems combining C_{60} with other carbon nanostructures such as CNTs and graphene and thus opens the door to explore the possible applications of such multifunctional nanomaterials.

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Notes and references

- (a) Fullerenes principles and applications, ed. F. Langa and J.-F. Nierengarten, Royal Society of Chemistry, 2008; (b) Carbon Nanotubes and Related Structures, ed. D. M. Guldi and N. Martín, Wiley-VCH, Weinheim, 2010.
- 2 G. Nasibulin, P. V. Pikhitsa, H. Jiang, D. P. Brown, A. V. Krasheninnikov, A. S. Anisimov, P. Queipo, A. Moisala, D. Gonzalez, G. Lientschnig, A. Hassanien, S. D. Shandakov, G. Lolli, D. E. Resasco, M. Choi, D. Tománek and E. I. Kauppinen, *Nat. Nanotechnol.*, 2007, 2, 156.
- 3 B. W. Smith, M. Monthioux and D. E. Luzzi, *Nature*, 1998, **396**, 323.
- 4 Y.-L. Zhao and J. F. Stoddart, Acc. Chem. Res., 2009, 42, 1161.
- 5 (a) J. L. Delgado, P. de la Cruz, A. Urbina, J. T. L. Navarrete, J. Casado and F. Langa, *Carbon*, 2007, **45**, 2250; (b) W. Wu, H. Zhu, L. Fan and S. Yang, *Chem.-Eur. J.*, 2008, **14**, 5981; (c) S. Giordani, J.-F. Colomer, F. Cattaruzza, J. Alfonsi, M. Meneghetti, M. Prato and D. Bonifazi, *Carbon*, 2009, **47**, 578; (d) Q. Wang and H. Moriyama, *Langmuir*, 2009, **25**, 10834; (e) N. Mackiewicz, T. Bark, B. Cao, J. A. Delaire, D. Riehl, W. L. Ling, S. Foillard and E. Doris, *Carbon*, 2011, **49**, 3998.
- 6 J.-F. Nierengarten, V. Gramlich, F. Cardullo and F. Diederich, Angew. Chem., Int. Ed. Engl., 1996, 35, 2101.
- 7 J.-J. Hwang and J. M. Tour, Tetrahedron, 2002, 58, 10387.
- 8 J. Iehl, I. Osinska, R. Louis, M. Holler and J.-F. Nierengarten, *Tetrahedron Lett.*, 2009, 50, 2245.
- 9 (a) M. S. Dresselhaus, G. Dresselhaus, A. Jorio, A. G. Souza Filho, M. A. Pimenta and R. Saito, Acc. Chem. Res., 2002, 35, 1070; (b) M. S. Dresselhaus, A. Jorio, M. Hofmann, G. Dresselhaus and R. Saito, Nano Lett., 2010, 10, 751.
- 10 (a) A. M. Rao, E. Richter, S. Bandow, B. Chase, E. C. Eklund, K. A. Williams, S. Fang, K. R. Subbaswamy, M. Menon, A. Thess, R. E. Smalley, G. Dresselhaus and M. S. Dresselhaus, *Science*, 1997, **275**, 187; (b) S. Iijima, T. Ichihashi and Y. Ando, *Nature*, 1992, **356**, 776.
- 11 K.-H. Le Ho, L. Rivier, B. Jousselme, P. Jégou, A. Filoramo and S. Campidelli, *Chem. Commun.*, 2010, 46, 8731.
- 12 H. P. Boehm, Carbon, 2002, 40, 145.
- 13 S. Stankovich, D. A. Dikin, R. D. Piner, K. A. Kohlhaas, A. Kleinhammes, Y. Jia, Y. Wu, S. T. Nguyen and R. S. Ruoff, *Carbon*, 2007, 45, 1558.
- 14 D. B. Mawhinney, V. Naumenko, A. Kuznetsova, J. T. Yates, J. Liu and R. E. Smalley, *Chem. Phys. Lett.*, 2000, **324**, 213.
- 15 E. Del Canto, K. Flavin, D. Movia, C. Navio, C. Bittencourt and S. Giordani, *Chem. Mater.*, 2011, 23, 67 and references therein.
- 16 J. H. Zhou, Z. J. Sui, J. Li, P. Zhu, D. Chen, Y. C. Dai and W. K. Yuan, *Carbon*, 2007, 45, 785.
- 17 M. Holzinger, J. Abraham, P. Whelan, R. Graupner, L. Ley, F. Henrich, M. Kappes and A. Hirsch, J. Am. Chem. Soc., 2003, 125, 8566.
- 18 N. Karousis, S. P. Economopoulos, Y. Iizumi, T. Okazaki, Z. Liu, K. Suenaga and N. Tagmatarchis, *Chem. Commun.*, 2010, 46, 9110.