

Photochemical Evidence of Electronic Interwall Communication in Double-Wall Carbon Nanotubes

María J. Gómez-Escalonilla,^a María Vizuete,^a Sergio García-Rodríguez,^b José Luis G. Fierro,^b Pedro Atienzar,^c Hermenegildo García,^{c,*} and Fernando Langa^{a,*}

^a Instituto de Nanociencia, Nanotecnología y Materiales Moleculares (INAMOL), Universidad de Castilla-La Mancha, 45071-Toledo, Spain.

^b Instituto de Catálisis y Petroleoquímica, CSIC, Cantoblanco, 28049, Madrid, Spain.

^c Instituto Universitario de Tecnología Química CSIC-UPV, Universidad Politécnica de Valencia, 46022-Valencia, Spain

Contact e-mail: MaríaJose.Gomez@uclm.es

Double-wall carbon nanotubes (DWCNTs)^[1] have attracted considerable attention when compared to single-wall CNT (SWCNTs), because show some advantages like higher thermal and chemical stability and are mechanically more robust.^[2] In addition, DWCNTs, being the simplest example of multi-wall carbon nanotubes (MWCNTs), are ideal structures for studying how the interwall interactions influence the properties of the CNTs with two or more walls for chemical^[3] and physical^[4,5] applications. The electronic communication between outer and inner tubes is observed by *in situ* Raman spectroelectrochemistry of unmodified DWCNTs; charge transfer from the outer tube to the inner tube occurs only if the electronic states of the outer tube are filled with electrons or holes and if these filled states are higher in energy than those of the inner tube.^[6]

Donor-acceptor nanohybrids prepared by covalent functionalization of SWCNTs with electron donors are very actively studied as donor-acceptor nanohybrid models and as building blocks for optoelectronic devices.^[7] Nevertheless, there are not examples in the literature where a valid comparison of the photochemical properties of DWCNT and SWCNT with identical degree of functionalization has been provided. Despite the interest in understand the role of the inner, intact graphenic wall in the properties of CNTs, there are scarce examples of functionalization of this kind of CNTs, but, from the available data, it is well established that the functional moiety is selectively attached to the sidewall of the outer shell of DWCNTs without disrupting the properties of inner tubes.

In the current work, we compare the behaviour of functionalized SWCNT and DWCNT in photoinduced electron transfer. Single and double wall carbon nanotubes (CNTs) having dimethylanilino (DMA) units covalently attached to the external graphene wall have been prepared by the reaction of dimethylaminophenylnitronium ion with the corresponding CNT. The samples have been characterized by Raman and XPS spectroscopies, thermogravimetry and high-resolution transmission electron microscopy where the integrity of the single or double wall of the CNT and the percentage of substitution (one dimethylanilino group every 45 carbons of the wall for the single and double walled samples) has been determined. Nanosecond laser flash photolysis has shown the generation of transients that has been derived from the charge transfer between the dimethylanilino as electron donor to the CNT graphene wall as electron acceptor. Time resolved spectroscopy data indicate that the charge mobility in DWCNT is much higher than in the case of SWCNT, suggesting that DWCNT should be more appropriate to develop fast response devices for nanoelectronics.

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