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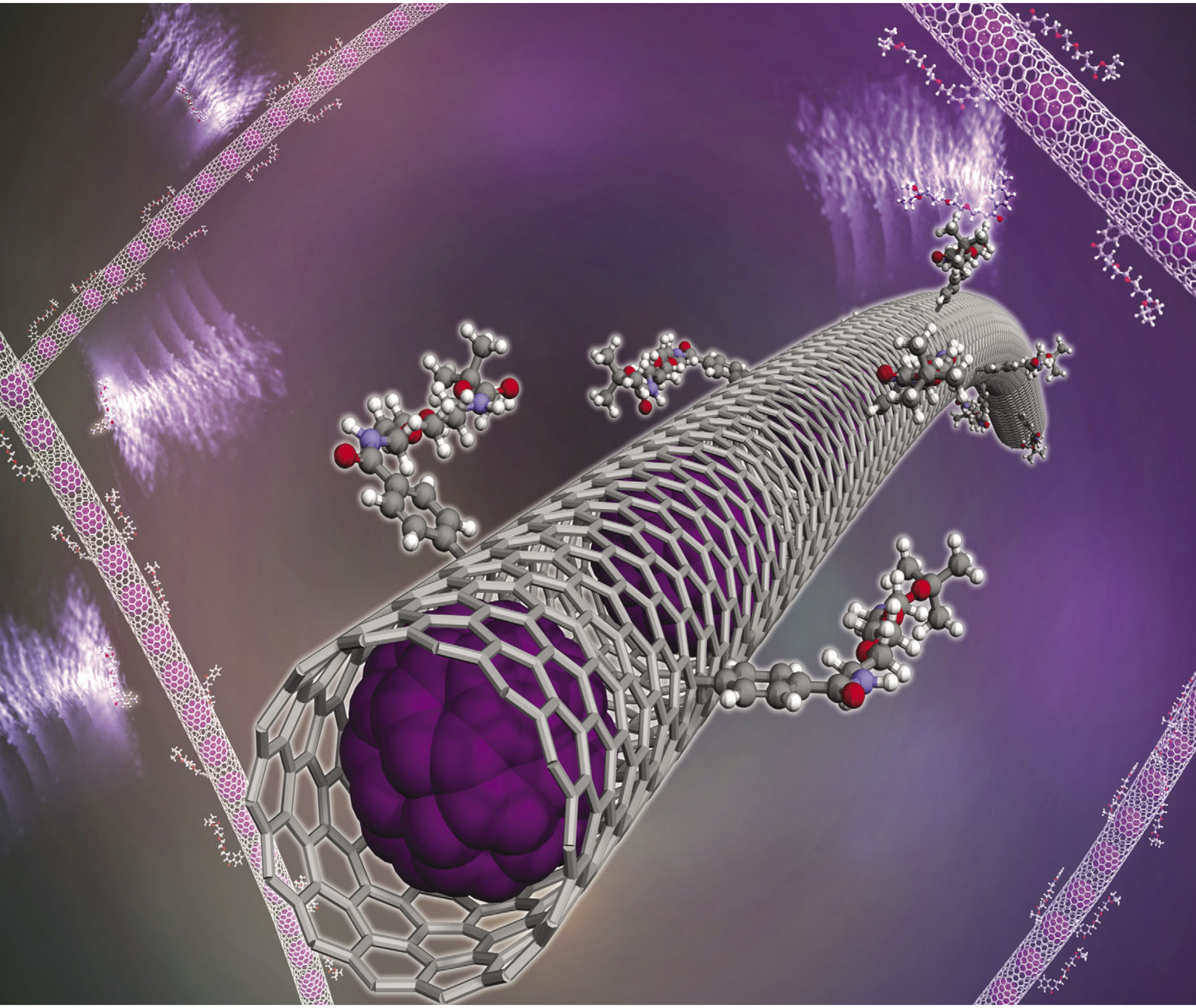

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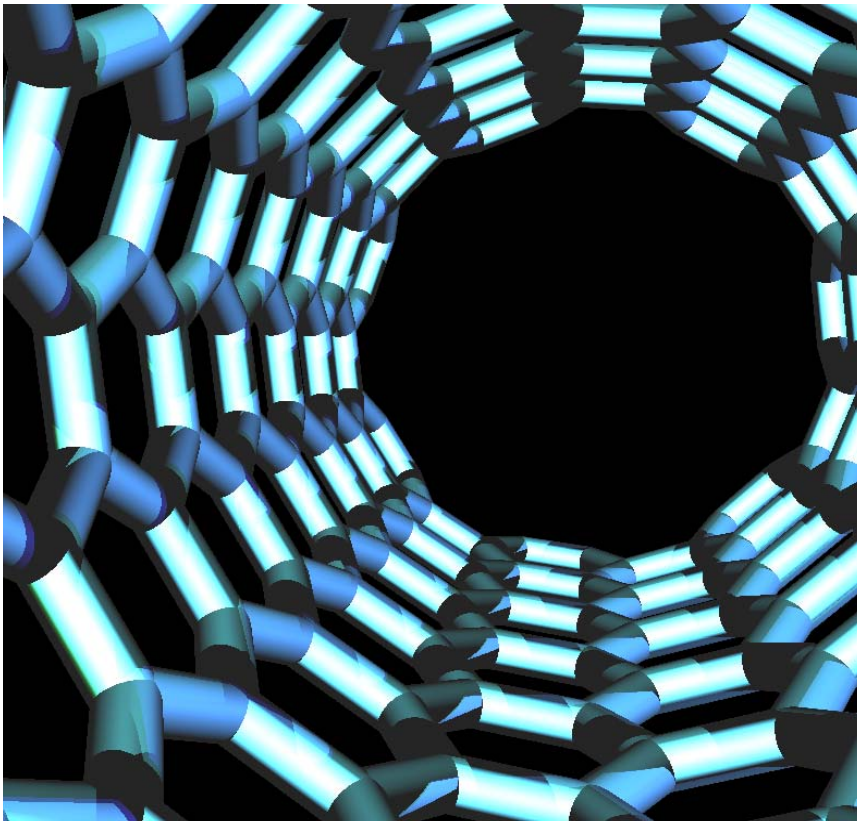

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Microwave assisted covalent functionalization of C_{60}@SWCNT peapods†‡

Nikolaos Karousis,[a] Solon P. Economopoulos,[a] Yoko Iizumi,[bc] Toshiya Okazaki,[bc] Zheng Liu,[c] Kazu Suenaga[c] and Nikos Tagmatarchis*[a]

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The covalent functionalization of the external wall of C_{60}@SWCNT peapods, by *in situ* generated aryl diazonium salts, assisted by microwave irradiation is reported. Spectroscopic, thermal and microscopy characterization was performed. Electrochemistry revealed the three reversible reductions of encapsulated C_{60}, however, shifted towards positive potentials when compared with those of intact C_{60}.

Single-walled carbon nanotubes (SWCNTs) hold great potential for electronic and biological applications because of their superior mechanical and electronic properties. One of the fundamental approaches to control the electronic structure of SWCNTs is molecular doping. Advantageously, SWCNTs possess fascinating hollow space to accommodate doping materials. A typical example is the so-called peapods,[1–3] materials in which fullerenes are entrapped inside the empty pseudo-one-dimensional nanoscopic space of SWCNTs. It is known that encapsulated fullerenes cause changes in the Fermi level and band gap of the host SWCNTs.[4] However, manipulation and processing of peapods is limited by their insolubility, similarly with pristine SWCNTs. In this context, functionalization and solubilization of peapods is a major issue that would allow us to study properties[5] in solution—especially when considering the rich electrochemistry of fullerenes—while enable better manipulation and handling, and therefore, practical applications.[6] Moreover, functionalized peapods become more useful than the original ones as the covalently grafted moieties on the outer skeleton of the nanotubes can be tailored for specific applications. Of course, an obvious question would be the behavior of peapods in solution, namely, would the encapsulated fullerene be affected and how, upon dissolution of peapods in an organic (or aqueous) environment? Would, for example, the encapsulated fullerenes remain entrapped in the hollow core of nanotubes,[7] or would they escape out?

Microwaves generate rapid intense heating of polar substances directly to the reaction mixture, which results in significantly lower reaction times. Moreover, if the reactants facilitate this, use of solvents can be omitted. These are important parameters when considering the presence of entrapped fullerenes within SWCNTs and the chemical modification of the outer skeleton of SWCNTs without affecting the fullerene and the inner wall of the tubes.[8]

Here, we report the covalent functionalization of the outer surface of C_{60}@SWCNT peapods, by *in situ* generated aryl diazonium salts, assisted by microwave irradiation. The dissolution achieved for aryl modified C_{60}@SWCNT peapods endows to perform a thorough spectroscopic as well as thermal and microscopy characterization. Moreover, electrochemistry revealed the three reversible reductions of encapsulated C_{60}, however, shifted towards positive potentials when compared with intact C_{60}, thus highlighting the importance of confinement in low-dimensional nanostructures.

C_{60} was inserted into SWCNTs by mixing an excess of solid fullerene with air-annealed, opened SWCNTs (major diameter 1.3–1.6 nm) following previously reported procedures.[9] Extensive washings with carbon disulfide, a solvent that dissolves best C_{60}, allowed the removal of any non-encapsulated fullerene material, as proved by continuous HR-TEM monitoring. At the same time, two-dimensional (2D) photoluminescence (PL) contour map of the produced C_{60}@SWCNT peapods show that the filling yield is more than 95% (see Fig. S1 in ESI‡).

Then, with the aid of microwaves, we departed from the methodology originally developed by Tour and Bahr,[10] utilizing *in situ* generated aryl diazonium salts, by screening and optimizing our modified reaction protocol, in relation with the applied microwave power, temperature and time. Thus, in order to find optimal conditions for high functionalization of C_{60}@SWCNTs, a test microwave reaction with intact SWCNTs was performed (see Table S1 and Fig. S2 and S3 in ESI‡). Moreover, blank experiments were performed in which only intact SWCNTs and C_{60}@SWCNTs peapods, namely in the absence of organic reactants (*i.e.* isoamyl nitrite and aniline derivative), were subjected to microwave power. The latter ensured that the microwave irradiation conditions chosen were not destructive and the nanosized morphology of C_{60}@SWCNTs was retained. Then, having in hand the optimized conditions for the microwave irradiation reaction, the covalent modification of C_{60}@SWCNTs was performed—see Scheme 1, where fullerenes are packed in the inner 1-D space of SWCNTs, while aryl units covalently decorate the outer wall of SWCNTs. The aryl-modified C_{60}@SWCNTs forms ink-like stable dispersions in chloroform, methanol and DMF, for at least several weeks.

The major concern was the fate of the entrapped C_{60} sphere and whether the fullerene packing inside SWCNTs and the

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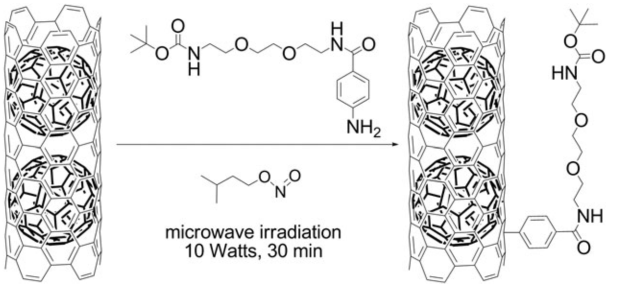

Scheme 1 Schematic illustration of the covalent functionalization of the outer surface of C_{60}@SWCNT peapods.

van der Waals interactions with the tube walls would be strong enough to avoid leaking out C_{60} into solution. Although, the color of the solubilized hybrid material markedly deviates from the characteristic magenta of C_{60}, direct proof for the accommodation of C_{60} inside the functionalized SWCNTs derived from careful HR-TEM inspection. It should be noted that the imaging conditions were set to minimize knock-on damage commonly occurring in fullerene structures under exposure to the electron beam. Fig. 1 shows such HR-TEM images of aryl-functionalized C_{60}@SWCNTs. The morphological characteristics of C_{60}@SWCNTs remain unaffected after the induction of microwaves for the modification of the outer skeleton of SWCNTs. Importantly, to our great expectations C_{60} molecules are settled well-packed in the inner 1-D environment of SWCNTs, as after examining a plethora of images there was not observed any fullerene spheres residing on the outer surface of nanotubes. Contrarily, the presence of the soft material that appears on the external framework of SWCNTs of the peapod hybrid material and is absent from intact C_{60}@SWCNTs (see Fig. S4 in ESI‡) is attributed to organic moieties that are covalently attached onto the sidewalls of the peapods (Fig. 1b and c).

The solubility of functionalized C_{60}@SWCNT peapods allowed to identify entrapped C_{60} with analytical techniques. The UV-Vis-NIR spectrum of aryl-functionalized C_{60}@SWCNTs (Fig. 1d) shows two bands at 257 nm and 344 nm which serve as fingerprints for C_{60}. Moreover, the characteristic van Hove transition features, which are routinely observed in the spectra of pristine SWCNTs, are preserved in the aryl-functionalized C_{60}@SWCNTs. Additionally, the 2D-PL contour plot of aryl-functionalized C_{60}@SWCNTs collected (Fig. 1e) and the strongest PL maxima from functionalized peapods are ascribed to (14,6), (13,8), (11,10), (15,5) and (16,3). The PL pattern of aryl-functionalized C_{60}@SWCNTs resembles the one obtained from intact C_{60}@SWCNTs peapods (*cf.* Fig. S1 in ESI‡), which not only verifies the presence of C_{60} inside SWCNTs after functionalization, but also reveals that the current modification of the outer skeleton of peapods does not significantly affect their electronic structure.

ATR-IR spectroscopy supports the covalent grafting of the aryl moieties onto the external skeleton of C_{60}@SWCNTs. Thus, C–H stretching vibration modes of aryl-functionalized C_{60}@SWCNTs are discernable at around 3000 cm^{-1}, carbonyl vibrations due to benzamide and BOC groups are present at 1649 cm^{-1} and 1707 cm^{-1}, respectively, while the characteristic upturn of the spectrum is attributed to the presence of C_{60}@SWCNTs (see Fig. S5 in ESI‡). Raman spectroscopy was also employed for the evaluation of the microwave-assisted functionalization of C_{60}@SWCNTs (see Fig. S6 in ESI‡). The Raman spectrum of pristine C_{60}@SWCNTs (λ_{exc} = 514 nm) shows a D-band with almost negligible intensity at 1347 cm^{-1} (D/G ratio is 0.01), while in the spectrum of the aryl-modified C_{60}@SWCNTs the D-band exhibits an increased intensity (D/G ratio is 0.07). The latter verifies the success of the covalent attachment of the aryl units on the external skeleton of C_{60}@SWCNTs. Thermogravimetric analysis (TGA) allows quantifying the functionalization degree of modified nanotubes. Intact C_{60}@SWCNTs exhibit thermal stability up to 550 °C, under nitrogen atmosphere. Aryl-functionalized C_{60}@SWCNT peapods show 19% weight loss at 200–550 °C, under inert conditions (see Fig. S7 in ESI‡), attributed to the degradation of the grafted organic addends.

The solubility enhancement achieved for the functionalized C_{60}@SWCNT peapods, allowed monitoring distinct Faradaic processes corresponding to redox of encapsulated C_{60}. Differential pulsed voltammetry (DPV) was utilized as a meaningful electrochemical probe because it removes the effect of electrode capacitive charging, resulting in only Faradaic processes, and hence in much higher signals than other conventional voltammetry methods.[11] Since modified C_{60}@SWCNT peapods exhibit optimum solubility in DMF, we opted to conduct all their electrochemistry measurements in that solvent, despite the fact that a mixture of *ortho*-diclorobenzene (*o*-DCB):acetonitrile

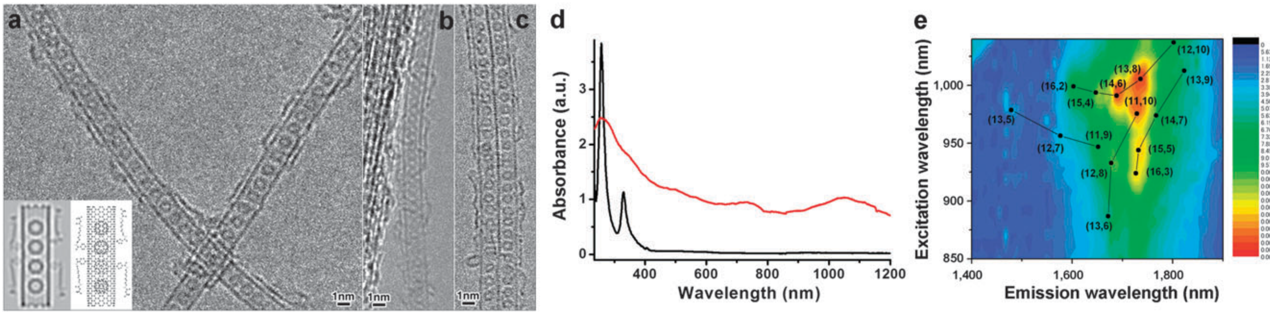

Fig. 1 (a–c) HR-TEM images, clearly showing encapsulated fullerene spheres inside SWCNTs and aryl addends as soft matter decorating the outer surface of SWCNTs. A simulated image and an atomic model of aryl-functionalized C_{60}@SWCNT peapods are inserted in image a, thus, highlighting the great similarity with the real HR-TEM images. (d) Steady-state electronic absorption spectra (UV-Vis-NIR) of C_{60} (black) and aryl-functionalized C_{60}@SWCNT peapods (red), obtained in DMF. (e) 2D photoluminescence contour map of aryl-functionalized C_{60}@SWCNT peapods with increasing PL intensity from blue to green to yellow to red.

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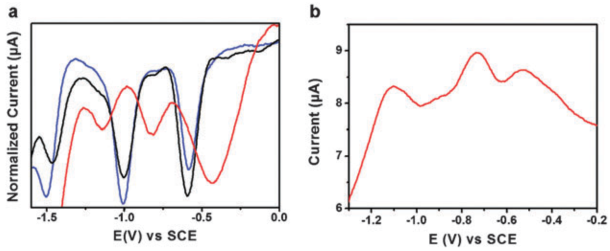

Fig. 2 (a) DPV (reduction run) of aryl functionalized C_{60}@SWCNTs (red) compared to C_{60} (black) and a mixture of C_{60} and aryl functionalized SWCNTs (blue). (b) DPV (oxidation run) of aryl functionalized C_{60}@SWCNTs. Measurements are obtained in 0.1 M $TBAPF_6$ in DMF or *o*-DCB : acetonitrile 5 : 1, using $Ag/AgNO_3$ as reference electrode at room temperature and referenced *vs.* SCE using Fc/Fc^+.

(5 : 1) is widely applied for electrochemical studies of intact C_{60}. The three reversible reductions of C_{60} are easily observed in the case of aryl functionalized C_{60}@SWCNTs peapods (Fig. 2). The reduction peaks are found shifted toward positive potentials as compared with the ones of pristine C_{60} and observed at −0.49 V (100 mV shift), −0.82 V (180 mV shift) and −1.14 V (350 mV shift). These shifts can be attributed to the confined environment of these molecules and/or interactions with SWCNTs, since the grafted aryl moieties onto the external surface of SWCNTs are not expected to affect their electrochemical properties in any appreciable way—a result in accordance with the PL measurements, *cf.* Fig. 1e. Moreover, when a blank CV measurement was conducted on C_{60} and aryl functionalized SWCNTs in a mixture of their respective solvents (*e.g.* *o*-DCB : acetonitrile 5 : 1 for C_{60} and aryl functionalized SWCNTs in DMF), the reduction potentials observed are basically overlapped with those of pristine C_{60} (Fig. 2a), thus highlighting the effect that confined space has on the redox properties of C_{60}. Similarly with intact C_{60}, three reversible oxidation peaks for aryl functionalized C_{60}@SWCNT peapods were observed during the oxidation DPV run (Fig. 2b).

In conclusion, we have functionalized the external surface of C_{60}@SWCNT peapods by covalently grafting aryl units following a microwave-assisted approach. In the modified peapods the fullerene remains encapsulated within SWCNTs regardless the solubility achieved. The latter allowed performing solution spectroscopic studies including photoluminescence and electrochemistry. The three reversible reduction peaks of encapsulated C_{60} on aryl modified peapods were identified, however, anodically shifted as compared with the ones found in intact C_{60}. This is a major result demonstrating the 1-D nanoconfinement effect of fullerenes inside SWCNTs, opening the way to applications in electrochemical sensing nanodevices. Currently we are exploring the strategy developed based on the microwave irradiation effect to functionalize other novel peapod materials.

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