

# Functionalization of Multilayer Fullerenes (Carbon Nano-Onions) using Diazonium Compounds and “Click” Chemistry

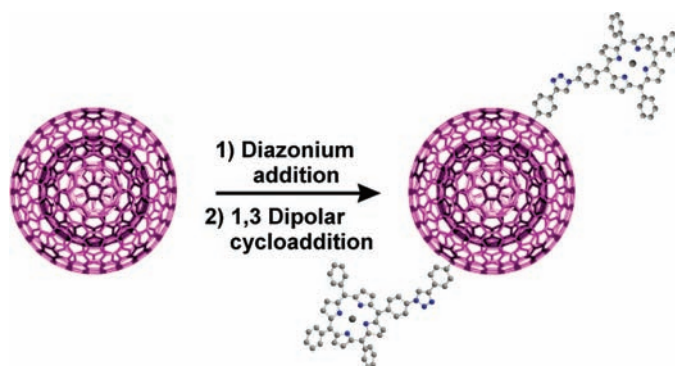
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Received December 22, 2009

## ABSTRACT



A novel versatile approach for the functionalization of multilayer fullerenes (carbon nano-onions) has been developed, which involves the facile introduction of a variety of simple functionalities onto their surface by treatment with in situ generated diazonium compounds. This approach is complemented by use of “click” chemistry which was used for the covalent introduction of more complex porphyrin molecules.

Both fullerenes and carbon nanotubes (CNTs) have attracted enormous attention since their discovery in 1985<sup>1</sup> and 1991,<sup>2</sup> respectively, as a result of their exceptional structural, physical, and chemical properties. The discovery of multi-shell fullerenes, also coined carbon nano-onions (CNOs), was subsequently made by Ugarte,<sup>3</sup> and although they have thus far not received such extraordinary interest as fullerenes or CNTs, they do display several very unique properties, such as a large surface area to volume ratio, a low density, and a

graphitic multilayer morphology,<sup>4</sup> which has made them appealing for several potential applications, such as catalysis,<sup>5</sup> electromagnetic shielding,<sup>6</sup> gas storage,<sup>7</sup> and optical limiting.<sup>8</sup>

An unfortunate attribute which CNOs share with CNTs is poor solubility and dispersibility in both aqueous and organic solvents. To enhance their applicability, compounds that are more suited for incorporation into composites and demonstrate greater solubilities are of considerable interest. The most obvious route toward achieving this goal is through

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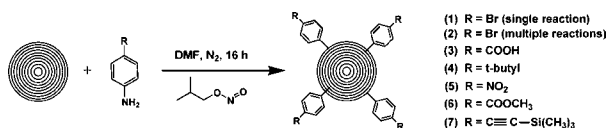
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chemical functionalization, which over recent years has been reported by a number of groups including our own. A number of approaches have been demonstrated including the 1,3-dipolar cycloaddition,<sup>8,9</sup> the [2 + 1] Bingel–Hirsch cyclopropanation reaction,<sup>10</sup> [2 + 1] cycloaddition of nitrenes,<sup>11</sup> and also amidation coupling reactions which take place directly with the oxidized defects on the graphitic surface.<sup>9,10</sup>

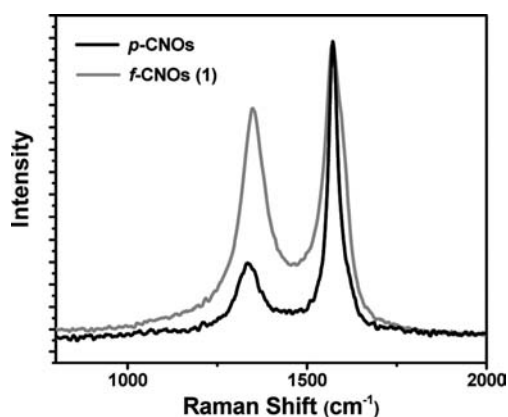
Treatment with diazonium-based compounds is one of the most efficient and effective methods for the covalent functionalization of CNTs, as previously demonstrated by Tour and co-workers.<sup>12</sup> However, the functionalization of CNOs by this method has never been reported. The question then presents itself as to whether the methodology in question could be extended for the functionalization of CNOs and whether the modified CNOs in turn could be further functionalized. Here we demonstrate the ease with which various simple functionalities can be introduced onto the CNO surface, using in situ generated diazonium compounds, in a facile and highly efficient manner. In a typical experiment, pristine CNOs (p-CNOs) were dispersed in DMF by sonication, and to this dispersion was added first the aniline derivative and subsequently isoamyl nitrite under an inert nitrogen atmosphere (Scheme 1). The reaction was stirred

**Scheme 1.** Functionalization of CNOs by in Situ Generated Diazonium Compounds



overnight at 60 °C, and the functionalized CNOs (f-CNOs) were subsequently separated from the reaction solution by centrifugation.

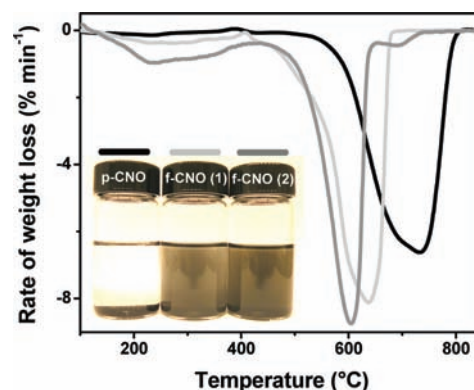
Raman spectroscopy was used to monitor the introduction of defects into the graphitic surface of the CNOs, as a conversion of sp<sup>2</sup> to sp<sup>3</sup> carbon causes an enhancement of the D-band (1354 cm<sup>-1</sup>) and is indicative of the creation of a new covalent bond.<sup>13</sup> Figure 1 illustrates spectra of the



**Figure 1.** Raman spectrum ( $\lambda_{\text{exc}} = 457 \text{ nm}$ ) of pristine and f-CNO (1) illustrating D and G bands.

CNOs before and after functionalization with aryl bromide, normalized with respect to the G-band (1575 cm<sup>-1</sup>). A substantial enhancement of the D-band is clearly evident, where the D/G increased from 0.30 to 0.77 and is indicative of successful functionalization.

Thermogravimetric analysis (TGA) was used to determine the efficiency of the reaction and allow an estimation of the degree of derivatization of the f-CNOs. Using this technique the thermal decomposition of the surface functionalities (below 400 °C) can be distinguished from the graphitic structure of the CNO (above 500 °C).



**Figure 2.** First derivative TGA weight-loss curves of pristine CNO (black), once treated (light gray) and three times treated with 4-bromoaniline (dark gray). Inset shows the enhanced dispersibility in THF.

Figure 2 compares the first derivative weight loss curves of pristine and functionalized CNOs (1 and 2), both of which were functionalized with aryl bromide moieties (where f-CNOs (2) were subjected to the entire functionalization procedure an additional two times). Two trends are evident from the analysis. First, there is a clear increase in weight loss below 400 °C from p-CNOs to f-CNOs (1) to f-CNOs (2), indicating increased surface functionalization. Second, the reduction of the graphitic decomposition temperature can be clearly seen indicating both the introduction of defects into the graphitic layer and also of more oxidizable functionalities onto the nano-onion structure. The functionalization procedure clearly enhances the solubility (inset in Figure 2) where dispersions of f-CNOs (1 and 2) in THF demonstrate far greater stability than the pristine materials.

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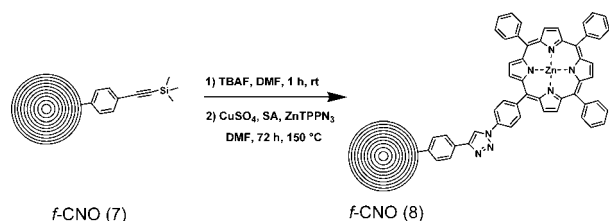
**Table 1.** Degree of Functionalization of f-CNOs (1–7)

	weight loss (%) 100–400 °C	functionalities per CNO	surface carbons per functionality
f-CNO (1)	7.9 ± 0.1	36	60
f-CNO (2)	19.2 ± 1.0	99	22
f-CNO (3)	12.3 ± 0.5	75	29
f-CNO (4)	10.8 ± 0.4	59	37
f-CNO (5)	11.7 ± 0.2	71	31
f-CNO (6)	10.5 ± 0.3	57	38
f-CNO (7)	10.7 ± 0.0	45	48

All TGAs were performed in triplicate, and weight losses ( $\pm$  standard deviation) from 100 to 400 °C were used to estimate the average number of functional groups per onion as previously reported.<sup>4</sup>

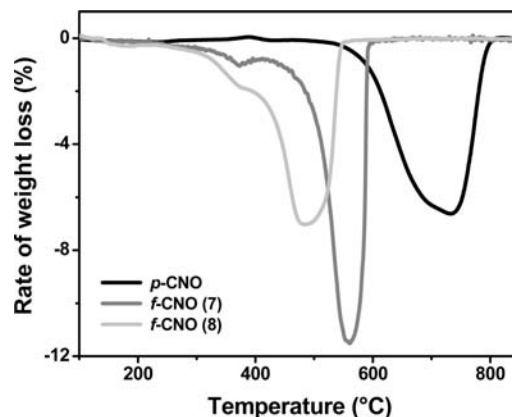
Table 1 shows the scope of the reaction and demonstrates the versatility of this functionalization procedure given the large number of different chemical functional groups that can be introduced onto the CNOs. A single reaction with any of the aniline derivatives utilized was shown to introduce between 36 and 75 functionalities per CNO, which can be enhanced as repetition of the derivatization procedure introduces further functionality.

In addition to introducing simple chemical functionalities onto the CNO surface, we are interested in derivatizing them with more sophisticated molecules with a view to preparing more complex or highly functional materials. The preparation of such complex CNO based materials is however limited by the difficulties associated with the general synthetic procedures often used to produce them, and there is a definite requirement for simple and flexible reactions which can be employed for their synthesis. For this purpose, we propose the use of “click chemistry”, more specifically a 1,3-dipolar cycloaddition, in which two molecules, one functionalized with an acetylene group and the other an azide, are joined in a versatile and clean reaction with a simple workup.<sup>14</sup> In addition to preparation of complex molecules using simple molecular building blocks, this type of reaction has been previously used for the facile functionalization of fullerenes<sup>15</sup> and CNTs.<sup>16</sup> Using a procedure developed by Campidelli et al.<sup>17</sup> f-CNO (7) was first deprotected using TBAF and subsequently “clicked” to the zinc monoazaporphyrin (Scheme 2).

**Scheme 2.** Deprotection of f-CNO (7) Followed by Coupling with the Zinc Monoazaporphyrin to Produce f-CNO (8)<sup>a</sup>

<sup>a</sup> TBAF = tetrabutylammonium fluoride; SA = sodium ascorbate; ZnTPPN<sub>3</sub>P = zinc triphenyl azidophenyl porphyrin.

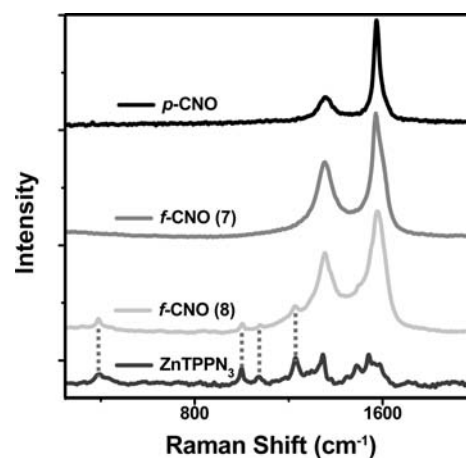
On comparison of p-CNOs and f-CNOs (7), two trends were again evident from the first derivative TGA curves (Figure 3). First the graphitic decomposition temperature

**Figure 3.** First derivative TGA weight-loss curves of pristine, aryl acetylene, and porphyrin functionalized CNOs.

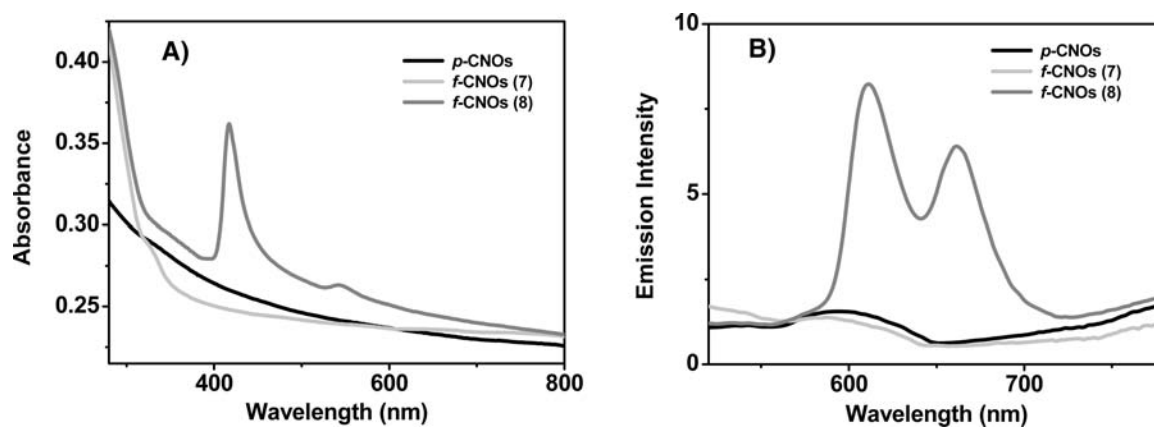
decreased upon defect introduction into the onion surface, and second, the weight loss at lower temperatures increased resulting from increased surface functionality.

Following the cycloaddition between f-CNOs (7) and the azide functionalized porphyrin, the weight loss below 400 °C displayed another significant increase due to the additional weight of the porphyrin. The graphitic decomposition temperature again decreased most likely due to the covalent attachment of the more oxidizable material.

On comparison of the Raman spectra for the CNOs before and after functionalization with the protected aryl acetylene group (Figure 4), a substantial enhancement of the D-band

**Figure 4.** Raman spectrum ( $\lambda_{\text{exc}} = 457$  nm) of ZnTPPN<sub>3</sub> (baseline corrected for clarity) pristine and functionalized CNOs (7 and 8).

of f-CNOs (7) is apparent, indicating covalent attachment. As expected, no further increase in the intensity of this band



**Figure 5.** (A) UV/vis absorption and (B) emission spectra ( $\lambda_{\text{exc}} = 425$  nm) of pristine and functionalized CNOs (**7** and **8**).

was seen following addition of the porphyrin, indicating addition to alkyne and not directly to the CNO structure.

The characteristic peaks for the porphyrin also appear in the spectrum of f-CNO (**8**). These are weaker than the D and G bands belonging to the CNO structure, as strong Raman resonance enhancement does not occur at this  $\lambda_{\text{exc}}$  for the porphyrin.

Absorption spectra of the p-CNOs and f-CNOs (**7** and **8**) dispersed in DMF are illustrated in Figure 5A. A strong enhancement in absorption below 350 nm is clearly evident following derivatization of p-CNOs with aryl acetylene moieties. Following addition of the porphyrin to the deprotected f-CNOs (**7**), two characteristic bands at 417 and 541 nm were observed, corresponding to the Soret- and the first Q-band of the Zn-chelated macrocycle, respectively. Figure 5B illustrates the emission spectra of p- and f-CNOs when excited at 425 nm. The two characteristic Zn porphyrin emission peaks can be seen at 612 and 662 nm, and as

expected a significant quenching of 94% is observed on comparison of f-CNOs (**8**) with the reference porphyrin (Figure S10, Supporting Information), presumably due to energy- or charge-transfer processes occurring between the two units. In conclusion, we have demonstrated a facile method for the introduction of simple functionalities onto CNOs by treatment with diazonium-based compounds. In addition to this, we have also demonstrated a convenient approach utilizing click chemistry for further functionalization with more complex molecules.

**Acknowledgment.** This work was supported by Science Foundation Ireland (PIYRA 07/YI2/I1052). The authors wish to thank Dr. Eoin Scanlan (School of Chemistry, Trinity College Dublin), Dr. Tatiana Perova (School of Engineering, Trinity College Dublin), and the support of the European Commission under framework 7. Financial support from the US National Science Foundation (Grant number DMR-0809129) is also greatly appreciated.

**Supporting Information Available:** Experimental procedures and characterization are given for all synthesized compounds including IR, Raman, TGA, UV-vis absorption, and emission where relevant for the f-CNOs. Enhanced solubility of the synthesized compounds is also demonstrated. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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