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Efficient functionalization of carbon nanotubes:
an opportunity enabled by flow chemistry

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KEYWORDS

Carbon nanotubes, microfluidics, flow chemistry, carbon nanostructures.

ABSTRACT

The covalent chemistry of carbon nanotubes has put forth a wide variety of interesting derivatives that widen the potential of these carbon allotropes in nanomedicine and materials science. However, the functionalization protocols often require long reaction times and frequently harsh conditions. This paper reports a flow approach to the functionalization of carbon nanotubes enabled by a Coflore ACR reactor that allows a precise reaction control through efficient heat and mass transfer. With the ACR setup we investigated the addition of an aryldiazonium salt to the mentioned carbon nanostructures and demonstrated that the solubility of the functionalized material is similar to that obtained with the flask synthesis, but can be achieved in shorter times with the potential advantage of a quick response when new solvents or the addition of new functional groups are explored.

INTRODUCTION

Carbon nanotubes (CNTs) are carbon allotropes characterized by a cylindrical structure with diameters between one and 50 nm, and typical lengths in the micrometre range. Their one-dimensional structure can be seen as derived from graphite layers rolled-up with a specific geometry. Depending on the number of concentric layers it is possible to distinguish between single-, double-, and multi-wall carbon nanotubes that, depending on the chiral angle, show semiconductor or metallic behaviour (1).

For their strong intertube interactions, CNTs are scarcely soluble in common solvents and require demanding chemical and physical processing to be functionalized and fully exploited for practical applications (2). However, it has been found that the use of microwave irradiation reduces reaction times for chemical modifications, yielding soluble materials with good degrees of functionalization (3).

A complementary enabling technology to microwave-assisted organic synthesis, namely, the continuous-flow approach to CNTs functionalization, has been recently reported by some of us (4) opening opportunities for the effective scale-up of the functionalization processing. In that paper we investigated the cycloaddition of azomethine ylides to CNTs with a simple flow-reactor setup, made of readily available components, and demonstrated that the same productivity of the flask synthesis could be achieved in much shorter times (7.5 h instead of 72 h at 140 °C) (4). Solubility and degree of functionalization of the resulting material were comparable in both flask and flow processing. But running the functionalization in a flow reactor offers the advantage of a quick response when new solvents or new functional groups are explored for the covalent modification of CNTs. The benefits of flow chemistry in micro/meso-structured reactors have received increased interest in the synthetic organic chemistry community over the past decade, following demonstration that in such systems large surface-area-to-volume ratios allow precise reaction control through efficient heat and mass transfer (5).

In this paper, we report the use of a Coflore Agitated Cell Reactor (ACR, Figure 1) for the diazonium-based functionalization of single wall CNTs (SWNTs) in 1-cyclohexylpyrrolid-2-one (CHP). The Coflore reactor has been specifically designed to tackle one of the drawbacks of flow chemistry: the processing of complex mixtures containing gaseous, liquid and solid (G/L/S) components, without reactor fouling (6). This challenge is illustrated by the well-known addition of aryldiazonium salts to SWNTs (7) that involves the processing of a solid carbon material (the tubes) dispersed in a solvent with nitrogen evolution.

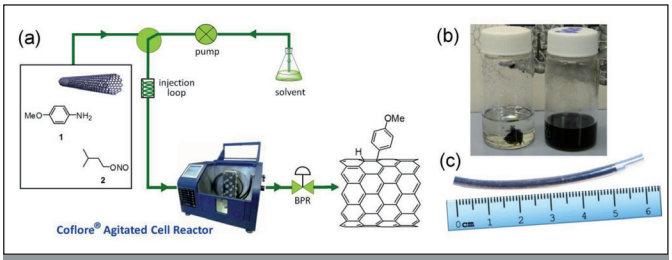

Figure 1. a) Functionalization of CNTs in a Coflore ACR reactor; b) Photo of pristine (left) and functionalized (right) CNTs dispersed in DMF; c) Photo of the reaction mixture.

EXPERIMENTALS

Figure 2 shows the schematic core of the Coflore ACR used for the functionalization of CNTs: a Hastellloy C-276 block mounted on a laterally shaking platform.

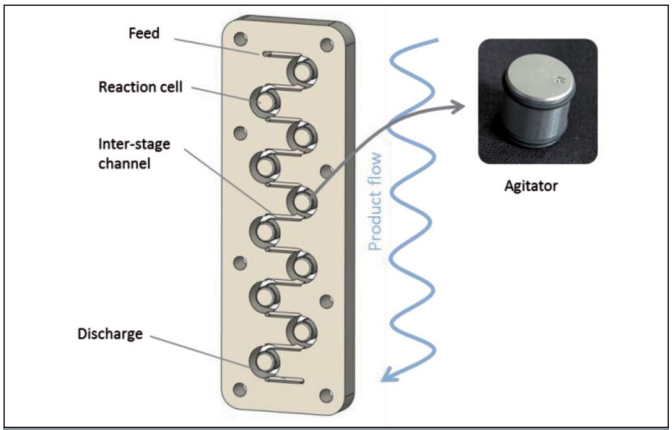

Figure 2. Details of the ACR used for the functionalization of CNTs.

The ten reaction cells, cut within the monolithic block, are connected by inter-stage channels of 4 mm diameter for a total volume of 20 ml. The top and the bottom reactor chambers are fitted with injection ports to allow feed and discharge of the reaction mixture, respectively. A third port is fitted with a thermocouple to monitor the effective temperature provided by a heating bath circulator connected to the reactor back plate. Freely moving hastelloy agitators are placed in the reaction cells to ensure efficient radial mixing and to prevent the solids in suspension from settling out. These agitators move inside the cells when the reactor is laterally shaken by the pneumatic circuit operating at 3 bar with a frequency adjustable from 1 to 9 Hz. The dispersion of nanotubes and reagents is prepared by sonicating a mixture of pristine SWNTs (HiPco, as produced grade, provided by Carbon Nanotechnologies Inc, lot # P2150, 3.0 mg, 0.25 mmol) and 4-methoxyaniline in 3.0 ml of CHP with a tip sonicator for 10 minutes (Misonix 3000, pulsed sonication, power: 6-9 W). Isopentylnitrite is added to this mixture immediately before loading into the main flow line through an injection loop (Teflon coil, V = 5 ml) connected to a switching valve. A HPLC pump provides a steady flow of the carrier solvent (i.e., DMF) with flow rate between 0.12 and 0.47 ml/min corresponding to residence times of 120 and 30 min, considering a free volume of 14.0 ml ($V_{reactor} - V_{agitator}$ = 20 ml – 6 ml = V_{free}). The setup comes with a vial placed after a backpressure regulator in which functionalized SWNTs are collected and treated with CH_3OH to remove CHP, unreacted reagents and byproducts. The mixture, that contains SWNTs with different solubilities and functionalization degree, is then extracted with DMF to remove insoluble pristine SWNTs and less soluble fractions (4a). The nanotubes in the soluble extracts were characterized by thermogravimetric analysis (TGA), dynamic light scattering (DLS), UV-Vis, ATR-IR and micro-Raman spectroscopy. While pristine HiPco nanotubes contain residual iron catalyst, the equivalents of reagents are calculated on the basis of a theoretical amount of 100 percent of carbon.

DISCUSSION AND RESULTS

In principle, a flow reactor allows a precise control of the critical parameters of a chemical process, such as residence time, temperature and mixing that, for the ACR, is implemented by the shaking frequency. Therefore, we expected reaction times (i.e. residence times) for the addition of a diazonium salt to SWNTs, inside the ACR, reasonably shorter than the 15 h reported for the same reaction in a flask (7). One to five equivalents of diazonium salt precursors, against the mmol of C that constitutes the SWNTs, have been used. The reaction was carried out at 70 °C, while the shaking rate was set to 4 or 9 Hz (f_{ACR}). Pertinent data summarizing the conditions and the results for ten additions of a diazonium salt to SWCNTs are reported in Table 1.

Run	f_{ACR} [Hz]	Flow (mL/min)	Residence time [min]	eq	c_{CNT} (mg/mL)	D/G	FG	Size (nm)
Prist.	/	/	/	/	0.02	0.06	/	/
1	9	0.12	120	1	0.13	0.29	1/40	350
2	9	0.12	120	5	0.32	0.48	1/29	250
3	4	0.47	30	5	0.29	0.41	1/30	250
4	4	0.30	47	3	0.21	0.30	1/35	300
5	9	0.30	47	3	0.05	0.20	1/55	350
6	9	0.47	30	1	0.05	0.13	1/51	>1000
7	4	0.12	120	5	0.48	0.49	1/25	<100
8	4	0.47	30	1	0.14	0.29	1/38	>1000
9	9	0.47	30	5	0.33	0.47	1/29	250
10	4	0.12	120	1	0.21	0.32	1/38	250

Table 1. Addition of the diazonium salt, generated in situ by the reaction of 4-methoxyaniline and isopentylnitrite in cyclohexylpyrrolidone, to SWNTs in the Coflore ACR reactor. Data for pristine (Prist.) nanotubes are reported for comparison.

Some of the characteristics of pristine nanotubes are reported for comparison as well.

The dispersions of SWNTs in CHP were processed smoothly yielding homogeneous plugs of functionalized material. The flow was set upwards to allow nitrogen leaving the reactor block with the liquid stream, without accumulating and hence affecting residence time (Figure 1c). ATR-IR spectrum (Figure 3) of the resulting material show alkyl and aryl C-H stretching bands (not observed for pristine SWNTs) consistent with the addition of 4-methoxyphenyl groups. The soluble extracts were analysed to provide a representative picture of the efficiency of the functionalization with the ACR. Solubility (c_{CNT} in Table 1) for all processed CNTs ranges from 0.05 to 0.48 mg/ml, corresponding to an increase between 2.5 and 24 times if compared to the pristine tubes. A closer inspection of Table 1 suggests that solubility gain depends on both flow rate (Flow) and relative amount of reactants (eq). Considering the effect of these parameters on the most soluble extract (run 7, Table 1), it turned out that by changing residence time from 120 to 30 min (run 3) a reduction of the solubility from 0.48 to 0.29 mg/ml was observed. On the other hand, a decrease of 4-methoxyaniline and isopentylnitrite equivalents from five to one (run 10) resulted in a drop of the tubes solubility to 0.21 mg/ml. Clearly, the solubility of the SWNT derivatives is a function of both residence time and amount of reactive diazonium salt. This was corroborated by the calculation of the degree of functionalization (FD) in Table 1, expressed as the ratio between the moles of functional groups and the moles of carbon in the tubes; FD = $mmol_{FG}/mmol_{C}$) (8) through TGA analysis of the functionalized samples. As expected, it has been found that higher FDs correspond to more soluble samples. Indeed, the values obtained range from one functional group every 55 carbon atoms for a sparingly soluble sample (run 5) to one group every 25 carbon atoms for the CNTs in the most soluble extract (run 7).

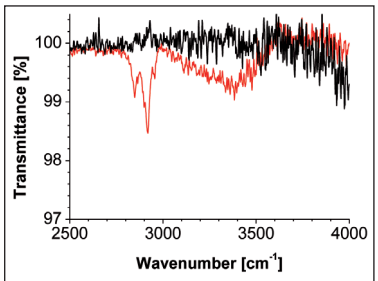

Figure 3. Detail of the IR spectra of pristine SWNT (black line) and SWNT functionalized through the ACR Coflore reactor (run 7, red line). The presence of alkyl and aryl C-H stretching following functionalization is consistent with the addition of 4-methoxyphenyl groups on SWNT.

As a demonstration of how challenging the chemistry of carbon nanostructures can be, it is worth mentioning that the amount of the diazonium salt that effectively functionalizes the CNT walls is less than 2.5 percent of the potentially available reactive salt for all tested conditions. A further confirmation of the successful derivatization of SWNTs in the ACR came from Raman spectroscopy characterization. Usually, the G and D bands, associated to the sp^2 graphitic structure and to sp^3 defects respectively, are monitored during CNTs functionalization (9). Saturation of the CNT double bonds by the diazonium salt increases the number of sp^3-hybridised carbons influencing, therefore, the Raman D/G bands ratio (Table 1).
For all SWNT derivatives prepared under continuous flow conditions, the D/G ratio increases, if compared to that of the pristine tubes. It has been estimated, from the D/G ratio, that the most soluble tube fraction is about eight times more defective than pristine SWNTs, while the least soluble only twice.
Also, we should consider that functionalized CNTs are not dispersed as individual nanostructures in solution, but they form aggregates. Indeed, DLS analysis of the obtained SWNT dispersions confirmed that the most soluble extract is made of aggregates with dimensions <100 nm, whereas the less soluble fractions have aggregate sizes around one micrometre.

CONCLUSIONS

In conclusion, the use of an ACR flow reactor enables the derivatization of SWNTs with tailored degree of functionalization, defect density, aggregation size and solubility.
The lateral shaking of the free agitators prevents the formation of clogs and handles well gas/liquid/solid mixtures that form during the addition of a model diazonium salt to SWNTs.
The advantage of the flow *vs.* flask approach is well expressed by the reduction of the reaction times (30 min *vs.* 15 h) with a functionalized tubes productivity (1 mg h^{-1} ml^{-1}) that is two orders of magnitude higher than that obtained with a standard flask synthesis. We believe that this approach has the potential to be scaled-up and further expanded to other CNTs functionalizations or to the modification of different carbon nanostructures.

ACKNOWLEDGEMENTS

C.C.D.F thanks *Fabbrica Italiana Sintetici SpA* for a PhD scholarship. We thank the U. of Padova (*HELIOS* project STPD08RCX5) and MIUR (*PRIN* 20085M27SS and *FIRB* RBFR08DUX6) for financial support.

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