ARYL DIAZONIUM GROUP FUNCTIONALIZED MULTI-WALL CARBON NANOTUBES: A NOVEL SURFACE TO ANCHOR NANOPARTICLES FOR VARIOUS APPLICATIONS

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Introduction
As-synthesized carbon nanotubes (CNTs) comprise impurities (by-product carbonaceous species, metallic catalysts, alumina, etc). Unmodified CNTs are insoluble in most solvents due to the existence of the strong van der Waals interactions that hold them together resulting in bundles. This limits the complete exploitation of unique properties of CNTs. Various methods of CNTs functionalization have been reported to enhance their dispersion in different solvents. Diazonium chemistry plays a very important role in the context of CNTs solubilization and decoration as it involves simple and very effective methodologies to obtain homogeneous functionalities and provide easy access to different side groups for their modifications. Nanoparticles possess unique optical, magnetic and chemical properties due to their nature and size. They provide large surface area. Their properties are most effective with small particles (< 10-20 nm). It is observed in many cases that these effects disappear essentially for sizes larger than 40-50 nm. Nanocomposites of multi-wall carbon nanotubes (MWCNTs) and metal or metal oxide/hydroxide nanoparticle are expected to have characteristics superior to the individual components. In this work, we have developed a simple and efficient technique using infrared irradiation (IR) to functionalize MWCNTs with mono and tricarboxylic aryl diazonium functions and utilize this functional group to decorate MWCNTs surface with different nanoparticles such as bismuth oxide nanocrystals, barium oxide nanoparticles, lanthanum hydroxide nanoparticles and maghemite nanocrystals. The aim is to control the size, nature, concentration and distribution of the desired nanoparticles on MWCNTs. This method is also applicable to prepare nanocomposites with other nanoparticles (work in progress). Bismuth oxide nanocrystals have been decorated on MWCNTs for the first time. Other nanoparticles decoration was already reported in the literature but in the present case, were decorated using tricarboxylic aryl diazonium functionalized MWCNTs for the first time. Our method of decoration overcomes significantly the most of the limitations reported in the literature. Some of these synthesized nanocomposites have been already applied for biomedical (electrochemical sensor), environmental (dye removal) and defense applications (energetic materials).
Materials and Methods
The method of purification involves a NaOH treatment to remove alumina. The purified MWCNTs are labelled as p-MWCNTs. 4-Aminobenzoic acid and 5-amino-1,2,3-benzenetricarboxylic acid were used to functionalize MWCNTs using IR irradiation method. They are referred to as p-MWCNTs-D1 and p-MWCNTs-D3, respectively. Diazonium salts were generated in-situ. The detailed procedure is reported in our previous work 8. Functionalized MWCNTs (p-MWCNTs-D1 or p-MWCNTs-D3) were treated with metal precursor’s solution under IR irradiation. The impregnated MWCNTs were calcined at an optimized temperature under a continuous flow of argon gas to get nanoparticles decorated MWCNTs. Bi$_2$O$_3$ was anchored using monocarboxylic aryl diazonium group (p-MWCNTs-D1) and the other nanoparticle decorated MWCNTs by using tricarboxylic aryl diazonium group (p-MWCNTs-D3).

Results and Discussion
Different techniques (XPS, FESEM, TEM, TGA, RAMAN, EDX, PXRD and UV-Vis) were used to characterize the prepared samples. Only XPS, TEM and PXRD results are reported here. Furthermore, some of the materials were tested for different applications: biomedical, environmental and defense. These are not described in the present paper but are available in references 5–7. Fig.1a shows the XPS survey spectra of p-MWCNTs, p-MWCNTs-D1, p-MWCNTs-D3, p-MWCNTs/Bi$_2$O$_3$ (bismuth oxide nanoparticles decorated MWCNTs), p-MWCNTs/BaO (barium oxide nanoparticles decorated MWCNTs), p-MWCNTs/LaH (lanthanum hydroxide nanoparticles decorated MWCNTs) and p-MWCNTs/MC (maghemite nanocrystals (MC) particles decorated MWCNTs).

Table 1. Atomic percentage composition of various materials obtained from XPS analysis.

<table>
<thead>
<tr>
<th>Materials</th>
<th>C%</th>
<th>O%</th>
<th>N%</th>
<th>S%</th>
<th>Bi%</th>
<th>Ba%</th>
<th>La%</th>
<th>Fe%</th>
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<tr>
<td>p-MWCNTs</td>
<td>98.50</td>
<td>1.50</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
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<tr>
<td>p-MWCNTs-D1</td>
<td>92.81</td>
<td>6.59</td>
<td>0.54</td>
<td>--</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
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<tr>
<td>p-MWCNTs-D3</td>
<td>72.85</td>
<td>23.87</td>
<td>3.28</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
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<tr>
<td>p-MWCNTs/Bi$_2$O$_3$</td>
<td>91.26</td>
<td>6.11</td>
<td>-</td>
<td>-</td>
<td>2.63</td>
<td>-</td>
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<tr>
<td>p-MWCNTs/BaO</td>
<td>92.71</td>
<td>5.65</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>1.64</td>
<td>-</td>
<td>-</td>
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<tr>
<td>p-MWCNTs/LaH</td>
<td>90.27</td>
<td>7.42</td>
<td>0.81</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>1.50</td>
<td>-</td>
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<tr>
<td>p-MWCNTs/MC</td>
<td>76.94</td>
<td>15.36</td>
<td>2.24</td>
<td>0.26</td>
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<td>5.19</td>
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Figure 1. (a) XPS survey and high resolution spectra (b) Fe2p, (c) La3d (d) Ba3d and (e) Bi4f.

Figure 2. Overall steps in the decoration process of MWCNTs with nanoparticles.

The percentage composition (%) obtained from the XPS (Table 1) clearly confirms the presence of the desired components in the sample. Fig. 2, explains the steps involved in the present work.
Figure 3. TEM images of (a) crude MWCNTs, (b) p-MWCNTs, (c) p-MWCNTs/Bi$_2$O$_3$, (d) p-MWCNTs/BaO, (e) p-MWCNTs/LaH and (f) p-MWCNTs/MC
Figure 4. Size distribution of nanoparticles (a) small size Bi$_2$O$_3$, (b) slightly bigger size Bi$_2$O$_3$ on the same sample (bimodal distribution), (c) BaO, (d) LaH and (e) $\gamma$-Fe$_2$O$_3$.

Crude MWCNTs (Fig. 3a) contain large species (alumina impurities) which are totally eliminated (Fig. 3b) after the purification without destroying the CNTs structure. This is a sure advantage over an acidic treatment, which causes severe damages to the CNTs structure and uncontrollable functionalization. Fig. 3c-f shows the presence of small nanoparticles decorated homogeneously on the nanotubes surfaces. Their size distributions are depicted in Fig. 4. Only, Bi$_2$O$_3$ nanoparticles exhibit a bimodal distribution (Fig. 4a-b).
Information regarding the crystal structure of the nanoparticles was obtained by PXRD (Fig. 5). In all cases, the diffraction peaks at $2\theta = 25.60$ and $2\theta = 42.79$ are due to the reflection from the (002) and (100) plane of MWCNTs, respectively. Nanoparticles signals are also found in Fig. 5. Bi$_2$O$_3$
and maghemite nanoparticles are crystalline in nature as the obtained peaks are very sharp. On the other side, BaO and LaH nanoparticles are amorphous. This may be due to the remains of amorphous functionalities around them or low temperature to organize them in the form of a crystals.

Conclusions
A simple, reliable, reproducible and efficient method to decorate multi-wall carbon nanotubes with nanoparticles has been reported. The efficiency of this novel methodology mediated by diazonium functions is exemplified by MWCNTs decoration with various kinds of nanoparticles (Bi$_2$O$_3$, La(OH)$_3$, BaO and Fe$_2$O$_3$). This method can be extended to other metals. These materials can also be used to make other nanocomposites. Some of these synthesized nanocomposites have been already applied for biomedical (electrochemical sensor), environmental (dye removal) and defense applications (energetic materials). Other different kind of diazonium functions can also be grafted on CNTs based on the same principle. This novel functionalization can be used for several applications such as biosensors, dye removal, catalysis, etc. The present methodology is also applicable to large scale preparations. This opens very interesting perspectives for nanotechnology.

Acknowledgment
Arvind K. Bhakta thanks the University of Namur for a CERUNA doctoral fellowship.

References