Carbon Nanoparticles-Decorated Carbon Nanotubes

Ahmed Awadallah-F & Shaheen Al-Muhtaseb*

Multi walled carbon nanotubes (MWCNTs) were decorated by activated carbon nanoparticles of resorcinol-formaldehyde aerogels. Carbon nanospheres and MWCNTs were mixed by equal mass ratios for different durations. The products were characterized by Raman spectroscopy, thermal gravimetric analysis, nanoscanning electron microscopy, transmission electron microscopy and x-ray diffraction. The results indicated that a significant decoration with carbon nanoparticles occurred onto the MWCNTs.

Carbon nanotubes (CNTs) drew a remarkable attention from their first discovery. This is attributed to their unique features, such as mechanical properties, electric properties, thermal stability, high chemical resistance and large surface areas. As a result of these characteristics, they became strong candidates for numerous applications; including catalytic processes, water treatment, drug delivery, gene transfer, transparent conducting membranes and electrochemical analysis. The idea of CNT decoration was introduced to widen their applications in different fields. It was reported in various works of literature that it was possible to decorate CNTs with either organic compounds or metallic nanoparticles. The importance of carbon aerogels is assigned to their hierarchical porous properties, which makes them suitable for use in numerous applications. For example, carbon aerogels are utilized in catalyst support, separation tools, electrocapacitor materials and battery construction.

It is noteworthy to mention that, to the authors' knowledge, the carbon-carbon decoration of multiwall carbon nanotubes (MWCNTs) by carbon nanoparticles (CNp) was not tackled in literature. Therefore, in this work, we disclose our method of decorating MWCNTs with resorcinol-formaldehyde activated carbon aerogel (RFA) CNp. The hybrid carbon nanoproducts will be characterized by various devices for tracking the changes of outcome carbon nanoproducts.

Results and Discussion

Figure 1(a–c) exhibits the characteristics of MWCNTs and RFA-CNp via XRD, Raman spectra and TGA, respectively. Figure 1a exposes the XRD patterns of MWCNTs (black line) and RFA-CNp (red line) samples. It was observed from Fig. 1a that the characteristic bands of MWCNTs are at $2\theta = 26^\circ$, $42^\circ$ and $53.8^\circ$; which refer to (002), (100) and (004) reflection of the MWCNTs, accordingly. Moreover, RFA-CNp has no crystalline peaks as seen from Fig. 1a. The higher crystallinity in MWCNTs than RFA-CNp is due to the graphitic portion that results in the high order of MWCNTs’ structures.

Figure 1b shows the Raman spectra of MWCNTs (black line) and RFA-CNp (red line) samples. The three fingerprint bands of pristine MWCNTs are the D-band at $1314$ cm$^{-1}$, G-band at $1576$ cm$^{-1}$ and G’-band at $2625$ cm$^{-1}$. The intensity of the D-band (I_D) indicates to disordered or amorphous carbon portions, while that of the G band (I_G) indicates to graphite or ordered carbon portions in the MWCNTs, and that of the G’ band indicates to a second harmonic of the D-band. Moreover, the relative crystallinity can be indicated by the I_D/I_G ratio. The values of I_D/I_G ratio are 0.48 and 1.25 for MWCNTs and RFA-CNp, respectively. Thus, the order (crystallinity) of MWCNTs is higher than that of RFA-CNp. Figure 1c shows the TGA thermograms of MWCNTs (black line) and RFA-CNp (red line) samples. It is observed that the thermal stability of MWCNTs is higher than that of RFA-CNp. This is attributed to the presence of graphic structure that resists the thermal decomposition in MWCNTs, contrary to the amorphous structure that has less resistance to thermal decomposition in RFA-CNp.

Figure 2(a–c) exhibits the characteristics of MWCNTs decorated with RFA-CNp via XRD, Raman spectra and TGA, accordingly; for samples decorated for various number of days as denoted by the sample codes in the form nD where the number n stands for the number of days in mixing. It is seen form the XRD patterns in Fig. 2a that the crystallinity of MWCNTs decreases by increasing the time of mixture stirring. The characteristic peaks of MWCNTs are at $2\theta = 26^\circ$, $42^\circ$ and $53.8^\circ$; which refer to the (002), (100) and (004) reflections of the MWCNTs,
Figure 1. (a) XRD patterns, (b) Raman spectra and (c) TGA thermograms of MWCNTs (black line) RFA-CNp (red line) samples.

Figure 2. (a) XRD patterns, (b) Raman spectra and (c) TGA thermograms of MWCNTs/RFA-CNp hybrids with 50/50 g/g at mixing times of 0, 185 and 415 days.
become decorated with RFA-CNp. Figure 4(g,h) shows the MWCNTs/RFA-CNp of 415D at two magnifications; led to new decorated carbon-carbon products with different features than the pristine MWCNTs or RFA-CNp.

Overall observation, the presence of RFA-CNp onto the surface of MWCNTs and RFA-CNp remain well intact. Figure 4(e,f) exhibits the MWCNTs/RFA-CNs after stirring of 185D at two amplifications; accordingly. Figure 4(c,d) shows the MWCNTs/RFA-CNp of 0D at two magnifications; 1 μm and 500 nm, respectively. Through the observation it can be deduced that the MWCNTs become decorated with RFA-CNp. Figure 4(g,h) shows the MWCNTs/RFA-CNp of 415D at two magnifications; 1 μm and 500 nm, respectively. It can be noticed from both photos that the MWCNTs become decorated densely and abundantly with RFA-CNp. Overall observation, the presence of RFA-CNp onto the surface of MWCNTs led to new decorated carbon-carbon products with different features than the pristine MWCNTs or RFA-CNp.

**Conclusion**

The carbon-carbon decoration, specifically MWCNTs with carbon nanoparticles, is a novel trend that can lead to expanding the potential applications of such nanomaterials. This work is just a trial to confirm that it is possible to decorate MWCNTs with carbon aerogel nanoparticles (RFA-CNp) as an example. This is done by mixing in methanol for long durations at a relatively high temperature. Various characterization techniques; including XRD, Raman spectra, TGA, NanoSEM and TEM were utilized to investigate the decorated products. The results referred to significant changes in the properties of pristine MWCNTs and RFA-CNp, which confirmed the formation of hybrid carbon nanoproducts. Moreover, in comparison to the pristine MWCNTs or RFA-CNp, the produced hybrid carbon nanoproducts are featured with unique morphologies, crystallinities and extents of order/defects in their structures. Overall, it was found that mixing for 185 days resulted in decorating the MWCNTs with RFA-CNp to a noticeable extent, whereas mixing for 415 days resulted in a significant (and in an abundance of) decoration. These hybrid carbon nanoproducts could be used in numerous applications and are worthy of further investigations.

**Experimental section**

**Materials.** MWCNTs (purity > 90%, with a diameter of 110–170 nm and length of 5–9 μm, resorcinol (purity 99%) and formaldehyde (containing 10–15% methanol as stabilizer, 37 wt.% in H2O) were purchased from Sigma-Aldrich, (Germany). Sodium carbonate anhydrous (Fisher Scientific, UK). Ultra-pure water supplied from Elix®70 Water Purification System from Millipore Sigma. Other reagents (Acetone, methanol, acetic acid, nitric acid and ammonium hydroxide) are of analytical reagent grade. All chemicals are utilized as-received.
**Preparation of aerogels.** Aerogels were synthesised from resorcinol and formaldehyde in presence of Na$_2$CO$_3$ as catalyst. The pH level of the starting solution is adapted at a neutral level with HNO$_3$ and NH$_4$OH buffers. The quantities of resorcinol (R), Na$_2$CO$_3$ catalyst (C), formaldehyde (F), and water (W) that were utilized in the preparation of the aerogel were 12.44 gram, 0.0240 g, 17.40 ml, and 32.60 ml, respectively. These quantities refer to molar ratios of R:F = 0.5, R:C = 500 and R:W = 0.05. The medium temperature is controlled at 70 ± 1°C.

**Figure 3.** NanoSEM photomicrographs of MWCNTs/RFA-CNp with 50/50 g/g mixing ratio at different mixing times and different scales of magnifications. (a,b) refers to pristine MWCNTs and CNp, respectively. Each couple of photomicrographs of (c,d) 0D, (e,f) 185D and (g,h) 415D refer to different scales of magnifications for the corresponding sample.
The gels were cured and dried by supercritical CO$_2$ extraction as detailed elsewhere\textsuperscript{23,24}. Supercritical drying is conducted by utilizing a critical point dryer (E3100 Critical Point Dryer, Quorum Technologies - Preparation for Excellence, UK).

**Preparation of activated carbon aerogels.** The dried resorcinol/formaldehyde aerogels are placed in a ceramic crucible into a tube furnace (Nabertherm GmbH, Germany), while flowing a stream of nitrogen gas ($1.0 \times 10^4$ cm$^3$/min). The tube furnace is firstly kept at ambient temperature for $1/2$ h to make sure that air is fully replaced with nitrogen. Afterwards, the temperature of the furnace is increased up to 500°C with a rate of 10°C/min.
kept at 500 °C for 180 min, and then let to cool down spontaneously to ambient temperature while flowing nitrogen. The outcome RF carbon aerogel is later activated within the same ceramic crucible (after cleaning thoroughly from previous residues) by switching the nitrogen gas with a carbon dioxide gas stream (1.5 × 10^3 cm^3/min), heating-up the sample again with a ramp of 10 °C/min up to 700 °C, keeping the sample at 700 °C for 1 h, and then cooling the product spontaneously to ambient temperature while still flowing CO_2 gas. The outcome sample is redeemed to be an activated carbon aerogel and is called resorcinol-formaldehyde carbon aerogel nanoparticles, which are denoted as RFA-CNp.

**Synthesis of carbon nanospheres-decorated carbon nanotubes.** MWCNTs and RFA-CNp were mixed in a fixed weight proportion of 1:1 (this ratio is selected as a fair example of the amount used between the two main ingredients) in reflux with methanol while stirring for 0, 185 and 415 days at 100 °C. The identity of these samples will be called hereafter; 0D, 185D and 415D, respectively. The sample 0D refers to mixing the samples manually in a dry state. All samples are then dried at 110 °C for 3 days.

**Characterization**

FT-Raman spectra were estimated by a Bruker FT-Raman spectrometer of type RFS 100/S. The morphological strutures of carbon materials were invetigated via a FEI Nova™ nanoscanning electron microscope 450. Thermogravimetric analyses (TGA) are conducted (from 30°C to 800°C with a heating rate of 10°C/min) utilizing a Perkin Elmer Pyris® TGA analyzer with a flow of nitrogen. Transmission electron microscopy of (TEM) was conducted with a FEI Tecnai G2 F20 FE-TEM. X-ray diffraction (XRD) tests are carried out by Miniflex II Benchtop XRD apparatus, manufactured by Rigaku Corporation Japan.

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Competing interests
The authors declare no competing interests.

Additional information
Correspondence and requests for materials should be addressed to S.A.-M.

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