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The effect of different chemical treatment on the structure and dispersion of multi-walled carbon nanotubes

E. G. Castro(1)*, R. A. de Morais(1), K. dos Santos(1), M. M. Oliveira(1), W. H. Schreiner(2) and A. J. G. Zarbin(1)

(1) Department of Chemistry, Universidade Federal do Paraná (UFPR), CP 19081, CEP 81531-990, Curitiba-PR, Brazil, email: eryza@quimica.ufpr.br
(2) Department of Physics, Universidade Federal do Paraná (UFPR), CP 19044, CEP 81531-990, Curitiba-PR, Brazil
* Corresponding author.

Abstract Multi-walled carbon nanotubes (MWNTs) offer a large number of opportunities of new applications. However, for some of this applications, CNT must be treated to improve their dispersion in different solvents and also their purity. In this work we present a study of the effect of different treatments on MWCNT samples. The main goal for this approach is creating carboxyl groups on the CNT surface, which is necessary for nanocomposites applications. Treated MWNTs were characterized by Raman spectroscopy, XRD, XPS and TEM.

A variety of promising applications, as in composite materials, require carbon nanotubes (CNTs) dispersions that remain stable in water. Usually, the as-produced CNT samples are therefore often a mixture of CNTs, metal catalyst and amorphous carbon. There are some methods of purification of CTN, but the oxidation treatments have the additional advantage to create a high density of carboxyl groups on the CNT's surface, which improve their stability in aqueous dispersion[1]. In this work we present a study of the effect of different chemical treatment (acids, acids mixture and hydrogen peroxide) on the CNTs structure.

The carbon nanotubes utilized in this work were prepared by a CVD route, starting from pure ferrocene, according our previous report[2]. Due this specific preparation route, the Fe/C molar ratio resulting in the final material is very high (1/10), which means that a great amount of iron-rich species is expected to be present in the resulting material. The product resulting from this synthetic route is essentially formed by multi-walled carbon nanotubes in which their cavities are filled with long crystals of iron-based species, mainly α-Fe, α-Fe_2O_3 (hematite) and Fe_3O_4. Some other carbonaceous species, as carbon nanopolyhedra, are also present in small quantities in the sample. The chemical treatments were conducted by refluxing the pristine MWCNTs in five different aqueous solutions, during 6 hours: (1) HNO_3 3.0 $mol.L^{-1}$; (2) H_2SO_4 3.0 $mol.L^{-1}$; (3) mixture H_2SO_4 3.0 $mol.L^{-1}$/HNO_3 3.0 $mol.L^{-1}$; (4) mixture HCl 1.0 $mol.L^{-1}$/HNO_3 3,0 $mol.L^{-1}$ and (5) H_2O_2 30% (w/w). After treatment, the MWCNTs were isolated by centrifugation and washed several times with distilled water. Samples were characterized by XRD, TEM, Raman spectroscopy and XPs

The TEM images show some differences on the morphologies of the MWNTs, mainly the sample obtained after the treatment (3) described above, which shows a roughness in the nanotubular surface. The occurrence of chemical changes in the walls of the CNTs was indirectly evidenced by XRD and Raman, in which the reduction on the sp^2-organization of the CNTs was observed for all treated samples. The most significant changes was observed in both the CNTs samples treated with the mixture H_2SO_4 3.0 $mol.L^{-1}$/HNO_3 3.0 $mol.L^{-1}$ and treated with H_2O_2. These procedures lead to samples with higher amount of functionalization than the others studied in this work. These initial observations were confirmed by X-ray photoelectron spectroscopy, XPS. The XPS spectra of pristine and all treated CNTs samples showed the presence of C1s main peak at 284,5 eV. In the pristine CNT spectra, we observed a single symmetric peak. However, in the spectra of the treated samples the C1s is composed by three peaks, assigned to graphitic sp^2 carbon (284,5 eV), carbon bonded to a hydroxyl group (286 eV) and carbon bonded to carboxyl groups (289 eV)[3]. These functional groups have been quantified through the XPS spectra confirming the high amount of surface chemical groups in the samples treated with H_2SO_4/HNO_3 and H_2O_2, corroborating the data obtained from Raman and XRD.

References

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