Purification of surface-modified arc-discharge single-walled carbon nanotubes by centrifugation processes

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Arc-discharge single-walled carbon nanotubes (SWCNTs) demonstrate well-defined spectroscopic responses and a high structural quality. In addition, the arc-discharge technique allows the synthesis of relatively large amounts of material, and the product is available at moderate prices. However, pristine arc-discharge SWCNTs contain large amounts of impurities, including catalyst metals, graphitic particles, and amorphous carbon. Well-purified commercial samples are expensive since current purification processes are time consuming and have low yields. Liquid media, which are necessary for the purification, change the physical aggregation of the SWCNTs or modify its chemical reactivity. Therefore, chemical studies on high-purity arc-discharge SWCNTs are limited.

In this communication, we present our results on SWCNT purification by centrifugation or ultracentrifugation in aqueous media. More specifically, we study the influence of surface chemistry on the separation of arc-discharge SWCNTs from their impurities during the centrifugation. The results of processing chemically modified materials are analyzed in terms of graphitic and amorphous carbon impurities, residual metal content, and SWCNT spectral characteristics.

Pristine SWCNTs were chemically modified through oxidative treatments in air, liquid phase (HNO_3, HNO_3/H_2SO_4), or combinations of both (air/HCl/HNO_3/H_2SO_4), and diazonium-mediated reactions for the attachment of aminated or fluoroalkyl groups. The SWCNT materials were dispersed in aqueous solutions containing a surfactant, usually sodium dodecylbenzene sulfonate (SDBS) or the block copolymer Pluronic F68. The dispersions were tip-sonicated, centrifuged or ultracentrifuged, and decanted. Purified SWCNT dispersions were directly analyzed by visible/near infrared spectroscopy, and the SWCNT purity was deduced from the relative intensity of the characteristic SWCNT spectral bands (M_{11} and S_{22}). Also, the dispersions were sometimes filtered in order to perform electron microscopy observations, X-ray diffractograms, and thermo-gravimetric analyses.

The purity of centrifuged SWCNT dispersions increases with the centrifugation speed, although yield is reduced proportionally [1]. Graphitic impurities are eliminated from the liquid dispersion and metal content decreases, while the reduction in amorphous carbon depends on the centrifugation medium, the starting SWCNT concentration, and the centrifugation speed. SWCNT purity particularly increases when the powder materials are air oxidized before high speed centrifugation [2]. It can be concluded that certain surface oxygen groups (anhydride and lactone) increase the relative stability of SWCNTs in the suspension.

Ultracentrifugation allows the preparation of high purity SWCNT dispersions when the starting powder is untreated or it has been air oxidized. However, purification seems to be less efficient when the starting powder has been oxidized with nitric acid or functionalized by the diazonium salts route.

References

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