Investigating the reactive sites and the anomalously large changes in surface pK_a values of chemically modified carbon nanotubes of different morphologies

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Abstract

"Bamboo-like" multiwalled (b-MWCNT), "hollow-tube" multiwalled (h-MWCNT) and single-walled carbon nanotubes (SWCNT), chemically modified with 1-anthraquinonyl (AQ) or 4-nitrophenyl (NP) groups, are characterized using voltammetric, electron microscopic and Raman spectroscopic techniques. The pK_a values of the AQ-modified CNTs are found to be shifted by greater than three units when compared to the pK_a values of anthrahydroquinone (AHQ, the reduced form of AQ) in aqueous solution to beyond pH 14. These large changes in the surface pK_a values of the modified CNTs are explored further by comparing the pK_a values of CNTs modified with an anthraquinonyl-2-carboxylic acid group. These groups are attached to the CNT surface via the formation of an amide bond with an aminophenyl "spacer" unit derived from the chemical reduction of NP modified CNTs. The location of reactive sites on the CNT surface is investigated and their influence on the pK_a of the modified materials is discussed. Comparison with modified pyrolytic graphite electrodes exposing pure edge-plane or pure basal-plane crystal faces indicates that the modifying aryl groups are predominantly located on edge-plane like defects at the tube ends of MWCNTs. The effect of polymer formation on electron transfer kinetics of b-MWCNTs and h-MWCNTs is also discussed. In contrast SWCNTs show both significant side-wall functionalisation and fast electron transfer kinetics which is attributed to their different electronic structure.

Indexed keywords

Engineering controlled terms: Chemical modification; Electron microscopy; Graphite; Raman spectroscopy; Single-walled carbon nanotubes (SWCN); Solutions

Engineering uncontrolled terms: Pyrolytic graphite electrodes; Reactive sites; Side wall functionalization

Engineering main heading: Multiwalled carbon nanotubes (MWCN)