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Mathematical models for the oxidative functionalization of multiwalled carbon nanotubes

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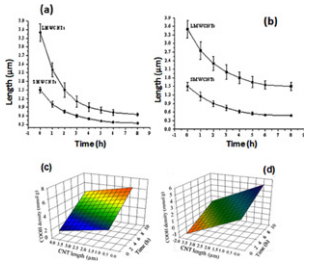
HIGHLIGHTS

- MWCNTs of different lengths were oxidized by two methods: reflux and ultrasonication.
- Oxidation was performed for different time periods.
- Empirical equation for MWCNTs length shortening was derived.
- Empirical equation for number of —COOH groups induced on MWCNTs was derived.
- These results were illustrated by mathematical models.

GRAPHICAL ABSTRACT



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ABSTRACT

A systematic, quantitative study has been conducted to elucidate the effect of oxidation protocol and time on the size, integrity and surface characteristics of multiwalled carbon nanotubes (MWCNTs). Pristine MWCNTs with initial lengths ranging between (i) 2–5 μm and (ii) 1–2 μm were selected for the study. Two oxidation protocols, sonication at 40 °C and reflux at 80 °C in a mixture of concentrated H_2SO_4 and HNO_3 (3:1 *v*/*v*) were examined with each variety of MWCNTs. Time dependence of oxidative shortening could be correlated by two empirical, exponential relationships: (i) $\sqrt{L_0} - \sqrt{L_t} = k \log t$ (Eq. (1)) and (ii) $L_t/L_0 = c \times \exp(kt)$ (Eq. (2)), where L_0 and L_t represented the initial and final length of the nanotubes oxidized separately for t hours under ultrasonication and reflux conditions respectively. Time and length dependence of surface carboxyl density was modeled using the following equations: (iii) COOH density (mmol/g, ultrasonication) = 3.088 + [0.353 × t(h)] − [1.185 × L_t (μm)] (Eq. (3)) (iv) COOH density (mmol/g, reflux) = 2.412 + [0.604 × t(h)] − [0.662 × L_t (μm)] (Eq. (4)), which suggest that oxidative shortening and carboxyl enrichment of MWCNTs is not only time-dependent but equally influenced by the oxidation protocol.

1. Introduction

Carbon nanotubes (CNTs) represent a novel class of nanomaterials, which made their appearance into the biomedical arena, less than a decade back. Ever since their emergence on the nanoplatform, their unique physicochemical properties such as high aspect ratio/ surface area, high mechanical strength, ultrahigh drug loading capacity, near infrared fluorescence detectability, Raman scattering and photoacoustic effects have made them potential candidates for drug delivery and diagnostic imaging. Although CNTs appear to be a promising material for various applications, their biomedical applicability is often fraught with certain toxicological concerns, closely associated with their high aspect ratio and hydrophobicity of the graphene side walls. These two factors, coupled with strong π–π interactions between the individual tubes, cause pristine (*p*-) CNTs to assemble as bundles, rendering them water-insoluble and toxic. One of the most promising approaches

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