

[0068] For individually dispersed SWCNTs, differences in the scaling of the buoyancy and frictional forces allows for length separation of the nanotubes via a rate separation scheme. Discounting convection of the fluid, a Nernst-Planck formulation can be used to model the flux, N_i , of each species i :

$$N_i = c_i F_{buoyancy} / f_i - D_i \nabla c_i + U c_i \quad (1)$$

Here, c_i is the concentration, f_i is the friction factor and $D_i = k_B T / f_i$ the diffusion coefficient of species i ; k_B is Boltzmann's constant, T is the temperature, and $k_B T$ is the thermal energy of the solution. U is the velocity of bulk fluid convection, which is expected to be zero in the absence of instrumental artifacts such as vibration or thermal gradient driven mixing. The buoyant force, $F_{buoyancy}$, is:

$$F_{buoyancy} = \pi r^2 \ell (\rho_s - \rho_{SWCNT,i}) G_i \quad (2)$$

in which r is the radius of the SWCNT plus the surfactant shell, ℓ is the tube length, ρ_s and $\rho_{SWCNT,i}$ are the density of the solution and the SWCNT (plus its surfactant shell) respectively, and G is the centripetal acceleration. Given average parameters for ultracentrifugation, $|c_i F_{buoyancy} / f_i| \gg |D_i \nabla c_i|$, and the diffusive flux can be eliminated from equation 1. The dependence of the friction factor suggests the possibility of length based separation. In the creeping flow limit, as indicated by a Reynolds number, $Re = V_i \rho_s \ell / \eta \ll 0.1$, in which $V_i = F_{buoyancy} / f_i$ is the ballistic velocity of an individual SWCNT, the friction factor for a long, thin rod can be represented as

$$f_{||} = \frac{2\pi\eta\ell}{\gamma} \left(\frac{1 + \frac{0.307}{\gamma}}{1 - \frac{0.5}{\gamma}} + \frac{0.426}{\gamma^2} \right), \quad (3)$$

$$f_{\perp} = \frac{4\pi\eta\ell}{\gamma} \left(\frac{1 + \frac{0.307}{\gamma}}{1 + \frac{0.5}{\gamma}} + \frac{0.119}{\gamma^2} \right),$$

where η is the fluid viscosity and $\gamma = \ln(\ell/r)$. Combining equations 1 to 3 yields an equation for the flux in which the nonlinear dependence on SWCNT length, approximately proportional to $\ln(\ell/r)$, is clearly apparent.

$$N_i(\ell) \approx c_i \frac{(\rho_s - \rho_{SWCNT,i}) Gr^2}{6\eta} \frac{2\gamma^4 + 0.614\gamma^3 + 0.544\gamma^2 - 0.136}{\gamma^3 + 0.614\gamma^2 + 0.638\gamma + 0.0135} \quad (4)$$

[0069] The consequence of the $\ln(\ell/r)$ dependence in equation (4) is that longer SWCNTs travel with a greater velocity in opposition to the applied acceleration.

[0070] Length separation, with minimal chirality differentiation, thus should occur in an experiment when $\Delta\rho = \rho_s - \rho_{SWCNT} \gg \Delta\rho_{SWCNT} = (\rho_{SWCNT} - \rho_{SWCNT,i})$, where $\rho_{SWCNT,i}$ is the density of an individual SWCNT chirality, and ρ_{SWCNT} is the average density of all the SWCNT types in solution. Alternatively, chirality separation should be maximized when $\Delta\rho = 0$ and different SWCNT types experience buoyancy forces in opposite directions.

[0071] Separation of single wall carbon nanotubes (SWCNTs) by length via centrifugation in a high density medium, and the characterization of both the separated fractions and the centrifugation process are further described herein. Significant quantities of separated SWCNTs ranging in average length from less than 50 nm to about 2 μm can be produced, with the distribution width being coupled to the rate of the separation. Less rapid separation is shown to produce narrower distributions. These length fractions, produced using sodium deoxycholate dispersed SWCNTs, were characterized by UV-Visible-near infrared absorption and fluorescence spectroscopy, dynamic light scattering, Raman scattering and atomic force microscopy. Several parameters of the separation were additionally explored: SWCNT concentration, added salt concentration, liquid density, rotor speed, surfactant concentration, and the processing temperature. The centrifugation technique is shown to support tens of milligrams per day scale processing and is applicable to all of the major SWCNT production methods: CoMoCat, HiPco, laser ablation, and electric arc. The cost per unit of the centrifugation based separation is also demonstrated to be significantly less than size exclusion chromatography based separations.

Results of Testing

[0072] In a first set of trials, the following were investigated.

[0073] Materials: CoMoCat process SWCNTs were purchased from SouthWest Nanotechnologies (Norman, Okla.). Sodium deoxycholate and iodixanol were purchased from Fisher Scientific (Pittsburgh, Pa.) and Sigma-Aldrich (Milwaukee, Wis.) respectively, and used as received.

[0074] Ultracentrifugation: Controlled length fractionation was achieved for HiPco, laser and CoMoCat process SWCNTs via ultracentrifugation. SWCNTs were dispersed with 2% by mass sodium deoxycholate surfactant. SWCNT preparation consisted of sonication (tip sonicator, 0.32 cm, Thomas Scientific) of the SWCNT powder loaded at (1.0 ± 0.2) mg/mL in the 2% surfactant solution in approximately 8.5 mL batches immersed in an ice water bath and tightly covered at 9 W of applied power for 2 h. Post-sonication, each suspension was centrifuged at 21,000 g in 1.5 mL centrifuge tubes for 2 h and the supernatant removed. The resulting rich black liquid contains primarily individually dispersed SWCNTs.

[0075] Density modified solutions were generated by mixing the appropriate surfactant or SWCNT solution with an iodixanol solution (OptiPrep, 60% mass by volume iodixanol) and 2% by mass sodium deoxycholate solution. Liquid layers were performed by careful layering in 15 mL polycarbonate centrifuge tubes. A Beckman-Coulter J2-21 centrifuge with a JA-20 rotor was used. Suspensions were spun for 20 h at 20,000 rpm, generating an average force of 32,000 g with a maximum force of approximately 45,000 g. The individual fractions were collected by hand pipetting off each layer in 0.75 mL increments.

[0076] In determining the velocity of an individual SWNT, the velocity will be proportional to the difference in the specific density of each SWNT and the medium, according to:

$$\Delta\rho_r = (\rho_s - \rho_{SWCNT,i}) \quad (5)$$

From the point at which the nanotubes stop being buoyant (known from experiment to be approximately 9% to 10% iodixanol for deoxycholate dispersion), ρ_{SWCNT} values cov-