Supplemental Information

Surface Esterification of Carbon Nanospheres and Carbon Nanotubes

Glacial acetic, butyric, and hydrochloric (37 wt%) acids were reagent grade from Sigma Aldrich. Hollow multiwalled carbon nanospheres (CNS) synthesized by laser pyrolysis of charred cellulose with average diameters of 40 nm were obtained from Fullerene Sciences Inc. (Boulder, CO). FTIR reveals a mixture of oxygen functionalities, including hydroxyl groups, on the surface of the CNS. Hydroxyl-functionalized multiwalled carbon nanotubes (MWCNT-OH) were obtained from CheapTubes.com (Brattleboro, VT). MWCNT-OH as-received were reported to have 1.76 wt% OH functionality and 20-30 nm outer diameters. CNS or MWCNT-OH were dried under vacuum (25 in Hg) for 24 hours at 100 °C in a round bottom flask. After drying, it was purged with argon, and acetic or butyric acid was added to give a solid concentration of 4 mg/ml. This suspension concentration corresponds to 4.14×10^{-3} mol/L OH groups and 17.5 mol/L acetic acid or 10.9 mol/L butyric acid. The flask was sealed and placed in a Bransonic laboratory sonicator for one hour to disperse the nanoparticles. Following sonication, hydrochloric acid catalyst was added to give a final catalyst concentration of 0.0268 M. The flask was fitted with a condenser and the mixture heated to 105 °C while stirring; the reaction was allowed to proceed 24 hours before cool deionized (DI) water was added to stop the reaction. The cooled water/acid mixture was filtered through a 0.2 μm nylon membrane and washed three times with DI water. The filter cake was removed, added to DI water and stirred overnight to ensure removal of all absorbed acid. The CNS or MWCNT were filtered again and washed three times with water. The filter cake was then dried at 100 °C under 25 in Hg vacuum for 24 hours.

Isolation and Surface Esterification of Cellulosic Nanowhiskers from Cotton Linter

Cotton linter pieces of about 1 cm^2 were soaked overnight in glacial acetic acid (AA) or butyric acid (BA) at 5 °C. The suspension was subsequently heated in an oil bath to 105 °C, and the desired amount of hydrochloric acid (HCl) and deionized (DI) water added to obtain a final concentration of 90 wt % organic acid in water (corresponding to 17.5 M acetic and 10.9 M butyric acid) and 0.0268 M HCl. The final solid to liquid ratio was 4

mg/ml. After a reaction time of 9 hrs, the suspension was quenched in an ice bath; this was followed by centrifugation at 8,600 g for 3 min and replacement of the clear supernatant with DI water to remove the acid (repeated for 3 cycles). The suspensions were then concentrated to about 10 wt% solid concentration and mechanically agitated in a Waring blender for 20 min. Subsequently, the suspensions were diluted with an equal volume of DI water. CNW were isolated by repeated centrifugation at 8,600 g for 3 min by replacing the initially clear supernatant with DI water until the supernatant remained turbid. After collection of the first turbid supernatant, the centrifugation cake was re-suspended and again centrifuged to obtain additional CNW in the form of a turbid supernatant suspension. The first three turbid supernatants were recovered and combined. For comparison, non-functionalized CNW were isolated using 2.5 M hydrochloric acid at the same temperature for 60 min. The isolation procedure was as described above. Fractions of the suspensions were freeze-dried for analysis.

Transmission Electron Microscopy (TEM)

Nanoparticles were examined using transmission electron microscopy in a FEI model CM200 (Hillsboro, OR) at 200 kV. A drop of dilute suspension was allowed to dry on a carbon coated copper grid. To enhance contrast for CNW, the grid was floated in a 2 wt% uranyl acetate solution for 3 min. Samples were dried under vacuum for 20 min at room temperature before examination.

Fourier Transform Infrared Spectroscopy (FT-IR)

A small amount of dried CNS, MWCNT or CNW was ground into a fine powder with KBr (IR-grade from Sigma Aldrich) and pressed into a pellet. Spectra were recorded on a Thermo Nicolet Nexus 670 FT-IR in the range of 400 to 4000 cm^{-1} using a liquid nitrogen cooled MCT detector (CNS, MWCNT) or a DTGS detector (CNW).

Thermal Gravimetric Analysis (TGA)

Thermal stability of the prepared materials was tested using thermal gravimetric analysis (Seiko SSC/5200, TG/DTA 220) calibrated against an indium standard. Small amounts of dried nanoparticles were heated from 30 °C to 800 °C (CNS, MWCNT) or 650 °C

(CNW) at 10 °C/min in an air atmosphere and mass as a function of temperature was recorded.