Systematic study of Lewis acid-catalyzed bromination and bromoalkylation of multi-walled carbon nanotubes

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Chemical functional groups govern the reactivity, wettability, and dispersibility of carbon nanotube (CNT). They play a central role in interactions of CNT with the environment, biological systems, composite matrix materials etc. Many different approaches to functionalize CNT are currently under research. The synthesis methods are studied and improved with respect to yield and uniformity of the resulting functionalization. Special attention is given to covalent functionalization strategies. Many promising molecules including polymers, peptides, and nucleic acids have been attached covalently to CNT.[1][2] Successful coupling strategies rely on S_N reactions with a nucleophile and require introduction of electrophilic sites on the CNT surface or ends.

Bromination and bromoalkylation reactions of CNT are very promising pathways to grafting of electrophilic sites. However, only sparse experimental data is available in the literature. The present work was a broad and systematic study to optimize the bromination and bromoalkylation of multi-walled CNT (Baytubes® C150P) using Lewis acids as catalysts. The bromine content was quantified using X-ray photoelectron spectroscopy (XPS) after thorough washing. Structural modifications were investigated by transmission electron microscopy and X-ray diffraction (XRD). The bromination and bromoalkylation of multi-walled CNT were investigated by varying the processing parameters. Eight different reaction times, three reaction temperatures, nine solvents, twelve catalysts and eleven electrophile reagents were studied with respect to optimum bromination yield. Also radical-initiated reactions were studied but resulted in low yields using dibenzoylperoxide at 95 ºC as well as ω-halo-1-alcohols and methanesulfonic acid or phosphoric acid at three different temperatures. In general, the highest bromination performance on CNT was found in apolar solvents like dichloromethane and hexane. Di- or triethylenglycoldimethylether can be used though if the Lewis acid like $AlBr_3$ is insoluble in an alkane. Most efficient Lewis acids were $AlBr_3$, $FeBr_3$, and $SnBr_4$. Higher temperatures are preferable and led to concentrations of up to 22 at.% Br according to XPS using Br_2 and significantly affected the graphitic order of the CNT as was shown by XRD. Finally, the substitutability of the introduced bromine was studied. For this, the reaction of brominated CNT with 4-(trifluoromethyl)benzyl mercaptane was investigated. Success and degree of substitution of bromine by this fluorinated compound was shown by XPS analysis.

References

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