

Aqueous Dispersion of Carbon Nanotubes  
for Electronic Type-Selective Reactions  
with Aryl Diazonium Salts



by

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## SUMMARY

In this work solutions of carbon nanotubes in water were obtained in a variety of different dispersants using a combination of ultrasonication and centrifugation. Suspensions containing nanotube samples possessing different diameter distributions were characterised using optical absorbance spectroscopy to compare the effectiveness of each dispersant. Larger diameter nanotubes were well-suspended by all dispersants while those of smaller diameter were best stabilised by smaller ionic surfactants as the bulkier polymeric variants were unable to conform to their higher degree of curvature. Differences in the stability provided by each dispersant and relative hydrophobic interaction strengths between the dispersing molecule and the nanotube sidewall were investigated, where ionic surfactants sodium dodecylbenzene sulfonate and sodium deoxycholate were found to be superior performers.

Altering the surfactant concentration was found to be more appropriate than tuning the surfactant to nanotube mass ratio to obtain optimally dispersed concentrations of nanotubes. The optimal surfactant concentration was determined for a number of different dispersants through analysis with both optical absorbance and Raman spectroscopy. At high dispersant concentration the nanotubes were found to be flocculated by attractive depletion interactions induced by the greater number of surfactant micelles in the solution volume. It was determined by atomic force microscopy that longer nanotubes are depleted first, leaving aggregates of short nanotubes in the solution.

Dispersions of nanotubes in sodium dodecylbenzene sulfonate were used to examine the sonication and centrifugation parameter space. The dispersion properties of concentration, mean length and degree of aggregation were probed by optical absorbance, Raman spectroscopy and atomic force microscopy to determine the relationship between these attributes and instrumental variables. It was found that both centrifugation and sonication have a significant influence on the mean length of the nanotube population, where the applied duration of both processes provides a large degree of control over this property, while the centrifugation step ultimately determines the average bundle size. The applied centrifugation force was found to affect the metallic impurity content in a more influential manner than either mean length or bundle size. The effect of sonication duration on the mean length of the nanotube population was examined in detail, while the relationship between the Raman D:G ratio

and the average nanotube length was determined for two different laser excitation energies. Increasing the sonication intensity was observed to induce surfactant foaming if the energy input was above a critical density. The input sonication energy density was determined to be a critical factor in controlling the dispersion properties for both tip and bath type ultrasonic instruments.

The decay mechanisms for aryl diazonium salts in aqueous solution were discussed and related to the possible mechanisms of nanotube functionalisation. Dediazoniation kinetics for the nitro- and bromo-benzenediazonium tetrafluoroborate salts in aqueous solutions containing a variety of dispersants were investigated and found to be uncorrelated with the reaction rates between the diazonium species and carbon nanotubes. The selectivity of the diazonium reaction towards metallic nanotubes was evaluated in a variety of dispersants and polyethylene-oxide containing variants were identified as superior performers, with Pluronic F-127 providing the greatest selectivity. Transfer of electron density between the dispersant and nanotube was observed to greatly affect the reaction selectivity. It was found that partial withdrawal of electron density by sodium dodecyl sulfate leads to increased functionalisation of semiconducting species relative to metallic nanotubes and produces similar effects to aggregation in the optical spectra of dispersions with this surfactant. Conversely, Pluronic F-127 strengthens the electron density of the nanotubes which enhances optical spectra and leads to improved selectivity in the diazonium reaction.

Conditions for which selectivity was improved were identified for the electric arc nanotube and Pluronic F-127 dispersant system. Reactions were performed in a number of dispersant-nanotube systems to the near exclusion of semiconducting species, indicating the potential for improved separation schemes with certain dispersant-nanotube type combinations.

## DECLARATION

I certify that this thesis does not incorporate without acknowledgment any material previously submitted for a degree or diploma in any university; and that to the best of my knowledge and belief it does not contain any material previously published or written by another person except where due reference is made in the text.

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Adam J. Blanch

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## PUBLICATIONS ARISING FROM THIS WORK

### Peer Reviewed Journal Articles

Blanch, A. J.; Lenehan, C. E.; Quinton, J. S., Dispersant Effects in the Selective Reaction of Aryl Diazonium Salts with Single-Walled Carbon Nanotubes in Aqueous Solution. *J. Phys. Chem. C*, **2012**, *116* (2), 1709-1723

Blanch, A. J.; Lenehan, C. E.; Quinton, J. S., Parametric Analysis of Sonication and Centrifugation Variables for Dispersion of Single Walled Carbon Nanotubes in Aqueous Solutions of Sodium Dodecylbenzene Sulfonate. *Carbon* **2011**, *49* (15), 5213-5228

Blanch, A. J.; Lenehan, C. E.; Quinton, J. S., Optimizing Surfactant Concentrations for Dispersion of Single-Walled Carbon Nanotubes in Aqueous Solution. *J. Phys. Chem. B* **2010**, *114* (30), 9805-9811.

### Peer Reviewed Conference Proceedings

Blanch, A.J., Lenehan, C.E., & Quinton, J.S., Optimising Surfactant Aided Dispersions of Carbon Nanotubes in Aqueous Solution, *Nanoscience and Nanotechnology (ICONN)*, 2010 International Conference on, pp.132-135, 22-26 Feb. **2010**