Electronic Supplementary Material (ESI) for Physical Chemistry Chemical Physics

Supporting information

Bio-functionalization of Multi-walled Carbon Nanotubes

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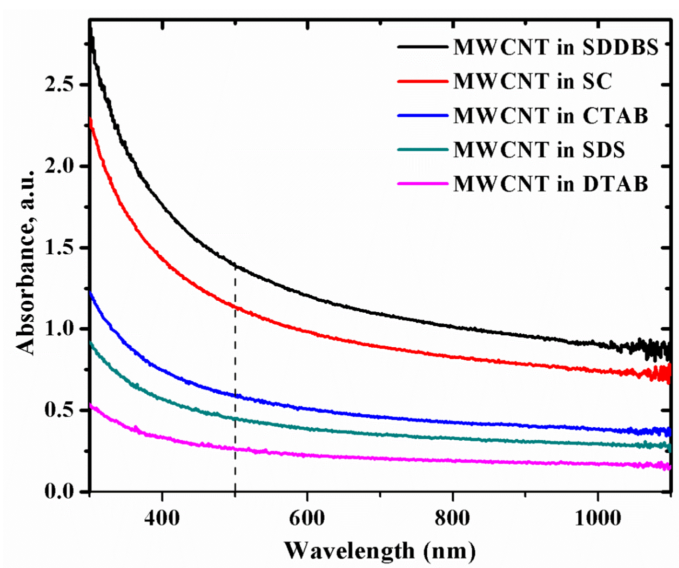
1. Comparative study of carbon nanotube dispersion using surfactants

Aqueous carbon nanotube dispersions were obtained by sonication tip using two cationic (DTAB and CTAB) and three anionic surfactants (SDDBS, SDS and SC). UV-Vis spectroscopy is a versatile method for characterizing the dispersion quality of CNTs in a solution. Bundles of MWCNTs are not active in the wavelength region between 200-1100 nm and only individual CNTs exhibit characteristic bands. UV-vis absorption spectra of these four samples were measured by subtracting the absorbance values of 1wt% surfactants from that of MWCNTs dispersion. Fig.1S (a) and figure 1S (b) illustrate the UV-vis spectra of these samples and their suspension photographs after centrifugation, respectively.

a)



b)

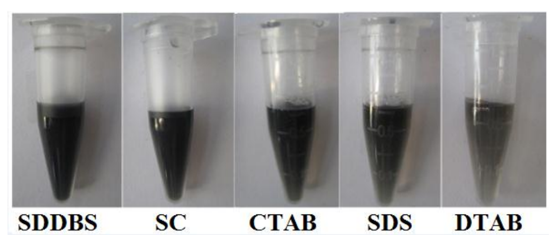


Figure 1S. *(a) UV-vis spectra of CNTs in SDDBS (black), SC (red), CTAB (blue), SDS (green) and DTAB (pink) . (b) Photograph of their supernatants after centrifuge.*

Comparison of the dispersion profiles of different surfactants at fixed wavelength shows explicitly that SDDBS enhanced the best nanotubes dispersibility. At the same time, DTAB is found to have lowest ability to disperse MWCNT comparing with the other surfactants used for this experiment. This experimentally observed trend can be explained by the chemical structure of surfactant molecules. Surfactants having benzene ring in their structures possess higher affinity for the tubes due to the strong π-π stacking type interaction with the graphitic surface of CNTs. Moreover, methylene groups in the surfactants tail groups can locate over the centers of the hexagonal structure of the graphite lattice, providing tail group lying on the tubes' sidewall.

The longer tail group provide higher adsorpsion affinity of surfactant to the carbon nanotube resulting in better dispersibility of CNTs in aqueous solutions by means of more steric repulsion between tubes. The better capabilities of SDDBS and SC compared to CTAB, SDS and DTAB to disperse MWCNTs can be ascribed to the presence of benzen ring in their chemical structures. As a consequence, it can be concluded whenever "tail group factor" and "benzen ring factor" compete, the latter has more effect on dispersion of CNTs. Among the remaining three surfactants, CTAB was showed the best observed distribution of MWCNTs which can be attributed to its longest tail group. Among the remaining two, they have the same tail group length but SDS has bulkier head group providing more electrostatic repulsion between tubes and consequently their better dispersibilities. Another characterization method to distinguish dispersion susceptibility of these surfactants was AFM. It is obvious that the more and longer tubes possess to dispersed ones with SDDBS. These cationic and anionic surfactants cover CNTs' sidewalls and the electrostatic repulsion between their ionic head groups leads to the distribution of CNTs in the aqueous solutions.

2. Determination of diameter and length distribution of dispersed MWCNTs

AFM and SEM studies have been implemented to specify characteristics of dispersed MWCNTs in SDDBS by taking the optimum sonication conditions into account. AFM images of dispersed MWCNTs by different surfactants is shown in Figure 2S.

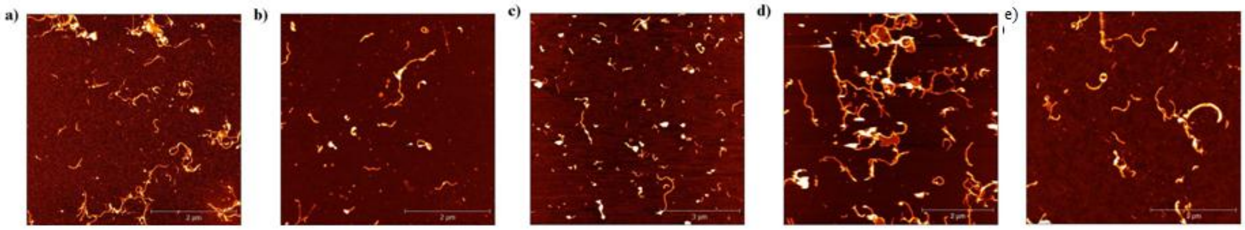


Figure 2S *AFM images of dispersed MWCNTs with (a) SDDBS, (b) SC, (c) CTAB and (d) SDS and (e) DTAB; (Height of 1-20 nm).*

The SEM images of these dispersed CNTs can be seen in Figure 3S.

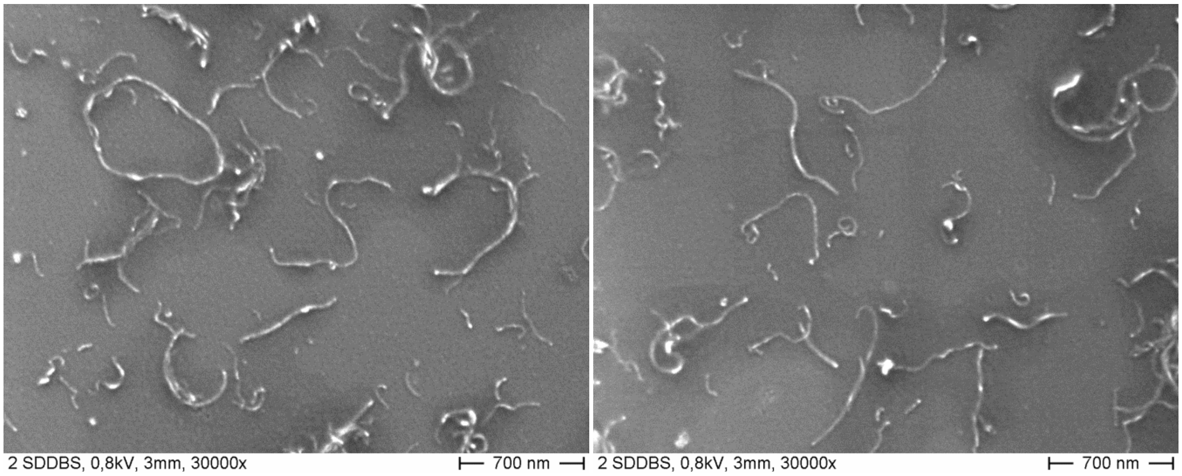


***Figure 3S** SEM images of dispersed MWCNTs in 1 wt% SDDBS.*

Subsequently analyzing the series of AFM and SEM images resulted in determination of the average diameter and length of dispersed CNTs. The diameter and length distributions of these tubes and the Gaussian fitted curves of them were presented in Figure 4S a and b. From these graphs, it can be deduced that the diameters of tubes after sonication process would be more in the range of 8.5-9 nm and their lengths are between 200-500 nm.

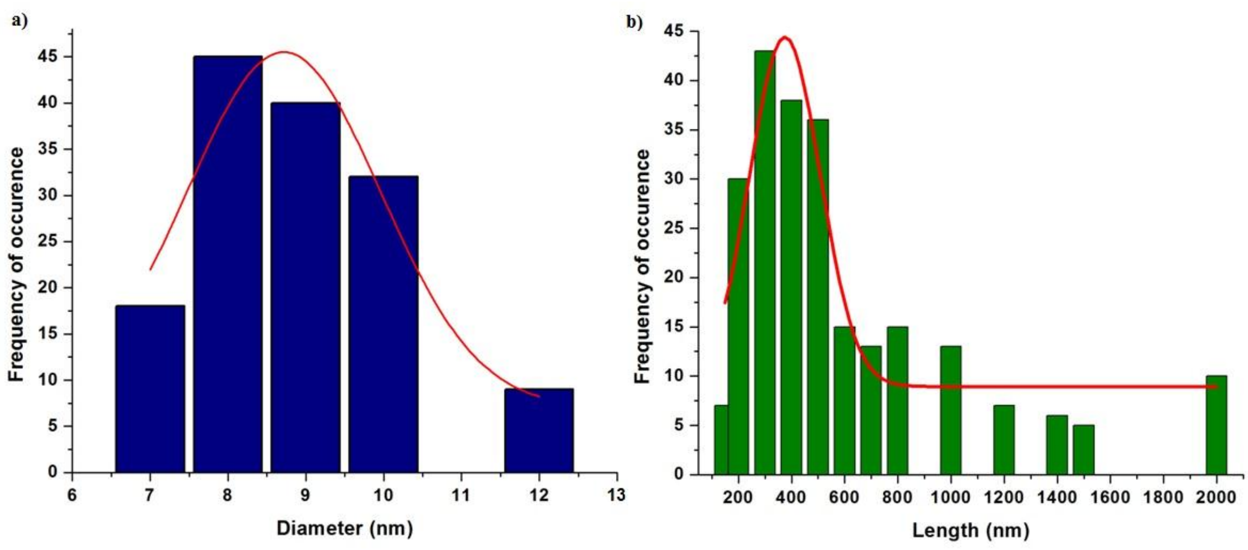


***Figure 4S** Diameter and length distributions of the dispersed MWCNTs with SDDBS*

Ultrasonication helps to exfoliate and disperse MWCNTs and afterwards SDDBS molecules are adsorbed on the MWCNTs' sidewalls. Dispersion of MWCNTs is attributed to the electrostatic repulsion between the negatively charged head groups of the SDDBS (anionic surfactant) on the MWCNTs' surfaces which prevent aggregation of them.