Electronic Supplementary Material (ESI) for RSC Advances.

Supplementary Information

A Simple Quantitative Estimate of the Number of Functional Groups on the Surfaces of Single-Walled Carbon Nanotubes

Quynh Bui Vu Ngoc,† Myung-Soo Choi,† Woo-Jae Kim*

[1]*Department of Chemical and Biological Engineering, Gachon University, Seongnam, Gyeonggi-do 461-701, Korea*

*Corresponding author. Phone: 82-31-750-8514. Fax: 82-31-750-8516. wjkim@gachon.ac.kr (W-J.K.)

†These authors contributed equally.

1. Reaction of different concentrations of 4-nitrobenzene diazonium tetrafluoroborate salt and SWNTs.

Various functionalized SWNT samples with different concentration of 4-nitrobenzene diazonium tetrafluoroborate salt are prepared to investigate the minimum concentration of diazonium reagent which can completely react SWNTs. When concentrations of diazonium are increased, the peak intensities of SWNTs are gradually decayed from 0.0167 mM to 0.0658 mM as shown in Figure S1, indicating that the extent of SWNT reaction with diazonium increases as the concentration of diazonium increases. However, below the reagent concentration of 0.0658 mM, SWNT absorption peaks are not fully decayed. This indicates that not all SWNTs are reacted with the reagents, which will complicate the analysis of density of functionalized SWNT. Therefore we raise the concentration of diazonium upto more than 0.11 mM to completely react SWNT with diazonium reagents as confirmed by Figure 1, and used these reacted samples for the analysis.

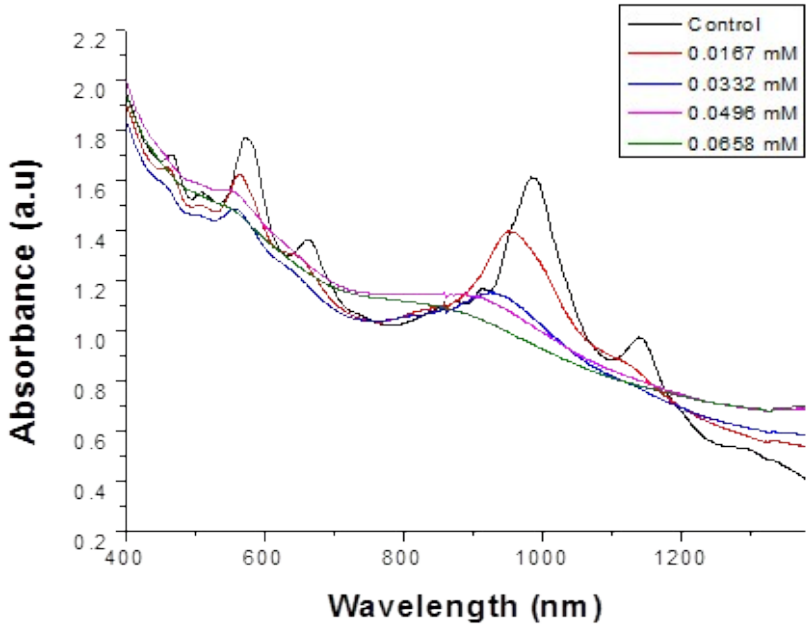

Figure S1. UV-vis-NIR absorption spectra of incompletely functionalized SWNT samples with different concentrations of 4-nitrobenzene diazonium tetrafluoroborate salt.

2. Preparation of the standard line of density according to the distance from meniscus.

We plot the line representing the relationship between the density along the tube and the distance from the meniscus. First, we fractionated the initial density gradient solution by every 200 µl using fraction recovery system (Beckman Coulter) and measured the mass of each fraction to calculate the density of each fraction. This gives rise to an initial density gradient profile, as shown in blue circle of Figure S2 below. This line was created by matching the density of each fraction with its distance from the meniscus. We plot two lines of initial and final density gradient (Figure S2), i.e., the densities along the tube before and after centrifugation, and these two lines are different because the centrifugal force applied during centrifugation changes the density of each fraction. The density gradient media (iodixanol) undergoes diffusion while simultaneously sedimenting towards the bottom of the centrifuge tubes in response to the centrifugal force (governed by the Lamm equation) as reported in our previous study [Langmuir, 24, 1790-1795, 2008]. We prepared the density gradient solution layers in the centrifuge tubes similarly to those of the centrifuge tube with functionalized SWNT sample, but used 1ml of iodixanol concentration of 50% (w/v) (without SWNT) instead of 1 ml of functionalized SWNTs with an iodixanol concentration of 50% (w/v). The final density gradient is used as standard line to determine the densities of the functionalized SWNTs in Figure 3.

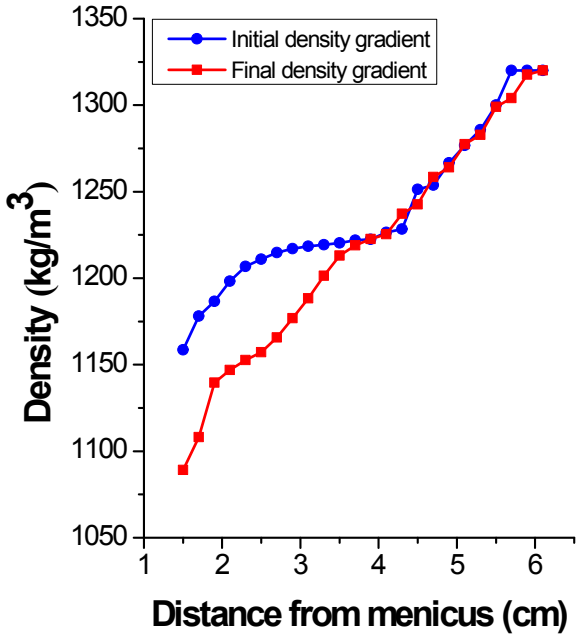

Figure S2. Density measurements: the density profile before and after 22 hours of centrifugation is shown. The graphs shows a relation between the density and the distance from the meniscus of the centrifuge tubes for the initial and final density gradient.

3. A correlation between the number of functional groups on the SWNTs and the D to G area ratios of Raman spectroscopy for 2nd batch of CoMoCAT SWNTs.

We performed the same experiment as done in the original manuscript using another batch of CoMoCAT SWNTs. The same concentrations of diazonium reagents used in the 1st Batch (Figure 1) were injected, i.e., 0.11 mM, 0.17 mM, 0.23 mM and 0.29 mM. As can be seen in Figure S3 (a), we also confirmed that all SWNTs are reacted as indicated by the complete decay of absorption intensities similar to the original 1st Batch (Figure 1). However, the extents of reactions were little different from those of the 1st Batch of CoMoCAT SWNTs (Figure 2) as indicated by the different D to G area ratio of Raman spectrum for four samples as shown in Figure S3 (b) and Table 1, compared to those of 1st Batch. This result indicates that the control of extent of surface functionalization of SWNTs by adjusting reagent concentrations is difficult as mentioned in the earlier section of this manuscript. We performed density-induced separations using these four samples to identify their densities to estimate the number of attached functional groups on SWNT surfaces and show the results in Figure S3 (c) and also listed the data in Table 1 of the original manuscript.

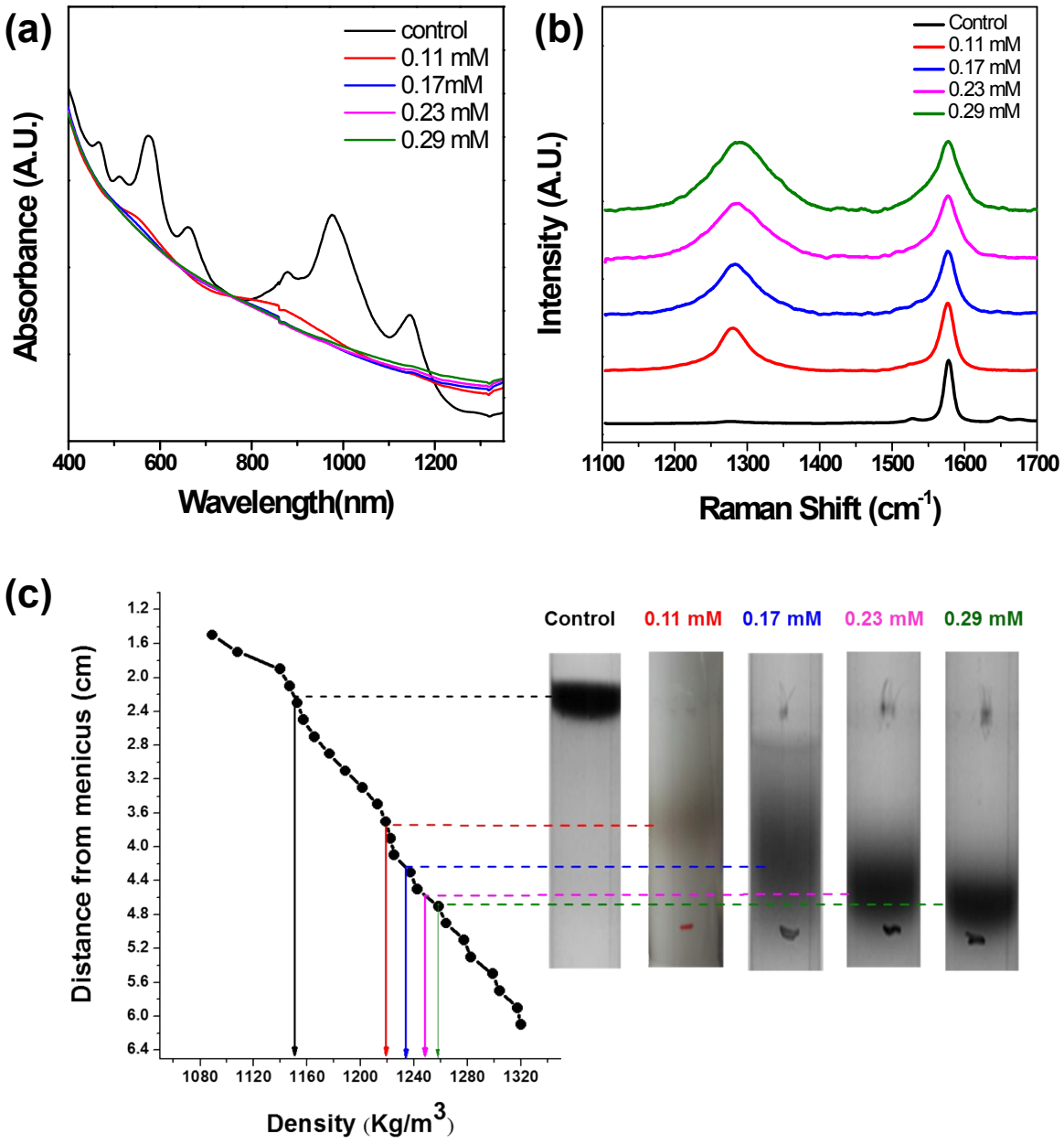

Figure S3. UV-vis-NIR absorption spectra of functionalized SWNT samples of 2nd Batch with different concentrations of 4-nitrobenzene diazonium tetrafluoroborate salt and a control sample as a reference (a), Raman excitation measurements (632.8 nm) for functionalized samples with different concentrations of diazonium reagents and a control sample as a reference, and the density measurements of functionalized SWNTs and a control sample (c) where, the density profile after 22 hours of centrifugation is shown. The inset shows a photograph of the centrifuge tubes for the functionalized samples and the control sample after centrifugation.

4. Estimating the number of functional groups per carbon atom for functionalized arc discharged SWNTs.

To confirm that the linear relationship between the D to G ratio and the number of functional groups per carbon atom developed in this study is also valid for other types of carbon nanotubes, we performed the same series of experiment using arc discharged SWNTs, which have larger diameters (1.3~1.5 nm) than CoMoCAT SWNTs (0.757 nm) used in this study.

We prepared fully functionalized SWNTs by injecting 0.143 mM nitrobenzene diazonium solutions into unreacted SWNT control solution. Both SWNTs were first dispersed in 1wt% SDS/H_2O and dialyzed to 2wt% SC/H_2O. We confirmed that the SWNTs were fully reacted using UV-vis-NIR spectrum (Figure S4 (a)) and measured the area ratio of D to G peak (1.564) as shown in Figure S4 (b).

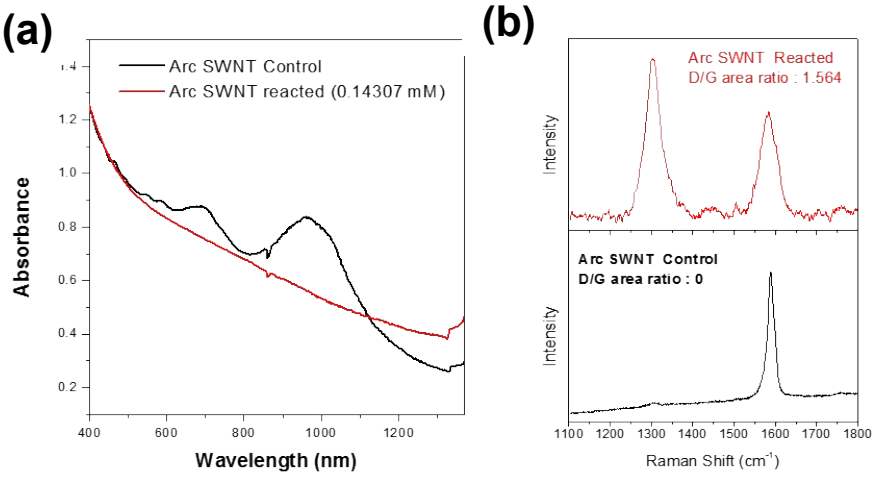

Figure S4. UV-vis-NIR absorption spectra of functionalized arc discharged SWNT sample and a control sample as a reference (a), Raman excitation measurements (632.8 nm) for functionalized samples and a control sample as a reference (b).

We performed density-induced separation of both SWNTs and measured their densities as shown in Figure S5. Because the arc discharged SWNTs have larger diameter distribution than CoMoCAT SWNTs, the band width of reacted SWNTs are broader than that of CoMoCAT SWNTs, originally used in this study. We used average density of functionalized SWNTs for calculation (1236.7 kg/m^3).

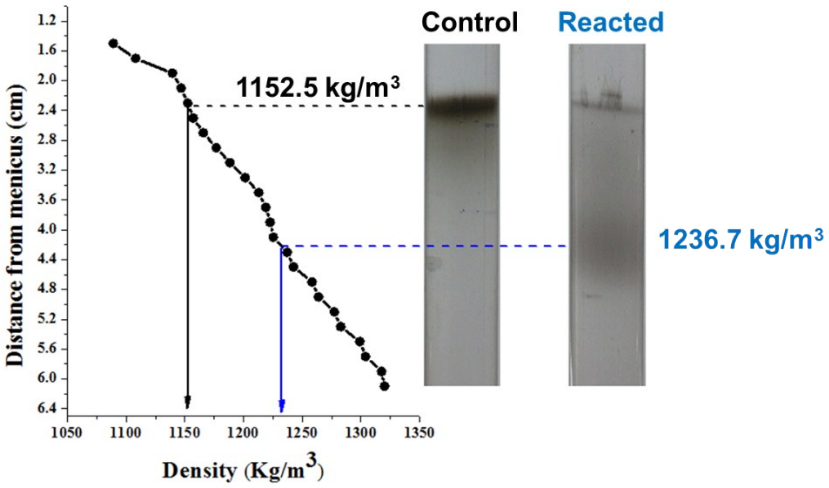

Figure S5. Density measurements of functionalized SWNTs and a control sample: the density profile after 22 hours of centrifugation is shown. The inset shows a photograph of the centrifuge tubes for the functionalized samples and the control sample after centrifugation.

The estimated number of functional groups per carbon atom for reacted arc discharged SWNTs using eq (9) developed in this study, is 0.0313, and the value estimated by the above experiment is 0.0306. Both numbers are in good agreement, as also shown in Figure S6 below. This result confirms that our simple quantitative estimation model developed in this study can be applied to various types of functionalized SWNT, irrespective of diameter ranges of SWNTs.

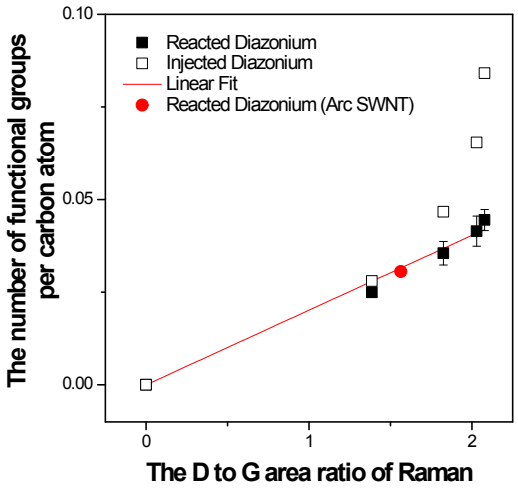

Figure S6. The relationship between the D to G area ratio and the number of 4-nitrophenyl functional groups per carbon atom for reacted arc discharged SWNTs (red circle)