Utilizing the Krafft Phenomenon to Generate Ideal Micelle-Free Surfactant-Stabilized Nanoparticle Suspensions**

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1 Supporting Information

1.1 Materials and preparation methods

CTAB was purchased from Acros Organics with a purity of at least 99 %. Hipco single-wall carbon nanotubes were purchased as purified (ash content less than 15%) from Unidym. The samples were sonicated for 30 minutes at 12 W (to the sample) by a Dr. Hielscher UIS250v ultrasound processor (3 mm diameter sonotrode tip, nominal power consumption 225 W) running in continuous mode, at 0°C (sample vial kept in an ice-water bath) and at 30°C, respectively.

Centrifugation was carried out with a Hettich centrifuge (Universal 320R, rotor type 1420-A), using 9180 RPM=8000 RCF for 20 minutes.

1.2 Optical spectroscopy investigations

Optical absorption measurements were done using a Varian Cary 4000 UV-Vis Spectrophotometer, on samples filled into a cuvette of 0.99 mm path length. The sample temperature was controlled by a tempered water circulator, allowing $T < T_K$ samples to be measured at 22°C and $T > T_K$ samples at 30°C. Any influence from the surfactant is negligible, as verified by measuring the absorption of a blank sample with 1wt.-% CTAB solution, without CNTs. This was essentially non-absorbing over the entire wavelength regime studied in this work.

Samples with up to 1.6 mg SWCNTs per mL of CTAB solution were prepared and investigated, but at nanotube concentrations greater than 1.2 mg mL^{-1} the resulting suspensions were so dark that the detector of the spectrophotometer could not measure the response, even with the reduced path length cuvette used in our study.

Fig. 1a and c show the same diagram as in Fig. 3a and c in the main paper, but here they are accompanied by zoomed-in versions in panes b and d, respectively. While only a part of the data is visible in this magnified section, the modulation as a function of wavelength is much clearer to see, thereby revealing also the weak modulation in the $T > T_K$ graphs. This is difficult to spot in the diagrams of the main paper since the scaling there was optimized for giving an overview of all data.

Apart from the difference in oscillation strength between the $T > T_K$ and $T < T_K$ samples discussed in the main paper, one may also note that the spectra from the former samples have a more pronounced background absorption that increases with decreasing wavelength. In general, there may be two origins of this phenomenon. First, metallic nanotubes have strong absorption at higher energies exhibiting characteristic peaks, and samples enriched with metallic tubes show such a background absorption that increases with decreasing wavelength, unlike samples enriched by semiconducting SWCNTs. This was observed e.g. by Weisman and co-workers [1]. The increase of absorbance could thus be the contribution of the metallic tubes. The second possible explanation, reported in the same paper, is that a general background absorption, increasing towards lower wavelengths, can get more pronounced for samples that have been sonicated long and/or to some extent chemically functionalized.
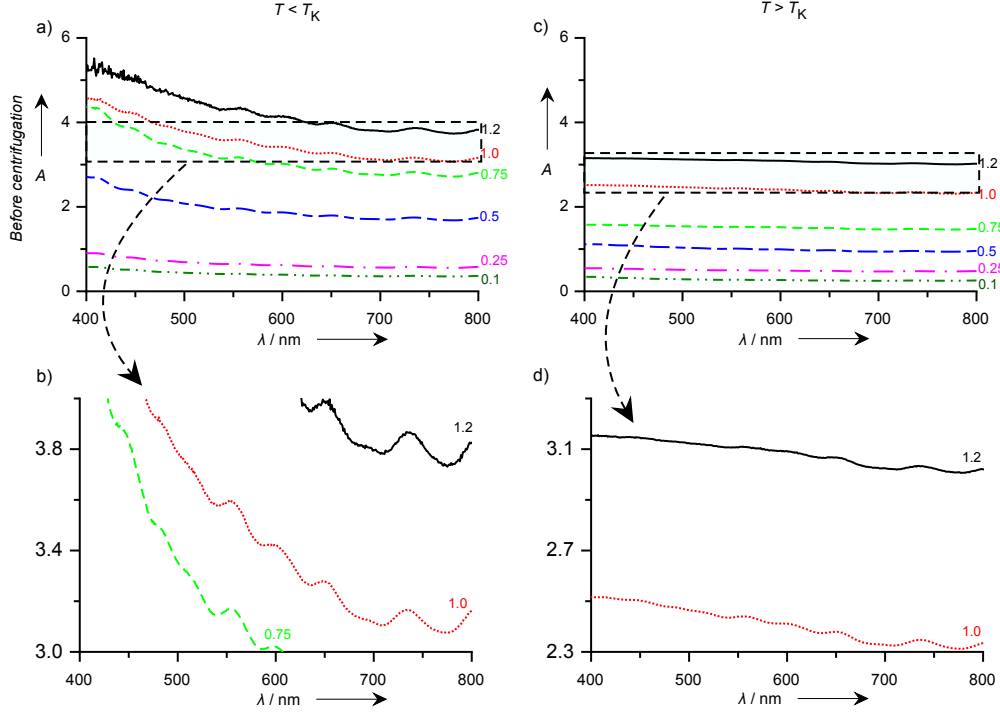
Figure 1: The optical absorption spectra of Fig. 3a and c in the main manuscript (top) together with zoomed-in plots of the same data (bottom), to reveal the weak modulation present also in the $T < T_K$ sample. The scaling is identical in b and d, although different sections of the vertical axis were chosen due to the different average absorption level in the two data sets.

As potential explanation why the background in our work is less pronounced for the more aggregated $T > T_K$ samples than for $T < T_K$ we may propose that since the CNT concentration appears lower in the first case, the reduced amount of metallic tubes affects strongly the considered part of the spectrum. We regard the possibility of chemical reaction on the sidewalls unlikely in our case, since our sonication conditions are fairly standard in terms of power and time and are not among the most aggressive. The real reason is however not trivial to assess and would require a new study, out of the scope of the present work.

1.3   Optical microscopy investigation

After leaving the samples standing for one week at $T < T_K$ and $T > T_K$, respectively, allowing CTAB crystallites to sediment in the $T < T_K$ sample, the supernatant was extracted and filled into a flat capillary for the microscopic investigation. At low magnification (2, top row) the tubes appear well dispersed in both samples but small aggregates can be distinguished upon increasing the magnification (2, bottom row). The $T < T_K$

sample contains fairly many aggregates but they are of small size, rarely beyond $\sim 1\mu m$ in extension. In the $T > T_K$ sample the number of aggregates is somewhat lower, but they are then on the other hand larger, not seldom on the order of 5 μm. This slight difference may have its origin in depletion attraction acting rapidly on large aggregates in the micellar sample but not in the micelle-free one.
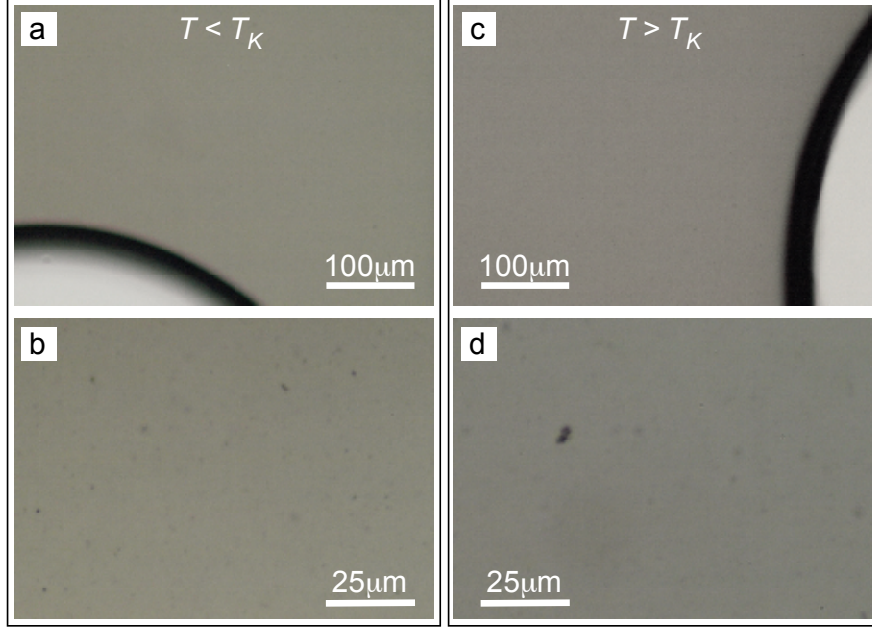

Figure 2: Optical microscopy pictures of two samples with 1 mg mL^{-1} Hipco SWCNTs, the sample on the left prepared below T_K, the sample on the right at $T > T_K$. For reference the edge of an air bubble is included in a) and c).

1.4 Atomic Force Microscopy investigations

For the preparation of the AFM samples we deposited 25 μL of the suspension on a 1.5 cm diameter circular Si wafer and performed a spin-coating process with up to 1000 rpm. Afterwards 500 μL of ultrapure water was deposited on the wafer which was then blotted. The blotting procedure was done three times. The samples were measured on a Multimode V AFM stage (Bruker Nanoscope V Controller) in Tapping Mode (res. freq. 300 kHz) using topside Al coated Si cantilevers (k = 42 N/m , Wetzlar NanoAndMore).

1.4.1 AFM investigation of samples with high CNT concentration

A quantitative height analysis of the 0.5 mg mL^{-1} nanotube concentration data shown in Fig. 3 reveals that the features of the $T > T_K$ sample have a typical thickness of

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15-20 nm, whereas those of the sample prepared below T_K are on the order of 2-7 nm. The small minimum feature size in the latter sample indicates the presence of very small bundles or even individual nanotubes even at this quite high CNT concentration, whereas the nanotubes clearly are much more aggregated in the $T > T_K$ sample. The feature width in that sample often varies in a quite irregular fashion and an uneven character in the phase as well as the topography images, with stripes that are not along the long axis of the aggregates, provides striking evidence that the CNTs are embedded in substantial amount of remaining surfactant.
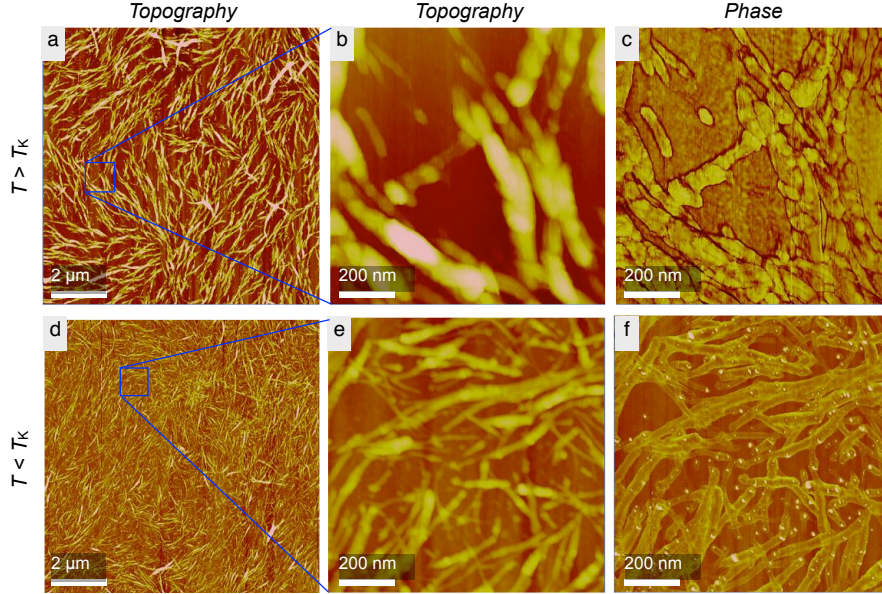

Figure 3: Atomic force micrographs of samples initially with 0.5 mg mL^{-1} SWCNTs, prepared above (a-c) and below (d-f) T_K.

1.5 Reference experiment at CTAB concentration equal to the solubility at 0°C ($< CMC$)

To further verify that the surfactant that is not initially in solution but present in the crystalline phase indeed contributes to the dispersion, we placed a 1 wt.-% aqueous CTAB solution in ice water bath until equilibrium was reached, all surfactant in excess of the solubility at 0°C falling out as a crystalline sediment. A sample of the crystal-free supernatant was then extracted and this was used for dispersing Hipco SWCNTs at a concentration of 1 mg mL^{-1}. The result was very poor with large aggregates and a suspension that was not stable. This shows that the small amount of CTAB that can enter solution at 0°C is far too small to stabilize an aqueous CNT suspension of this concentration.

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1.6 Determination of optimum CTAB:CNT ratio based on analysis of sediment from $T < T_K$ samples

The optimum ratio of CTAB to CNTs that is achieved after sedimentation of excess CTAB in the the samples prepared at $T < T_K$, after storage at a temperature of 20°C for about one week, was determined as follows. Four samples were prepared following identical dispersion procedures, all with 1 mg SWCNTs in 1 mL of 1% CTAB solution. When the sedimentation process was complete, we removed as much of the supernatant as possible from each sample without disturbing the sediment significantly. Nevertheless, it was impossible to avoid a small amount of the CTAB from the sediment to be removed together with the supernatant, due to the effect of the shear flow while extracting the supernatant.

1 mL of ethanol was now added to the sediment and small remaining amount of suspension of each sample, followed by a brief vortex mixing. When all CTAB had been dissolved in ethanol the small amount of remaining CNTs and impurities, which do not disperse well in ethanol, were sedimented to the bottom of each vial by centrifugation. The supernatant ethanol, now containing only dissolved CTAB but essentially no nanotubes or impurities, was now extracted from each sample and saved in a separate vial (one per original sample) that had previously been weighed when empty. New ethanol was now added to the remaining sediment and this washing, centrifugation and extraction procedure was repeated ten times for every sample, each time saving the extracted CTAB-containing ethanol in the collection vial. In this way the CTAB component in the sediment was completely separated from the component consisting of CNTs and impurities. After the final extraction step, each vial with the CNT/impurity sediment as well as each collection vial with all the extracted CTAB-ethanol solution were now placed in a vacuum oven, which was gently evacuated and heated to 60°C. The vials were left in the vacuum oven until all ethanol had evaporated. After the vials had cooled down to room temperature again they were weighed, yielding the masses of CNTs + impurities and of CTAB, respectively, that were in each sample's sediment.

The result was that the mass of CNTs and impurities in every sample was below the resolution limit of the balance used (0.1 mg) and the masses of CTAB were 7.6, 6.3, 7.6 and 7.6 mg, respectively, yielding an average CTAB content of 7.3 mg in the sediment. The remaining 2.7 mg were thus in the suspension together with almost the full 1 mg of nanotubes, giving us a first estimate of the optimum surfactant to nanotube ratio for our samples. However, this is by necessity an over estimate, since a small share of the sediment was always removed together with the supernatant at the first separation stage. Therefore, we conclude that the optimum CTAB:SWCNT ratio in our samples, following our preparation procedure, is about 2:1, and this was thus the ratio chosen for the reference experiment described in the following.

1.7 Reference experiment at $T > T_K$ with optimized CTAB concentration

We finally prepared samples with 0.25 mg and 1 mg, respectively, of SWCNTs, each in 1 mL of CTAB solution with a concentration set to yield a CTAB:SWCNT ratio of 2:1 for each sample, as had been found to be optimal in the experiment described above. This was dispersed following our standard procedure but at 30°C, i.e. above the Krafft temperature T_K. After dispersion the sample was stored for two days at 30°C before carrying out optical spectroscopy, and then the samples were centrifuged, followed by new optical spectroscopy measurements. 25 μL of the centrifuged low CNT concentration sample (0.25 mg mL^{-1}) was now deposited on a Si wafer for investigation by AFM.

Topography and phase images from the AFM investigation of this sample are shown in Fig. 4. Comparing with the images for the corresponding $T < T_K$ sample (Fig. 4d-f in the main paper) we note that most of the features are substantially larger in this reference sample, suggesting that the exfoliation of the tubes was less efficient that in the case of dispersion below T_K. The amount of excess surfactant however seems to be smaller, as expected, since the features appear relatively uniform in the phase image. The features in the sample prepared with 1% CTAB solution at $T > T_K$ were strongly non-uniform in texture, indicating substantial coverage by surfactant, cf. Fig. 4a-c in the main paper.
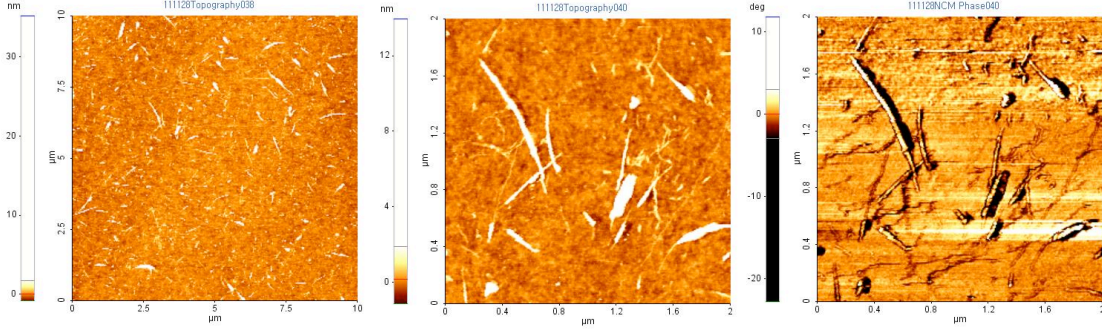

Figure 4: Atomic force micrographs (the first two showing topography data and the third the phase corresponding to the second image) of a reference sample with 0.25 mg mL^{-1} SWCNTs, prepared above T_K but with a CTAB:CNT ratio of 2:1.

The absolute optical absorption spectra of the reference samples are shown in Fig. 5a, together with the spectra obtained with the corresponding $T < T_K$ samples, here repeated from the main paper. The general absorption level is somewhat higher than in the $T < T_K$ samples, in particular prior to centrifugation, a difference that we attribute primarily to some loss of absorbing species in the $T < T_K$ sample during the sedimentation phase. In order to simplify the comparison we have therefore plotted the same results in b but with the data for the new reference samples rescaled to match the average absorption levels of the $T < T_K$ samples. While the characteristic SWCNT peaks are
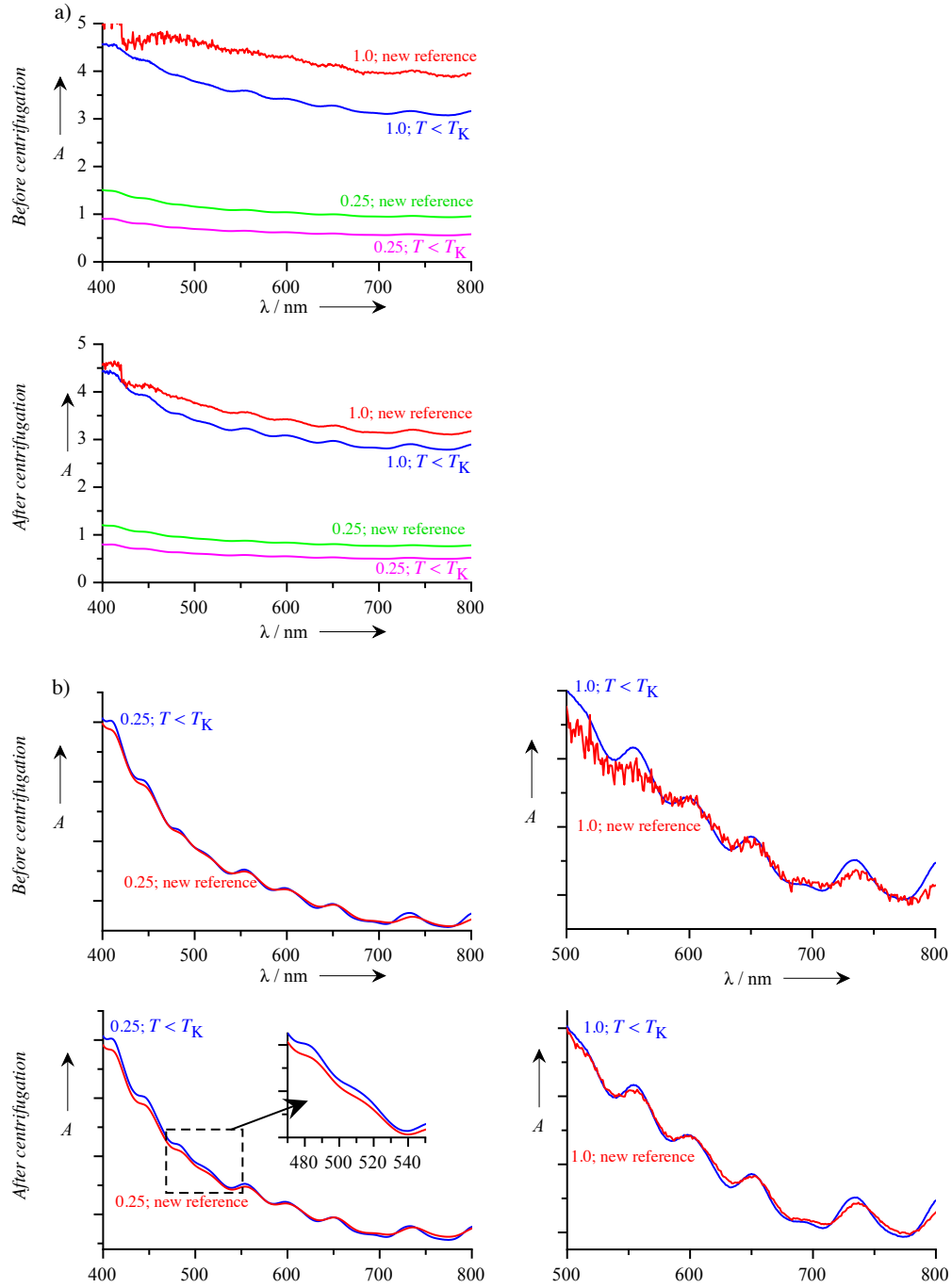
Figure 5: Optical absorption spectra of the reference samples prepared above T_K with optimized surfactant concentration (new reference) compared to the data for corresponding samples prepared at $T < T_K$ (these curves are identical to those in the main paper). In a the absolute values are plotted, in b the new reference data have been rescaled to match the general absorption level of the $T < T_K$ spectra, thus the y-axes have arbitrary units in these diagrams. For clarity, a detail has been highlighted in the post centrifugation 0.25 mg mL^{-1} diagram.

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clear in all spectra, they are slightly weaker in the spectra from the reference samples than in those from the $T < T_K$ samples, although the reference samples had been stored only two days while the spectra from the $T < T_K$ samples were obtained after a month of standing. Although a long-term stability study of the reference sample has not yet been carried out this already indicates that dispersion below T_K is more efficient in exfoliating the SWCNTs than above T_K, even compared to a $T > T_K$ sample with optimized surfactant concentration. This matches the results from the AFM investigation and it is further corroborated by the greater reduction in absorbance upon centrifugation for the reference samples than for the corresponding $T < T_K$ samples.

References

[1] A. Naumov, S. Ghosh, D. Tsyboulski, S. Bachilo, and R. Weisman, "Analyzing absorption backgrounds in single-walled carbon nanotube spectra.," *ACS Nano*, vol. 5, no. 3, pp. 1639–1648, 2011.