Shear-induced ordering of micellar arrays in the presence of single-walled carbon nanotubes†

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Single-walled carbon nanotubes were found to induce elongation and alignment of surfactant micelles in thin films under the action of shear, leading to the formation of ordered arrays over micron lengths.

Surfactant molecules in aqueous solutions are known to exhibit rich phase diagrams, where self-association results in the formation of micelles above the critical micellar concentration (CMC). Upon increasing the concentration, elongated micelles may become stable, and further aggregate and orient into lyotropic liquid crystalline (LC) phases.[1] LC phases are important in a variety of applications, ranging from cosmetics and paints to molecular sensors.[2,3] In addition, LC phases have been shown to template the self-assembly of inorganic molecules, leading to the formation of well-defined structures and symmetries, as in mesoporous silica.[4]

It is well known that LC mesophases are sensitive to the presence of inclusions due to their orientational ordering. Thus, dispersed molecules and nanostructures that induce elastic distortions in the LC phase give rise to long range inter-particle interactions at mesoscopic length scales.[5,6] Recently, significant efforts have been devoted to the utilization of LC phases for orienting of nanoparticles and nanostructures embedded within LC phases.[7–9] It was found that the mutual interaction and stability of the combined system was sensitive to the size and shape of the inclusion, the local ordering of the liquid crystal molecules at the surface of the particle, the orientation of the LC director field, as well as the location on the phase diagram of the LC phase. For example, it was shown that spherical particles are only stable within the lamellar LC phase if the bilayers are soft and fluctuating.[7] In the hexagonal LC, phase additives were found to be depleted from the inner walls of the cylinders.[8]

An interesting and relevant question is whether, under specific conditions, nanometric inclusions may *induce* orientational ordering and the formation of LC-like regions in a surfactant system that is otherwise located in an isotropic regime of the phase diagram. The resulting structures may be thermodynamically stable, or trapped, non-equilibrium structures.

Previous studies reported that additives may change the phase boundaries[10] or the spacing of ordered LC phases,[11] as well as induce the alignment of aggregates.[12] In the latter case, kinetic trapping of ordered structures was reported.[12]

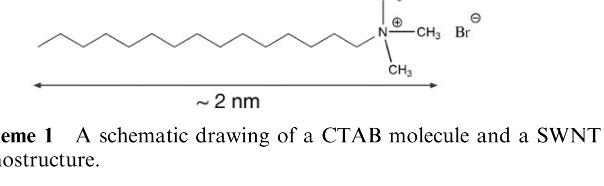
Among the more relevant additives are functional nanostructures, such as single-walled carbon nanotubes (SWNTs). SWNTs are crystalline graphitic rods characterized by a diameter in the range 0.8 to 1.2 nanometers and a typical length of microns.[13] SWNTs exhibit a unique combination of electrical and mechanical properties,[13] making them a desired component in nanohybrid materials. Combining a molecular diameter and a mesoscopic length (Scheme 1), dispersed SWNTs may affect the phase diagram of self-assembling molecules, as well as the response of the system to external constraints and the formation of non-equilibrium structures.

Here, we report our observations of the formation of well-aligned arrays of elongated micelles in a system composed of anisotropic molecules (cetyl trimethyl ammonium bromide (CTAB)) and a low concentration of well-dispersed individual SWNTs. We focus our study on nanometrically-thin films and characterize their structure using electron microscopy at cryogenic temperatures (cryo-TEM).

CTAB forms lyotropic LC phases in aqueous solutions at room temperature[14] at concentrations above 22 wt%, as presented in Scheme 2.

SWNTs[15] were dispersed in isotropic CTAB solutions[16] at concentrations ranging from 5 to 20 wt% (Scheme 2). The dispersions were observed to de-mix into two macroscopic phases: an upper (transparent) phase and a lower (black) phase. The lower phase was enriched with well-dispersed individual SWNTs (as indicated by TEM and small angle X-ray, SAXS (not shown)). The upper phase was depleted of nanotubes. Similar de-mixing was observed in dispersions of multi-walled carbon nanotubes (MWNTs)[17] and carbon black (CB)[18] at a wide range of CTAB concentrations (see ESI†).

Nanometrically-thin films, prepared from the lower phase of the CTAB-SWNT dispersions, were found to exhibit long-



Scheme 1 A schematic drawing of a CTAB molecule and a SWNT nanostructure.

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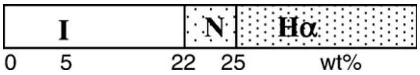
† Electronic supplementary information (ESI) available: SAXS scattering curves of SWNT in CTAB dispersions and a discussion of de-mixing.



Scheme 2 Phase diagram of aqueous solutions of CTAB (25 °C): I-isotropic, N-nematic and Hα-hexagonal liquid crystalline phases.

range ordering of the elongated CTAB micelles, well-observed *via* cryo-TEM imaging (Fig. 1). Thin films were prepared by placing a micro-droplet on an electron microscope (EM) grid, blotting the excess liquid and ultra-fast cooling to a temperature of −182 °C.[18] The resulting film was confined between two concave air–solution interfaces.[19,20] Using a vitrification robot (Vitrobot[21]), we were able to control the blotting force exerted on the samples, the number of blotting actions and their duration.

As can be seen in Fig. 1, the dominant features in the TEM images are almost half micron-long cylindrical micelles, oriented parallel to individual SWNTs (indicated by the arrows). The aligned micelles form large arrays (typically several hundreds of nanometers) of ordered micelles of well-defined periodicity. The micelles' orientation is dictated by the direction of the SWNT, as can be seen in Fig. 1. We observed that the diameter of an individual SWNT coated with adsorbed CTAB was ∼3.5 nm, similar to that of a native CTAB micelle. Similar behavior was observed at different CTAB concentrations in the range 9–15 wt% and a SWNT concentration of 0.1 wt%. SAXS measurements of bulk SWNT–CTAB–water dispersions at relevant concentrations did not indicate the presence of orientational ordering (not shown). Had similar micron-range domains of oriented micelles been present in the bulk, they would have resulted in a characteristic peak pattern in the SAXS measurements. We noted that the SAXS scattering curves clearly showed the presence of SWNTs and CTAB micelles (see ESI†) of no orientational preference. The effect was found to be unique to SWNTs: other carbonaceous additives of similar composition and surface area but of different diameter (MWNTs, of typical diameter 20 nm) or geometry (CB, spherical particles of typical diameter 30 nm) did not induce the alignment of elongated micelles under similar processing, as can be seen in Fig. 2.

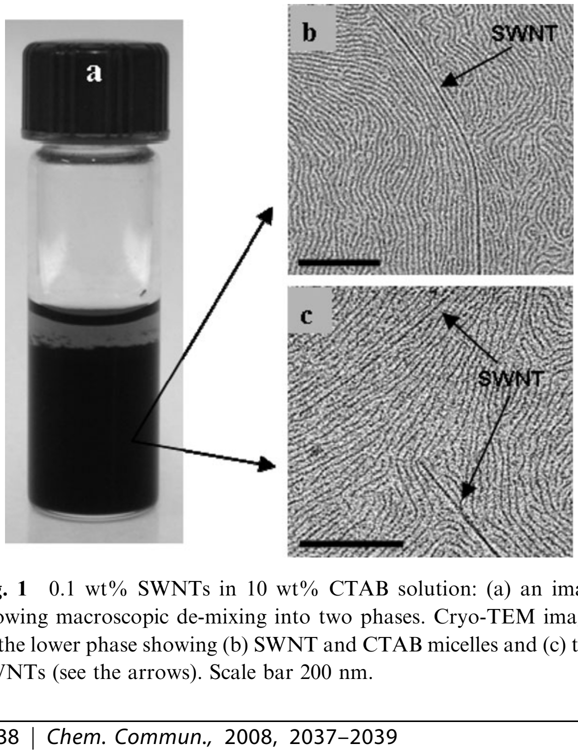


Fig. 1 0.1 wt% SWNTs in 10 wt% CTAB solution: (a) an image showing macroscopic de-mixing into two phases. Cryo-TEM images of the lower phase showing (b) SWNT and CTAB micelles and (c) two SWNTs (see the arrows). Scale bar 200 nm.

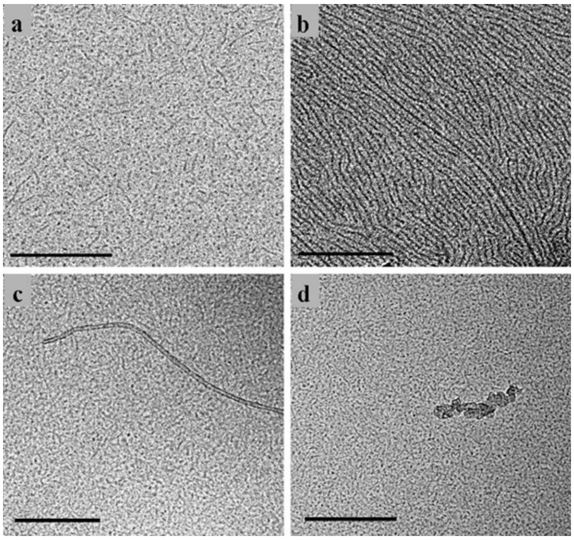


Fig. 2 Cryo-TEM images of 10 wt% CTAB solution: (a) The native solution, (b) a dispersion of 0.1 wt% SWNTs, (c) a dispersion of 0.1 wt% MWNTs, (d) a dispersion of 0.1 wt% CB. Scale bar 200 nm.

What is the origin of the observed effect?

The preparation process of ultra-thin films for cryo-TEM involves a step of blotting that subjects specimens to high shear rates ($\sim 10^3$–10^6 s^{-1}).[19,22] It has been shown previously that the flow fields that develop during shearing may cause alignment of structures in the liquid specimen prior to vitrification of the sample. In cases where the relaxation time of the structure is short, the original structure may be restored during a relaxation period of some tens of seconds. To test the effect of relaxation on the structures presented here, we performed a series of on-the-grid[22] relaxation experiments, where samples were incubated for up to 90 sec in a controlled environment prior to quench-cooling. The images (Fig. 3) suggest that a relaxation process indeed takes place, leading to the loss of orientational ordering, and that a structural transformation from elongated to spherical CTAB micelles occurs. Thus, we may conclude that micelle elongation and orientational ordering result from shearing of the combined SWNT–CTAB dispersions.

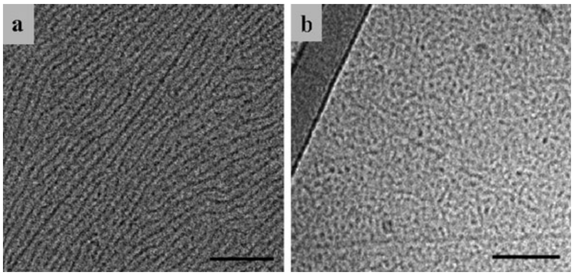
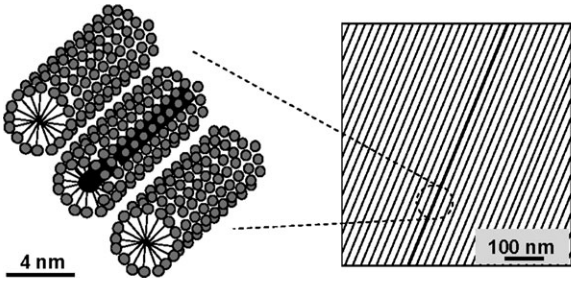


Fig. 3 Cryo-TEM images of a dispersion of 0.1 wt% SWNTs in 10 wt% CTAB solution following on-the-grid relaxation periods of (a) 0 sec and (b) 60 sec. Scale bar 100 nm.



Scheme 3 A schematic presenting the structure of the building blocks comprising the ordered arrays, as imaged by cryo-TEM.

Both the shear-induced transitions from spherical to elongated worm-like micelles and the shear-induced alignment of thread-like micelles in solutions of surfactants have been reported previously.[19,20,22] Here, we show that the combination of a low concentration of well-dispersed SWNTs and shear induces both micelle elongation and the alignment of elongated micelles over micron-sized domains. The effect is exclusive to SWNTs and is probably related to dimensional matching between the surfactant-coated SWNTs and the native micelles on the one hand, and the mesoscopic length of the tubes on the other, as schematically presented in Scheme 3.

To conclude, we have found that a low concentration of dispersed SWNTs may induce the alignment and ordering in an ultra-thin film of a complex fluid, well below the ordered region of the native surfactant phase diagram. The ordered micellar arrays span over mesoscopic length scales. The effect is unique to SWNTs, and has not been observed in other additives of similar chemical composition and surface area.

Understanding of the role played by the SWNT additives in the formation of the ordered arrays requires further investigation. The role of the tubes' dimensions, the effect of confinement, induced by the thin film configuration, and the role of shear forces is not clear. It is evident that techniques beyond cryo-TEM imaging and SAXS will be required to elucidate the mechanism leading to the observed phenomenon. Once achieved, such understanding will open up new possibilities for the processing of molecular entities into desired structures. We suggest that the ordered arrays presented here may be further used for templating the preparation of nanometrically-thin layers of mesoporous materials of desired structures and architectures to meet the emerging needs of advanced technologies.

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