

Order–disorder transition induced by surfactant micelles in single-walled carbon nanotubes dispersions†

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The observation of spontaneously formed microns-long islands of orientationally ordered SWNT in isotropic dispersions of spherical surfactant micelles is reported. The micelles co-exist with surfactant-coated individual SWNT of like charge. Inter-tube distances of 25 to 16 nanometres and an unexpected first order transition into a random phase induced by an increased ionic strength cannot be explained by classical depletion interactions or electrostatic repulsion. We suggest that coupling between the nanostructures and the assembled molecules modifies the effective interactions in an unexpected way. As the nanometrically thin SWNT share common features with rigid polymers, rod-like particle suspensions, and biological polymers such as microtubules and actin in crowded cellular environments, the observed phenomenon is believed to be general and expected in other systems.

Single walled carbon nanotubes (SWNT) with their all-carbon composition, micron-long spherocylindrical geometry and nanometric diameter (0.8–2 nm) are characterized by a unique combination of electrical and mechanical properties.^{1–3} Dispersion of SWNT in aqueous media is a prerequisite for processing of SWNT and their utilization in a variety of applications.^{4,5} Dispersions of individual SWNT in a variety of aqueous solutions were reported^{6–8} below and above the critical micellar concentration (cmc)⁹ of the native surfactant solutions. While lyotropic liquid crystalline (LC) phases orient dispersed nano-structures and in particular carbon nanotubes,^{10–15} isotropic phases of spherical micelles are not expected to show such behavior. Yet, it is becoming evident that the coupling between molecular and colloidal interactions^{8,16,17} leads to non-trivial structures when the dimensions and geometry of the nanostructures are commensurate. Here we report the observation, *via* transmission electron microscopy at cryogenic temperatures (Cryo-TEM), of spontaneously formed microns-long islands of orientationally ordered SWNT in macroscopically homogeneous dispersions of ionic surfactant micelles. In Fig. 1a, b and d we present images taken from dispersions of SWNT (0.5–1 wt%) in solutions of spherical micelles of an ionic surfactant, cetyl trimethyl ammonium bromide (CTAB). The solution concentrations are above the cmc of the native surfactant but within the isotropic phase of the spherical micelles and far from their

LC transition (Scheme S1, ESI†). The SWNT dispersions are optically isotropic, and the viscosity of the dispersion is similar to that of the native surfactant solution.

The Cryo-TEM images (Fig. 1a and b) present CTAB coated SWNT dispersed in a solution of like-charged CTAB micelles. The SWNT are aligned almost parallel to each other with a typical inter-tube separation that depends on the concentration of the surfactant solution. The micron-long areas of orientationally ordered surfactant-coated SWNT coexist with an isotropic background of nanometric CTAB micelles (a typical diameter of 5 nm⁹). Higher magnification (Fig. 1d) reveals that the dispersed SWNT are coated by adsorbed surfactant molecules, forming a periodic structure on the SWNT surface with a typical periodicity of 5 nm. The adsorbed surfactant molecules seem to form close-packed quasi-spherical micelles on the surface of the SWNT. Similar images were reported before.^{18,19}

These structures result from the optimization of the interactions between the hydrophobic surfactant tail and the SWNT,

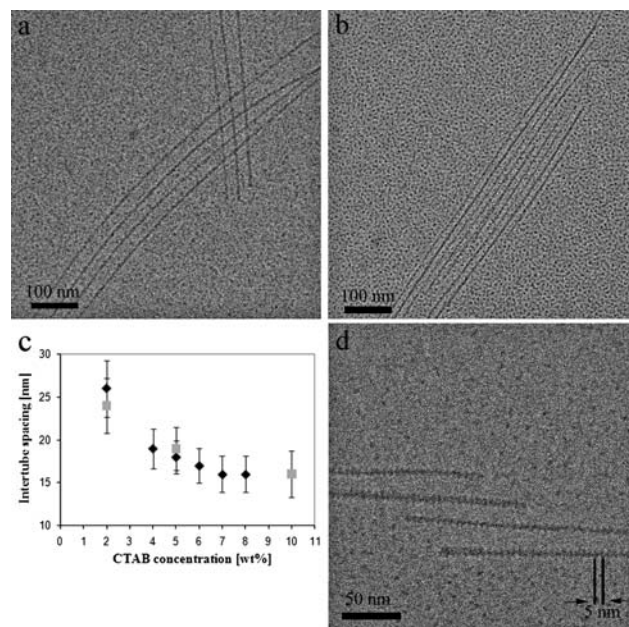


Fig. 1 Aligned SWNT in aqueous solutions of CTAB are observed in Cryo-TEM images of individual SWNT (1 wt%, dark lines in the image) dispersed in aqueous solutions of CTAB (the granular background) at CTAB concentrations of (a) 2 wt% and (b) 7 wt%. (c) Mean values of the inter-tube spacing as a function of CTAB concentration, for SWNT (◆) and DWNT (■). (d) A higher magnification presenting aligned SWNT in a dispersion of 5 wt% CTAB. The typical distance between the surface structures seen on the SWNT surface is 5 nm.

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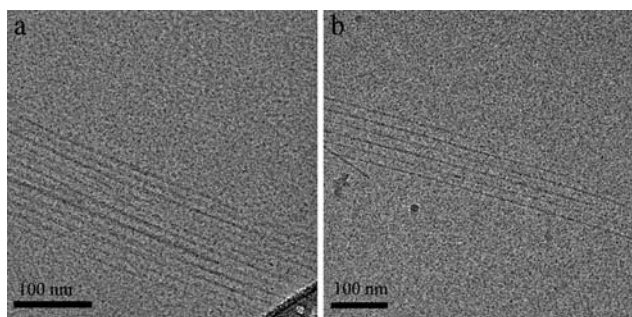


Fig. 2 Cryo-TEM images of SWNT (1 wt%) dispersed in aqueous solutions of (a) 5 wt% SDS, showing a mean inter-tube spacing of 19 nm and (b) 2 wt% CTAC, showing a mean inter-tube spacing of 16 nm.

minimization of the contacts between the hydrophobic moieties and the water, and maximization of the CTAB head group–water interactions. We observed similar alignment of dispersed SWNT in the anionic surfactant sodium dodecyl sulfate, SDS, and in cetyl trimethyl ammonium chloride (CTAC), (Fig. 2a and b and Fig. S1 in the ESI†).

The inter-tube spacing of the orientationally ordered SWNT islands is found to be sensitive to the bulk concentration of a given surfactant. For CTAB dispersions the inter-tube distance decays from about 25 nm to 16 nm as the bulk CTAB concentration increases from 2 wt% to 8 wt% (Fig. 1c). We note here that spacing of about 20 nm between adjacent SWNT is one order of magnitude higher than what would be expected from electrostatic repulsion between charged SWNT as the Debye length is less than 2 nm at these surfactant concentrations.²⁰ We also found that the number of co-

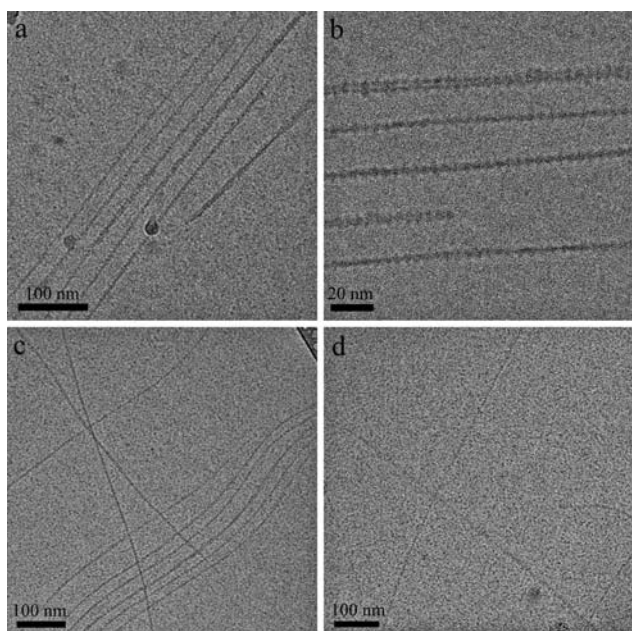


Fig. 3 Cryo-TEM images of SWNT (1 wt%) dispersed in 2 wt% (55 mM) CTAB and (a and b) 3.5 mM KBr (b presents a higher magnification of (a)), (c) 7 mM KBr and (d) 20 mM KBr. A transition from aligned to randomly oriented SWNT phase was measured at KBr concentrations of 70 mM in CTAB dispersions of 5 wt% (137.5 mM).

aligned SWNT within an island was below 10 tubes (typically 4–8), and did not depend on the concentration of the surfactant.

Experiments performed in SWNT dispersions using nonionic surfactants such as Brij-78 (1–3 wt%) and Triton ×-100 at 5 wt% (see Table S1 and Fig. S2, ESI†) showed only randomly dispersed SWNT. Orientationally ordered islands of dispersed SWNT were not observed in any of these dispersions at a variety of concentrations, located at a similar regime of the relevant surfactant phase diagram.

To further test the effect of electrostatic interactions on the spontaneous alignment of the surfactant-coated tubes, a salt (KBr) was added to CTAB dispersions at different concentrations. We observed that the presence of salt up to a threshold salt concentration (C_{thresh}) did not alter the orientational ordering (Fig. 3a) or affect the typical inter-tube spacing (Table 1). At the vicinity of the threshold concentration randomization of the orientationally ordered SWNT occurred, leading to an intermediate regime at which random networks of dispersed SWNT co-existed with orientationally aligned SWNT phases (Fig. 3c).

This coexistence suggests a first order phase transition between the isotropic and nematic domains controlled by the ionic strength, suggesting that the interaction is of an electrostatic origin. At a higher salt concentration the nematically ordered regimes disappeared, and only randomly oriented SWNT were observed (Fig. 3d). The value of C_{thresh} was found to depend on the concentration of the surfactant (Fig. 3).

As can be seen in Fig. 3b, addition of salt does not modify the local structure of the adsorbed surfactant. Visual inspection (and cryo-TEM images) shows that the bulk dispersions do not coagulate or agglomerate in these salt concentrations.

In a different set of experiments multi-walled carbon nanotubes (MWNT) with diameters ranging from 2 nm (double-walled nanotubes, DWNT) to about 80 nm were dispersed in aqueous solutions of CTAB. We found that while the DWNT formed regimes of co-aligned tubes with typical inter-tube distances similar to those of the SWNT (Fig. 4a), a similar phenomenon was not observed for the thicker MWNT.

Cryo-TEM images show random orientation of the dispersed MWNT at all CTAB concentrations. Random orientation was also observed in MWNT dispersions in DTAB, CTAC and SDS (not shown). Interestingly, images of dispersed MWNT do not show the surface structure typical for dispersed SWNT. Namely while the ionic surfactants adsorb to the surface of the MWNT and disperse them, spherical-like micelles are not seen, suggesting that the adsorbed surfactants coat the MWNT homogeneously. The different surface structure probably results from the different diameter and curvature of the MWNT which do not match the dimensions of the native micelles and thus do not lead to the formation of the surface micelles.

To test the role of the ionic surfactant in the observed phenomenon, two additional sets of experiments were performed. In the first,

Table 1 Inter-tube spacing as calculated from cryo-TEM images of SWNT dispersed in 2 wt% CTAB solutions and different salt (KBr) concentrations

Salt (KBr) concentration/mM	Inter-tube spacing/nm
0	26 ± 3
3.5	26 ± 3
7	24 ± 5

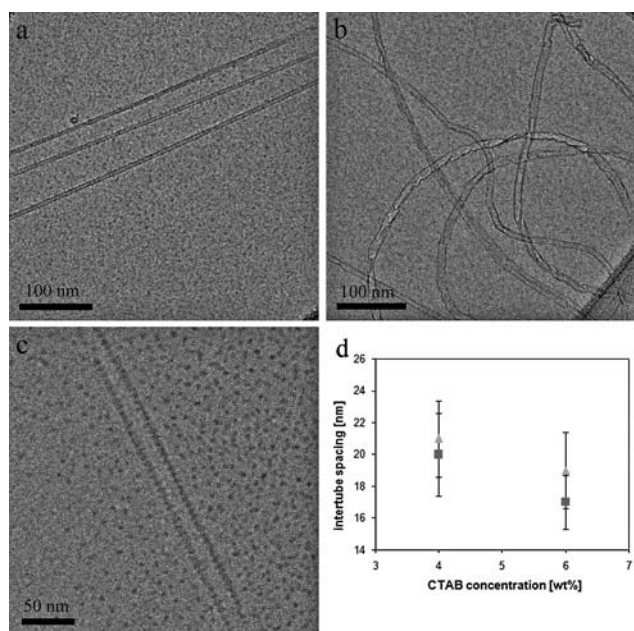


Fig. 4 Cryo-TEM images of dispersed CNT. (a) DWNT (1 wt%) dispersed in 2 wt% CTAB, (b) MWNT (1 wt%) dispersed in 2 wt% CTAB, (c) SWNT (1 wt%) in a mixed dispersion of 2 wt% CTAB and 2 wt% Brij-78. (d) Intertube spacing as a function of the overall surfactant concentration in CTAB–Brij-78 mixtures: (■) 0.3% CTAB + 3.3 wt% Brij-78, (▲) 2% CTAB + 2 wt% Brij-78.

a low concentration of CTAB (0.3 wt%) was used for dispersing SWNT, and the non-ionic surfactant Brij-78 (Table S1, ESI†) was added to the dispersions to final concentrations of 4 wt% and 6 wt%. In a second set of experiments a mixture of 2 wt% CTAB and 2 wt% Brij-78 was used to disperse SWNT. In all of these experiments cryo-TEM images of the dispersed SWNT show islands of aligned SWNT (Fig. 4c). Moreover, the observed inter-tube distances were similar to those observed in CTAB dispersions of concentrations corresponding to the overall (Brij-78 + CTAB) concentrations (Fig. 4d).

The appearance of islands of co-aligned charged rods coexisting with an isotropic phase of like-charged spherical surfactant micelles (or non-charged surfactants, Fig. 4c and d) in dispersions of ionic surfactants is non-trivial. The presence of a tightly packed monolayer of charged surfactant molecules at the highly curved surface of the SWNT, forming a non-homogeneous structure of hollowed spherical-like micelles, seems to be necessary for the appearance of this novel phase, as it is not observed in dispersions of MWNT or in SWNT dispersions of non-ionic surfactants where no such surface-structure is observed. Interestingly, the absence of the ordered phase in the MWNT also suggests that Onsager orientational interactions are not the source of the effect. It is not yet clear whether the observed phase is a transient or an equilibrium phase, yet shear-relaxation and aging experiments performed on the TEM grid (see Fig. S3, ESI†) suggest that the phase is long-lived, and thus a metastable or an equilibrium phase. At equilibrium, the observed coexistence would indicate an equality of the pressure and the chemical potential in the two phases. However, before a calculation could be made one would need to identify the dominant interactions controlling the system. A reasonable suggestion would be entropic interactions, known as osmotic depletion effect.²¹ Poulin *et al.*¹³ reported the observation of

macroscopic phase separation in hyaluronic acid–SWNT–water system, and attributed the effect to excluded volume (entropic) interactions. Yet, depletion interactions are intensified in the case of non-ionic surfactants, contrary to the observations presented here.²²

Extensive calculations show that depletion interactions would result in an oscillatory free energy whose minima are found at multiples of the spherical micelles diameter, they weaken with distance, and become negligible at an inter-particle distance of around 20 nm, see Fig. S4, ESI†. In addition, molecular calculations that include both electrostatic interactions and depletion forces (see ESI†) suggest that the overall interaction should be repulsive. Furthermore, they suggest that the addition of salt should screen the electrostatic repulsions and lead to dominance of depletion interactions, promoting SWNT alignment. The experimental observations, however, clearly show the opposite behavior. Namely, the attractions leading to the nematic-like ordering of the surfactant coated SWNT disappear at salt concentration above C_{thresh} . As described above (Fig. 1 and 3) the observed typical spacings are an order of magnitude higher than the characteristic Debye length and correspond to the spacing expected from a nematic phase of the native surfactant, if such a phase would have existed at the low concentrations described here. Furthermore, note that the observed alignment disappears upon the addition of salt to a concentration above C_{thresh} , though the surface packing of the surfactant is not destroyed (Fig. 3b). The combination of the experimental observations and the lack of agreement with the molecular calculations suggest that the origin of the nematic order is due to a novel long range electrostatic driven attraction. Moreover, its origin is probably similar to that of van der Waals attractions. Namely, it is of the type of induced dipole–dipole interactions that arise from the specific organization of the surfactants on the surface of the SWNT, and maybe partial adsorption of counterions. These attractions would not be modified by the charge of the solution micelles, thus a similar behavior is observed when either CTAB or the non-ionic surfactant Brij-78 comprises the bulk micelles. The latter observation suggests that these are not analogous to electrostatic attractions mediated by multivalent counterions.²³ However, note that the presence of a tightly packed charged surfactant layer at the surface of the SWNT is a necessary condition for the onset of SWNT alignment. Taking into account the described observations, we propose that the key observation pointing to the mechanism responsible for the formation of the aligned phase is the non-homogeneous coating of the SWNT by the surfactants. The latter results in an inhomogeneous distribution of charges, because the effective charge of the head-groups depends on the area per surfactant and on the local curvature.²⁴ Namely, surfactants in regions of concave curvature should exhibit a different degree of dissociation than those in convex regions. This charge distribution, which depends strongly on salt concentration²⁵ leads to the intertube attraction responsible for the alignment of the CNT.

To summarize, spontaneously formed microns-long islands of orientationally ordered SWNT in macroscopically homogeneous dispersions of ionic surfactants were observed *via* cryo-TEM. The islands of the nematic-like phase, with inter-tube distances of 16 to 25 nanometres, form in dispersions where spherical surfactant micelles co-exist with surfactant-coated individual SWNT. An unexpected first order transition was induced by an increased ionic strength. It is evident that the classical depletion interaction as such is not the origin of the observed phenomenon and the combination of

a good size matching between the surfactant micelles and the diameter of the dispersed nanostructures, as well as electrostatic interactions, are necessary for the onset of the unexpected behavior.

Experimental section

Materials and methods

Raw SWNT synthesized by arc discharge were purchased from Carbolex, Inc. USA (<http://carbolex.com>) (SWNT (AP) batch no: CLAP8420) and used as received. MWNT produced by Catalytic Chemical Vapor Deposition were purchased from INP (Toulouse, France). DWNT produced by chemical vapor deposition (CVD) process were purchased from Helix Materials Solutions Inc. CTAB (product no. H5882, 99% purity), Brij-78 (product no. P4019) and Triton \times -100 (product no. \times -100 batch#027K0127) were purchased from Sigma (Israel). SDS (product no. 71727, 99% purity) and CTAC (product no. 52366, 98% purity) were purchased from Fluka (Israel). All surfactants were used as received. KBr (product no. P5510, IR grade) was purchased from Sigma (Israel).

Methods

Aqueous surfactant solutions in concentrations of 0.3–10 wt% (surfactant in water) were prepared by dissolving the surfactant in water (Millipore water, resistance of 18.2 M Ω cm) at room temperature (25 °C). Liquid dispersions of SWNT, MWNT and DWNT were prepared by sonicating the powder of the raw material (typical concentration of 0.5–1.0 wt%) at very mild conditions (mini super-sonic cleaner, Delta DG-1, 50 W, 43 KHz) for 30–40 minutes in 1 wt% surfactant solution. The dispersions were centrifuged (at 4500 rpm for 30 min) and the supernatant was decanted from above the precipitate. Dispersions in higher surfactant concentrations were prepared by adding the surfactant to the dispersion. KBr in the desired concentration was added to the dispersion. Samples for cryo-TEM imaging were prepared by depositing a droplet of 5 μ L on perforated polymer film supported on a 300 mesh carbon coated electron microscope grid (copper, Ted Pella–lacey substrate). Ultra-thin films (10–250 nm) were formed as most of the solution was removed by blotting. The process was carried out in a controlled environment vitrification system where the temperature and the relative humidity are controlled using an automatic system termed Vitrobot (FEI). The samples were examined at -178 °C using a FEI Tecnai 12 G² TWIN TEM equipped with a Gatan 626 cold stage.

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Notes and references

- 1 M. S. Dresselhaus, G. Dresselhaus and Ph. Avouris, *Carbon Nanotubes, Topics in Applied Physics*, 80, Springer-Verlag, Berlin Heidelberg, 2001.
- 2 C. Joachim, J. K. Gimzewski and A. Aviram, *Nature*, 2000, **408**, 541.
- 3 J. N. Coleman, U. Khan and Y. K. Gun'ko, *Adv. Mater.*, 2006, **18**, 689.
- 4 M. Moniruzzaman and K. I. Winey, *Macromolecules*, 2006, **39**, 5194.
- 5 Y. Lin, et al., *J. Mater. Chem.*, 2004, **14**, 527.
- 6 V. C. Moore, M. S. Strano, E. H. Haroz, R. H. Hauge, R. E. Smalley, J. Schmidt and Y. Talmon, *Nano Lett.*, 2003, **3**, 1379.
- 7 H. Wang, *Curr. Opin. Colloid Interface Sci.*, 2009, **14**, 364.
- 8 I. Szleifer and R. Yerushalmi-Rozen, *Polymer*, 2005, **46**, 7803.
- 9 J. N. Israelachvili, *Intermolecular and Surface Forces*, Academic Press, London, 2nd edn, 1992.
- 10 V. Weiss, R. Thiruvengadathan and O. Regev, *Langmuir*, 2006, **22**, 854.
- 11 M. D. Lynch and D. L. Patrick, *Nano Lett.*, 2002, **2**, 1197.
- 12 X. Xin, et al., *Langmuir*, 2010, **26**, 3562.
- 13 S. E. Moulton, M. Maugey, P. Poulin and G. G. Wallace, *J. Am. Chem. Soc.*, 2007, **129**, 9452.
- 14 W. Song and A. H. Windle, *Macromolecules*, 2005, **38**, 6181.
- 15 W. H. Song, I. A. Kinloch and A. H. Windle, *Science*, 2003, **302**, 1363.
- 16 E. Nativ-Roth, O. Regev and R. Yerushalmi-Rozen, *Chem. Commun.*, 2008, 2037.
- 17 E. Nativ-Roth, R. Yerushalmi-Rozen and O. Regev, *Small*, 2008, **4**, 1459.
- 18 C. Richard, F. Balavoine, P. Schultz, T. W. Ebbesen and C. Mioskowski, *Science*, 2003, **300**, 775.
- 19 Y. Wu, J. A. S. Hudson, Q. Lu, J. M. Moore, A. S. Mount, A. M. Rao, E. Alexov and P. C. Ke, *J. Phys. Chem. B*, 2006, **110**, 2475.
- 20 Debye length is of less than 2 nm at these surfactant concentrations see for example: D. F. Evans and H. Wennerström, *The Colloidal Domain*, Wiley-VCH, 1994.
- 21 S. Asakura and F. Oosawa, *J. Chem. Phys.*, 1954, **122**, 1255.
- 22 F. Mondain-Monval, J. P. Leal-Calderon and J. Bibette, *Phys. Rev. Lett.*, 1995, **75**, 3364.
- 23 K. C. Lee, I. Borukhov, W. M. Gelbart, A. J. Liu and M. J. Stevens, *Phys. Rev. Lett.*, 2004, **93**, 128101.
- 24 R. Nap, P. Gong and I. Szleifer, *J. Polym. Sci., Part B: Polym. Phys.*, 2006, **44**, 2638.
- 25 P. Gong, J. Genzer and I. Szleifer, *Phys. Rev. Lett.*, 2007, **98**, 018302.