COMMUNICATION www.rsc.org/chemcomm | ChemComm

Self-assembled lamellar structures with functionalized single wall carbon nanotubes†

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Received (in Cambridge, UK) 22nd June 2007, Accepted 20th July 2007
First published as an Advance Article on the web 8th August 2007
DOI: 10.1039/b709499j

Highly ordered self-assembled multi-layer structures with denatured collagen wrapped single wall carbon nanotubes and surfactant systems were obtained through bioinspired methodology.

Lessons from living systems offer strategies for designing and synthesizing new solid state materials. In living systems, complex morphologies are obtained in a variety of length scales through cooperative self-assembly of organic and inorganic species. It remains a great challenge to mimic these natural pathways in order to synthesize new materials.

The interactions of nanomaterials with biomolecules and the formation of nano-bio hybrid complexes have only recently been studied and are still not well understood. Single wall carbon nanotubes (SWNTs) are among the most promising objects in the field of nanotechnology and nano-biotechnology.[1–3] Extensive interdisciplinary studies of SWNTs are underway due to their wide range of applications in materials science, sensor technology[4,5] and biomedicine including biochemical sensing[6–8] and substrates for *in vitro* nerve cell growth.[9,10]

Development of SWNT-based materials into engineered macroscopic systems is still at an early stage, since particular applications need unique processing routes. Nanotubes must be modified to achieve solubility and integration in ordered structures. In particular, their use for biomedical and biological applications requires their processing in aqueous media. For the synthesis of structures with preferential orientation containing SWNTs, the most successful methods include preparing fibers and ribbons of SWNTs,[11] polymers doped with SWNTs[12,13] and ionic-liquid-based surfactant and nematic liquid crystal functionalized SWNTs.[14–16] Evaporation assisted self assembly of SWNTs has also been explored on solid substrates like glass.[17,18] So a simple and easy way to form ordered structures with carbon nanotubes has been a major, unmet need for application perspectives.

In this communication we show that the *in situ* denaturation of type I collagen in the presence of sodium dodecyl sulfate (SDS) stabilized SWNTs leads to the wrapping of SWNTs by collagen peptide and thereby to solubility in water. The denaturation of collagen is probed by circular dichroism: the disappearance of a positive peak observed for the complex at 220 nm indicates the denaturation of the collagen (data not shown). Details of the synthesis procedure can be found in the supplementary information†. This water-soluble complex can self assemble into highly ordered lamellar structures on glass, mica and silicon by slow evaporation of the water. We have recently shown that this complex is very efficient for reinforcing the semicrystalline polymer polyvinyl alcohol.[19] The scheme for synthesizing the SWNTs/SDS/collagen complex is shown in Fig. 1.

The morphology of a monolayer of this complex on a mica surface has been characterized by AFM and by TEM by forming the monolayer on a carbon-coated TEM grid. The structure of the multilayers formed on glass and silicon has been characterized by X-ray diffraction.

A TEM micrograph of a monolayer formed by this complex on the grid is shown in Fig. 2, the SWNTs are clearly visible within the layer of the complex and these SWNTS are well wrapped with denatured collagen (inset of Fig. 2). From the figure it can be inferred that the SWNTs are well complexed with the SDS and collagen and embedded within the layer. To examine the morphology and to measure the thickness of the monolayer, AFM has been carried out on a monolayer formed on a mica surface by spin coating. Fig. 3a shows a topographical image of the monolayer, which has a uniform thickness of 40 Å. A topographical image of a multilayer formed on a microscope glass slide by slow evaporation of water is depicted in Fig. 3b. The layer was scanned near a scratch made by sharp knife in order to see the layered structure. We observe different layers with thickness equal to an integral multiple of 40 Å indicating a multilayer structure with each layer being 40 Å thick. It should be noted that in the case of the multilayer it is almost impossible to observe the SWNTs, possibly due to the fact that the nanotubes are well embedded within the layers. In order to observe the nanotubes, we heat the

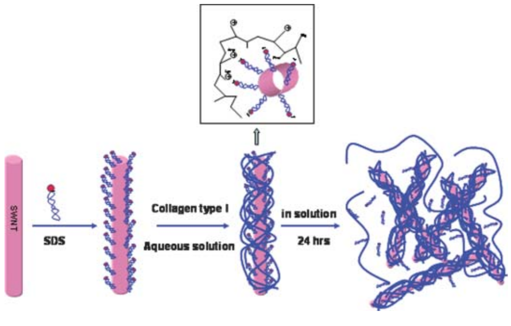

Fig. 1 Schematic diagram showing the synthesis of the SWNTs/SDS/collagen complex.

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† Electronic supplementary information (ESI) available: experimental. See DOI: 10.1039/b709499j

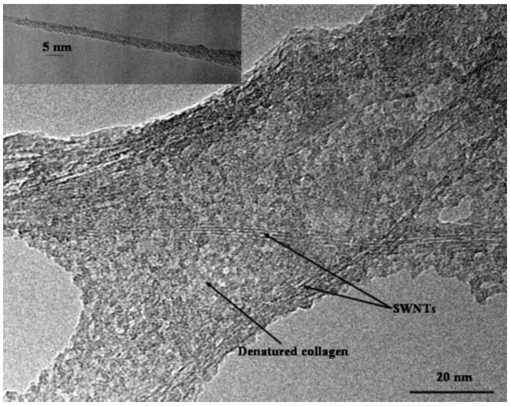

Fig. 2 TEM micrograph of monolayer of SWNTs/SDS/collagen complex.

sample at 350 °C in air for 2 h to destroy the structure and get rid of the collagen and after which the nanotubes are clearly visible on the substrate (see supplementary information†). To confirm the presence of the nanotubes within the multilayer structure and investigate their interactions with collagen and SDS we performed Raman spectroscopy on this sample. The characterization of SWNTs by Raman spectroscopy is well documented:[20] a typical spectrum contains two main regions of interest, one in the range of 100–300 cm^{-1} with several peaks arising from radial breathing mode (RBM),[21,22] and the other in the range of 1500–1600 cm^{-1}, the so-called G peak, arises from tangential C–C stretching vibrations both parallel and perpendicular to the nanotube axis.[23] A peak known as the D band, is found in the 1300–1400 cm^{-1} region and is attributed to scattering from sp^2 carbons associated with defects; its strength is related to the amount of disordered graphite and the degree of conjugation disruption in the graphene sheet.[24] Successful attachment of macromolecules to the SWNT surfaces results in an up shift of the G peaks due to an increase in the elastic constant of the functionalized SWNT.[25] Fig. 4 shows the Raman spectra of the multilayer structure formed on glass in which we can see all the characteristic peaks of SWNTs, proving the presence of SWNTs within the layers; the inset shows the up shift of G peak by 9 cm^{-1} for the SWNTs within the layered structure compared to the bare SWNTs used to prepare the complex. This result together with the increased intensity of the D peak, confirms that the SWNTs are interacting with the collagen and with the SDS.

X-ray diffraction (XRD) patterns of the films, with Cu K_α radiation with λ = 1.5418 Å, reveal a high degree of long-range order with peaks extending to 8th order (Fig. 5A). The average *d*-spacing is 40 Å. The XRD pattern is most consistent with a lamellar-phase structure with alternating surfactant and SWNTs wrapped in denatured collagen.[26,27] To go further in the structural investigation, samples deposited on thin silicon wafers have been studied using a 2D planar detector. We were able to record scattering patterns at small, medium and wide angles (Fig. 5B (a to c)), by choosing different distances between the sample and the two-dimensional detector. The results are displayed in Fig. 5B, where the incident beam was parallel to the substrate surface. The diffraction peaks resulting from the substrate and from a powder

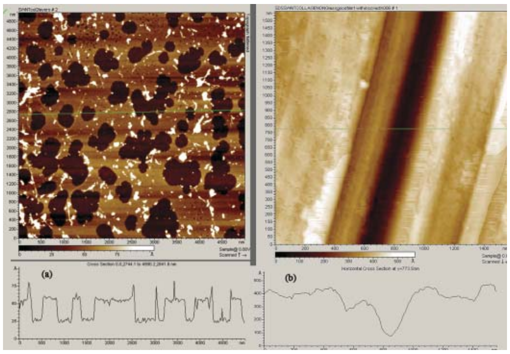

Fig. 3 AFM topograph of the (a) monolayer of the complex on mica, (b) multilayers on glass slide.

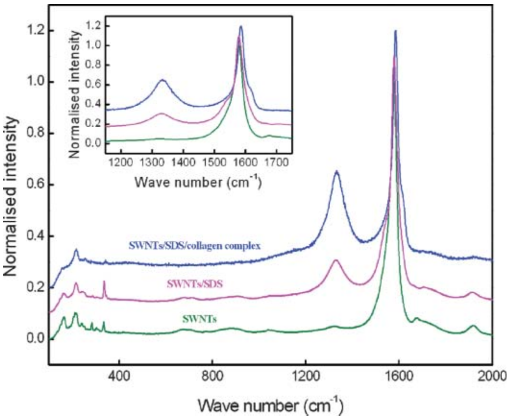

Fig. 4 Raman spectra of starting SWNTs, SWNTs/SDS and SWNTs/SDS/collagen complex taken with a laser of 633 nm wavelength.

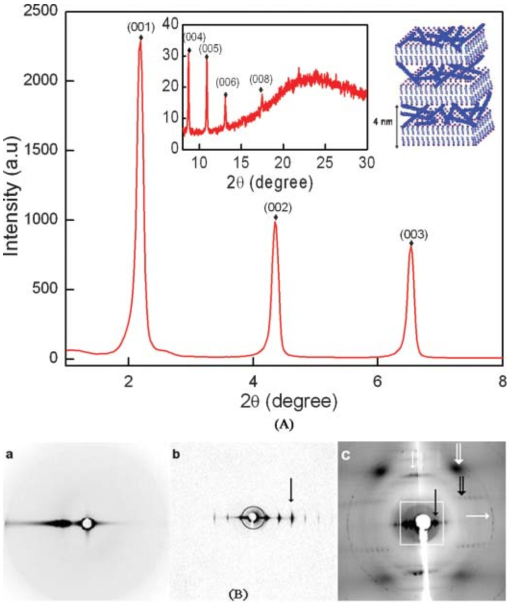

Fig. 5 (A) X-ray diffraction pattern of SWNTs/SDS/collagen multilayers structure on glass. The peaks from the lamellar phase structure are indexed and labeled with asterisks. (B) X-ray scattering patterns of a SWNT/SDS/collagen multilayer deposited on a silicon wafer. The scattering pattern (a) corresponds to the measurement in the *d* range of 50–500 Å, (b) and (c) correspond to the measurements in the *d* range of 10–70 Å. Black arrows point toward diffraction peaks characteristic of the lamellar structure, white arrow corresponds to the diffraction peak of another powder-like phase and double white arrow points toward the signal coming from the silicon substrate.

phase are indicated by white arrows (Fig. 5B(c)). No lower wavevector values having been observed, the powder-like phase should not contain nanotubes, since the diameter is of about 10 Å. The peaks indicated by black arrows located on the equatorial line in Fig. 5B (b) and (c) correspond to a lamellar period of about 40 Å, in good agreement with the pattern shown in Fig. 5A. The angular width of the spots in Fig. 5B(b) indicates the presence of lamellar regions slightly disorientated with respect to the substrate surface. Small angle X-ray scattering measurements shown in Fig. 5B(a), in the d range 50–500 Å, did not allow us to detect larger periodicity. In Fig. 5B(c), peaks corresponding to the 40 Å spacing in the horizontal direction are measured out of the equatorial plane, the period along the vertical direction being about 8.3 Å and corresponding to in-lamellae periodicity. Diffraction patterns taken for the sample perpendicular to the X-ray beam indicate that the structure is powder-like in two dimensions inside the lamellae. In brief, the SWNT/SDS/collagen multilayers are made of domains disordered in two-dimensions. As a reference, we studied a pure SDS sample prepared under the same conditions and found similar diffraction patterns. The ordered structure is thus related to the arrangement of the SDS molecules. This absence of modification of XRD pattern compared to bare SDS would suggest that most of the NT–collagen macromolecules are probably aggregated in grain boundaries. However, AFM investigations on mono, bi, tri layers and thick films do not agree with this picture. No aggregates of SWNTs were observed in any sample. Moreover, optical microscopy shows a good homogeneity of the deposits. Therefoe we suggest that most of the SWNTs wrapped up with collagen might be randomly incorporated in the hydrophilic part between SDS layers, without perturbing the interlamellar spacing. A similar observation has been made by Huang *et al.*[26] for silica/SDS lamellar composites. As already mentioned, calcination at 350 °C for 2 h removes all the organic species and destroys the complex, leaving behind only the inorganic SWNTs, with consequent loss of XRD peaks (not shown).

Gelatin (denatured collagen) has already been used for the dispersion of carbon nanotubes in water.[28,29] The strong interaction of gelatin and SDS demonstrated that the system behaves like a polyelectrolyte surfactant complex in solution.[30–32] In our case, a fraction of the SDS molecules are initially adsorbed hydrophobically onto the surface of the SWNTs and act as a denaturating agent for the collagen. The denaturation results in the wrapping of the SWNTs by collagen peptides; this complex interacts with rest of the SDS in solution in a manner similar to a polyelectrolyte/surfactant system. When the water is slowly evaporated this part of the SDS forms a lamellar structure incorporating the SWNTs wrapped in denatured collagen within the hydrophilic region of the structure. We have observed that, below a certain concentration of SDS, this lamellar structure cannot be formed. In that case all the surfactant molecules are adsorbed on the SWNT surfaces and none are available to interact with denatured collagen wrapped SWNTs.

In conclusion, we have demonstrated a simple and easy way to functionalize SWNTs which are well dispersed in an aqueous environment. Highly ordered lamellar structures can be formed with this material by evaporation-assisted self assembly on solid substrate. These structures could have potential applications in electronics and bio-nanotechnology, especially in the field of biosensors.

Authors would like to acknowledge Jean-Claude Maurizot of CBM, Orleans for CD measurement, Patrick Davidson and Doru Constantin from Laboratoire de Physique des Solides at Orsay, for their help in SAXS experiments.

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