Hierarchical carbon nanotube assemblies created by sugar–boric or boronic acid interactions†

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We previously found that polysaccharide "schizophyllan (SPG)" can entrap as-grown and cut single-walled carbon nanotubes (as-SWNTs and c-SWNTs, respectively): we here reported that the c-SWNT–s-SPG (single stranded SPG) composites thus obtained can be aligned regularly using the covalent bond formation between boric acid or boronic acid derivatives and the 4,6-dihydroxyl group of the glucose side-chain unit.

Since the discovery of single-walled carbon nanotubes (SWNTs),[1] they have been postulated as a potential source of new functional materials. However, their strong cohesive nature and poor solubility have caused researchers trouble for a long time as these properties seriously hamper efforts to obtain reproducible data in solution. Therefore, many research efforts have been directed towards the solubilization or dispersion of SWNTs in solvents.[2–4] However, controlled ordering of these discretely dissolved SWNTs, in order to design various SWNTs-based functional materials, is in its infancy.[5]

Schizophyllan (SPG) is a natural polysaccharide produced by the fungus *Schizophyllum commune*, and its repeating unit consists of three β-1,3-glucoses and one β-1,6-glucose side-chain linked at every third main-chain glucose (Fig. 1a). SPG adopts a triple helix (t-SPG) in nature, which can be dissociated into a single chain (s-SPG) by dissolving in dimethyl sulfoxide (DMSO). The s-SPG chain can recover the original triple helix by exchanging DMSO for water (Fig. 1b). Similar properties were observed for t-curdlan and s-curdlan which have a β-1,3-glucan main-chain structure but no side-chain substituent (Fig. 1a). We recently demonstrated that natural polysaccharide β-1,3-glucans act as one-dimensional hosts for hydrophobic guest polymers, such as single-walled carbon nanotubes (SWNTs),[6] poly(aniline),[7] and poly(thiophene),[8] and encapsulate them in the tubular hollow constructed by the helical structure inherent to β-1,3-glucans,[9] resulting in the creation of water-soluble one-dimensional nanocomposites. If the functional group on the surface of these nanocomposites can be utilized as an interaction site for the construction, they would acquire a potential self-assembling ability to create the specific hierarchical superstructures. It thus occurred to us that the SPG–SWNT composites may be aligned using the sugar–boric or boronic acid interactions: that is, in the side-chain glucose unit of SPG the 4-OH and the 6-OH group remain unsubstituted and can form cyclic complexes with boric acid or boronic acid derivatives.[10] In other words, they may act as covalently-bonded "Velcros" to align SWNTs wrapped by polysaccharide sheaths. We here report that SPG–SWNT composites are regularly aligned in aqueous solution in one dimension in the presence of boric acid or di- and tetra-boronic acid derivatives but not in the presence of mono-boronic acid derivatives (Fig. 1c). To the best of our

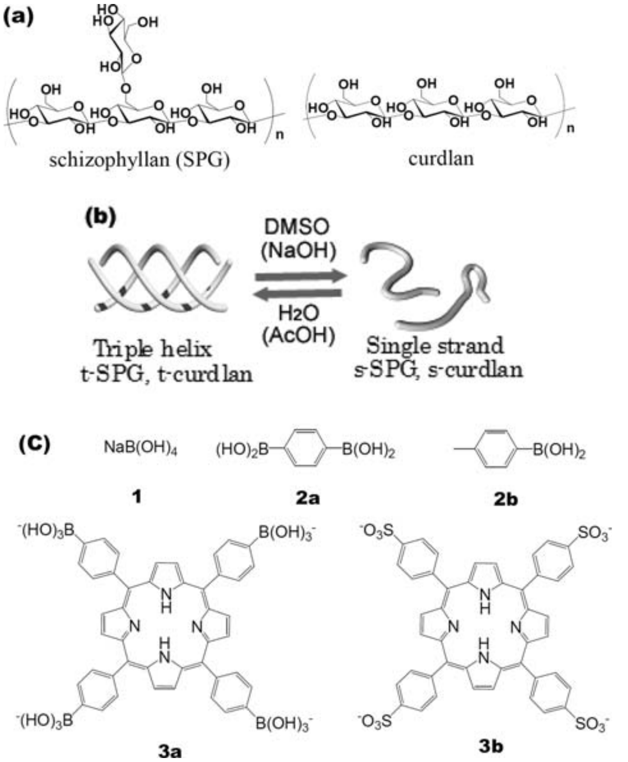

Fig. 1 (a) Chemical structure of SPG and curdlan, (b) renature and denature processes of SPG and (c) chemical structure of boric acid and boronic acids.

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† Electronic supplementary information (ESI) available: SEM images of c-SWNT–**1** composites, additional TEM images, absorption, CD, fluorescence spectra and POM images of c-SWNT–**3a** composites. See DOI: 10.1039/b808599d

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knowledge, this is the first example where SWNTs have been aligned by specific covalent bond formation.

SWNTs cut to 1–2 μm length (c-SWNTs: for the preparation see ref. 11) dispersed in an aqueous solution (1000 μL) were mixed with 200 μL of a DMSO solution containing s-SPG (5.0 mg mL^{-1}, M_w = 150 000). At this stage, the water–DMSO mixed solution contained 300–600 μg mL^{-1} of c-SWNTs and 830 mg mL^{-1} of s-SPG, and the composition of water–DMSO (v/v) was 84 : 16 (v/v). After being left for 2 days at room temperature, the mixture was treated in a centrifuge (8000 G) for 1 h and the supernatant containing uncomplexed s-SPG was pipetted off. The precipitated c-SWNT–s-SPG composites were recovered and then dispersed into water (400 μL). After repeating this centrifugation process five times, a clear aqueous solution was obtained. The pH of the solution was 7.8. The c-SWNT–s-curdlan (M_w = 9570) composites were prepared using the same procedure. An aqueous solution (400 μL) containing sodium tetrahydroxyl borate decahydrate (**1**: 400 μL, 0.5 mg mL^{-1}) was added to the aqueous solution containing c-SWNT–s-SPG composites or c-SWNT–s-curdlan composites. The pH of the final solution was estimated to be 9.3. As the borate ion forms covalently-bonded complexes with 1,2-diol and 1,3-diol groups at this pH,[10] it should also form complexes with the side-chain glucose in SPG. The samples thus obtained were subjected to transmission electron microscopy (TEM) observations.

It is seen from the results of TEM observation that in the presence of **1** the c-SWNT–s-SPG composite gives sheet-like structures with periodical stripes (Fig. 2a). We could recognize the sheet-like structure extending several micrometres, the size of which is almost consistent with that observed in scanning electron microscopy (SEM) images (Fig. S1†). On the other hand, this kind of ordered structure could not be obtained either from the c-SWNT–s-SPG solution without **1** (Fig. 2d) or from the c-SWNT–s-curdlan solution with **1** (Fig. S2†). These differences clearly support the view that the presence of both the side-chain glucose and **1** is indispensable to form this ordered structure. From the aqueous solution containing t-SPG and **1**, we could not obtain the sheet-like structure (Fig. S2†). From high resolution TEM (HR-TEM) observations (Fig. 2b), we confirmed the highly regular alignment of fibers in the sheet-like morphology, and the electron diffraction pattern revealed that this sheet-like morphology has some crystalline nature, suggesting that the components are tightly packed. The distance between the periodical dark lines could be estimated to be 2.0 nm by utilizing the Fourier-filtered image, the value of which was consistent with that estimated from the periodical pattern of Fig. 2c. One may propose, therefore, that **1** can act as a "covalent Velcro" to assemble and order the c-SWNT–s-SPG composites, as illustrated in Fig. 2e.

To further confirm the above proposal, we employed phenyl-1,4-diboronic acid (**2a**). We could observe a c-SWNT-ordered structure, like that in Fig. 2b, with periodical stripes for the c-SWNT–s-SPG composite (Fig. S3†). On the other hand, such an ordered structure was not formed at all in the presence of 4-methylphenylboronic acid (**2b**) (Fig. S3†). These results indicate that the prerequisite for the "covalent Velcro" is a bifunctional diboronic acid capable of cross-linking c-SWNT–s-SPG composites. Under boric conditions **1** can act as the equivalent of a diboronic acid.

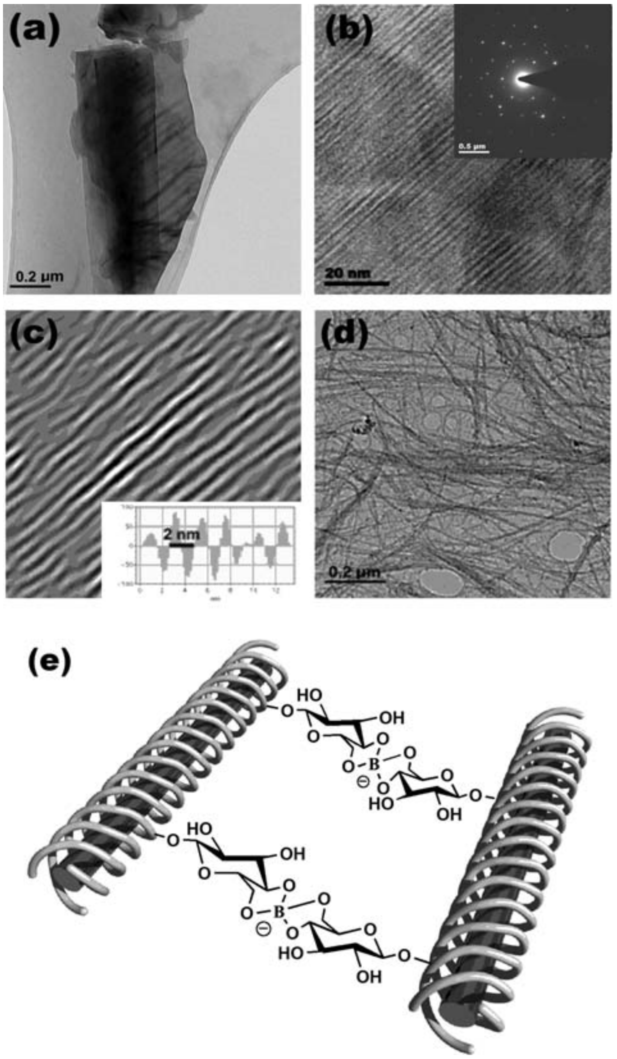

Fig. 2 (a) TEM images of c-SWNT–s-SPG with **1**, (b) HR-TEM image of c-SWNT–**1** composites (inset: electron diffraction pattern obtained from the sheet), (c) Fourier translation image of c-SWNT–s-SPG with **1** composite and an extracted periodical pattern, (d) TEM image of c-SWNT–s-SPG without **1** and (e) schematic illustration of c-SWNT–s-SPG cross-linked by **1**.

5,10,15,20-Tetrakis(4-boronylphenyl)porphine (**3a**) has frequently been used as a molecular sensor for saccharides dissolved in water.[12] As **3a** has four boronic acid groups, the porphyrin rings may be arranged in a one-dimensional fashion among the ordered c-SWNT–s-SPG composites with the aid of the boronic acid–side-chain glucose interaction. As a reference compound, we used 5,10,15,20-tetraphenyl-21*H*,23*H*-porphine-p,p',p'',p'''-tetrasulfonic acid tetrasodium salt hydrate (**3b**) which cannot form any covalent bond with the side-chain glucose. The sample solution was prepared by mixing a DMSO solution (12.8 μL) containing **3a** or **3b** (1.0 mg L^{-1}) and an aqueous carbonate (0.10 mol L^{-1}) solution (787 μL) with an aqueous c-SWNT–s-SPG composite solution (900 μL). The pH of the final solution was 9.9, which is suitable for complexation between the boronic acids and the side-chain glucoses. In the

TEM images (Fig. S4†), one can again recognize the presence of a well-ordered stripe structure. Interestingly, the morphology features moiré fringes which are scarcely seen for the superstructures created from **1**- or **2a**-cross-linked c-SWNT–s-SPG composites. The presence of the moiré fringes could be further confirmed by the HR-TEM image (Fig. S4†): the distance between the stripes is about 2.4 nm. This distance is in accord with the sum of the t-SPG (1 nm), c-SWNT (1 nm) and **3a** sizes. These findings indicate that the distance between the stripes can be controlled by the size of cross-linking boronic acid derivatives.

The presence of **3a** in the sheet-like morphology was confirmed by energy-dispersive X-ray (EDX) spectroscopy. Fig. S4 shows an EDX spectrum of the c-SWNT–s-SPG composite with **3a**.† Several elements (N, O, Cu and Si) were detected from the EDX spectrum. Particularly, the presence of nitrogen strongly supports the view that **3a** exists in the morphology observed by the TEM observations. On the other hand, the presence of SWNTs in the ordered structure was clearly evidenced by Raman spectroscopy (Fig. S5†). An aqueous solution of the c-SWNT composite with **1** was cast on a glass plate and dried under reduced pressure. A radial breathing mode (RBM) peak (205 cm^{-1}), a D band (1348 cm^{-1}) and a G band (1610 cm^{-1}) could be seen in the Raman spectrum. This result indicates that c-SWNTs exist in the sheet-like morphology obtained from TEM. We could obtain the similar results from the c-SWNT–s-SPG composite with **3a** (Fig. S5†).

Fig. S6 indicates the results of absorption, circular dichroism (CD) and fluorescence spectroscopies of **3a** in the presence and the absence of the c-SWNT–s-SPG composite.† In the absorption spectra, the Soret band maximum decreased with the increase in the concentration of the c-SWNT–s-SPG composite (Fig. S6(a)). Such a change was not observed for **3b** at all. Fig. S6(b) shows the CD spectra. One can confirm that **3a** becomes CD-active in the presence of the c-SWNT–s-SPG composite: an intense split-type ICD appears at 428 nm, which is close to the absorption maximum of the Soret band. This implies that **3a** interacts with s-SPG and is chirally oriented. As expected, such an ICD was not observed for **3b**. These results strongly support the view that the interaction between the c-SWNT–s-SPG composite and **3a** occurs *via* covalent bond formation between the side-chain glucoses of s-SPG and the boronic acid groups in **3a**. The fluorescence spectra are shown in Fig. S6(c). Interestingly, the drastic fluorescence intensity decrease was observed only for the combination of the c-SWNT–s-SPG composite and **3a**. The finding again supports the view that **3a** is in close proximity to the c-SWNTs owing to the covalent bond formation with s-SPG and efficient energy transfer is taking place from **3a** to the c-SWNTs.

In conclusion, we have achieved regular organization of c-SWNT–s-SPG composites by the ‘‘chemical reaction’’ between boric or boronic acid derivatives and the side-chain glucose units of SPG. Undoubtedly, this is a very convenient method to assemble one-dimensional architectures into two- and three-dimensional ones. Taking the reversibility of boronic acid–sugar interactions into account, superstructure formation should be reversibility controlled by the medium's pH. In addition, as various boronic acid derivatives are already available, one can design various superstructures, by simply changing the structure of boronic acid cross-linkers.

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