

# Facile preparation of stabilized polymeric nanotubes using sacrificial yttrium hydroxide nanotubes as template and block copolymer micelles as precursor†

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We report here facile preparation of stabilized polymeric nanotubes with a hair-like shell using yttrium hydroxide nanotubes as the sacrificial template and block copolymer micelles as the precursor, and orientation of the polymeric nanotubes encapsulating magnetic particles under magnetic field.

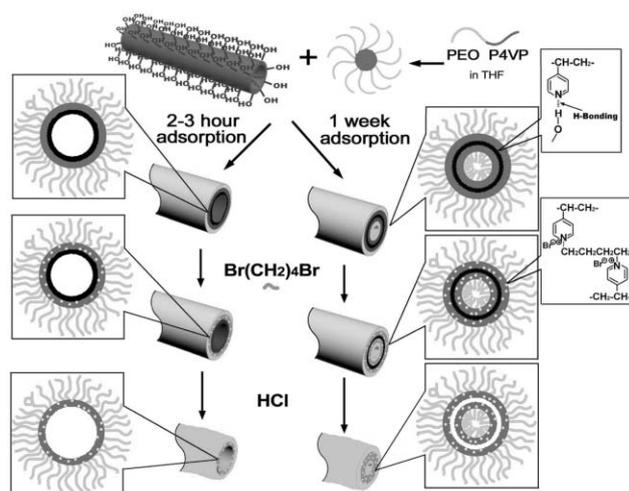
Polymeric nanotubes (PNTs) have drawn a lot of scientific attention due to their diverse applications in advanced materials, controlled drug delivery and biotechnologies.<sup>1–3</sup> A number of approaches have been reported to prepare PNTs. Self-assembly of a rod-coil block copolymer with designed structure parameters in a selective solvent for the coil block forms PNTs directly.<sup>4</sup> Cross-linking the outer layer of cylindrical domains formed *via* self-assembly of ABC triblock copolymers and then degrading the core of the cylinder can also produce PNTs.<sup>5</sup> Besides, template-directing approaches for preparing PNTs have been developed with membranes with cylindrical pores used as the templates.<sup>6</sup> When nano-rods or nano-wires were used, layer-by-layer method<sup>7,8</sup> or polymerization of a styrene layer surrounding the nanorods, which were dispersed in water by a surfactant, was applied.<sup>9</sup> Both assembly-based and template-directing methods have their advantages. The former leads to PNTs with a distinct hierarchical structure and the latter is usually more efficient and allows facile control over the size of PNTs.

Herein, we report a novel facile approach to the preparation of PNTs with a hierarchical structure (*i.e.* PNTs with a hair-like shell) in a relatively large quantity using yttrium hydroxide nanotubes (YNTs) as the sacrificial template and poly(ethylene oxide)-*block*-poly(4-vinylpyridine) (PEO-*b*-P4VP) micelles as the precursor. This approach involves the following steps: (1) YNTs were mixed with the block copolymer micelles in THF. After the mixing, the micelles transformed to a block copolymer layer coated on the surface of YNTs due to adsorption of a P4VP layer on the surface, resulting in water-dispersible hybrid nanotubes (HNs). (2) After cross-linking the adsorbed P4VP layer, HNs were readily purified by centrifugation and then dissolved in water. By removing the template, PNTs were prepared (Fig. 1). The as-prepared PNTs were stabilized by the cross-linking and had a single walled or a

tube-in-tube structure, depending on the time interval allowed for the adsorption of the micelles on the surface of YNTs. It is confirmed that the PNTs can be dissolved in water at various pH and ionic intensities as well as in many organic solvents. Besides, these PNTs are capable of encapsulating functional species. By encapsulating a large amount of magnetic particles, they can be oriented under a magnetic field.

YNTs with a diameter of *ca.* 200 nm and an inner diameter (the diameter of the channel) *ca.* 80 nm (S1 in ESI†) were prepared according to the procedures reported.<sup>10</sup> PEO-*b*-P4VP was synthesized by ATRP and purified according to ref. 11. The molecular weight (MW) and MW polydispersity (PDI) of PEO is 5000 and 1.02, respectively. The MW of the P4VP block is 6500 based on <sup>1</sup>H NMR characterization and PDI of the block copolymer is 1.13 measured by GPC using DMF as the fluent.

Cöfen *et al.* reported that P4VP blocks above a certain MW are insoluble in THF.<sup>12</sup> The polymeric micelles formed by PS (polystyrene)-*b*-P4VP in THF with P4VP as the core were also reported by Antonietti *et al.* (in one of the polymers used to form the micelles, MW of the P4VP block was 6900).<sup>13</sup> In the present study, we found that a 0.5 mg mL<sup>-1</sup> solution of PEO-*b*-P4VP in THF showed a light opalescence. Dynamic light scattering (DLS) measurement revealed the formation of polymeric micelles with an average hydrodynamic diameter  $\langle D_h \rangle$  of 62.4 nm. Our TEM observations also confirmed the formation of PEO-*b*-P4VP micelles in THF (S2, ESI†). It is known that PEO block chains have a good solubility in THF.‡ Therefore, the micelles formed in



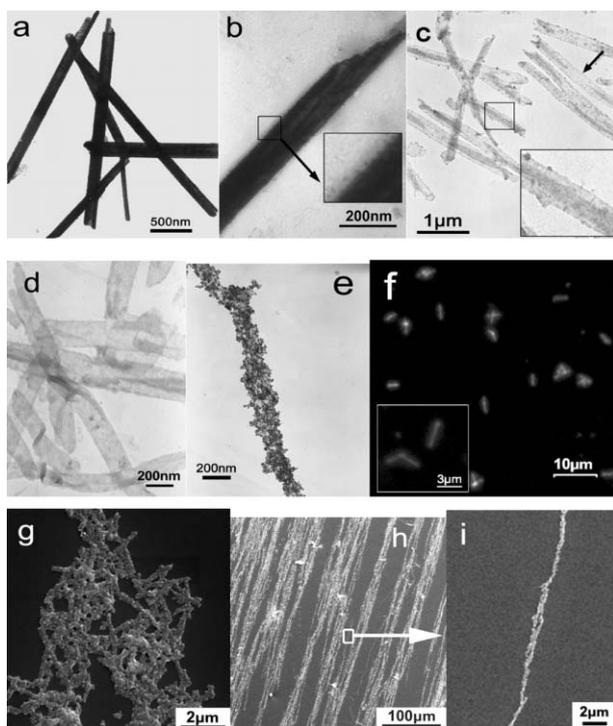
**Fig. 1** Procedures to prepare polymeric nanotubes using inorganic nanotubes as the template and polymeric micelles as the precursor.

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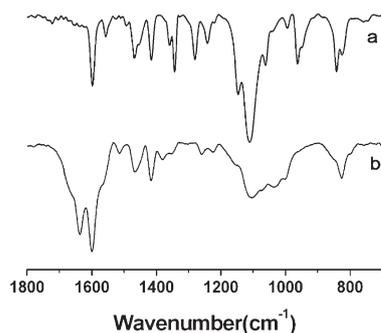
THF are with P4VP as the core and PEO as the shell. On the other hand, pristine YNTs are insoluble in THF. However, mixing 500 mg YNTs with 500 mL THF solution containing 250 mg PEO-*b*-P4VP led to dispersion of YNTs in THF. After the mixing, the PEO-*b*-P4VP micelles transformed into the block copolymer layer composed of a dense P4VP inner layer and an extended PEO outer layer surrounding YNTs, detailed as below. FT-IR characterization demonstrated that the adsorption of the P4VP layer on the surface of YNTs was due to the hydrogen bonding between the pyridine units of the P4VP block and surface hydroxyl groups of YNTs (S3, ESI†). The hydrogen bonding between surface hydroxyl groups of solid silica and pyridine units of P4VP was reported previously.<sup>14</sup> Under gentle stirring, HNs can be individually dispersed in THF for weeks, due to the solubilization of the PEO block chains. The adsorbed P4VP layer was locked by chemically cross-linking P4VP chains with excess 1,4-dibromobutane (the molar ratio of 1,4-dibromobutane to the pyridine units is 16/1) at 40 °C for 48 h.<sup>15</sup> After the cross-linking, HNs were still individually dispersed in THF since no considerable change in the  $\langle D_h \rangle$  during the cross-linking reaction was detected by DLS. The block copolymer layer surrounding YNTs was observed by TEM after the layer was stained by H<sub>2</sub>AuCl<sub>4</sub> (H<sub>2</sub>AuCl<sub>4</sub> can complex with the pyridinium and/or pyridine units. The molar ratio of H<sub>2</sub>AuCl<sub>4</sub>/ (pyridine + pyridinium) is 1/10). Due to the staining, in the TEM images, a polymer layer surrounding YNTs with a low contrast was observed (Fig. 2(b)), whereas the pristine YNTs do not show such a layer (Fig. 2(a)).



**Fig. 2** TEM images of (a) pristine YNTs, (b) PEO-*b*-P4VP/YNT with the adsorbed P4VP layer being cross-linked and then stained by H<sub>2</sub>AuCl<sub>4</sub>, (c) PNTs with a tube-in-tube structure, (d) single walled PNTs, and (e) a PNT encapsulating magnetic particles (MPs); (f) Confocal fluorescence microscopy images of PNTs encapsulating a fluorescent dye; SEM images of (g) PNTs encapsulating MPs and (h, i) their orientation under a magnetic field.

After the cross-linking, HNs in THF were purified by centrifuging the solution at 1000 rpm for 5–10 min and then discarding the supernatant solution. An additional two cycles of dispersing the sediments in THF and subsequent centrifuging were applied to guarantee the purity of HNs. 550 mg of as-purified HNs were dissolved in 500 mL water, followed by addition of 44 mL of hydrochloric acid (38%, w/w) to remove the template. 3 min after the addition, the mixture solution was dialyzed against water to remove YCl<sub>3</sub> (S4, ESI†). Finally, individually dispersed PNTs were obtained, as evidenced by TEM observations (Fig. 2(c), (d)). We found that the as-prepared PNTs had either a single walled (Fig. 2(d)) or a tube-in-tube (Fig. 2(c)) structure, depending on the length of the time interval between the mixing of the micelles with YNTs in THF and the cross-linking reaction, which allowed for the adsorption of the block copolymer on the surface of YNTs. When the time interval was 2–3 h, single walled PNTs were produced; whereas when extended to 6–7 days, PNTs with a tube-in-tube structure were obtained. The latter should result from the adsorption on both the outer and the inner surfaces of YNTs. It is noted that, in the PNTs with a tube-in-tube structure, the *inner tube* breaks at the middle of the PNTs (indicated by the arrow in Fig. 2(c)). Obviously, the block copolymer layer adsorbed in the channel near the ends of YNTs made further diffusion of the block copolymer in the channel difficult. We further confirmed that in PNTs with either a single walled or a tube-in-tube structure, the template was removed completely because the X-ray energy diffraction (EDX) analysis focused on a PNT detected no yttrium (S5, ESI†).

In the present study, the PEO-*b*-P4VP micelles in THF were used as the precursor. Although only one block copolymer layer was adsorbed on the surface of YNTs, fully formed PNTs were produced (Fig. 2(c) and (d)). However, in a control experiment, when we replaced THF by chloroform and prepared PNTs under the same conditions and procedures, pieces of the polymer layer rather than fully formed PNTs were mostly obtained, based on TEM observations (chloroform is the usual solvent for PEO-*b*-P4VP). DLS characterization detected no aggregates in solutions of the block copolymer in chloroform (*i.e.* the PEO-*b*-P4VP was molecularly solubilized in chloroform). We believe that the P4VP layer resulting from direct adsorption of the micelles in THF is denser than that formed by adsorbing free chains of the same block copolymer in chloroform. Actually, in THF the density of the adsorbed P4VP layer is comparable to that of the core of the micelles; while in chloroform, when the free chains (the random coils) of the block copolymer adsorb individually onto the surface of YNTs, it will be difficult to form such a dense layer. We noted that the adsorption of polymeric micelles from solution on substrate surfaces has been extensively studied.<sup>16–21</sup> It was stated that in the cases that the interaction between core-forming block chains of polymeric micelles and surface of substrate was strong enough to overcome the repulsion between the shell-forming block chains and the surface, the micelles transformed into a layer composed of a dense inner interacting layer and an extended outer layer on the surface.<sup>16</sup> In the present study, we believe that the hydrogen bonding interaction between the surface hydroxyl groups of YNTs and the pyridine units of the P4VP core of the micelles are strong enough to form a dense P4VP inner layer on the surface of YNTs. The adsorption of one of the micelles may involve the following steps: (1) the pyridine units in the P4VP core



**Fig. 3** FTIR spectra in the range of 700–1800  $\text{cm}^{-1}$  of (a) pure PEO-*b*-P4VP copolymers and (b) the resultant PNTs.

near the core–shell interface contacted with the surface of YNTs due to the fluctuation of the shell-forming PEO block chains<sup>22</sup> and thus some of the pyridine units were hydrogen bonded by the surface hydroxyl groups; (2) with more and more pyridine units in the core being hydrogen bonded, the micelle deformed and finally spread on the surface.

As mentioned before, the PNTs were obtained by removing YNTs in HCl aqueous solution and subsequent dialysis against water. As the block copolymer was prepared using PEO-Br as the macroinitiator, the PEO and P4VP blocks were linked by an ester bond. The etching and dialysis possibly led to breaking of the ester bond and leaving of the PEO block chains from PNTs. We characterized the PNTs after the dialysis by FT-IR (Fig. 3(b)) (the FT-IR spectrum of PEO-*b*-P4VP is shown in Fig. 3(a)). The peaks at 1110 and 1600  $\text{cm}^{-1}$  in both spectra are assigned to the stretch vibration of the C–O bonds of the PEO and that of the pyridine rings of the P4VP, respectively. The peak at 1639  $\text{cm}^{-1}$  in spectrum (b) is associated to pyridinium in PNTs while the peak at 1100  $\text{cm}^{-1}$  in spectrum (b) reveals the presence of PEO block chains in PNTs. As the solution was contained in a dialytic bag with 14 kDa cut-off membrane and dialyzed against water for 3 days (S4, ESI†), the PEO chains (MW = 5000) unconnected with the PNTs should have been removed. In other words, the peak at 1100  $\text{cm}^{-1}$  in spectrum (b) should be assigned to the PEO block chains grafting on the cross-linked P4VP tubular layer. From spectrum (b) we can also see the coexistence of the pyridinium and pyridine signals. Therefore, in PNTs the P4VP block chains were only partially cross-linked.<sup>15</sup>

The as-prepared PNTs with a hierarchical structure in which PEO block chains graft on the cross-linked P4VP tubular layer exhibited good solubility in solvents such as chloroform, DMF, THF, methanol, ethanol, water and 1 M aqueous solutions of NaCl, HCl and NaOH. This should be related to the solubilization of the hair-like PEO shell. Besides, the PNTs are capable of encapsulating species that can complex with the pyridinium groups. For example, the fluorescent dye, potassium 3,4,9,10-perylenetetracarboxylate, was encapsulated in the PNTs (Fig. 2(f)). Citrate capped magnetic particles (MPs)<sup>23</sup> with a diameter *ca.* 10 nm were also encapsulated (Fig. 2(e) and (g)) due to the interaction between the  $\text{COO}^-$  groups on the surface of MPs and the pyridinium in PNTs. In Fig. 2(e) and (g), we can see that each of the PNTs encapsulates a large amount of MPs. This implies that, in a dilute solution, each of the PNTs carries a large amount of net charge since it contains positive charges (the pyridinium cations) only. SEM observations demonstrated that without a

magnetic field, the PNTs/MPs were randomly located on the surface of mica (Fig. 2(g)). When under a magnetic field, all the PNTs were oriented (Fig. 2(h)). The SEM image at a large magnification (Fig. 2(i)) reveals that the nano-objects oriented are the PNTs encapsulating MPs *rather than* MPs alone. We also confirmed that the PNTs encapsulating a large amount of MPs could be separated from a solution conveniently under a magnetic field.

In conclusion, we have prepared PNTs using YNTs as the sacrificial template and PEO-*b*-P4VP micelles as the precursor. The adsorption of the micelles on the surface of YNTs formed a dense P4VP inner layer and an extended PEO outer layer surrounding YNTs, so that cross-linking the P4VP layer and removing the template resulted in integrated PNTs with a hair-like shell. The PNTs are capable of encapsulating a large amount of negatively charged species. When PNTs encapsulated a large amount of magnetic particles, they can be oriented under a magnetic field or separated from the solution. We believe the results will generate much interest of researchers in fields such as nanotechnology, material chemistry and physics.

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## Notes and references

† In a control experiment, we confirmed that PEO<sub>329</sub>-*b*-P2VP<sub>128</sub> can be molecularly solubilized in THF. This indicates that PEO block chains with even a larger molecular weight are soluble in THF. Different from P4VP, P2VP block chains are soluble in THF.

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