

## NOTE

# Noncovalent functionalization of boron nitride nanotubes using water-soluble synthetic polymers and the subsequent preparation of superhydrophobic surfaces

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In recent years, one-dimensional (1-D) nanomaterials have attracted scientific interest from a broad range of fields because of their diverse physicochemical properties and their broad range of prospective applications.<sup>1</sup> Carbon nanotubes (CNTs) are a well-known 1-D nanomaterial<sup>2</sup> and show promise for applications in many electronic, optical, bio-related, and composite materials fields. Specifically, the use of CNTs as essential building substrates (or blocks) for protein immobilization<sup>3</sup> in biological devices and for polymer composites in hydrophobic materials<sup>4</sup> have been widely studied. However, the optoelectronic properties of CNTs are complex functions of tube chirality, diameter, and length, and this complexity is a disadvantage in many cases.<sup>5</sup> For polymer composite applications, the interfaces between CNTs and the polymer play a key role in the successful fabrication of high-performance materials; however, the control of such interfaces is difficult, mainly owing to the sidewalls of CNTs being inert.

Boron nitride nanotubes (BNNTs) have a geometry similar to CNTs, except that the C atoms in the graphene networks of CNTs are substituted with B and N atoms in BNNTs.<sup>6</sup> In contrast to CNTs, both theoretical and experimental investigations have verified that BNNTs possess a stable electrical band-gap independent of the tube chirality, diameter, and length.<sup>6</sup> The combination of their superb resistance to oxidation and a much high thermal stability than CNTs make BNNTs a notably promising nanomaterial in materials science and nanotechnology.<sup>6</sup> Moreover, recent studies have suggested that BNNTs strongly interact with polymers due to tube polarization originating from the broken symmetry of B-N bonds.<sup>7</sup> Such unique properties make BNNTs more suitable than CNTs as building

substrates (or blocks) for integration with various polymers when the goals are immobilizing proteins<sup>8</sup> and fabricating composite materials with superhydrophobic surfaces.<sup>9</sup>

However, progress toward the actual application of BNNTs is hindered because pristine structures frequently exist as entangled bundles as a result of strong van der Waals forces, and BNNTs are therefore not dispersible in conventional organic and aqueous solvents.<sup>6</sup> Hence, the chemical functionalization of BNNT sidewalls to make them disentangled and dispersible in various solvents should lead to a significant breakthrough. Both covalent<sup>10</sup> and noncovalent<sup>11</sup> approaches have been developed to overcome these problems. In comparison to covalent approaches, noncovalent ones have a minimal impact on the original properties of BNNTs, and may be the better choice in many cases.<sup>11</sup> In this paper, we compare the ability of representative water-soluble synthetic polymers to disentangle and disperse BNNTs in an aqueous phase and find that polymers with conjugated and/or aromatic structures work efficiently via noncovalent  $\pi$ - $\pi$  stacking interactions. Although it has been reported that water-soluble poly(*p*-phenyleneethynylene) disperses CNTs well in water via helical wrapping,<sup>12</sup> information on the dispersion of BNNTs by water-soluble synthetic polymers is still limited. To test the feasibility of a new potential application of a BNNT-polymer mixture, we converted cast films (composed of polymer-functionalized BNNTs) into superhydrophobic surfaces by a chemical conversion of the adhered original polymers.

Conjugated polymers have been used extensively in the fabrication of composite materials and organic electronic devices.<sup>13</sup> The existence

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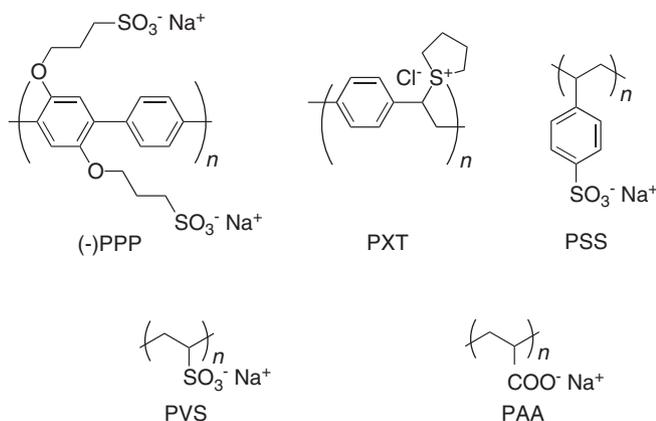
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of  $\pi$ -electrons in their main chains allows preferable  $\pi$ - $\pi$  stacking configurations to form. On the other hand, the incorporation of different functional groups in their side chains makes them selectively dissolvable in either polar or nonpolar solvents. In this sense, the functionalization of BNNTs with water-soluble conjugated polymers enables BNNTs to be dispersed in an aqueous phase. Here, five types of water-soluble polymers were tested, including a conjugated poly (*p*-phenylene) derivative ((-)-PPP) and four other polymers: poly(xylylene tetrahydrothiophenium chloride) (PXT), poly(sodium styrene sulfonate) (PSS), poly(sodium vinyl sulfonate) (PVS) and poly(sodium acrylate) (PAA). (-)-PPP was one of the polymers tested here not only because it is water-soluble but also because it can form self-assembled macrostructures<sup>14</sup> and has negatively charged side chains (due to sulfonate groups). The chemical structures of all of the polymers used here are shown in Scheme 1. In a typical experimental run, pristine BNNTs were mixed with aqueous solutions containing polymers, followed by sonication for dispersing the mixture. Then, the mixture was centrifuged to remove any insoluble materials, and the supernatant was collected for further characterization (see Supplementary Information for details).

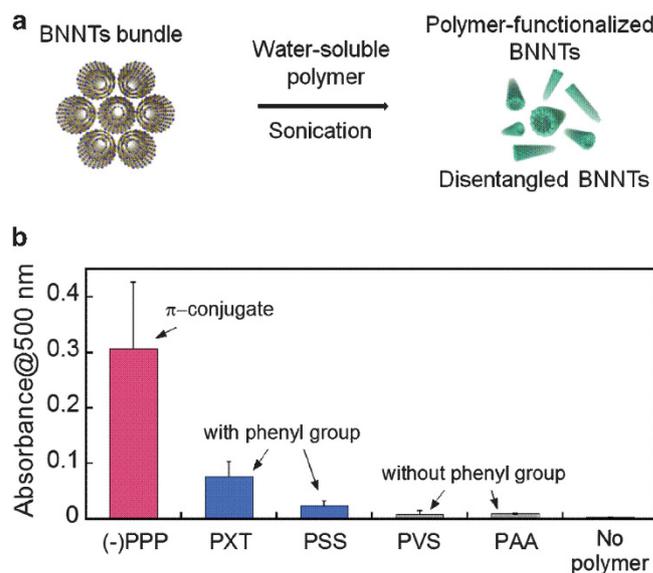
As shown in Figure 1 and Supplementary Figure S1, the list of polymers in order from best to worst ability to disperse BNNTs in aqueous solution was found to be (-)-PPP > PXT > PSS > PVS > PAA. Both the dispersing and functionalizing of BNNTs were dependent on the chemical structure of the individual synthetic polymers. Specifically, (-)-PPP showed the greatest potential for dispersing BNNTs in an aqueous phase. PXT was the second best among the five polymers studied. In general, polymers with conjugated  $\pi$ -electrons ((-)-PPP, PXT, and PSS) showed greater potential than the polymers without such  $\pi$ -electrons (PVS and PAA), suggesting that the  $\pi$ - $\pi$  stacking interactions play a key role in interactions with the BNNT sidewalls. Furthermore, (-)-PPP was better than the polymers with simple aromatic rings (PXT and PSS). These findings are in good agreement with the previous theoretical computations for interactions occurring between single-walled BNNTs and various polymers,<sup>7</sup> as well as with small aromatic molecules.<sup>15</sup> To characterize the dispersed BNNTs in detail, we focused on (-)-PPP-functionalized BNNTs in the following sections.

The supernatant after centrifugation was slightly turbid, suggesting the presence of dispersed BNNTs (Figure 2a). The morphologies of dispersed BNNTs were characterized by atomic force microscopy (AFM). Figure 2b shows a representative AFM image of

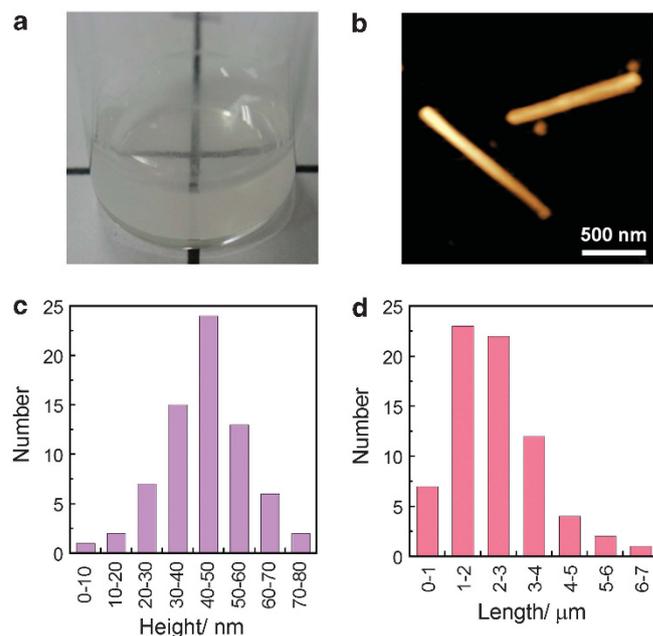


**Scheme 1** Chemical structures of the water-soluble synthetic polymers used in this study.

(-)-PPP-functionalized BNNTs. Isolated needle-like features are observed on the substrate surface, suggesting the presence of excellently disentangled BNNTs. The statistical topography analysis revealed that the BNNTs had heights ranging from 10 to 80 nm (Figure 2c), these are slightly greater than those for the original BNNTs (10 to 70 nm).<sup>16</sup> The BNNT lengths are distributed up to



**Figure 1** (a) Schematic image of disentanglement and dispersion of pristine BNNTs using water-soluble synthetic polymers and (b) comparative potentials of the polymers for dispersing BNNTs in an aqueous phase. The absorbance at 500 nm analyzes the intrinsic absorption of BNNTs without interference from the absorptions of the synthetic polymers.



**Figure 2** (a) Aqueous dispersion of (-)-PPP-functionalized BNNTs, (b) AFM image of (-)-PPP-functionalized BNNTs, statistical analysis of (c) height and (d) length distributions of (-)-PPP-functionalized BNNTs (the total number of BNNTs analyzed was 71).

7  $\mu\text{m}$  (Figure 2d), which are slightly shorter than those for the original BNNTs (up to 10  $\mu\text{m}$ ).<sup>16</sup> These observations suggest that the BNNT sidewalls were coated by (-)PPP after disentanglement and that the tubes were shortened during the sonication process. It is noteworthy that the similar height and length distributions were observed for PXT-functionalized BNNTs (see Supplementary Figure S2).

Then, we investigated the interactions between (-)PPP and the BNNT sidewalls using ultraviolet-visible (UV-vis) spectroscopy. Figure 3a compares the UV-vis absorption spectra of the original BNNT, (-)PPP, and (-)PPP-functionalized BNNTs. There are apparent changes that can be seen in these three spectra. Specifically, the band-gap absorption of the original BNNTs appeared at 200 nm,<sup>16</sup> while it was shifted to 212 nm in the spectrum of (-)PPP-functionalized BNNTs. Meanwhile, three small bulge peaks at approximately 236, 288, and 344 nm are visible in the spectrum of (-)PPP-functionalized BNNTs. These peaks correspond to the peaks at approximately 221, 279, and 325 nm in the spectrum of (-)PPP, which are associated with the  $n-\pi^*$ ,  $\pi-\pi^*$  and  $n-\sigma^*$  electron transitions,<sup>17</sup> respectively. All of these changes suggest that there are indeed strong interactions occurring between the conjugated main chains of (-)PPP and the graphene-like BNNT sidewalls.

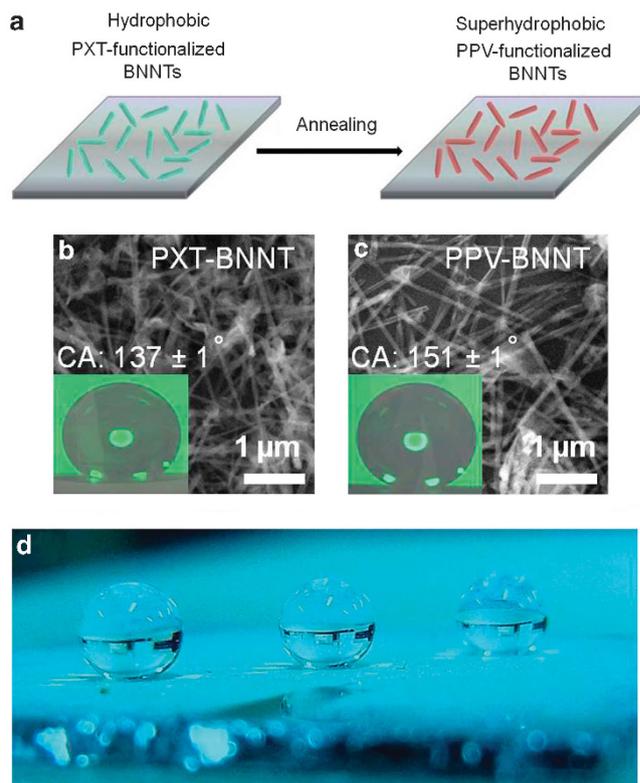
Further investigation of the interactions was conducted using fluorescence spectroscopy. Figure 3b compares the fluorescence spectra of the original BNNTs, (-)PPP, and (-)PPP-functionalized BNNTs. The peak of the original BNNTs appeared at 330 nm and was assigned to B or N defects,<sup>16</sup> and the corresponding peak was shifted to 333 nm in the spectrum of (-)PPP-functionalized BNNTs. A peak appeared at approximately 400 nm for (-)PPP-functionalized BNNTs, which originates from the main chains of (-)PPP,<sup>18</sup> and it was shifted from 412 nm for standard (-)PPP. These changes provide further evidence of the presence of strong  $\pi-\pi$  stacking interactions between (-)PPP and BNNT sidewalls. In addition, Fourier transform infrared (FT-IR) absorption spectra showed other changes in the absorption peaks that were assigned to BNNTs and (-)PPP (see Supplementary Figure S3), suggesting that BNNTs are successfully functionalized by (-)PPP, mainly via  $\pi-\pi$  stacking interactions.

Superhydrophobic coatings are attractive because of their prospective applications in self-cleaning glasses and clothes.<sup>19</sup> The hydrophobicity of pristine, as-made BNNTs makes them promising building blocks for the construction of functional materials with superhydrophobic surfaces.<sup>9</sup> However, it is difficult to use pristine BNNTs directly as coating materials because of their poor level of dispersion in any solvent. Therefore, we hypothesized that PXT, which showed the second strongest potential for dispersing BNNTs in this study, should be converted to poly(*p*-phenylene vinylene) (PPV) via thermal treatment for the preparation of superhydrophobic films composed of

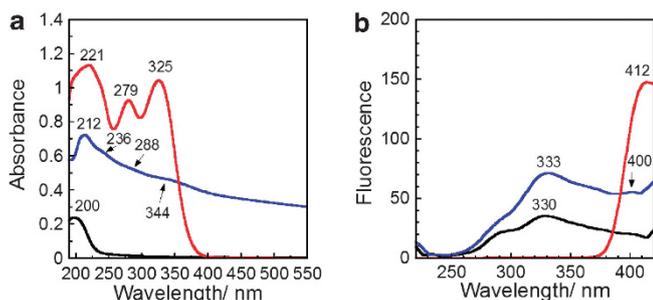
post-functionalized PPV-coated BNNTs. It is noteworthy that thermal treatment can be performed because of the excellent thermal stability of BNNTs.

PXT-functionalized BNNTs were deposited onto a Si wafer, followed by thermal treatment at 240 °C for 6 h (see Figure 4a and Supplementary Information for details). The chemical conversion of PXT into PPV on the BNNT sidewalls was confirmed by the changes in the UV-vis (Supplementary Figure S4) and FT-IR absorption spectra (Supplementary Figure S5). As shown in the insets of Figures 4b and c, the contact angles before and after the thermal treatment were measured to be  $137 \pm 1^\circ$  and  $151 \pm 1^\circ$ , respectively. These observations suggest that the film surface composed of PPV-functionalized BNNTs has superhydrophobic properties (see Figure 4d). The morphologies of the coatings were then compared using scanning electron microscopy (SEM). As shown in Figures 4b and c, and Supplementary Figure S6, a loosely packed nanotubular structure network is observed and has been identified to be important for the origin of the superhydrophobicity of nanotube materials.<sup>4</sup>

In summary, we have experimentally shown that various water-soluble synthetic polymers are able to disentangle and disperse BNNTs in an aqueous phase without forming covalent bonds. Among the synthetic polymers tested here, a conjugated polymer of (-)PPP showed the greatest potential for dispersing BNNTs, thereby suggesting that  $\pi-\pi$  stacking interactions play a key role in BNNT functionalization. As a possible application of polymer-functionalized BNNTs, we have demonstrated the fabrication process for superhydrophobic coatings with post-functionalized processing BNNTs.



**Figure 4** (a) Schematic image of the conversion of PXT into PPV on the BNNT sidewalls via thermal treatment, SEM image of the film surfaces coated with (b) PXT- and (c) PPV-functionalized BNNTs coated on a Si wafer, and (d) an optical photo of water droplets on a superhydrophobic PPV-functionalized BNNT. The insets in (b) and (c) show water droplets used for contact angle measurements.



**Figure 3** (a) Comparative UV-vis absorption and (b) fluorescence spectra of the original BNNTs (black), (-)PPP (red), and (-)PPP-functionalized BNNTs (blue).

The fabrication process is based on the conversion of PXT into PPV on BNNT sidewalls via a simple thermal treatment process that is allowable because BNNTs are thermally stable. These findings should be significant for the development of BNNT/polymer composite materials in various engineering fields.

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