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Research Article

Covalent Surface Functionalization of Boron Nitride Nanotubes Fabricated with Diazonium Salt

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The chemical inertness and poor wetting properties of boron nitride nanotubes (BNNTs) hindered their applications. In this work, BNNTs have been functionalized with aniline groups by reacting with diazonium salt and the graft content of aniline component was calculated as high as 71.4 wt.%. The chemical structure, composition, and morphology of functionalized BNNTs were carefully characterized to illustrate the modification. The anilinocarbocation generated by decomposition of diazonium salt reacted not only with NH_2 sites, but also with B-OH sites on the surface of BNNTs. Meanwhile, the reaction applied a hot strong acid environment, which would help to open parts of B-N bonds to produce more reactive sites and enrich the functional groups grafted on the surface of BNNTs. Consequently, the functionalized BNNTs exhibited significantly improved dispersion stability in chloroform compared with pristine BNNTs. Amino surface functionalization of BNNTs offered more possibilities for surface chemical design of boron nitride and its practical application.

1. Introduction

As a structural analogue to carbon nanotubes (CNTs) [1], boron nitride nanotubes (BNNTs) containing boron and nitrogen atoms distributed equally in hexagonal rings have attracted much attention due to their excellent mechanical properties, high thermal conductivity, superb thermal and antioxidation stabilities, excellent biocompatibility, and effective light emission properties [2–5]. These make BNNTs great potential to be applied in many aspects, such as semiconductor devices and thermal conductive composite that work under high temperature, as well as photoelectric and neutron radiation shield materials [6–9].

Despite the advantages mentioned above, there are still some problems of BNNTs that hinder their further application. For one thing, BNNTs are extremely difficult to dissolve in organic solvents and water and are almost insoluble in all acids, bases, and solvents, so their solubility and dispersibility have greatly limited their application. For another, experimental modifications of BNNTs are much fewer than theoretical investigations due to their chemical inertness and poor wetting properties [10]. However, BNNTs can disperse well in certain solvent and polymer matrix after surface modification, which would expand their potential applications [11]. To this end, the development of new methods to realize the modification of BNNTs with functional groups attracted more and more attention.

To date, a variety of chemical methods by means of weak interactions and covalent bonding have been suggested to develop functionalized and dispersible BNNTs. Ciofani et al. implied the chemical reaction of the residual amino on the surface of the BNNTs and octadecyl chloride was used to make it graft long molecule chains, and the BNNTs after grafting could be dispersed in many solvents [12]. Maguer et al. used dimethyl sulfoxide to weaken the B-N bonds through cycloaddition, which make the part of B-N bonds on the surface of BNNTs hydrolysis and stripping the stripping BN molecular layer will be embedded in the BNNTs to form Y loop structure BNNTs [13]. The localized ionization structure enabled BNNTs to interact with substrates through stacking interactions and electrostatic interactions [10, 14, 15]. Actually, the covalent bonding chemistry of BNNTs, which could react at either N sites or B sites to achieve surface modification of BNNTs, has not been studied until recent years [16, 17]. The N site reaction mainly relied on the reactivity of surface amino group; however, there were usually few amino groups on the surface of BNNTs [18, 19]. Ikuno et al. developed a method to increase concentration of active N sites through NH_3 plasma treatment, but the surface damage cannot be avoided [20]. On the other hand, since most of the organic reactions are based on the C and N species, studies on B site reaction were not as sufficient [21]. Various chemical functionalization could be achieved by esterification between hydroxyl and carboxyl groups when B-site-activated BNNTs were used as the starting materials. Zhi et al. found that B sites could be activated by oxidizing BNNTs in H_2O_2 at high temperature and high pressure conditions [22]. Hydroxyl groups were attached on B sites of BNNTs and the hydroxylated BNNTs could be well dispersed in water opposed to pristine BNNTs. However, several problems have yet to be addressed. The major issue is represented by the lack of an effective method to graft a high density of functional groups on BNNTs and thus make BNNTs chemically active, which could allow for further efficient surface modification [23]. In addition, the understanding of the reaction mechanisms and the development of new functionalization methods for BNNTs are also challenging tasks.

In this work, we have proposed an innovative and simple approach to achieve chemically functionalized boron nitride nanotubes, which were abundantly decorated by aniline groups through the hydrolysis of the diazonium salt. The mechanism of the reaction was also studied, which suggested that the high active anilinocarbocations generated by the hydrolysis of diazonium salt reacted not only with N active point, but also with B active point on the surface of BNNTs. Therefore, the surface functionalized BNNTs could be greatly dispersed in the solvent of chloromethane, which greatly improves the compatibility with organic solvents.

2. Materials and Methods

2.1. Materials. Multiwalled boron nitride nanotubes (BNNTs) were purchased from Boron Nitride Research Center of Hebei University of Technology. The reagents used for the synthesis of diazonium chloride, including p-phenylenediamine, sodium nitrite ($NaNO_2$), concentrated hydrochloric acid (HCl), and iron powder were purchased from J&K Scientific Ltd. Other chemicals and reagents were used directly without further purification. Deionized water was generated by a Milli-Q integral ultrapure water purification system.

2.2. Sample Preparation. The synthesis of NH_2Ph-BNNTs was shown in Figure 1. The first step was the synthesis of diazonium chloride by using a modified diazotization reaction, followed by the hydrolysis of the diazonium salt and the introduction of aniline groups on the surface of BNNTs. Detailed procedures were given as follows. Firstly, 1.6 g of p-phenylenediamine was dissolved in 20 mL of deionized water and then 11 mL of 0.5 mol·mL^{-1} HCl was added dropwise under stirring within 30 min to form amaranth suspension. Then the suspension was cooled in ice bath (<5°C), and 1.02 g of $NaNO_2$ dissolved in aqueous solution was slowly added under stirring to generate the diazonium chloride, which was immediately added to BNNTs suspension under stirring within 30 min at room temperature. Then 1.2 g of ironic powder and 50 mL of 0.5 mol mL^{-1} HCl were added to the mixture successively and stirred for 2 h to obtain the targeting product. The product was washed with deionized water and methanol successively, followed by the treatment of ultrasonic and centrifugation to remove the extra diazonium chloride. In order to ensure that the impurities were fully removed, in the process of further postprocessing, the product was extracted by refluxing ethanol for 4 h in a set of Soxhlet apparatus. The resultant product was dried at 60°C for 24 h in vacuum oven and named as NH_2Ph-BNNTs.

2.3. Characterization. Fourier transform infrared spectroscopy (FT-IR) analysis was carried out using a Perkin-Emler System 2000 infrared spectrum analyzer in the wave number range of 4000–650 cm^{-1} with KBr pellets. Thermogravimetric analysis (TGA) was carried out using Perkin-Elmer Pyris 1 and TGA 7 thermogravimetric analyzer in air atmosphere. The thermal behavior was characterized by temperature programming from 50°C to 700°C at a heating rate of 10°C min^{-1}. The content of the grafted functional groups was calculated by thermogravimetric loss between 250°C and 600°C. X-ray photoelectron spectroscopy (XPS) data were obtained with an ESCALab 220i-XL electron spectrometer from VG Scientific using 300 W Al Kα radiation. The base pressure is about 3×10^{-9} mbar. The binding energies are referenced to the C1s line at 284.6 eV from adventitious carbon. Elemental composition analysis was obtained using Flash EA 1112 elemental analyzer. Scanning electron microscope (SEM) image was taken on a JEOL S-4300F field emission scanning electron microscope at 10 kV. Transmission electron microscope (TEM) image was obtained using a JEOL (Japan) JEM-2200FS instrument with an accelerating voltage of 150 kV. Specimen of TEM was prepared by placing a droplet of water-diluted sample on a carbon-coated microscope grid and dried in air.

3. Results and Discussion

3.1. Dispersity Analysis. As a consequence, lots of organic aniline groups were irregularly grafted on the surface of BNNTs, which could improve the dispersity of BNNTs in chloroform, as shown in Figure 2. The BNNTs and NH_2Ph-BNNTs images captured by supersonic treatment followed by standing for 24 h in chloroform are shown in Figure 2. It is obvious that the obtained NH_2Ph-BNNTs were more stable than the pristine BNNTs in chloroform. The reason for the excellence dispersibility of NH_2Ph-BNNTs is likely to be a result of the atomic degradation of the crystallinity [20]. These results suggested that aniline groups were attached on the surface of NH_2Ph-BNNTs and could increase the affinity between BNNTs and chloroform solvent.

3.2. FT-IR Analysis. Figure 3 shows the FT-IR spectra of BNNTs and NH_2Ph-BNNTs. Main IR peaks corresponding to

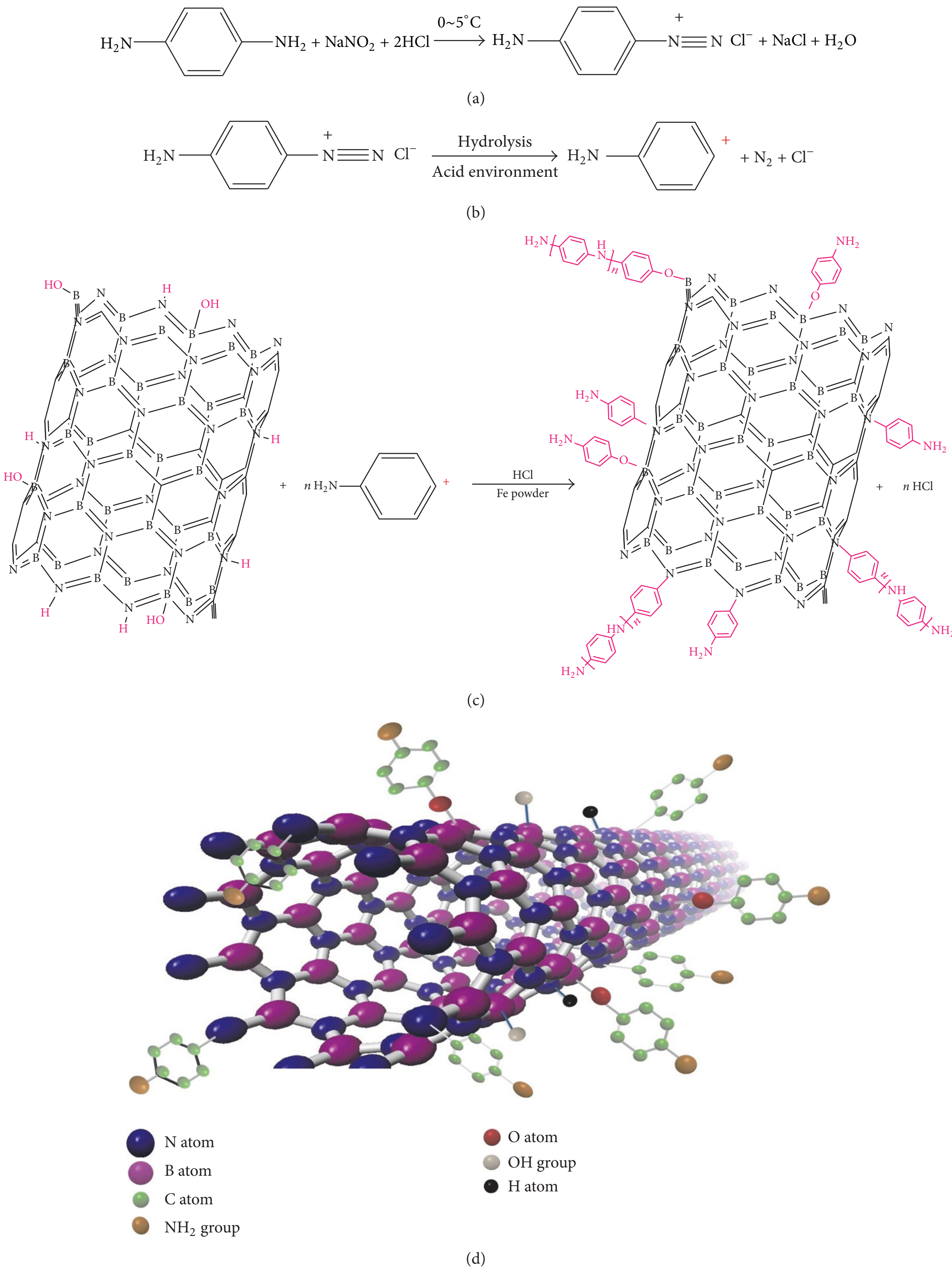

Figure 1: (a) The synthesis of diazonium salt chloride. (b) The hydrolysis of diazonium salt chloride. (c) The surface grafting between anilino-carbon cations and BNNTs. (d) The grafted schematic of single-NH_2Ph-BNNTs.

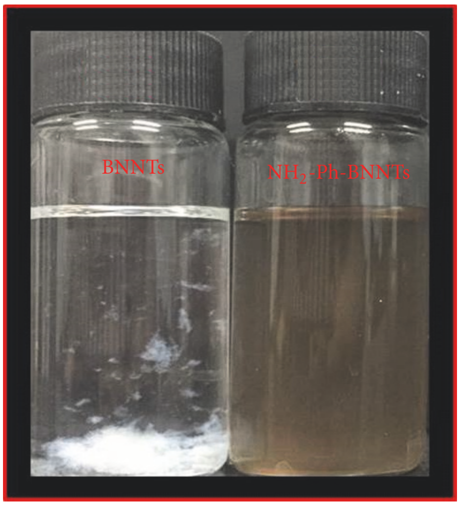

Figure 2: Photographs of vials containing the BNNTs and the NH_2Ph-BNNTs in chloroform after standing for 24 h.

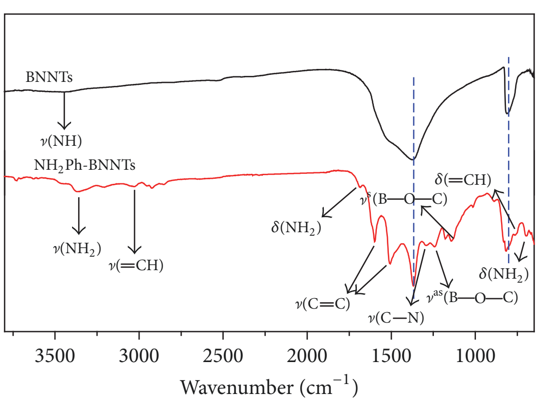

Figure 3: FT-IR spectra of BNNTs and NH_2Ph-BNNTs.

literature values and their assignments were given in Table 1. Two main featured peaks were found for BNNTs sample, which were marked by two blue lines in the figure. The broad absorption band near 3424 cm^{-1} can be resulting from the N-H bonds on the surface of BNNTs. These values were in good agreement with the reports concerning the FT-IR spectra of BNNTs [24, 25]. Compared with the spectra of BNNTs, some new peaks were observed in the spectra of NH_2Ph-BNNTs. These peaks indicated the existence of aniline groups in NH_2Ph-BNNTs. More importantly, the peaks at 1239 cm^{-1} and 1141 cm^{-1} were attributed to B-O-C bonds, which was the result of the reaction between anilinocarbocation and B-OH. This directly proved the success of grafting reaction. Moreover, slight blue shift of two featured peaks of NH_2Ph-BNNTs was also observed, which may result from the grafting of the electronegative aniline groups.

3.3. TGA Analysis. Furthermore, we utilized thermogravimetric analysis (TGA) to evaluate the grafting efficiency, as shown in Figure 4. The results of the thermogravimetric curves showed that there was almost no heat loss of BNNTs,

Table 1: The main characteristic peak values of BNNTs and NH_2Ph-BNNTs.

FT-IR peak values (cm^{-1})	Reference values (cm^{-1})	Assignments
1324	1343	$\beta_{B\text{-}N_f}$
783	789	$\gamma_{B\text{-}N\text{-}B}$
3424	3500~3300	$\nu_{N\text{-}H}$ of amine group
697	750~600	$\gamma_{N\text{-}H}$ of amine group
3025	3100~3000	$\nu_{C=H}$ of benzene
1598 and 1507	1600 and 1500	$\nu_{C=C}$ of benzene
1253	1340~1250	$\nu_{C\text{-}N}$ of aromatic amine
794	860~790	$\gamma_{C=H}$ of benzene
1239 and 1141	1300~900	$\nu_{sB\text{-}O\text{-}C}$ and $\nu_{asB\text{-}O\text{-}C}$

Table 2: The concentration of each element from XPS for BNNTs and NH_2Ph-BNNTs.

Sample	Chemical composition (at.%)			
	B1s	N1s	C1s	O1s
BNNTs	52.55	44.65	1.84	0.96
NH_2Ph-BNNTs	2.08	3.88	81.1	12.93

illustrating the thermal stable structure of BNNTs. On the contrary, obvious heat loss of NH_2Ph-BNNTs was observed. The weight loss of NH_2Ph-BNNTs mainly resulted from surface organic components, indicating the existence of organic ingredients in NH_2Ph-BNNTs. Moreover, the graft content was calculated as 71.4 wt.%. For one thing, the high grafting rate benefited from the broken of B-N bonds on the surface of BNNTs in the acidic environment, producing more reactive sites. For another, we used largely excess diazonium chloride salt to decorate BNNTs. As we know, the excess diazonium salt could further react with the Ph-NH_2 group that has been grafted on the surface of BNNTs to form polyaniline-like oligomers. Therefore, this reaction would increase the grafting content. However, the high grafting content would significantly contribute to BNNTs' compatibility with organic substance.

3.4. XPS Analysis. XPS technique was applied to detect the chemical structures of BNNTs and NH_2Ph-BNNTs. Figure 5 shows the wide-scan spectra of BNNTs and NH_2Ph-BNNTs. The element content data were calculated and summarized in Table 2. As shown in Figure 5, the peak intensity of Bls and Nls in NH_2Ph-BNNTs was obviously decreased compared to that of BNNTs. The decrease in the detectable boron and nitrogen elements was caused by the grafting layer on the surface of BNNTs. As mentioned above, polyaniline-like oligomers could form a coating layer, which would hinder the detection of the inner BNNTs. Actually, the electron microscope observation below would verify this point. In addition, due to the introduction of nitrogen carried by aniline groups, the N/B ratio of NH_2Ph-BNNTs was increased to 1.87, which was much higher than that of BNNTs (0.85).

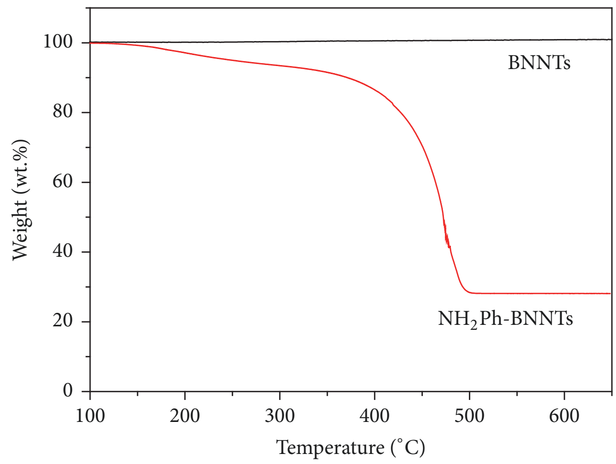

FIGURE 4: TGA curves of BNNTs and NH_2Ph-BNNTs.

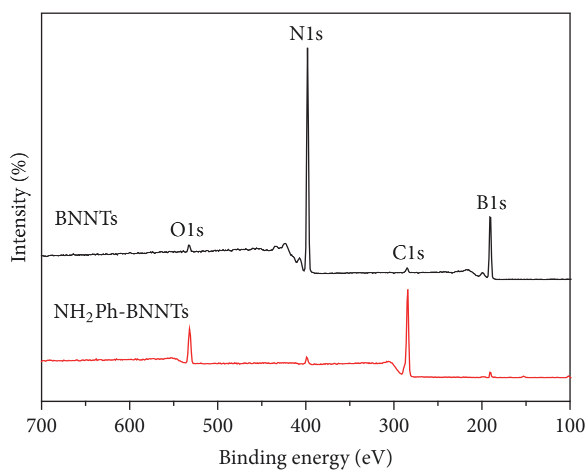

FIGURE 5: The wide-scan spectra of BNNTs and NH_2Ph-BNNTs.

The N1s photoelectron spectroscopy of BNNTs and NH_2Ph-BNNTs is shown in Figure 6. The N1s of BNNTs perfectly presented a single peak with binding energy at 397.9 eV, corresponding to B-N-B [26, 27]. Obviously, the N1s peak of NH_2Ph-BNNTs was not a single peak. It could be divided into four peaks by peak-fitting process located at 397.9 eV, 399.4 eV, 402.4 eV, and 400.8 eV, attributed to B-N-B, Ph-NH_2, C-N-B, and B-N-H, respectively [28]. These results indicated that the aniline groups existed in NH_2Ph-BNNT. From the existence of C-N-B structure, we concluded that during the reaction anilinocarbocation also reacted with N-H on the surface of BNNTs, in addition to reacting with B-OH as FT-IR suggested.

The B1s photoelectron spectroscopy of BNNTs and NH_2Ph-BNNTs is shown in Figure 7. The peak at 190.3 eV was found in both the BNNTs and NH_2Ph-BNNTs, which was assigned to B-N in BNNTs [24, 27]. There was another peak obtained from the peak-fitting; however, for this peak BNNTs and NH_2Ph-BNNTs showed slight different binding energy values. The peak at 191.4 eV in BNNTs belonged to the -B-OH while the peak at 191.9 eV in NH_2Ph-BNNTs belonged to -B-O- group. The replacement of H atom by electronegative aniline groups caused the rise of inner electron bonding energy of boron, and this was in accordance with the literatures results, simultaneously verifying the above FT-IR result [6, 19].

The O1s photoelectron spectroscopy of BNNTs and NH_2Ph-BNNTs is shown in Figure 8. The peak at 523.3 eV corresponding to the -B-OH group was found both in BNNTs and in NH_2Ph-BNNTs. Additionally, one peak assigned to -B-O-C- group at about 533.3 eV was also found in NH_2Ph-BNNTs, suggesting again that aniline was reacted with the -B-OH groups on the surface of BNNTs [19].

The C1s photoelectron spectroscopy of NH_2Ph-BNNTs is shown in Figure 9. The peak at 284.6 eV caused by the contamination carbon in the raw materials was found both in the BNNTs and in NH_2Ph-BNNTs. In addition, three peaks at 284.9 eV, 286.5 eV, and 288.9 eV were also observed in NH_2Ph-BNNTs and they were assigned to the -C-C-, -C-O-, and -C-N- groups [28]. The existence of -C-O- and -C-N- indicated again that the aniline reacted with both -B-OH and -N-H groups on the surface of BNNTs.

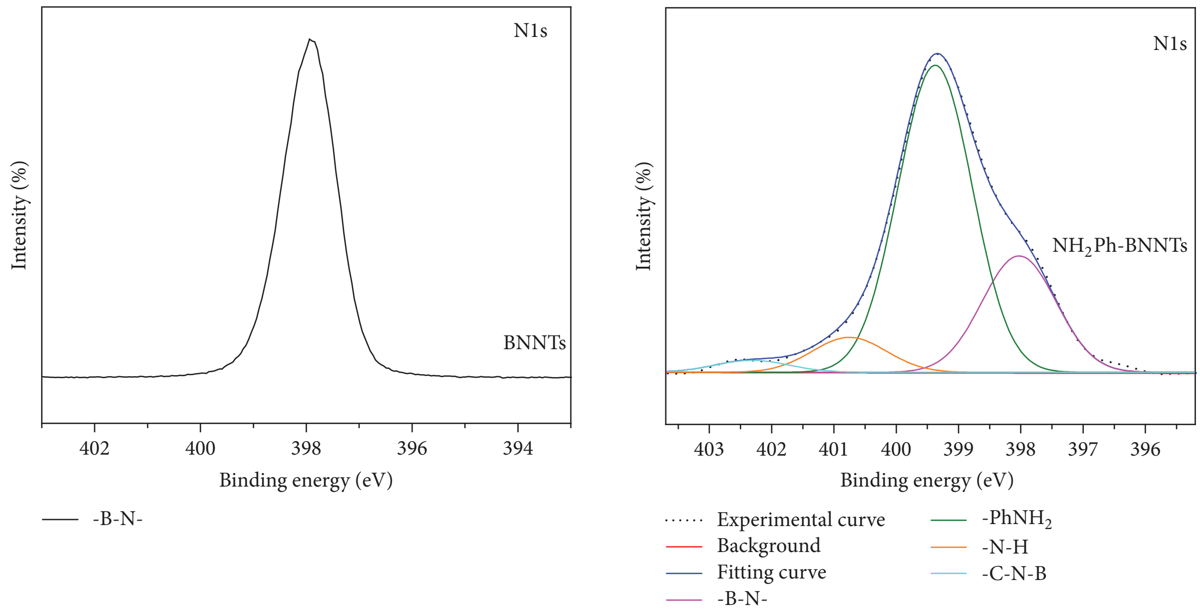

FIGURE 6: The N1s core level spectra of BNNTs and NH_2Ph-BNNTs.

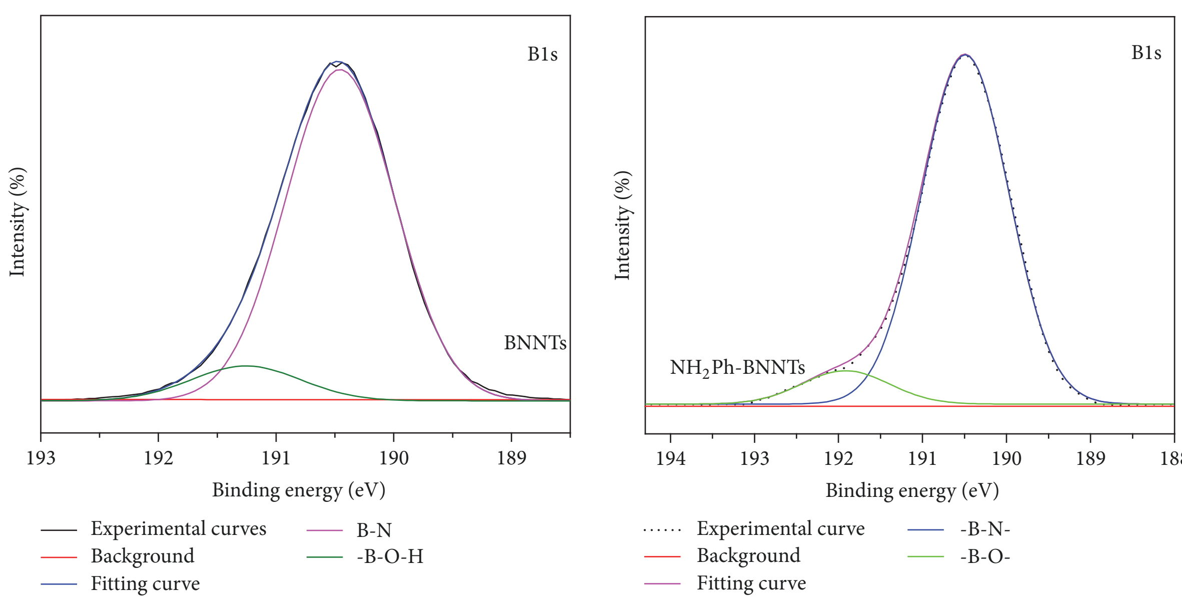

FIGURE 7: The B1s core level spectra of BNNTs and NH_2Ph-BNNTs.

3.5. Electron Microscope Analysis. The electron microscope presented the morphology of BNNTs and NH_2Ph-BNNTs. SEM images of BNNTs were shown in Figures 10(a) and 10(b). The naked BNNTs were about dozens of micrometers in length, with diameter of ~150 nm and their surfaces were smooth. After the grafting, amorphous organic coating layers were observed on the surface of nanotubes, introducing a rough surface of NH_2Ph-BNNTs. According to TEM images in Figures 10(c) and 10(d), the coating layer was 15~25 nm, but a single *para*-phenylenediamine molecule is about 1 nm in length. The difference between theory and actual thickness was too big, which might result from the largely excess diazonium chloride salts used to decorate BNNTs during the reaction. The excess diazonium salt could further react with the Ph-NH_2 group that has been grafted on the surface of BNNTs to form polyaniline-like oligomers. Therefore, the grafting reaction formed organic coating layer, wrapping the nanotube all up. Consequently, the surface structure and wetting properties of NH_2Ph-BNNTs became totally different from the naked BNNTs, just as discussed above. Moreover, Figure 10(b) captured one nanotube with part of BNNTs exposed, which presented the smooth surface of BNNTs, indicating there was no serious damage upon the integrity and tubular structure of BNNTs after the functionalization.

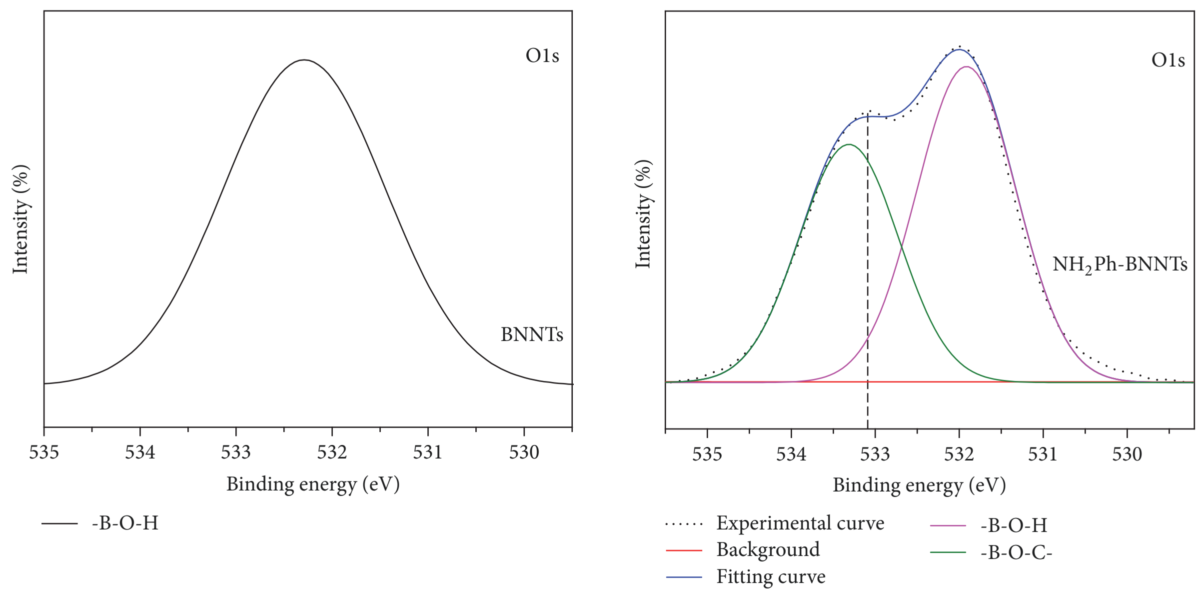

Figure 8: The O1s core level spectra of BNNTs and NH_2Ph-BNNTs.

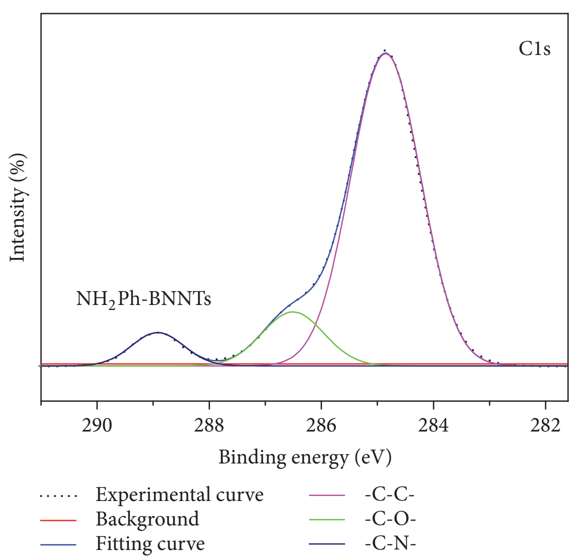

Figure 9: The C1s core level spectra of NH_2Ph-BNNTs.

3.6. The Functionalization Mechanism. Finally, the functionalization mechanism was concluded as follows. At the first step diazonium chloride salt was synthesized. Then, in the BNNTs dispersion, diazonium salt chloride was decomposed to generate anilinocarbocations, which was active in acid environment. Meanwhile, under this strong acid environment, the surface B-N bonds of BNNTs were fractured to generate more -B-OH and -NH groups [25, 29]. Due to the high activity of anilinocarbocations, it could immediately capture the hydrogen atoms of -NH and -B-OH groups on the surface of BNNTs. The grafting schematics were shown in Figures 1(c) and 1(d). The excess anilinocarbocations could react with the Ph-NH_2 that has been grafted on the surface of BNNTs to form polyaniline-like oligomers. There formed the coating layer upon the surface of BNNTs and the coating component was covalently bonded with BNNTs.

4. Conclusion

In this paper, we have proposed an innovative and simple approach to achieve chemically functionalized boron nitride nanotubes. High active anilinocarbocations generated by the hydrolysis of diazonium salt reacted both N-H and B-OH active sites on the surface of BNNTs. The hot acid aqueous environment helped to introduce more N-H and B-OH reactive sites. As a result, BNNTs were abundantly coated by organic polyaniline-like components and their dispersibility in organic solvent was greatly improved. It is expected that the

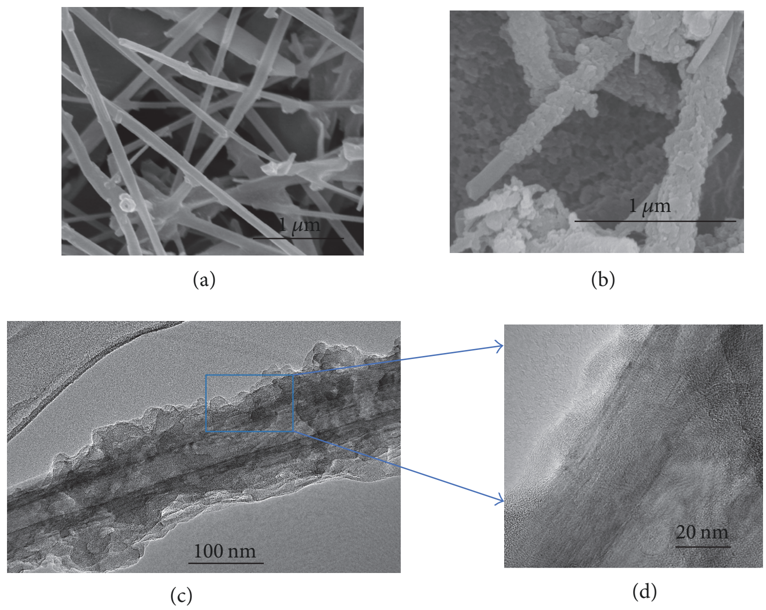

Figure 10: (a) SEM imaging of BNNTs. (b) SEM imaging of NH_2Ph-BNNTs. (c) TEM imaging of NH_2Ph-BNNTs. (d) High resolution TEM images of NH_2Ph-BNNTs.

modified BNNTs could be used as filler to directly mix with polymer matrix and prepare nanocomposites. The reactive aniline groups decorated upon the surface of BNNTs would contribute to the potential applications and further chemical design.

Conflicts of Interest

The authors declare that there are no conflicts of interest regarding the publication of this article.

Acknowledgments

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