Facile Grafting of Ionic Liquids onto Halloysite Nanotubes via An Atom Transfer Radical Polymerization Method

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ABSTRACT

Ionic liquids (ILs)-based organic–inorganic nanocomposite materials are a new class of hybrid materials which can be used in lithium batteries, fuel cells, dye-sensitized solar cells and pressure sensors. Halloysite nanotubes (HNTs, $Al_2Si_2O_5(OH)_4{\cdot}nH_2O$) are hollow like aluminosilicate clay, similar to commonly used platy clay kaolin, which open up various attractive applications including catalysis, anticorrosion, adsorbent, drug delivery, enzyme immobilization, fiber spinning and so on. However, the inorganic characteristics of clay-based halloysite nanotube result in a limited application in electronic field, making it difficult to capture attentions as extensively as carbon nanotubes. Herein, we develop a feasible and versatile approach to prepared ILs grafted HNTs, by coupling the arylboronic acid and Al-OH groups on the HNTs. ILs are grafted to the modified HNTs via a typical atom transfer radical polymerization (ATRP) method. The modified halloysite nanotubes (HNTs) are characterized by (FTIR), thermogravimetric analysis (TGA), scanning electron microscopy (SEM) and transmission electron microscope (TEM).

KEY WORDS: *Halloysite nanotube, Ionic liquid, ATRP, Chemical modification, Arylboronic acid*

1. INTRODUCTION

In the past decades, increasing research efforts were devoted to investigate organic–inorganic nanocomposite materials. Compared to nanospheres, tubular systems usually exhibit superior aerodynamic and hydrodynamic properties and thus better processability with the same amount of cargo. Like other tubule

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materials, halloysite nanotubes (HNTs) share a similar geometry but exhibit many excellent advantages such as biocompatibility, environmental friendliness, large surface area, high porosity, as well as low-cost and widely spreadable properties[1-4]. HNTs ($Al_2Si_2O_5(OH)_4{\cdot}nH_2O$) are hollow like aluminosilicate clay, similar to commonly used platy clay kaolin[5]. The size of HNTs often ranges from 15 to 100 nm in external diameter with a length from 500 to 1000 nm. Furthermore, the tubule shape of HNTs with length/diameter ratio of 10–50 provides optical and mechanical anisotropy[6]. Generally, the internal surface of HNTs consists of a gibbsite octahedral array (Al-OH) groups, whereas the siloxane groups (Si-O-Si) overspread on the external surface. Usually, the inner and outer-compositions of these tubes allow for quite a few feasible modification methods by immobilization of functional groups via different chemical reactions, which can open up some attractive applications including catalysis[7, 8], anticorrosion[9], adsorbent[10], drug delivery[11, 12], enzyme immobilization[13], aerogel[14], sensor[15], rubber filler[16], and fiber spinning[17]. However, the inorganic characteristics of clay-based halloysite nanotube result in a limited application in electronic field, making it difficult to capture attentions as extensive as carbon nanotubes possessed.

Ionic liquids (ILs)-based nanocomposites are a new class of hybrid materials which can be used as high performance gel electrolytes in lithium batteries[18], fuel cells [19], dye-sensitized solar cells[20], and pressure sensors[21] due to their major advantages such as improved safety, negligible vapor pressure and the fact that they allow easy shaping. Previously, our group reported a feasible approach to prepare ILs-based nanocomposite polymer electrolytes by immersing HNTs-based aerogel in an excess of ILs, which exhibited desirable conductivity property and significant anisotropy[22]. So, it would be also full of significance to prepare an poly(ionic liquid)s-grafted HNTs with better stability and processibility so that to meet widely in-depth applications.

Herein, we develop a feasible and versatile approach to prepared poly(ionic liquid)s-grafted HNTs, which starts from a selective modification of the alumina innermost surface by arylboronic acid by referring to the method we reported previously[23-26]. Then 2-bromoisobutyryl bromide is used to couple with amino-functionalized HNTs to give a HNTs-based initiator for the surface initiated-ATRP polymerization. Poly(ionic liquid)s are grafted to HNTs following a typical atom transfer radical polymerization (ATRP) procedure[27, 28]. We hope the poly(ionic liquid)s-grafted HNTs can be further developed as conductor nano wires in the following investigations.

2. EXPERIMENTAL

2.1. Materials and methods

HNTs were obtained from Guang Zhou Shinshi Metallurgy and Chemical Company Ltd (Guangzhou, China). Ionic liquids of 1-butyl-3-vinylimidazolium hexafluorophosphate and polyvinyl alcohols with the molecular weight of 130000 $g{\cdot}mol^{-1}$ were purchased from Sigma-Aldrich and used as received. *m*-aminophenyl boronic acid was purchased from Soochiral Chemical Science & Technology Co., Ltd. Dimethylaminopyridine (DMAP), α-bromoisobutyryl bromide and 2,2'-bipyridine (bpy) were purchased from Aladdin Industrial Incorporated. Reagents purchased from commercial suppliers were used without further purification. The solvents were dried and distilled by a standard process before use. Distilled water was used throughout the study.

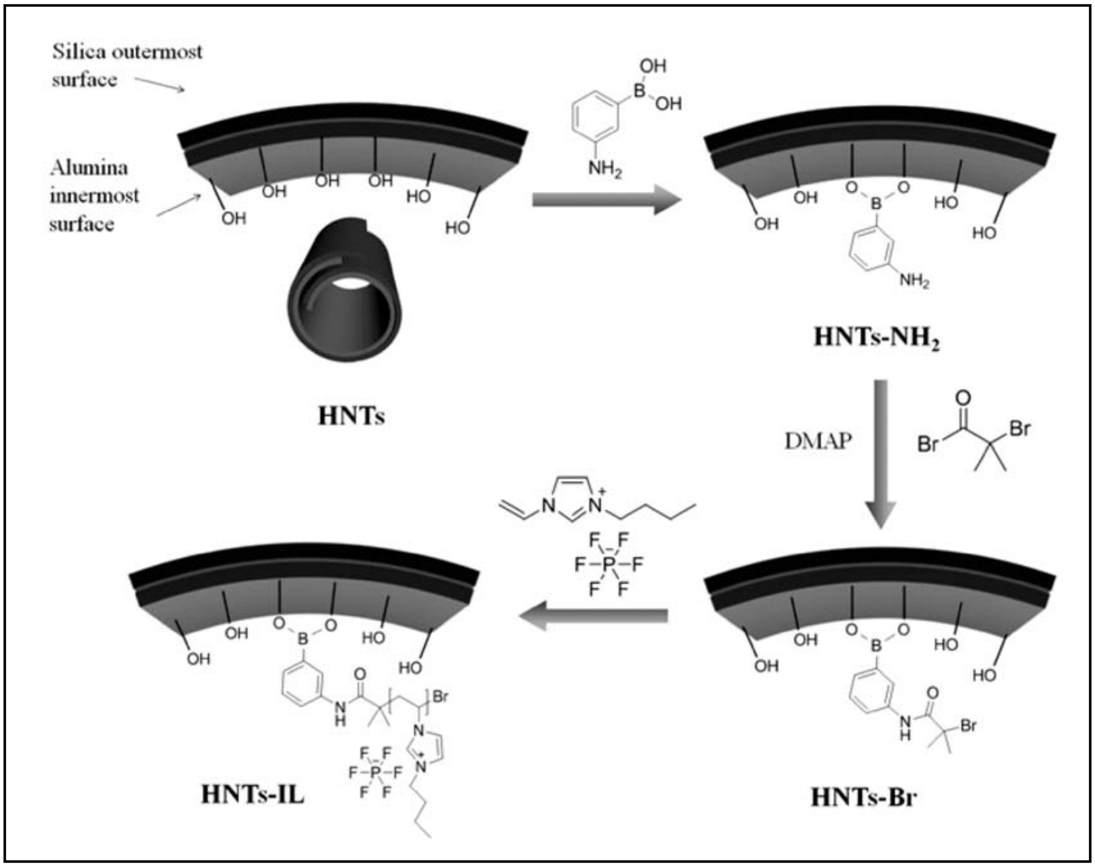
2.2. Preparation

2.2.1. Purification of HNTs

HNTs were purified according to our previous work[29, 30].

2.2.2. Preparation of HNTs-NH_2

A mixture of purified HNTs (2.00 g) and *m*-aminophenyl boronic acid (4.00 g) in anhydrous DMSO was carefully degassed. The system was heated at 80 °C for 6 h under stirring. The mixture was cooled to ambient temperature and then washed triply and sequentially by ethyl acetate, methanol and dichloromethane. The residue was collected by centrifugation. After vacuum-drying, the HNTs-NH_2 was obtained as a gray solid.



Scheme 1. Synthetic route to HNTs-IL

2.2.3. Preparation of HNTs-Br

Triethylamine (4.0 mL, 28.8 mmol) and DMAP (1.5 g, 12.3 mmol) were dissolved in dry dichloromethane (30 mL) suspension of HNTs-NH_2 (1.5 g) at 0°C. Then, 2-bromoisobutyryl bromide (1.7 mL, 14 mmol) dissolved in 2 mL DCM was injected into the HNTs-NH_2 solution directly. After stirred for 2 h, the reaction was continued at room temperature for 48 h. The mixture was washed as above mentioned. Resulted HNTs-Br was obtained after centrifugation and dryness successively.

2.2.4. Preparation of HNTs-IL

HNTs-Br (100 mg), monomer (1-butyl-3-vinylimidazolium hexafluorophosphate) (1.0 g) and 5 mL DMF were charged in a well-dried glass tube with a stopcock and carefully degassed. CuCl (50 mg, 0.51 mmol) and 2,2- bipyridine (150 mg, 1.0 mmol) were introduced into another glass tube, which was degassed by three cycles of vacuum pumping and flushing with N_2. The copper catalyst solution was injected to the monomer solution. The resulting reaction mixture was again degassed by three cycles to remove the oxygen and stirred in an oil bath at 60 °C for 24 h to graft poly(ionic liquid)s onto the HNTs. The reaction was stopped by opening the glass vessel to air. The reaction mixture was poured into methanol to precipitate the crude product. The HNTs-IL was then washed with acetate, methanol and dichloromethane and centrifuged for three times to remove the weakly bound polymer adsorbed on halloysite surface. The crude product was dried under reduced pressure to give the final product HNTs-IL.

2.3. Characterizations

The morphological characterizations were performed by using a Tecnai G2 F20 S-TWIN transmission electron microscope (TEM) with an accelerating voltage of 200 kV. A JEOL Ltd. JSM-7500F Cryo field emission scanning electron microscopy (SEM) was also used to characterize the micromorphology of prepared hydrogels. The fluffy samples were carefully put on fiat substrates precoated with carbonic glues and then were coated with gold for SEM observations. TGA was performed on Perkin-Elmer Pyris 6 under a nitrogen flow. Accurately weighted amounts of samples were heated at a scanning rate of 10 ^{o}C/min from 40 to 800 ^{o}C. FTIR spectra were recorded in the region of 400-4000 cm^{-1} for each sample on a Varian-640 spectrophotometer. Samples were previously grounded and mixed thoroughly with KBr. The spectrum for each sample was obtained from averaging 32 scans over the selected wave number range. X-ray diffraction (XRD) patterns were performed at room temperature with a D8 ADVANCE X-ray powder diffractometer system (Bruker, Faellanden, Switzerland). The patterns were recorded on a quartz plate at a tube voltage of 40 kV and a current of 40 mA in a 2θ range of 5-70^{o} using a step size 0.06^{o} at a scan speed of 1 s/step. The molecular weight and polydispersity and were determined by Viscotek 270-doul detector-Size Exclusion Chromatography which equipped with differential refractive index (RI).

3. RESULTS AND DISCUSSION

3.1. Synthesis

To explore a grafting approach to combine the poly(ionic liquid)s and HNTs via a copper-catalyzed ATRP method, we initially functionalized HNTs with amino groups based on the condensation reaction between the -OH groups on HNTs and the arylboronic acid groups in *m*-aminophenyl boronic acid. Previously we have demonstrated that the modification method by using arylboronic acid derivatives should be a selective modification of halloysite lumen. The overwhelming majority modification occurred in the inner surface of HNTs. While some components may be also immobilized on the outer surface result from the curly structure and hydrolysis of Si-O-Si groups. 2-Bromoisobutyryl bromide was coupled to HNT-NH_2 under alkaline condition, resulting in active bromine groups on HNTs to give the bromide product (HNTs-Br) which can be further used as an initiator for the surface initiated-ATRP polymerization. Then the poly(ionic liquid)s were introduced on HNTs by the Cu(I)- catalyzed surface initiated-ATRP polymerization to give HNTs-IL. The HNTs-IL and intermediate products were carefully characterized by FTIR and TGA. The micromorphology of HNTs-IL was revealed by TEM and SEM.

The FTIR spectra of the samples were measured and shown in Fig. 1. The FT-IR spectrum of original HNTs featured two distinct peaks at

3703 and 3625 cm^{-1}, which can be attributed to the stretching vibrations of inner and surface -OH groups. Inner hydroxyl groups, lying between the tetrahedral and octahedral sheets, give the absorption near 3625 cm$^{"1}$. The other strong band at 3703 cm$^{"1}$ is related to the surface hydroxyl groups in the lumen of the nanotubes. Characteristic band of in-plane Si-O-Si stretching vibration was observed around 1036 cm^{-1}. The bands less than 1000 cm^{-1} can be assigned to symmetric or perpendicular stretching vibrations of Si-O or Al-O groups. Compared to original HNTs, HNTs-NH_2 exhibited the vibration bands for C-N group at 1431 cm^{-1} and an obvious reduction of intensity the peak assigned to the -OH groups spread on inner surface. It indicated that *m*-aminophenyl boronic acid was facilely attached to HNTs following the coupling reaction. Moreover, the absorption band at 1651 cm^{-1} in the spectrum of HNTs-Br is assigned to the -C=O groups. In the spectrum of HNTs-IL, the bands at 3081, 1603 and 1441 cm^{-1} were related to the aromatic stretches. These changes suggested that the poly(ionic liquid)s was chemically grafted onto the surface of HNTs-N_3 successfully following the modification and ATRP method.

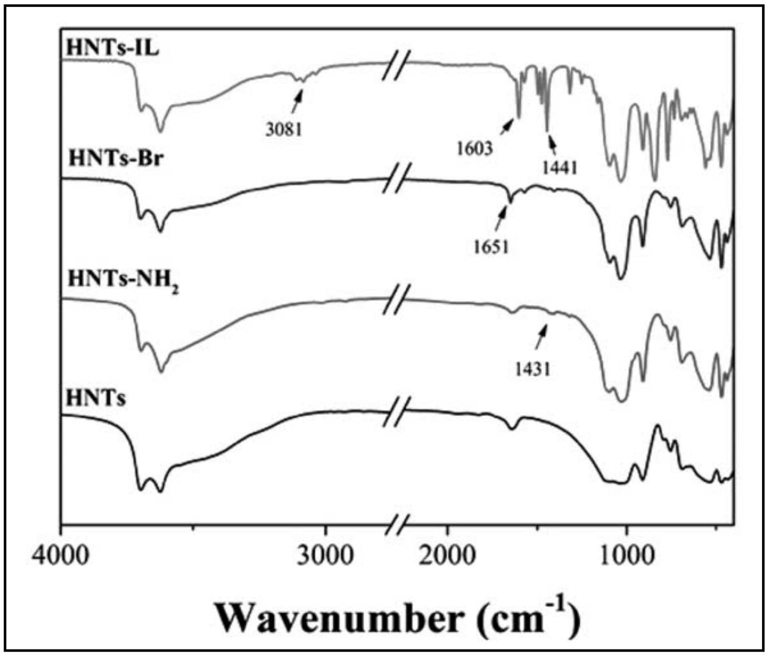


Fig. 1. FTIR spectra of HNTs, HNTs-NH_2, HNTs-Br and HNTs-IL

Thermogravimetric analysis (TGA) curves of original HNTs and modified HNTs are shown in Fig. 2. To estimate the grafting degree of the HNTs derivative, we analyzed the obtained curves in three steps: the slight mass loss before 200°C can be attributed to the adsorbed water existing in the surface, cavity or inter-layers of HNTs; the distinct mass loss range from 200-550 °C or 200-650 °C was relating to the degradation and volatilization of the organic fractions; the grafting degree (the mass ratio of grafted organic units to the pure nanotubes) was evaluated by comparing the residual masses at 800 °C. The different grafting degrees of HNTs-NH_2 and HNTs-Br were calculated from the TGA curves and the values are 7% and 13%, respectively. Moreover, grafting degree of HNTs-IL can be calculated as 51 %, suggesting a high value in the field of grafting polymers onto inorganic nanomaterials. The high-efficiency grafting may be attributed to the using of ATRP method which was proved to have the nature of high productivity and few side reactions.

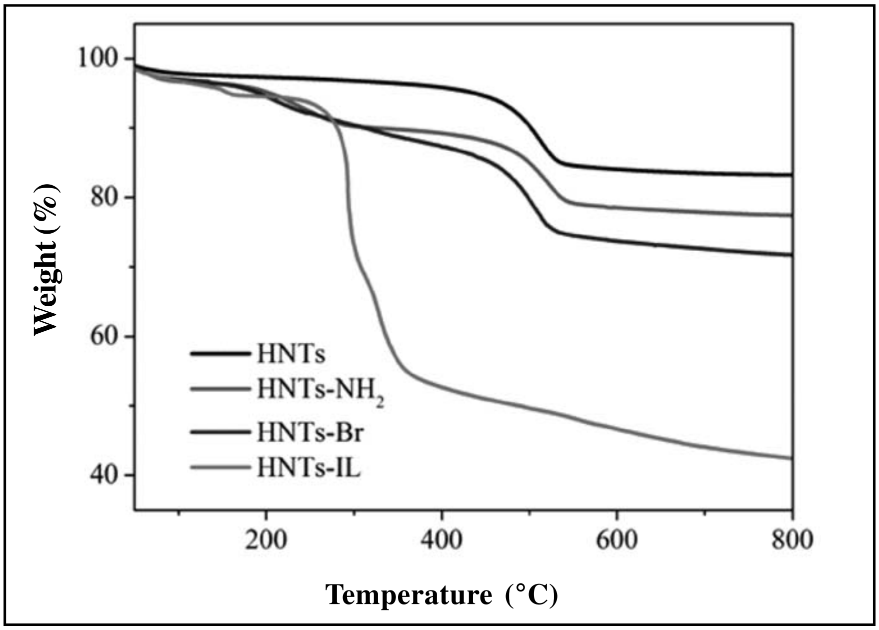


Fig. 2. TGA curves of HNTs, HNTs-NH_2, HNTs-Br and HNTs-IL

TEM images of original HNTs and HNTs-IL are shown in Fig. 3. & Fig. 3A revealed that the original HNTs are cylindrical-shaped with an open-ended lumen along the nanotubes. The nanotubes have an outer diameter of 40-60 nm and a lumen diameter of 15-25 nm, while the wall thickness is about 20 nm. For HNTs-IL shown in Fig.3B, the lumen is almost completely filled or blocked and the outer is also coated by polymer. Therefore, it can be inferred from the TEM micrographs that the polymer was successfully grafted on the HNTs. According to our previous studies, the modification of HNTs by arylboronic acid would result in selective modification that the overwhelming majority modification occurred in the inner surface of HNTs. While the TEM image shown in Fig. 3B gave the result that plenty of poly(ionic liquid)s were also grafted on the outer surface. The outer alumosilicate sheets of the rolls are not tightly bound and the very last one is often loose. So, this very last sheet has an essential part of alumina surface opened to the bulk. The treating of HNTs by *m*-aminophenyl boronic acid may result in some modifications occurred on the edge of the last sheet and the defect on outer surface. The immobilized initiators for the surface initiated-ATRP polymerization may initiate much more polymerizations than those on the inner surface which can be owing to the space effect. On the other hand, the 2-bromoisobutyryl bromide can also react with the hydroxy groups on the outer surface of HNTs-NH_2, which may result in the grafting reaction occur in the outer surface in the Cu(I)-catalyzed ATRP polymerization.

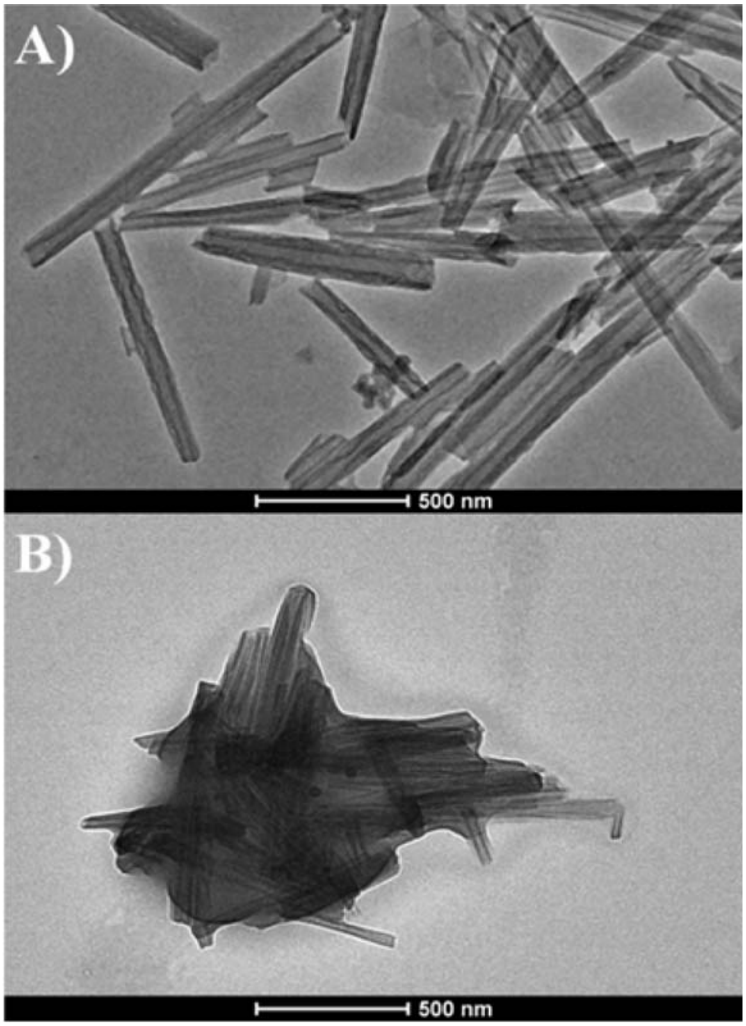


Fig. 3. TEM images of HNTs and HNTs-IL

The microstructure of the obtained HNTs-IL was also observed by SEM. The sample was gold-coated by cathodic spraying (Polaron gold). Fig. 4 shows the SEM photograph of HNTs-IL. The result indicates that the nanotubes retain the regular tubular structures, which implies that the HNTs underwent little damage during the modification and ATRP procedures.

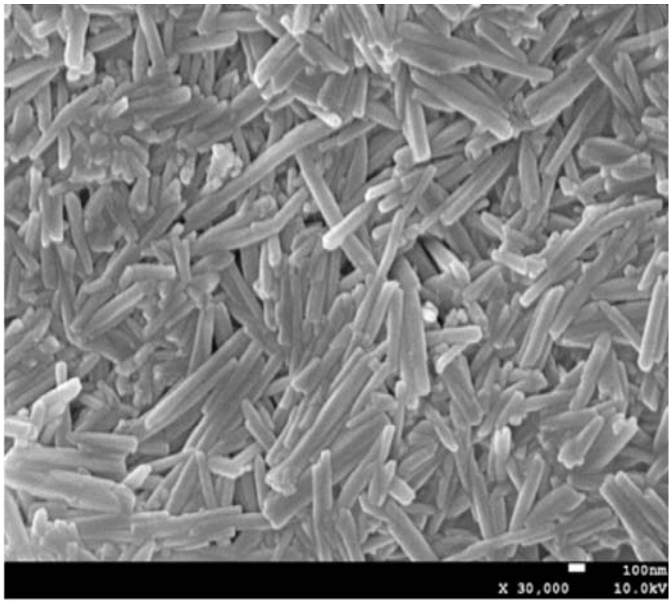


Fig. 4. SEM images of HNTs-IL

The XRD patterns of HNTs and HNTs-IL were shown in Fig.5. The XRD pattern of HNTs features a diffraction peaks at ca. 11.9°, corresponding to a basal spacing of layer spaces. Other diffraction signals at ca 20.0°, 24.6°, 35.1°, 38.2°, 54.9° and 62.3° can also be observed, which are in good agreement with the literatures[31, 32]. As for HNTs-IL, the diffraction peaks assigned to the HNTs can also be detected with slight shifts and decreases of intensity, which can be owing the introduction of poly(ionic liquid)s.

The established B-C link in HNTs-IL can be degraded in the presence of H_2O_2[23, 24] (Scheme 2). To estimate the molecular weight for grafted chains, the product (HNTs-IL) was dispersed in 0.1 M H_2O_2 aqueous solution for 12 h and then the suspension was centrifuged. The supernatant was collected and freeze-dried. The obtained poly(ionic liquid)s were dissolved in 0.1 mol/L $NaNO_3$ aqueous solution and subjected to a Size Exclusion Chromatography (SEC). The elution curves of the obtained poly(ionic liquid)s and standard sample (M_n=1.18 × 10^4 g/mol) are given in Fig.6. The M_n of the grafted chains was calculated as 8.9 × 10^3 g/mol with a polydispersity index of 2.1.

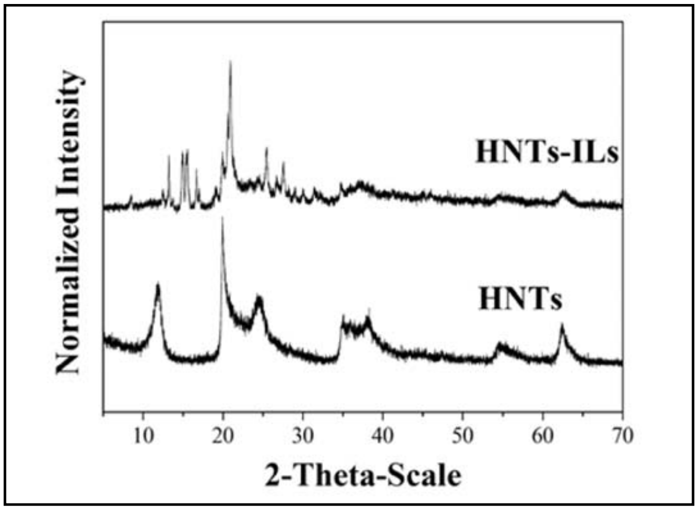
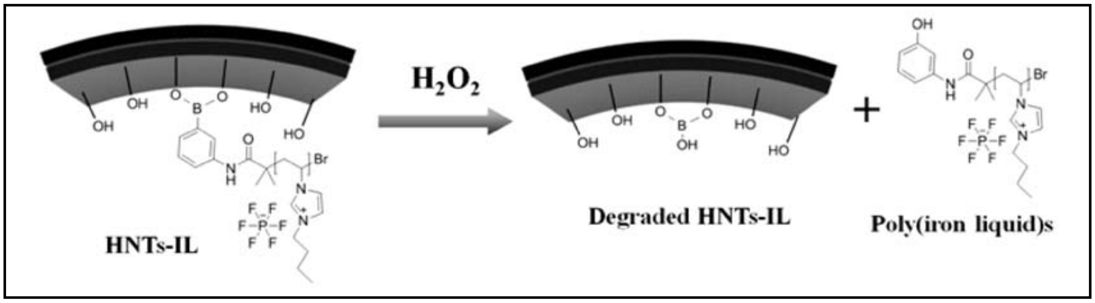


Fig. **5.** XRD Patterns of HNTs and HNTs-IL



Scheme 2. H_2O_2-triggered degradation of HNTs-IL

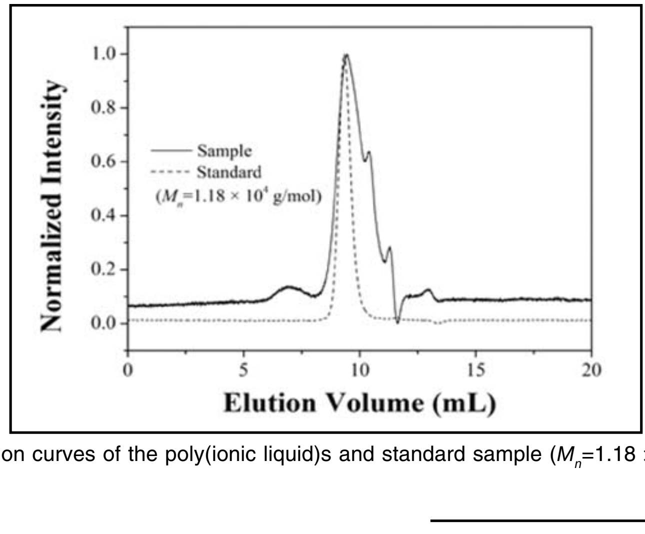


Fig. 6. Elution curves of the poly(ionic liquid)s and standard sample (M_n=1.18 × 10^4 g/mol)

4. CONCLUSION

In this study, the poly(ionic liquid)s-grafted HNTs has been prepared via arylboronic acid-based modification and ATRP process. The structure was well-characterized by FTIR, TGA, TEM and SEM. TGA results show that the HNTs-IL possesses a high grafting ratio at 51%. The micromorphology observation by TEM and SEM indicated that the nanotubes underwent little damage during the modification and ATRP procedures. The obtained product may expand the application of HNTs in the field of conductor material.

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