SIMPLE, ECONOMICAL, SCALABLE AND ENVIRONMENTALLY SUSTAINABLE ROUTE FOR FUNCTIONALIZATION BNNTS

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Abstract

Boron nitride nanotubes (BNNTs) were synthesized at 1150 °C under atmosphere of NH_3/N_2 gas by chemical vapor deposition (CVD) technique. A simple mechanical method (ball milling in the presence of urea) is proposed for functionalization of BNNTs. FTIR results indicate that amine functional groups (N-H and $-NH_2$) were introduced on the nanotubes and the X-ray photoelectron spectroscopy showed that the obtained values for the B:N rates are slight different which may be an indication of the functionalization occurrence. TEM and MEV images after ball milling showed an evidence of small fragments of tubular particles by the parallel fringes corresponding to multiple stacked layers of h-BN sheets. Successful of functionalization of the BNNTs structure was evidenced by stability of the dispersions in water, DMF and acetone. Additionally, the result suggests that the amino termination of the functionalized BNNTs makes it possible to covalently bond to polymers for manufacturing nanocomposites.

1. INTRODUCTION

The fact that carbon nanotubes (CNTs) have unique properties motivated the search for other materials that could also present themselves in the form of nanotubes and bring with this morphology different properties [1,2]. Thus, after the assumption about the existence of boron nitride nanotubes (BNNTs) raised in 1994, research groups engaged and succeeded in the synthesis of this new type of nanomaterial [2]. Results from several studies described in the literature showed that BNNTs were as attractive as researchers imagined. These materials exhibit unique properties such as visible light transparency and electrically insulating nature associated with high thermal conductivity, high thermal and chemical stability and mechanical strength [3,4,5,6].

In addition, when compared to CNTs, BNNTs exhibited a greater homogeneity in their electronic properties, since these properties are not influenced by chirality and geometry [2, 7]. The properties cited above make BNNTs promising for applications in nanoelectronics devices, gas sensors, applications involving high temperature and aggressive environments, as well as in high performance and structural composites [8, 9].

Despite the remarkable properties, BNNTs present low solubility in solvents due to their low surface chemical reactivity (especially when they have a high degree of crystallinity) and a high tendency to self-aggregation [10]. Thus, its applicability is considerably reduced, especially when it becomes necessary to disperse them in a given solvent or even in a polymeric material [8, 11].

Functionalization is considered one of the solutions to overcome these problems. Experimentally, it was proved that different BN surfaces can be modified by –NH_2 and –NHR groups. In 2007, using NH_3 plasma, Zettl's group reported that –NH_2 groups could be covalently attached to BNNTs, followed by the amorphization of BNNTs' walls [12]. Furthermore, Liao and co-workers [13] found that BNNTs could be etched in ammonia solution under sonication. As a result, entangled and freestanding BN nanoribbons were detected in the products due to –NH_2 functionalization and unzipping. Lei and co-workers [14] synthesized NH_2- boron nitride nanosheets (NH_2-BNNSs) via ball milling and using urea and the resultant NH_2-BNNSs exhibited good solubility in water and formed colloidal solutions.

However, finding a process that is easy and effective to add functional groups to BNNTs' surface is not a trivial task, so functionalization is still seen as a challenge in the scientific environment. Thus, the aim of the present work was to develop a simple, economical, scalable, reproducible and environmentally sustainable route to functionalize BNNTs with urea so that it would be possible to disperse this nanomaterial in different solvents and polymeric matrices, promoting its applicability and allowing the scientific environment to profit from its outstanding properties. Urea is a low-cost reactant that was chosen to perform the functionalization of BNNTs. It acts as a chemical supply of nitrogen groups to perform the chemical modification of BNNT samples as well as the process control agent (PCA) of the high energy milling, since it protects the BNNTs from excessive mechanical damage, and minimize an extensive formation of lattice defects.

2 - MATERIALS AND METHODS

2.1 - Materials

The boron nitride nanotube samples that were used in this study were synthesized by CVD method using amorphous boron and iron oxide as a catalyst. This synthesis has been published in previous studies [15]. Acetone 99.5%, Ethyl alcohol 99.8%, Urea 99.0%, were of analytic grade obtained from Sigma Aldrich and were used without further purification.

2.2 - Chemical modification of Boron Nitride Nanotubes by high energy ball milling

The chemical modification of the BNNTs was obtained by high energy ball milling. BNNTs and urea were mixed together in a 1:60 weight ratio inside a stainless steel milling container (1.4435 vessel; 316L) using a planetary ball mill (PM 100, from Restch, Germany) at a rotation speed of 500 rpm for 10h under nitrogen atmosphere. The ball:powder ratio used was 1:100 and the ball size was 10 mm. The milling was stopped in the first half period of the process (after 5h), for 30 minutes, and rotated counterclockwise the second half period. At the end of the milling, the vessel was kept closed overnight for reducing internal temperature and pressure induced by the high energy ball milling.

2.3 - Purification of functionalized Boron Nitride Nanotubes

When the process was complete, the resulting loose powder as well as the material adhered to the grinding balls and reaction vessel were submitted to an exhaustive cleaning process with deionized water and vacuum filtration. At the end, the sample was washed with pure ethanol and submitted to vacuum filtration through a polytetrafluoroethylene membrane filter (47 mm diameter, 0.45 mm pore size, from Whatman) followed by drying at 60°C for 24 hours in a vacuum drying oven. To confirm the absence of any traces of urea as well as other degradation products, FTIR analysis was conducted in the purified functionalized boron nitride nanotubes (BNNTs-U2).

2.4 – Evaluation of the solubility behavior of the functionalized samples

In order to obtain a qualitative response of the change in chemical behavior of the samples due to the functionalization, the BNNTs-U2 sample was added in different solvents: distilled water, ethyl alcohol, acetone and dimethylformamide (DMF), in the proportion of 10mg/10ml and kept in an ultrasonic bath (from Elma) for 30 minutes to promote their dispersion. Dispersion stability was evaluated visually by photographs, which were taken one hour and one week after dispersion.

2.5 - Materials characterization

SEM analysis was performed using an electron microscope (model Sigma VP, from Carl Zeiss). The acceleration voltage used was 20-15kV. TEM analysis was performed in a Tecnai model G2 at 200 kV. FTIR analysis was conducted in a Frontier Single & Dual Range equipment (from PerkinElmer). The measurements were performed in the range of 4000 to 650 cm^{-1} with a resolution of 4 cm^{-1} and 64 scans min^{-1}. XPS spectra were obtained using monochromatic Al Kα radiation (1486.6 eV) and an electron energy analyzer (Specs, Phoibos-150).

3 - RESULTS AND DISCUSSION

3.1 –Visual, SEM and TEM characterization of the BNNTs after the high energy ball milling

When removing the resulting powder from the reaction between BNNTs and urea in the planetary ball mill, a change in color was observed, which also happened after washing it successively in distilled water. The white color of the pristine BNNTs changed to a greyish color after their removal from the planetary ball mill and finally, to a brownish color after their washing. This change in color readily suggests an evidence of change in chemical environment of BNNT sample due to functionalization. A similar result was obtained by Xie and co-workers [16] for BNNTs functionalized with amine-terminated oligomeric poly(ethyleneglycol).

Fig. 1 a-b shows a typical SEM image of the raw BNNT sample that was used in this work. It shows a web-like morphology and it is relatively rich in nanotubes. The sample consisted of nanotubes of tens of microns in length (Fig. 1c) with a large diameter distribution. Also, a soot material that consists of amorphous boron nitride is also present in the sample. The TEM image suggests that the nanotubes in the raw sample consist of thin hollow tubular particles with walls formed by multiple stacked layers of h-BN sheets. By the TEM high resolution mage (Fig. 1-d) it is also possible to calculate the interlayer spacing of the BNNT sample giving a mean value of the ≈ 0.34 nm that agrees with d(002) spacing in bulk h-BN (0.332 nm).
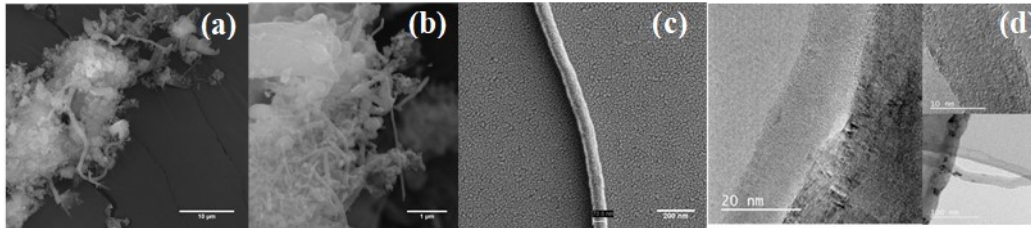
Fig. 1 - SEM (a-c) and TEM (d) images of raw BNNT sample.

After mechanical milling, BNNTs of relative large lengths and diameters disappear giving place to small compact particles (Fig. 2 a-b) and few small nanotubes can be found in some areas near the particle boundary (Fig. 2c). This modification suggests that the high energy of the milling can break the large nanotubes into small fragments and allow only the smallest nanotubes to be incorporated into these compact particles.
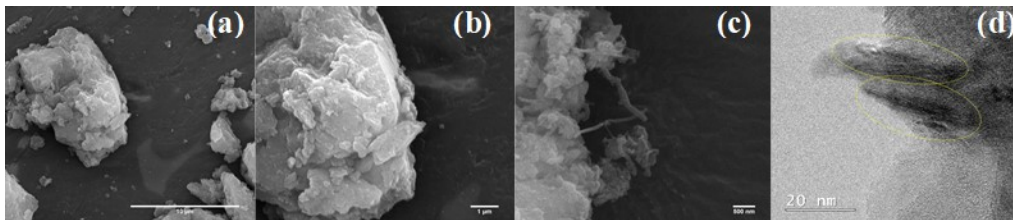

Fig. 2 - SEM (a-c) and TEM (d) images of BNNT sample after functionalization procedure in high energy mechanical milling.

The TEM image of BNNTs-U2 (Fig 2d) samples after ball milling shows evidences of small fragments of tubular particles by the parallel fringes corresponding to multiple stacked layers of h-BN sheets. These results agree with the SEM observations.

3.2 – Evaluation of the functionalization

3.2.1 - Fourier transform infrared spectroscopy (FTIR)

The FTIR spectra of the BNNTs, functionalized BNNTs before washing (BNNTs-U1), and after washing (BNNTs-U2) and urea are shown in Fig. 3a, 3b, 3c and 3d, respectively. It can be observed that bands at 1156, 1599, 1679, 3258, 3342 and 3437 cm^{-1}, assigned to functional group vibrations present in urea [17], are also identified in the FTIR spectrum of BNNTs-U1 (Fig. 3b). As the ratio used in this functionalization was 60:1 (urea/BNNTs), there was a high amount of urea in contact with the nanotubes, which explains the similarity between the BNNTs-U1 and urea spectra. After the successive washes in distilled water, all the adsorbed urea was removed (Fig. 3c), and a broad signal around 4000 and 2700 cm^{-1} can be observed which cannot be observed in the pristine BNNTs spectrum. This signal (inset in Fig. 3c) was attributed to the N-H and NH$_2$ stretch vibration modes by a peak-fitting procedure. Besides that, characteristic bands of urea, such as 1153 cm^{-1} (attributed to N-C-N) and 1683 cm^{-1} (attributed to C = O), are no longer present in the BNNTs-U2 sample after washing. Therefore, one can say that washing was efficient, removing all adsorbed urea on the walls of the nanotubes.
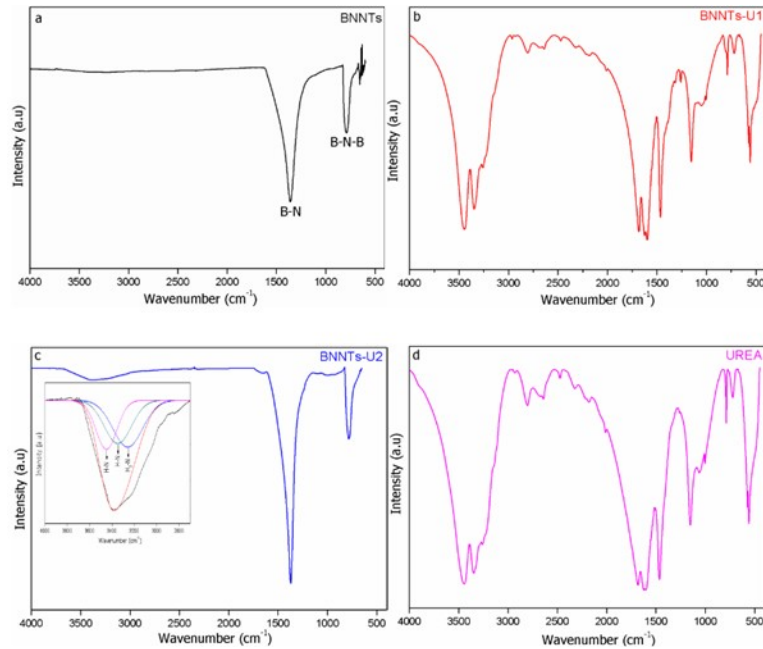
Fig. 3 – FTIR spectra for a) BNNTs, b) BNNTs-U1, c) BNNTs-U2 and d) urea.

Based on the results obtained in the spectroscopy analysis, where characteristic bands of the -NH and NH_2 bonds were found, it was inferred that functionalization occurred. It is thought that -NH or NH_2 groups have bounded to sites containing defects or on the walls of nanotubes.

3.2.2 - X-rays photoelectron spectroscopy (XPS)

XPS spectra were obtained in the regions of the main elements of interest (B, N, C and O). Fig. 4 shows the survey XPS spectra of the BNNTs and BNNTs-U2 samples. All samples show photoemission peaks for B 1s (~190.5 eV), N 1s (~198.8 eV), C 1s (~284.5 eV) and O 1s (~533.4 eV). The C, O and Si signals identified in the BNNT sample before chemical modification (Fig. 4a) are related to the surface contamination that generally occurs during the preparation process and to the exposure of the sample to air, as commonly observed in XPS measurements. The stoichiometry rate of boron to nitrogen atoms (B:N) is confirmed from the peak areas of the XPS survey spectra. The obtained values for the B:N rates are 1.05 for BNNTs and 0.96 for BNNTs-U2, indicating almost stoichiometric samples. Similar results were obtained by Li and co-workers [18]. However, for BNNTs-U2 sample a slight excess of N atoms was observed, which may be an indication of functionalization occurrence. Two additional peaks were identified in the Fig. 4b at 712.0 (Fe 2p) and 578.0 eV (Cr 2p). Both peaks are associated with the contamination from the stage of chemical modification carried out in the planetary mill.
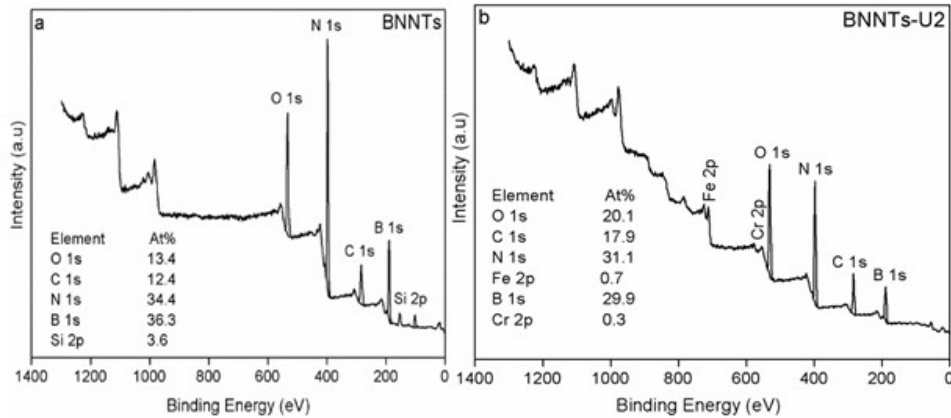
Fig. 4 – XPS spectra for a) BNNTs and b) BNNTs-U2.

3.2.3 - Evidence of the change in the chemical environment of the BNNTs-U2 sample

Fig. 5 shows BNNTs-U2 dispersed in distilled water, DMF, acetone and ethyl alcohol one hour and one week after the dispersion process. Visually, it is possible to observe that BNNTs-U2 showed better dispersibility in DMF, followed by acetone, water and ethyl alcohol. In all cases, BNNTs sedimentation was observed, but more noticeable in alcohol. The latter presented the least satisfactory result, since a short period of time after the dispersion process, it was possible to see a big quantity of sedimented BNNTs, which indicates the little interaction between the BNNTs-U2 and ethyl alcohol.

Tiano and co-workers [11] conducted a study of the dispersivity of BNNTs in several solvents and concluded that they did not disperse in water. To explain such behavior, the Hildebrand solubility parameter (δ^2_t) was used, which is a function of the Hansen parameters ($\delta^2_d, \delta^2_h, \delta^2_p$), as one can see in Equation 1.

$$\delta^2_t = \delta^2_d, \delta^2_h, \delta^2_p \quad (1)$$

Where δ^2_t is the dispersion parameter, δ^2_h is the hydrogen interaction parameter, δ^2_p is the polar interaction parameter. Hansen parameters may explain why certain solutes can be dispersed in certain solvents and others cannot. Each solute and solvent have their own Hansen parameters and there is an optimal range in which the parameters of a given solvent must be contained in order to disperse certain solutes. Thus, all parameters will have a contribution that will permit the dispersion. Tiano and co-workers [11] observed that water was not able to disperse BNNTs, however in the present work, some dispersion was observed. This can be explained by the fact that the functionalization of BNNTs may have changed their Hansen parameters allowing water to disperse them.

These results are still preliminary for conclusions. Other ways to evaluate the dispersion of the functionalized nanotubes should be performed in the future, since in the present work focused on the visual aspect.
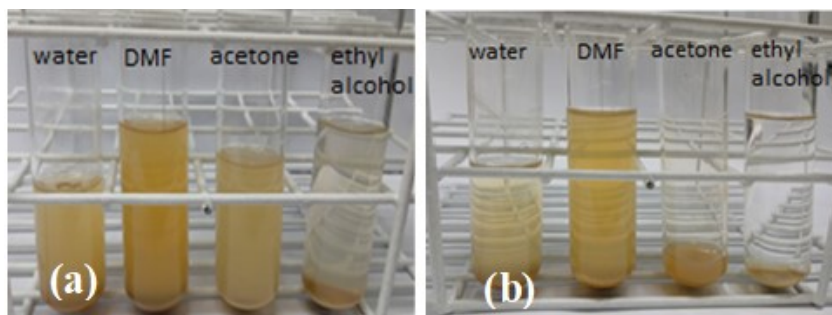
Fig. 5 - Dispersion of BNNTs-U2 in different solvents a) one hour after dispersion and b) one week after dispersion

4 - CONCLUSIONS

An efficient route for amino functionalization of BNNTs is proposed in this paper. The results clearly demonstrate that the urea induced functionalization is a good method for the successful functionalization of BNNTs with the advantages that functionalization can be carried out in a simple manner. Based on the results obtained in the FTIR spectroscopy, where characteristic bands of the -NH and NH_2 bonds were found it was inferred that functionalization occurred. It is thought that -NH or NH_2 groups have bound to sites containing defects or on the walls of nanotubes. Besides the X-ray photoelectron spectroscopy showed that the obtained values for the B:N rates are slight different which may be an indication of the functionalization occurrence. TEM and SEM images show that the high energy of the milling broke the large nanotubes into small fragments and possibly allowed only the smallest nanotubes to withstand the process. Successful of functionalization of the BNNTs structure was evidenced by stability of the dispersions in water, DMF and acetone. However, other ways to evaluate the dispersion of the functionalized nanotubes should be performed in the future.

ACKNOWLEDGMENTS

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