

Amine Functionalization of Boron Nitride Nanotubes through Exposure to a Capacitively Coupled Radio-Frequency Plasma

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Abstract: Boron nitride nanotubes possess many commercially exploitable properties; however, surface functionalization is required to harness these properties. This is typically done using wet chemistry methods that have a number of drawbacks associated with them. In this work, we demonstrate a novel scalable and solvent-free approach to achieve amine functionalization using an Ar/NH₃ capacitively coupled RF plasma. The surface functionalization was confirmed by thermogravimetric-infrared spectroscopy.

Keywords: Boron nitride nanotubes, amine functionalization, capacitively coupled plasma

1. Introduction

Boron nitride nanotubes (BNNTs) are structurally similar to carbon nanotubes (CNTs) [1] and feature similar impressive properties. Some of the extraordinary properties of BNNTs include their high mechanical strength, chemical and thermal stability [2], and wide bandgap semiconducting capabilities [3]. These properties make BNNTs appealing for many applications. However, the high aspect ratio of BNNTs favours agglomeration and the van der Waals force makes interfacial interactions between BNNTs and matrices difficult to achieve [4]. These issues can be resolved using chemical functionalization by improving the solubility and stability of BNNTs [4-6], but this is typically done using wet chemistry approaches [7-9]. Wet chemistry functionalization methods have multiple drawbacks associated with them, such as the generation of large amounts of chemical waste, scale-up limitations, and the high cost of solvents [10]. Furthermore, agglomeration reoccurs when removing the solvent.

Exposure to a reactive plasma can be used as a method for chemical functionalization of BNNTs. The reactive species present in the plasma can produce defects on the surface of BNNTs where different chemical functional groups can bind to [5,6,11]. Plasma functionalization has the potential to overcome the main difficulties associated with chemical functionalization without the use of solvents, therefore making this technique environmentally friendlier, more scalable and less expensive.

Amine functionalization, both NH and NH₂, has been chosen because of the importance of these functional groups to the chemical industry, particularly for epoxides [12,13]. Amine functionalized BNNTs can significantly impact their applications as the epoxide resin market is estimated to be \$US 11 billion by 2021 [14]. Additionally, there is theoretical calculations that show both NH and NH₂ can bind to the BNNTs' surface favourably [15].

In this work, we show that amine functionalization of BNNTs can be achieved using a 100% dry and solvent-free

non-thermal plasma process. The reactive species in the plasma and surface functionalization are analysed using characterization techniques such as optical emission spectroscopy (OES) and tandem thermogravimetric-infrared analysis (TGA-IR) spectroscopy.

2. Methods

The BNNTs were produced from the NRC's Nanotube Manufacturing Facility from pure hexagonal boron nitride (h-BN) powder (99.5 %, avg. 70 nm, MK-hBN-N70, M K Impex Corp.) using the Hydrogen-Assisted Boron Nitride Nanotube Synthesis (HABS) method, previously reported by Kim et al [16]. The as-produced BNNTs (R-BNNT) were purified with chlorine gas, as described recently [17]. The purified BNNTs are referred to as P-BNNT hereafter. The reactive species present in the non-thermal plasma were analysed by OES using a modular spectrometer (JAZ-EL200-XR1, Ocean Optics, with 1.7 nm FWHM resolution). The light emission was collected and guided to the spectrometer using an optical fiber (QMMJ-55-UVVIS-200/240-2PCBL-0.25, OZ Optics Ltd., with a core size of 200 μ m). The functionalized BNNTs (F-BNNT) were characterized using TGA that collected IR absorption data concurrently using a Netzsch STG 449 F1 instrument coupled to a Bruker Tensor 27 FTIR spectrometer.

The plasma functionalization reactor, shown in Fig. 1 below, was custom-built to sustain a large volume of continuous wave capacitively coupled radio-frequency (RF, 13.56 MHz) plasma at low pressure. The reaction chamber, enclosed in a Faraday cage, consists of a glass tube with inner diameter and length of 1.5 in. and 14 in., respectively. Five copper straps (0.5 in. wide) wrapped around the exterior of the glass tube serve as the electrodes for staged capacitive coupling. The electrodes alternate between live and ground, where the live electrodes are powered by an Advanced Energy RFX600A, 13.56 MHz generator and a VM-100 automatic matching network. The P-BNNTs are baked for 3 hours at 110 °C to remove any moisture prior to being added to the conical reducer located

at the base of the reactor. The glass tube reactor is evacuated to a pressure of 25 mTorr using a dual stage rotary vane vacuum pump (Alcatel, Pascal Series 2005 SD) for 1 hour to remove any remaining moisture from the P-BNNTs. The reactor is then backfilled to a pressure of 2 Torr using an Ar/NH₃ gas mixture at 98/2 sccm, respectively. The P-BNNTs are pulsed into the glass tube using a 3-way solenoid air directional control valve at a cycle time and duty cycle of 1 s and 5 %, respectively. Each sample undergoes a 100 min treatment time at 100 W of continuous RF power. After plasma exposure, the samples remain under vacuum for 20 min and then exposed to Ar for 10 min to stabilize the surface before exposure to air [6].

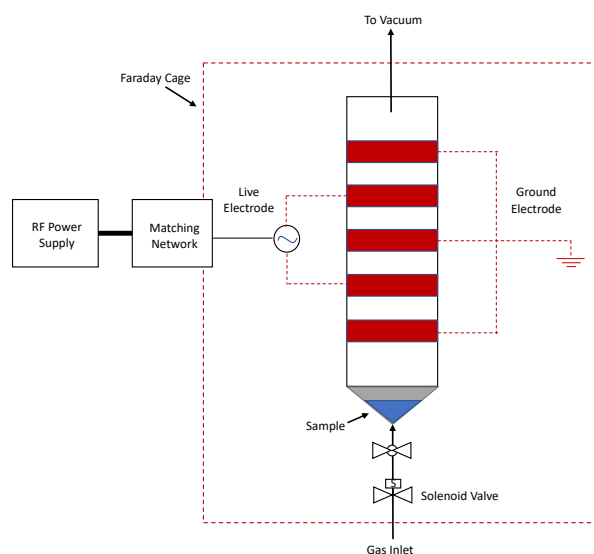


Fig. 1. Schematic of custom-made RF plasma functionalization reactor.

3. Results and Discussion

OES was used to identify the chemical species generated by the plasma and emitted in the near-UV-visible range, and to determine the gas composition that resulted in the highest concentration of the active chemical species. Fig. 2 shows a typical spectrum obtained with various Ar/NH₃ gas ratios. We are particularly interested in the NH radical as it is highly reactive and has been used to covalently functionalize h-BN nanosheets [15]. Additionally, NH₂ cannot be detected using the OES setup [18]. The measured spectrum identifies the following reactive species: N₂⁺ at 388 nm, H^α and H^β at 656 and 486 nm, respectively [19]. The most prominent peak is the NH molecular emission line at 336 nm. The peaks in the range of 700-900 nm are from atomic Ar lines [19]. As observed in Fig. 2, the intensity of the peaks is drastically enhanced when the concentration of ammonia decreases, suggesting that the concentration of the desired radicals, specifically NH, is maximized at 2 % NH₃.

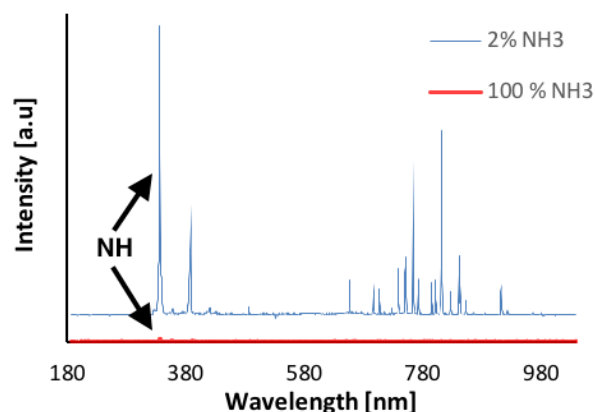


Fig. 2. Optical emission spectrum for two plasma compositions.

TGA-IR spectroscopy was used to identify the reaction time and operating power that resulted in the highest degree of amine functionalization. From the TGA oxidation data in Fig. 3 below, the 100 min treatment time results in the most mass loss. There are two prominent oxidation peaks that can be observed: one at 81 °C and the other at 250 °C. The peak at 81 °C is associated with the desorption of water, which is attributed to the physical adsorption of water onto the F-BNNTs after plasma treatment. This physical adsorption drastically increases with plasma treatment, particularly with the 100 min sample, suggesting that the addition of amine groups potentially changed the F-BNNTs' surface from hydrophobic to hydrophilic.

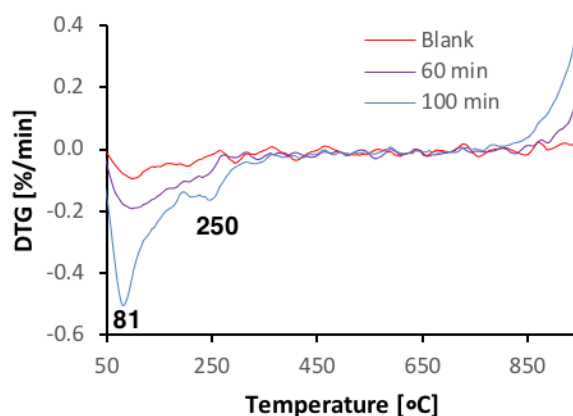


Fig. 3. Derivative thermogravimetric (DTG) graph for the P-BNNTs exposed to different plasma treatment times.

In-line FTIR was used to analyse the species evolved at 250 °C (results not shown). Absorption bands appeared at 930, 965 and 3334 cm⁻¹, which are characteristic signatures of ammonia [20]. This suggests that the F-BNNTs were functionalized with amine groups because the release of ammonia at 250 °C is not observed with the untreated sample. Additionally, the operating power was also varied from 20 to 200 W for reaction times of 100 min and it was

found that 100 W resulted in the highest degree of P-BNNT functionalization.

4. Conclusion

We have demonstrated that amine functionalization of BNNTs can be achieved through exposure to an Ar/NH₃ capacitively coupled plasma. The presence of amine groups on the surface of F-BNNTs was confirmed using tandem TGA-IR spectroscopy. The plasma chemical make-up was analysed and optimized using OES by varying the NH₃-to-Ar ratio. This functionalization method allows for BNNTs to be functionalized using a new impactful solvent-free method, resulting in a more environmentally friendly, scalable and inexpensive process than the current wet chemical functionalization methods used.

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