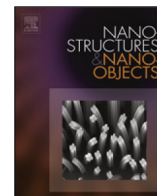




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## Efficient sensitive polymer-grafted boron nitride nanotubes by microwave-assisted process

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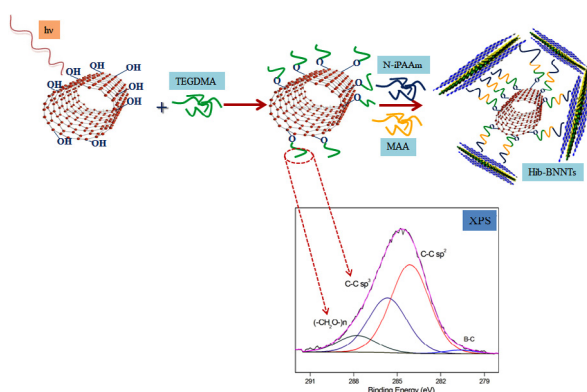
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## HIGHLIGHTS

- Oxidized BNNTs were covalently functionalized with TEGDMA by microwave reaction.
- The presence of attached functional groups linked to the BNNTs was investigated.
- Hib-BNNT has a potential application as drug delivery thermo and pH sensitive.

## GRAPHICAL ABSTRACT



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## ABSTRACT

Boron nitride nanotubes (BNNTs) have been growing in notoriety in the development of systems aiming bioapplications. Hybrids formed between these inorganic structures and sensitive polymers are regarded as potential and safe drug delivery device as they can respond strongly to temperature and pH changes. In this work the synthesis of a BNNT-Poly[(N-iPAAm)-co-(MAA)] system was explored and the functionalization process was achieved by a microwave-assisted route, in order to create a highly specific environment based drug delivery device as a new perspective for the pharmaceutical industry. Due to the diffusion modulation shown by these polymers in response to external factors, the drug release can be controlled and directed when it is needed. The thermal chemical vapor deposition, TCVD-formed BNNTs were oxidized in acidic medium and functionalized via microwaves with triethylene glycol dimethacrylate (TEGDMA), a crosslinking agent with two unsaturated carbon bonds from which one reacted with the oxidized BNNT and the other one is expected to bond to the polymeric network, thus covalently linking the two phases. The hybrids were formed by polymerizing Poly[(N-iPAAm)-co-(MAA)] with the functionalized BNNTs. The samples were characterized using Fourier-transform infrared spectroscopy (FTIR), thermogravimetric analysis (TGA), X-ray photoelectron spectroscopy (XPS), elementary analysis (CHN), Zeta potential, scanning electron microscopy (SEM) and high-resolution transmission electron microscopy (HRTEM) to evaluate the chemical modifications that were introduced along the tubes. The material's chemical bonds were identified and the amounts of the elements in the nanohybrid were

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measured. Both parameters indicate the BNNTs functionalization and hydrogel presence in their structure. Stability tests have been conducted to check the interaction between the phases in the nanocomposites. The results confirm the successful synthesis of these hybrid systems and stimulate their investigation as anticancer drugs carriers.

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## 1. Introduction

An important historical reference about boron nitride nanotubes (BNNTs) synthesis is the work of Chopra and co-workers published in 1995 [1]. Since then, the BNNTs have emerged as a key material in the field of nanotechnology due to their extraordinary thermal stability, high resistance to oxidation and high Young's modulus besides of the ability to suppress thermal neutron radiation [2–4]. However, since BNNTs have a hydrophobic surface due to typical  $sp^2$  hybridized B–N bonds, they are incapable of forming stable hydrogen bonds with water molecules. Furthermore, the low dispersibility of BNNTs in most of the organic and inorganic solvents, combined with poor chemical compatibility, has become a major issue, since it may impair their applicability [5]. Therefore, adequate functionalization of BNNTs by covalent or non-covalent methods can expand their potential applicability. The functionalization or chemical modification of BNNTs through the covalent attachment of atoms or molecules on the surface has been used to introduce chemical specificity and processability in different environments [6–8]. In nanomedicine, for example, the covalent modification of the BNNT surface would open interesting perspectives for the use of these nanomaterial in drug delivery and cell targeting [9].

Currently, functionalized BNNTs with different functional groups have been widely used in biological studies. In the study of Ferreira et al. [7], for example, the BNNTs were oxidized and functionalized with folic acid through a covalent approach. Biological tests with HeLa cells demonstrated an increased cellular up-take of the functionalized BNNTs, with respect to the pristine BNNTs, due to the enhanced receptor-mediated endocytosis. Özlem et al. [10] functionalized BNNTs with oligonucleotides. The studies suggest that BNNTs can be used as a potential vector to transfect cells. Daniel et al. [11] functionalized BNNTs with glycol chitosan polymer and radiolabeled them with technetium ( $^{99m}\text{Tc}$ ) as a means of studying their *in vivo* biodistribution behavior in mice. The results showed a massive reduction of radiation in the organs where the nanostructures had previously accumulated, in part due to intense renal excretion and partly due to a possible metabolism of a glycol chitosan polymer coating, with a consequent bioaccumulation of BNNTs in the studied organs [11]. Depending on the functional group grafted in the nanoparticle surface, such as folic acid, functionalization process allows the production of materials that are recognized by specific cellular receptor. These materials may show impact the uptake efficiency, allowing the active accumulation on tumor sites due to the system of ligand–receptor interactions that induce receptor-mediated endocytosis and internalization inside the cells. Then, a suitable surface modification is essential to allow an adequate performance of these materials.

As drug delivery devices, BN nanotubes offer a number of advantages when compared to traditional nanovectors. More specifically, they have a larger inner volume, which allows more drug molecules to be encapsulated, and they have distinct inner and outer surfaces for functionalization. In addition, the volume and the surfaces of the nanotube are more readily accessible since the end caps can be easily removed [12]. Nevertheless, pure BNNTs present a major problem as far as drug release is concerned. There is the limited control of the drug release whose major mechanism is diffusion, and the van der Waals forces between the sidewalls of

adjacent nanotubes, which causes the BNNTs to aggregate in liquids when they are packed together by surface tension, hindering their prospective applications in biological contexts. Therefore, it is indispensable the development of new materials with optimal tailored characteristics, especially hybrid materials based on polymer and inorganic nanostructures, seeking to improve their biological applications [13–15].

Responsive hydrogels are reticulated polymers which are able to swell or collapse depending on external factors, such as pH, ionic strength or temperature, the latter having been more extensively studied [16]. For these materials, the phase transition between swelled and collapsed states brings no immediate harm to the structure due to the reversibility of the hydrogen bonds formed between the polymeric chains in the net, and can be repeated, characterizing the process as reversible [17,18]. The response to stimuli depends on the susceptibility of the repeating units to these external factors and also their molecular fraction in the polymer [19]. For temperatures under the lower critical solution temperature (LCST), the polymeric net of hydrogels such as poly(*N*-isopropylacrylamide) [P(*N*-iPAAm)] is swollen, hydrated and hydrophilic and, above that, it becomes collapsed, dehydrated and hydrophobic [20]. For pH-sensitive hydrogels, the same phase transition is caused by the ionization of carboxyl groups from the methacrylic acid (MAA) molecules grafted into the polymeric net [21,22]. As smart polymers, sensitive hydrogels present the possibility to predict and control the release behavior of compounds such as drugs or even water, thus finding application varying from agriculture and reforestation [23] to the pharmaceutical industry [24].

Combining sensitive hydrogels into a matrix that is simultaneously thermally and hydrothermally resistant, highly porous, chemically stable and biocompatible expands their application perspectives [16,25] and highlights the best features of both phases [26]. It is important to note that the properties of the polymeric matrices are highly dependent on the structure of the crosslink network. In this sense, the functionalized BNNTs can contribute to the improvement of mechanical properties of hybrid systems.

It is known in organic chemistry that certain reactions can be microwave-assisted to improve selectivity and reduce reaction times [27]. Several studies concerning the functionalization of different nanotubes, especially carbon nanotubes (CNTs) by microwave method have been reported [28]. Microwave process may also result in lower structural defects on the nanotubes surface compared to conventional methods [29]. The traditional methods utilize strong acid mixtures to introduce OH functional groups into BNNTs and COOH into carbon nanotubes, or strong oxidizing agents such as potassium permanganate (Hummer's Method) to oxidize expanded graphite. In order to introduce these groups, it is necessary to introduce defects in the tube structure by changing its hybridization from  $sp^2$  to  $sp^3$ . These functional groups can also be inserted into defect sites (Stone–Wales defects) from the synthesis process [9,30–32]. Despite many years of experimental synthesis and characterization of functionalized nanotubes materials, BNNTs have not been studied extensively when compared to CNTs. As far as we know, no study describes the functionalization of BNNTs by microwave-assisted process and only limited investigation of the chemical interactions between the organic moieties and the

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