



Perspectives on Chemical Modification of Carbon Nanomaterials Assisted by Microwave Radiation



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Abstract

Carbon nanomaterials (CNMs) as graphene and carbon nanotubes (CNTs) have attracted attention of scientific community due to their high performance and applications. However, their potential applications as nanofillers, depends necessarily of their production which high structural quality, great compatibility with the host system. For instance, in polymeric matrices this issue involves several challenges due to their low dispersibility in water and organic solvents, thus different process of chemical modification of CNMs surfaces have been reported. In cases of functionalization with amino groups, most of them use in one of their chemical steps thionyl chloride (SOCl₂) as intermediate reagent. In general, the use of SOCl₂ limits the chemical process, due to of its dangerous nature and high level of toxicity. Another drawback found in this kind of methodology is the time spent on reflux lasting days and making it a very onerous process. In this context, the chemical modification of CNMs assisted by microwave radiation has been explored in synthesis, purification and chemical modification processes of these nanostructures resulting in simpler and faster procedures that allow its used on a large scale and with low environmental impact.

Keywords: Carbon nanomaterials; Graphene; Carbon nanotubes; Chemical functionalization; Microwave irradiation

Mini Review

CNMs as graphene and carbon nanotubes exhibit exceptional physical properties that have generated great interest from the scientific and technological community [1-4]. Graphene can be understood as a single stable 2D graphite layer formed only by carbon atoms hybridized in sp² and arranged in hexagonal rings, that theoretically is considered as a fundamental block for the construction of other allotropic covalent carbon solids, such as graphite, fullerenes and CNTs [5]. In order, the development of several methods of production of graphene and carbon nanotubes has been gaining relevance because their nanostructure exhibits excellent electrical, thermal and mechanical high flexibility. In special, CNTs have been studied in approximately the last two decades by many researchers due to their great potential application in different fields [6]. Their important features such as light weight, high aspect ratio, and impressive tensile strength, thermal and electrical conductivity make them useful as nano additives in different polymers and ceramics systems [7]. On the other hand, it was observed that graphene presents high electrical mobility (200.000cm²V⁻¹s⁻¹) [8], two orders of magnitude greater than the silicon and its electric transport occurs from ballistic form at room temperature [5]. Graphene showed thermal conductivity of approximately 5.000Wm⁻¹K⁻¹ [9], and high surface area (2.630m²g⁻¹) [10]. Moreover, it is important to mention that

graphene presents a modulus of elasticity of 1.1GPa and tensile strength of 125GPa, 200 times greater than steel [11].

Different methods of synthesis of CNMs, such as chemical vapor deposition (CVD), electric arc discharge, epitaxial growth on SiC substrate, reduction of CO, opening of CNTs (bottom-up) and graphite exfoliation (top-down) [12-16], have been reported. Microwave-assisted procedures have been used in methodologies for the growth of graphene films via CVD [17], as well as chemical exfoliation processes of graphite to produce graphene oxide (GO) nanosheets [15,18,19]. Chemical functionalization of CNMs and their applications such as reinforcing polymers composites, supercapacitors, cells solar cells, memory devices, biosensors, drug dispensers [4,12,20-32] among other, also have been reported.

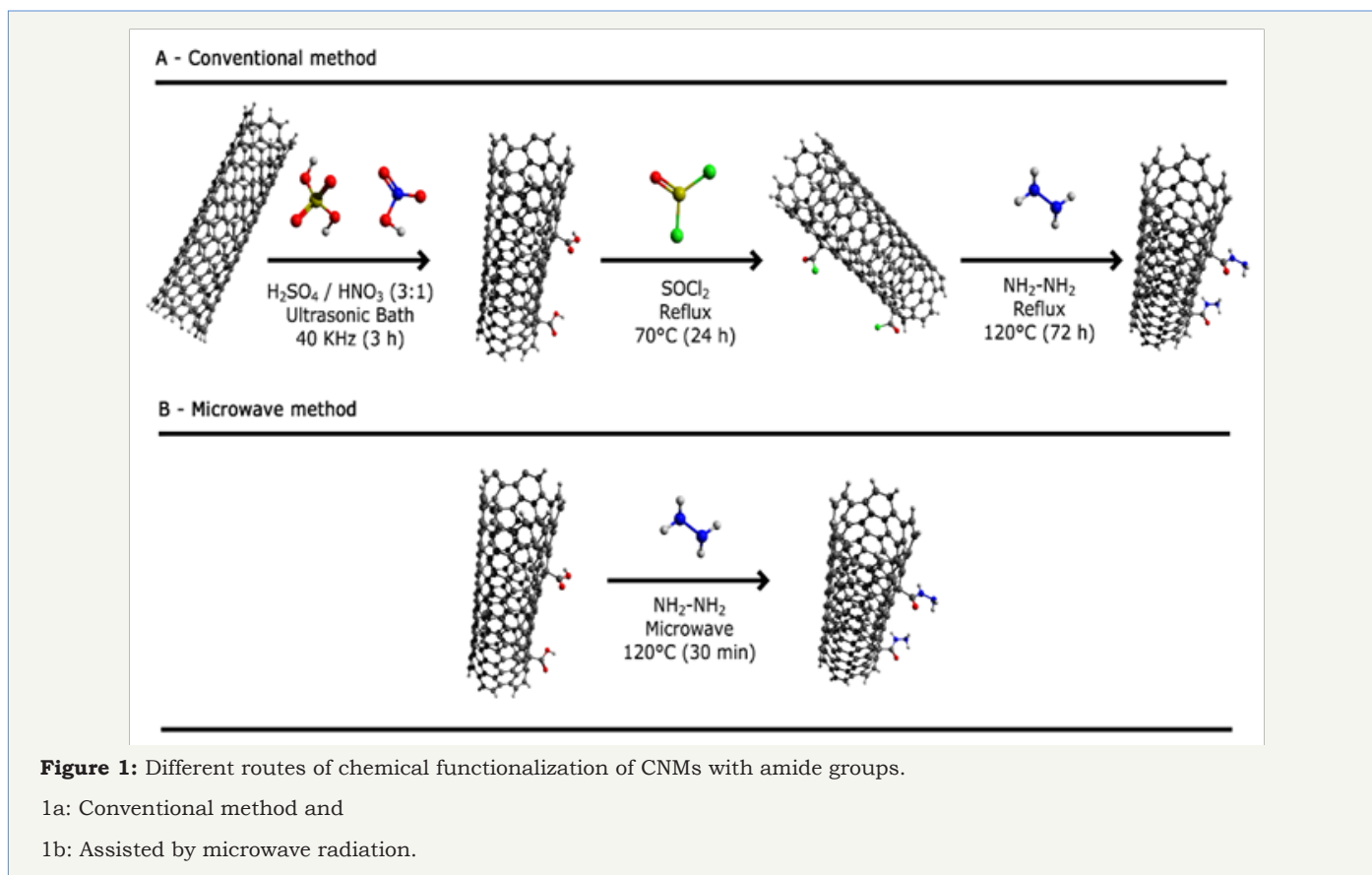
The ability to control the functionalities of CNMs surface is importance for exploring and building blocks in the engineering of supra-molecular structures, that imparting them specific solubility in specific solvents or host matrices [33]. In general, to produce a more reactive CNMs surface in different substrates, chemical groups may be covalently introduced on their surface [5,24,34]. In case of graphene, graphite and CNTs, this type of procedure needs to be controlled duo to the inherent re-hybridization process of carbon atoms sp² to sp³. This process is accompanied by the partial

or total loss of π - π electronic conjugation that alter significantly their electrical properties [5,22,26,35,36]. To overcome this issue, one strategy adopted is the doping of the crystalline network of CNMs with heteroatoms such as N, P and B without destroying their structural integrity, thus preserving their potential properties [20,22,37] however, this task is not easy.

Several studies have been carried out to develop effective CNMs functionalization process, and most of them adopted the strategy based on processes of carboxylation. This reaction has advantages in that the carboxylated groups can be derivatized to ester, amides and isocyanates [33,38]. However, many works with amino-functionalization reaction in CNMs, report processes via SOCl_2 (Figure 1). Niyogi et al. [34] reported an effective way of obtaining graphene oxide functionalized with octadecylamine (ODA) after the treatment of graphite oxide with sulfuric acid, followed by treatment with thionyl chloride (SOCl_2) and ODA, forming GO-ODA. Hu Y et al. [6] were able to functionalize CNMs with 4,4'-diaminodiphenylsulfone (DDS) in dimethylformamide (DMF) at 130 °C under inert atmosphere at reflux for 6 days. Silva et al. [7] modified covalently CNTs with triethylenetetramine groups (TETA). Initially, they used as the reaction mixture in the presence of distilled SOCl_2 and maintained under reflux for 24 hours. After reflux, all SOCl_2 was extracted from the medium by distillation. Then,

excess TETA was added in volumetric flask and kept under reflux for 72 hours [7]. This classical amino-functionalization reaction with SOCl_2 has resulted in some difficulties and inconveniences, since thionyl chloride has a high degree of toxicity, and high carcinogenic potential. SOCl_2 reacts violently in contact with water, releasing acid gases and, in contact with metal surfaces, can generate flammable and explosive hydrogen. Generally, this methodology requires approximately 96 hours or up to 6 days, which makes the procedure very onerous [7,39].

On the other hand, several chemical modification methodologies assisted by microwave have been reported [16,19,20,40-46]. In general, the irradiation process can be used in mild conditions, with controlled temperatures and reduced time reaction, when compared to conventional techniques (Figure 1) [13,33,41,46-48]. An advantage of use microwave radiation that only 3 minutes of irradiation in CNTs samples (in $\text{H}_2\text{SO}_4/\text{HNO}_3$ mixture) is sufficient to produce carboxyl groups promoting their dispersibility in water [48]. Amidation, esterification and cycle addition reactions in CNMs surface assisted by microwave in several solvent systems and ionic liquids have also been reported [49-52]. The introduction of amide groups in GO surface in only 30 minutes without the use of SOCl_2 , was reported by Ribeiro et al. [33].



Several other methodologies of chemical modification of CNMs assisted by microwave have led to the formation of CNMs

functionalized with different groups in a smaller reaction time [46], some of them are summarized in the Table 1.

Table 1: Synthesis and chemical functionalization methodologies of CNMs assisted by microwave radiation.

Nanomaterials	Methodology	Reference
Graphene Oxide	The addition of a small amount graphene oxide leads to deoxygenation reaction of GO under microwave irradiation and graphene formation.	[41]
MWCNTs	Multi-walled carbon nanotubes (MWCNTs) synthesized by thermal chemical vapor deposition have been successfully purified by high efficient microwave acid digestion method.	[53]
Carbon nanotubes	Interaction study of carbon nanotubes and microwaves, responses, and applications	[46]
MWCNTs-NCO	Microwave-assisted functionalization of carbon nanotubes with isocyanate groups allowed a reduction of functionalization time from 24h to 30 minute with no change in the degree of functionalization or in the nanotube characteristics.	[38]
Carbon black	Carbon black surfaces were sequentially modified with ethylenediamine by microwave irradiation.	[54]
Graphite	Versatile method to achieve the exfoliation and reduction of graphite oxide assisted by microwave reaction.	[55]
Graphene	Chemical reduction method assisted by microwave irradiation for the synthesis of chemically converted graphene sheets and metal nanoparticles dispersed on the graphene sheets.	[44]
Graphene-chitosan	Chitosan (CS) modified graphene nanosheets were prepared under microwave irradiation in N,N-dimethylformamide medium.	[19]
Mos2/graphene	Graphene-based molybdenum disulfide catalyst was prepared via a microwave irradiation assisted route.	[51]
MWCNTs- bisphenol-A-polycarbonate	MWNTs were grafted with bisphenol-A-polycarbonate in a solid state reaction at 110 °C using microwave irradiation.	[56]

These techniques have also been used in several CNMs grafting procedures in polymeric molecules [56,57], and in catalytic systems such as hydrodesulfurization reactions [51]. Thus, chemical manipulation processes of CNMs assisted by microwave have often used in methodologies for the synthesis, purification and functionalization of CNMs samples, providing simple, easy methodologies that allow us used it in large scale.

Conclusion

The microwave-activated chemical reactions cover a wide spectrum of potential applications for the chemical manipulation of CNMs, providing a fast, compact, simple, selective, and economical technique. In addition, the reaction system can evolve under mild conditions in the absence of toxic reagents (such as SOCl_2), and without the use of long heating time, as seen in the classical refluxes. Further studies on the behavior of CNMs as graphene and CNTs in different systems activated by microwaves should be explored opening new perspectives in their applications in different areas of science and technology.

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