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Multi-wall Carbon Nanotubes Decorated with Barium Oxide Nanoparticles

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Abstract

A simple, reproducible and efficient technique to decorate multi-wall carbon nanotubes (MWCNTs) with barium oxide nanoparticles (BaO NPs) using infrared (IR) irradiation is developed. NaOH treatment leads to the purification of MWCNTs (p-MWCNTs). Functionalizing p-MWCNTs with tricarboxylic aryl diazonium salts generated in-situ and then reacting it with barium acetate in the presence of IR irradiation is the key step in efficiently impregnating p-MWCNTs-D3 with barium acetate (p-MWCNTs-D3/BA). Materials are characterized using XPS, TEM and PXRD. Homogeneous distribution of BaO NPs on MWCNTs is evidenced, with a Gaussian mean diameter of 5.1 nm. This method is also applicable to large scale preparation which opens interesting perspectives for nanotechnology applications.

Keywords: Multi-wall carbon nanotubes; Barium oxide nanoparticles; Sonication; Infrared irradiation; Nanocomposite

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Introduction

Carbon nanotubes (CNTs) are among the most effective allotropes of carbon. They exhibit very interesting properties such as high chemical stability, extraordinary tensile strength, desired electrical and thermal conductivities and large surface area [1]. These properties help CNTs to find potential applications in the field of chemical and biosensors, hydrogen storage, solar and fuel cells, supercapacitors, and lithium ion batteries [2]. Crude CNTs not only contain impurities such as alumina (residual impurities from the synthesis process), but they are also difficult to solubilize in most of the solvents. These problems can be solved by purification and functionalization of the CNTs [3]. Nanoscale dimensions providing high surface area make them to be considered as efficient templates for the assembly of nanoparticles. In the current years, substantial interest has been noted for metal or metal oxide nanoparticles decorated carbon nanotube hybrid materials [4].

Alkaline earth metal oxides have been identified as materials which catalyze many types of reactions. BaO is a catalyst with strong basic sites which play very important role in isomerization and co-isomerization reactions [5]. It also catalyzes transesterification reactions [6]. Barium oxide (BaO) is an important direct band gap II–VI semiconductor material having a large band gap (4.4 eV), robust mechanical strength, high thermal stability and oxidation resistance in harsh environments [7]. It is a potential candidate for field emission devices [8] , hydrogen separation membranes [9] and gas storage materials, to cite a few. Amorphous barium oxide plays a very important role in solid oxide fuel cells [10].

CNTs absorb radiation near- infrared (IR) area, rapidly transferring electronic excitations into molecular vibration energies which produce heat. These interesting properties: photo-absorption and photo-thermal have been also used for CNTs decoration [11] .

To the best of our knowledge, there is an only one work [12] reporting on the decoration of CNTs with barium oxide

nanoparticles. However, this method suffers from limitations such as very large particles size and very low concentration of particles on CNTs. In the present method, we have successfully controlled the size, nature and distribution of BaO NPs on MWCNTs. The present method using IR irradiation to decorate CNTs with BaO NPs is simple. Thus, present methodology is advancing the science by substantially improving the reported work. Also, our strategy has not been reported before for Ba, hence the motivation for this work. The nanocomposite material as a result of combination of MWCNTs and BaO NPs can lead to effective integration of properties of both constituents in new hybrid material which is important for the nanotechnology applications, nanocatalysis, for example.

Materials and Methods

Chemicals

All the chemicals are of analytical grade or higher purity. The thin MWCNTs (NC 7000) (>95%) purchased from Nanocyl SA (Belgium) have an average diameter of 10 nm with lengths ranging from 0.1 – 10 µm. Barium acetate (99%) is purchased from MERCK. All aqueous solutions are prepared using ultra-pure water.

Apparatus

XPS spectra are carried out on a Thermo Scientific K-Alpha spectrometer using monochromatized Al Kα radiation (1486.6 eV). Transmission electron microscopy (TEM) studies are carried out using Tecnai 10 philips microscope, operating at 80 kV accelerating voltage and 5 µA emission current. Powder X-Ray diffraction (PXRD) analysis is performed using PAN analytical XPert PRO Bragg-Brentano diffractometer with tube current of 30 mA and an operating voltage of 45 kV with Cu Kα (λ= 1.5418 Å). Irradiation of the samples are carried out using a Petra IR 11 IR lamp

Purification of crude MWCNTs and tricarboxylic aryl diazonium functionalization of p-MWCNTs

The process of purification and tricarboxylic aryl diazonium functionalization of MWCNTs are carried out using the method reported in the literature [13]. The purified MWCNTs and tricarboxylic aryl diazonium functionalized MWCNTs are referred to as p-MWCNTs and p-MWCNTs-D3, respectively.

Impregnation of barium acetate on p-MWCNTs-D3

Mixture of an aqueous solution (100 ml) of 0.255 g of barium acetate (BA) and the functionalized CNTs (p-MWCNTs-D3) are sonicated for 5 minutes and then IR irradiated for 2 hours under constant magnetic stirring. The mixture is cooled down to room temperature, filtered and the residue is washed with water then by acetone and finally dried in air. The impregnated p-MWCNTs thus obtained are referred to hereafter as p-MWCNTs-D3/BA.

Calcination of p-MWCNTs-D3/BA

The p-MWCNTs-D3/BA are calcined in a furnace at 400°C for 2 h under a continuous flow of argon gas. The achieved material is labeled as p-MWCNTs/BaO

Results and Discussion

Carbon nanotubes are characterized by XPS, TEM and PXRD. They are compared at each step of their modifications i.e. purification, functionalization, impregnation and calcination.

Materials chemical composition by XPS

XPS was carried out to assess the chemical composition of the different samples and the results are displayed in **Table 1**. XPS general survey spectra of p-MWCNTs, p-MWCNTs-D3, p-MWCNTs-D3/BA, and p-MWCNTs/BaO are shown in **Figure 1**. The absence of alumina in p-MWCNTs **(Figure 1a)** is indicative of the purity of the sample and the efficiency of the purification method. The increase in the amount of O1s and the presence of a N1s peak (**Figure 1C)** proves that the MWCNTs are functionalized with the tricarboxylic aryl diazonium group. Furthermore, the presence of barium (**Figure 1c)** indicates the successful impregnation of barium acetate on the tricarboxylic functionalized MWCNTs. As expected, the Ba peak exists after calcination (**Figure 1d)** but there is a decrease in the amount of barium from the impregnation to the calcination steps.

The high resolution Ba3d XPS spectrum of p-MWCNTs/BaO is displayed in **Figure 2**. The $Ba3d_{5/2}$ and $Ba3d_{3/2}$ are formed at 780.69 and 795.97 eV, indicating the presence of Ba in +2 oxidation state, which agrees well with the literature [14].

Materials morphology by TEM

Figure 3 shows the TEM images of the prepared materials. TEM micrographs of crude MWCNTs **(Figure 3a)** point to a

Table 1 Chemical composition of different materials obtained from XPS analysis.

Materials	C%	O%	N%	Al%	Ba%
crude MWCNTs	97.18	1.98	-	0.84	-
p-MWCNTs	98.27	1.73	-	-	-
p-MWCNTs-D3	71.97	24.89	3.14	-	-
p-MWCNTs-D3/BA	86.08	10.83	1.15	-	1.94
p-MWCNTs/BaO	92.71	5.65	-	-	1.64

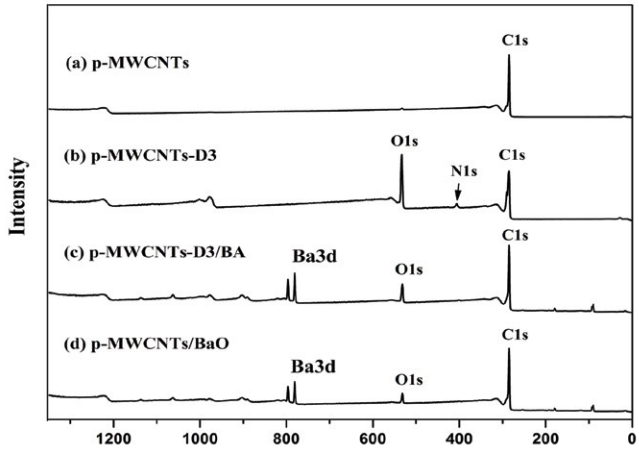

Figure 1 XPS survey spectra of (a) p-MWCNTs, (b) p-MWCNTs-D3, (c) p-MWCNTs-D3/BA, and (d) p-MWCNTs/BaO.

substantial amount of alumina (impurity) which is eliminated in the p-MWCNTs **(Figure 3b)**. This evidences the effectiveness of the purification method. **(Figure 3c)** is a TEM image of tricarboxylic aryl diazonium functionalized MWCNTs. Nanotubes are intact even after the purification and functionalization steps. This evidences the effectiveness of the purification and functionalization methods. This is a definite advantage over acid treatments which causes severe damages to the tubes [15]. As shown in TEM images **(Figure 3d)**, small size BaO NPs, with a Gaussian mean diameter of ~5.1 nm **(Figure 4)** are uniformly distributed over CNTs surface. No BaO NPs are detached from the MWCNTs indicating that they are strongly anchored on the CNTs surface.

Characterization of materials by PXRD

PXRD patterns of p-MWCNTs and p-MWCNTs/BaO are displayed in **(Figure 5)**. In all the samples, the diffraction peak at 2θ=25.66° is due to the reflection from (002) plane of graphitic carbon forming the MWCNTs structure. The diffraction patterns of the sample p-MWCNTs/BaO match with those of barium oxide nanoparticles decorated CNTs reported in the literature [12] indicating that the nanoparticles formed in our case are barium oxide nanoparticles.

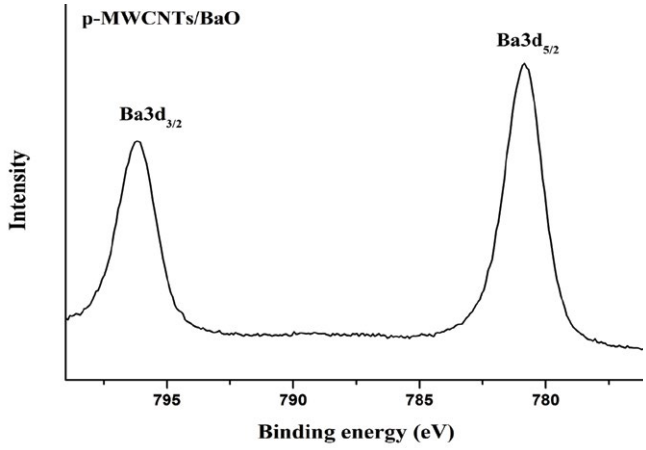

Figure 2 High resolution XPS spectra of Ba3d of p-MWCNTs/BaO.

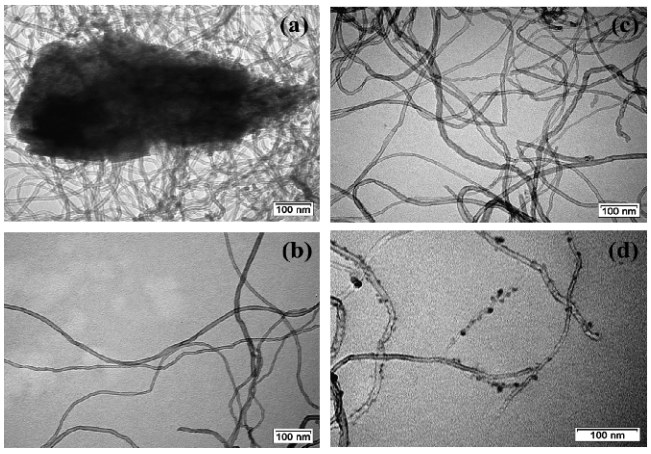

Figure 3 TEM images of (a) crude MWCNTs, (b) p-MWCNTs, (c) p-MWCNTs-D3, (d) p-MWCNTs/BaO.

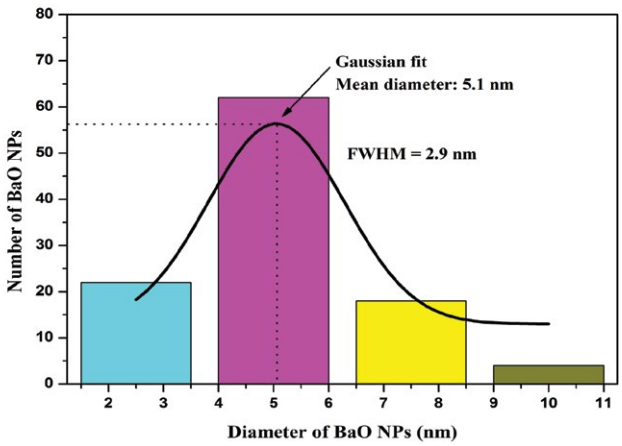

Figure 4 Diameter distribution of BaO NPs of p-MWCNTs/BaO.

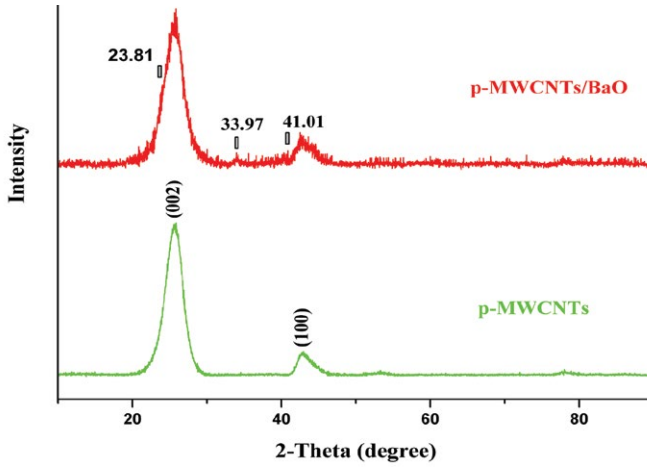

Figure 5 PXRD patterns of p-MWCNTs and p-MWCNTs/BaO.

This is in accordance with XPS data. The obtained peak is not sharp indicating that the NPs are amorphous in nature. Amorphous BaO NPs are very important for nanotechnology applications [10] .

Conclusions

We are reporting a simple method for decorating MWCNTs with BaO nanoparticles (NPs) by making use of diazonium chemistry and infrared irradiation. These NPs exhibits Gaussian mean diameter of ~5.1 nm. NPs (amorphous nature) are uniformly distributed over the MWCNTs surface. As BaO is very usefull in many fields, the hybrid material obtained from MWCNTs and BaO NPs could lead to the successful integration of properties of both the constituents in the new nanocomposite which will play important role in catalysis and nanotechnology.

Though there are still some limitations of the present method since the results are not as promising compared to results reported for other nanoparticles [13] but it advances the science by substantially improving the method for decorating CNTs with BaO NPs. Some modifications such as varying the nature of salt, duration of IR irradiation, solution of process etc. in the present approach can be done to further improve the results.

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Conflict of Interest

The authors declare that there is no conflict of interest.

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