



## Ceramic composites from mesoporous silica coated multi-wall carbon nanotubes



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### ABSTRACT

The addition of multi-wall carbon nanotubes (MWCNTs) to ceramic matrices could provide nanocomposites with enhanced properties. Efforts to produce these materials are normally frustrated by two major issues: firstly, the difficulty of attaining a homogenous distribution of MWCNTs in the matrix and secondly the poor bonding between the MWCNTs and the ceramic matrix. Herein, a processing method that overcomes these problems by using a sol–gel route to produce a low-melting point silica matrix, in combination with a dispersion method for the MWCNTs that is compatible with the sol is reported. This universal method was used to coat mesoporous silica on conventional, nitrogen-doped (CN<sub>x</sub>) and boron-doped (CB<sub>x</sub>) produced using aerosol assisted chemical vapour deposition (AACVD) as well as commercially available MWCNTs. After hot-pressing the powders, record improvements (*ca.* 50%) in hardness for the nanocomposites over the silica were observed and this improvement is enhanced by 50% if spark plasma sintering is used to consolidate the nanocomposites. Nanocomposites containing conventional nanotubes produced from AACVD and commercially available nanotubes have near identical hardness even though the nanotubes have different properties and characteristics.

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### 1. Introduction

Ceramics have high stiffness and excellent thermal stability with relatively low density, but their brittleness impedes their use as structural materials. Multi-wall carbon nanotubes (MWCNT) might be effective reinforcement materials for ceramics because of their exceptional mechanical properties [1]. The combination of nanotubes with a ceramic matrix could potentially create composites that have high-temperature stability as well as exceptional toughness and creep resistance [2]. Efforts to produce these composites are routinely frustrated by two major issues: firstly, the difficulty of attaining a homogenous distribution of MWCNTs in the matrix and secondly the poor interface between the MWCNTs and the ceramic matrix [3–7]. Both of these issues can lead to agglomeration of carbon nanotubes in the final nanocomposite; these agglomerates are essentially defects which can cause premature failure.

Much work has been carried out on using mesoporous silica (Meso-SiO<sub>2</sub>) as a matrix material for carbon nanotubes due to its highly ordered and tunable porous structure [8]. Two main techniques have been used to create MWCNT/Meso-SiO<sub>2</sub> nanocomposites: firstly, an *in situ* growth method of MWCNTs by chemical vapour decomposition (CVD) in which catalytic nanoparticles, placed in the silica pores, are used as catalysts for the growth of MWCNTs [9–12]. Secondly a sol–gel process, where pre-prepared MWCNT's are mixed with the synthesis gel of mesoporous silica, has been used [13,14]. The *in situ* growth method has a number of intrinsic problems, primarily the inhomogeneous distribution of catalyst nanoparticles leads to an uneven growth of nanotubes throughout the matrix and hence, the properties of the final nanocomposite are not uniform. The sol–gel method has numerous advantages. Primarily, as a dispersion of the nanotubes is first created, agglomerates of MWCNTs can be avoided, making it easier to achieve a homogenous distribution of MWCNTs in the resultant nanocomposite. Secondly, by adjusting the surface chemistry of the MWCNTs using surfactants, an improved interface with the silica matrix can be achieved, which should prevent agglomeration of the MWCNTs during densification. Additionally,

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the produced powders can be consolidated without further treatment as a fine powder without large clumps is produced. Finally, as the MWCNTs are coated prior to consolidation, they should not be damaged during the high temperature treatments normally associated with densification processes.

This universal method is applicable to all types of MWCNTs, including “doped” MWCNTs. It has previously been demonstrated that the modification of MWCNTs with other elements results in significant changes in their structure and hence mechanical and electronic properties [15]. The insertion of these doped nanotubes into ceramic matrices should lead to nanocomposites with unique properties, unobtainable with conventional MWCNTs. Recently, Belmonte *et al.* [16] demonstrated this by creating a SiN<sub>4</sub>/N-doped MWCNT composite which reached an electrical conductivity of 2174 S/m, the highest value reported for carbon nanotubes/Si<sub>3</sub>N<sub>4</sub> nanocomposites. Additionally, they claimed that the nitrogen doping favoured a strong mechanical interlocking between the nanotubes and the Si<sub>3</sub>N<sub>4</sub> matrix; when compared to conventional carbon nanotubes.

Herein, we demonstrate that mesoporous silica (Meso-SiO<sub>2</sub>) can be used to coat conventional, commercial, nitrogen-doped (CN<sub>x</sub>) and boron-doped (CB<sub>x</sub>) nanotubes. The produced powders were consolidated *via* hot-pressing and/or spark plasma sintering to form nanocomposites. As the same method was used to create all the nanocomposites, a direct comparison between their properties could be made for the first time.

## 2. Experimental

For the generation of the nanocomposite materials various types of nanotubes, exhibiting different surface chemistries, were employed. These included conventional MWCNTs, CN<sub>x</sub> and CB<sub>x</sub> nanotubes produced in-house [15,17]. Additionally, commercial MWCNTs were obtained from Bayer Technologies and are referred to as Baytubes. Briefly, synthesis experiments were carried out using an aerosol-assisted chemical vapour deposition (AACVD) system consisting of a piezo-driven aerosol generator (RBI Pyrosol 7901), a quartz tube (2.2 cm inner diameter) and a 50 cm long horizontal electrical furnace, equipped with a gas flow controller and a gas trap filled with acetone. Solutions of 5 wt% ferrocene (Aldrich 98%), in a mixture of toluene (Fluka 99.7%) for the conventional MWCNTs, benzylamine (Fluka 99%) for CN<sub>x</sub> and a mixture of 1 M solution of triethylborane in hexane (TEB) ((CH<sub>3</sub>CH<sub>2</sub>)<sub>3</sub>B, CH<sub>3</sub>(CH<sub>2</sub>)<sub>4</sub>CH<sub>3</sub>, Aldrich) in toluene (5 vol. %/vol. 95%) for CB<sub>x</sub> were prepared in an ultrasonic bath (30 min). For conventional MWCNT and CN<sub>x</sub> nanotubes the furnace was operated at 800 °C, whilst the CB<sub>x</sub> nanotubes were generated at 900 °C. All experiments ran for 10 min while the argon flow was kept at 2500 sccm. During heating and cooling of the furnace the aerosol generator and the quartz tube were flushed with 100 sccm argon. The soot was collected from the inner wall of the quartz tube with a sharp metal tool. The MWCNTs (0.1 g) were dispersed in 100 ml of a 1 wt% sodium dodecyl benzene sulfonate (SDBS, Aldrich) aqueous solution by high shear mixing and ultrasonication (600 W, 20 kHz).

The synthesis of mesoporous silica was adapted from a previously described method [5]. Briefly, 4.0 g P85 (BASF) in 120 ml of

2 M HCl (Aldrich 37%) and 30 ml deionised H<sub>2</sub>O was stirred for 30 min. The mixture was subsequently placed in a water bath and heated to 40 °C. 11.3 g of tetraethyl-orthosilicate, TEOS (Fluka) was added. The solution was stirred at this temperature for 24 h after which it was placed in an oven (60 °C) for 5 days. This enabled the silica to reproduce the surfactant network. Mesoporous silica samples containing MWCNTs were prepared in the same way except that 30 ml of the SBDS/nanotube solution is used in place of the deionised water. The resultant products were recovered by filtration and dried at 60 °C for 12 h. The samples were then heated in air to 450 °C at a rate of 2 °C min<sup>-1</sup> to remove the surfactant template. The dried powder was formed into a disc by hot pressing at 1100 °C at 10 MPa. Selected samples were also consolidated by Spark Plasma Sintering (SPS) at 1100 °C at 45 MPa for times between (5 and 25 min) for comparative purposes.

In order to obtain microstructural and microanalytical information, the composite materials were characterized at different stages of the process by scanning electron microscopy (SEM, JOEL 840-F), transmission electron microscopy (TEM, JEOL 3000F), Raman spectroscopy (recorded at room temperature using a 532 nm laser and a power density of 100 mWmm<sup>-2</sup> (LabRam Aramis)), Thermogravimetric analysis (TGA, Perkin Elmer Pyris 1), x-ray powder diffraction (XRD, D5000 diffractometer Siemens), and nanoindentation (Micromaterials Nanotest Platform). Density measurements were carried out by the dimensional method using the average value from at least three samples of each composition. An intrinsic MWCNT density of 1.65 cm<sup>3</sup>/g was used, typical of MWCNTs [18]. The pore size distribution of the MWCNTs and the nanocomposites were analysed by the N<sub>2</sub> adsorption–desorption isotherms and the t-plot method (Micromeritics Gemini VI) [19,20].

## 3. Results and discussion

Raman, TGA, N<sub>2</sub> adsorption–desorption isotherms analysis along with SEM and TEM micrographs of the conventional MWCNTs, CN<sub>x</sub> and CB<sub>x</sub> along with the Baytubes were obtained and are shown in the [Supplementary Information \(SI Figs. 1–4\)](#). Raman spectra demonstrated that the Baytubes were the most defective with regard to their graphitisation followed by the CB<sub>x</sub>, CN<sub>x</sub> and conventional MWCNTs respectively. All the nanotubes had a high oxidation resistance, all survive temperatures in excess of 500 °C which demonstrated that they are compatible with mesoporous silica synthesis. The surface area and pore volume figures of all the nanotubes are collected in [Table 1](#); Baytubes are seen to have the highest surface area (204 m<sup>2</sup>/g) and all nanotubes have negligible micropore volumes (*ca.* 0.002 cm<sup>3</sup>/g, [Table 1](#)). SEM images showed that the conventional and CN<sub>x</sub> nanotubes formed as flakes with lengths of *ca.* 500 μm and 30 μm respectively. CB<sub>x</sub> tubes formed as cotton wool-like bundles whilst the Baytubes were present as agglomerates with diameters of hundreds of micrometres. All the AACVD produced nanotubes had average diameters larger than the Baytubes (14 nm); MWCNTs (60 nm), CN<sub>x</sub> (50 nm) and CB<sub>x</sub> (80 nm) [17].

It was previously demonstrated nanotube agglomerates are detrimental, especially in ceramic matrices, as they can act as defects leading to premature failure [18]. In order to establish an

**Table 1**  
Surface areas and volumes of the Baytubes, conventional MWCNTs, CN<sub>x</sub> and CB<sub>x</sub> nanotubes.

Sample	Raman D/G ratio	BET surface area (m <sup>2</sup> /g)	Total pore volume (cm <sup>3</sup> /g)	Micropore volume (cm <sup>3</sup> /g)	Micropore area (m <sup>2</sup> /g)	External surface area (m <sup>2</sup> /g)
MWCNT	0.40	104 ± 3	0.145	0.002	5	99
NMWCNT	0.90	75 ± 0.2	0.116	0.001	3	72
BMWCNT	1.12	16 ± 0.2	0.026	0.003	6	10
BayMWCNT	1.51	204 ± 1	0.518	0.001	5	199

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