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A microwave cured flux for the adhesion of ceramic particles using silica coated carbon nanotubes

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ABSTRACT

We report the application of multi-walled carbon nanotubes (MWCNT) to facilitate the fusing of ceramic particles together by the creation of a silica flux through localized microwave heating of the carbon nanotubes. When pre-formed Stöber SiO_2 nanoparticles (120 nm) and MWCNT are co-mixed with alumina microbeads (369 ±47 μm) the SiO_2 nanoparticles act as anchor points and attach the MWCNT to the larger alumina surface. Upon microwave irradiation (2 x 1 min @ 1000 Watt) large silica plates of a few nanometers in length are formed. The localized heat that MWCNT generate under microwave irradiation produces sintering within the silica. Mixing of preformed SiO_2-coated MWCNT with the alumina particles results in the formation of "patches" on the surface of alumina, that upon exposure to microwave irradiation causes the melting of the silica and its flow as "bridges" between the particles effectively "welding" the microbeads together. The microwave heating of the MWCNT can be thus be used to create interaction and adhesion between particles.

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1. Introduction

The creation of hierarchical structures by bringing together molecules into nanostructures offers a solution to a number of challenges in the creation of macroscopic structures or networks [1-5]. A similar approach can be used for the joining of nano or micron sized particles into macroscopic structures. For example, ceramic powder 3D printing allows for complex structures to be created which fit together and adhere; however, the bonding (or fusing) of the ceramic particles ordinarily requires thermal processing, which generally results in decreased permeability [6]. Although densification is often desirable there are cases where the creation of an immobilized structure with permeability is desired. For example, we have previously demonstrated that alumina nanoparticles can be arranged to create hierarchical structured membranes in which two levels of porosity are formed, unfortunately, significant chemical and thermal processing is required [7].

Sand (quartzite) or ceramic particles are extensively used as proppants in the oil and gas industry [8]. The proppant provides a highly porous conductive pathway from the reservoir to the well by holding the fracture open and so enhance the ability of fluids (oil and/or gas) to migrate through the fractures. One significant problem is the loss of proppant from a fracture (usually referred as flowback), which can generate problems as any reduction of fracture conductivity results in a negative impact on production. If the proppant volume in the fracture is significantly reduced, the fracture can become closed reducing hydrocarbon production and in extreme cases resulting in the need to re-drill the well. This causes increased water and chemical usage per well and a rise in the associated environmental impact, as well as significant financial losses. Current approaches for improved proppant performance involve modifying them with different resins, polymers, and fibres [9-11]. The use of polymers or resins as coatings can cause undesirable effects on the reservoir permeability, e.g., partially cured coatings used in proppants can interfere with the viscosity profile of the fluid used to carry the proppant, be eroded or cured prematurely. On the other hand, pre-cured coatings, are not effective enough to prevent the flowback of the proppant in the well [12], hence new alternatives in the proppant design should be developed. One approach is to partially fuse the proppants *in-situ* creating a network, an alternative is to *ex-situ* fuse the particles into dimers, trimers, etc., that would mechanically interlock and provide greater resistance to flowback. Irrespective of the in-field application we are interested in the development of methods that allow for the triggered fusion of ceramic particles without

significant loss of permeability. We have therefore investigated the potential routes to creating a process for the adhesion of ceramic particles.

Microwave energy has been extensively applied for chemical synthesis [13-17] and processing of new materials [18] due to; rapid heating, decreased sintering temperatures, improved physical and mechanical properties and the formation of unique properties, which are not observed in conventional heating processes. Unlike convective or radiation heating, fast and direct heating of the active materials is achieved under microwaves [18]. Microwave absorbing properties of certain types of carbon nanotubes (CNTs) make then very attractive when use as a nexus for fast and direct heating [19-23]. Rapid temperature increase has been observed with CNTs under microwave irradiation [24,25] and "superheating" processes have been used to cure ceramic/CNT composites [19] and induce welding in composites [26-29]. We have proposed that the localized high temperatures generated by microwave adsorption of CNTs should be sufficient to create a flux of a suitable material that can then act as an adhesive between individual ceramic particles.

Most bonding of ceramic systems has concentrated on dental and related medical applications, while traditional sintering involves high levels of heating to ensure fusing even in the absence of grain growth. In this study, we proposed that the surface of ceramic spheres could be modified by two approaches: (a) nanometric silica spheres acting as anchor points to fix
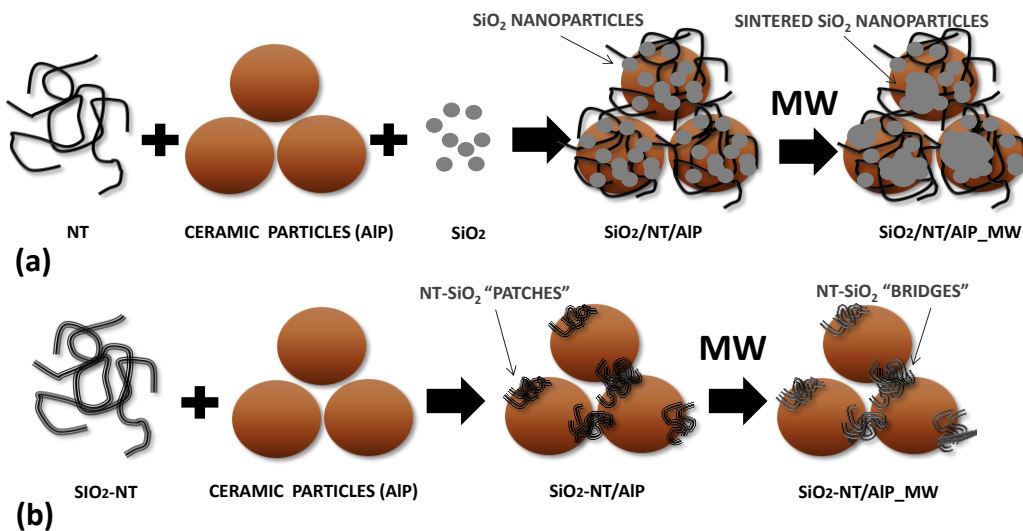

Fig. 1 - Schematic of the approaches used to modify the surface of the alumina ceramic particles. (A colour version of this figure can be viewed online.)

multiwall carbon nanotubes (MWCNT) and (b) MWCNT coated with silica (Fig. 1). The use of MWCNT allows microwave irradiation to control the extent of the ceramic particles interaction. When silica coated MWCNT are exposed to a microwave source, the MWCNT create a localized heat that causes sintering in the silica. By adding patches of this hybrid material to the ceramic surface and treating them under microwave irradiation the goal is to create irreversible bridges between the ceramic particles pack. Therefore, microwave radiation can be used as an in-situ trigger to create twins, triplets or higher-order linked particles.

2. Experimental

2.1. Materials

Kuhmichael alumina microparticles (F240, Kuhmichel Abrasiv GmbH), denoted **AlP**, were used as received. Tetraethyl orthosilicate (≥99.0%, TEOS), absolute EtOH, and ammonium hydroxide solution 28.0-30.0% NH_3 basis were purchased from Aldrich). MWCNT were prepared using a Nanotech Innovations SSP-354 tabletop horizontal tube reactor as previously reported [30].

2.2. Modification of alumina particles

The two approaches used to modify the surface of the alumina particles are shown in Fig. 1. All samples studied are described in Table 1.

In the first approach (Fig. 1a), uniform 120 nm silica spheres were synthesized by the Stöber [31] method in which ammonium hydroxide solution was added under magnetic stirring to a solution of TEOS (4 mL) in EtOH (50 mL) in the presence of multiwall carbon nanotubes (MWCNT, 0.5 mg/mL solution used) and Kuhmichael particles (1.0 g). The resulting material was ultrasonicated during 2 h and thoroughly washed with EtOH several times and dried at 70 ºC during 24 h. The result is Stöber SiO_2 nanoparticles and MWCNT coated alumina particles (**SiO_2/NT/AlP**).

In the second approach (Fig. 1b) silica coated carbon nanotubes (**SiO_2-NT**) were prepared by dispersion of the MWCNT over 30 min in an ultrasonic bath to form a 0.5 mg/mL dispersion in absolute EtOH. TEOS (4 mL) and the correspondent amount of ammonium hydroxide solution were added and the mixture stirred at ambient temperature for 1 hour. The

reaction was then centrifuged and washed three times with EtOH and the resultant precipitate of silica coated MWCNT (**SiO$_2$-NT**) dried in air at room temperature. Kuhmichael alumina particles were added to a suspension of **SiO$_2$-NT** (100 mg) in EtOH, followed by ultrasonication (30 min). The resulting SiO$_2$-MWCNT coated alumina particles (**SiO$_2$-NT/AlP**) were dried at room temperature. A full list of denotations of sample names is given in Table 1.

Table 1. Summary of the denotations for sample names.	
Sample name	Synthesis
SiO$_2$	SiO$_2$ nanoparticles made by Stöber method
AlP	Alumina particles as supplied
NT	Multiwalled Carbon Nanotubes
SiO$_2$/NT/AlP	Three way mixture
SiO$_2$-NT	Pre-formed multiwalled carbon nanotubes covered with SiO$_2$
SiO$_2$-NT/AlP	Deposition of SiO$_2$-NT onto the alumina particles
_MW$_x$	Additional microwave treatments of samples with x = number of 1 minute irradiations at 1000 W.

2.3. Microwave treatment

A 1000 W microwave oven (Panasonic NN-CT579SBPQ) was used in all the experiments. In all microwave reactions the sample was placed in a glass vial and microwaved for a number of 1 min periods at 1000 W power. The microwave oven incorporated inverter technology allowing control of oven power between 0 and 1000 W. A similar domestic microwave has been used previously in the literature [16] producing waves at a frequency of 2.45 GHz. Rotating the sample on the standard table enclosed enabled a uniform distribution of power. The microwaved samples are indicated by the addition of "**MW$_x$**" to their name (see Table 1).

2.4. Characterization

Samples were characterized by scanning electron microscopy using an Ultra-High Resolution FE-SEM S-4800 coupled with an energy dispersive X-ray analyser (Inca X-ray analysis system,

Oxford Instruments, Abingdon, UK) was used for the EDX analysis. Some of the samples were sputter coated with chromium to prevent charging. Thermogravimetric analyses (TGA) of the samples were performed on a TA Q600 instrument. The samples were heated under flowing air (100 mL/min) from room temperature to 1300 °C with a heating rate of 20 °C/min. the exhaust gas from the TGA was monitored using a heated sample transfer line (350 °C) and a Thermoscientific i510 FTIR. Scans were taken approximately every 36 seconds for the duration of the TGA heating cycle. The XRD analysis was performed by using a Rigaku D/Max Ultima II Powder XRD, with Cu-K$_\alpha$ radiation, and the data was analysed using Jade 10 software and the ICDD PDF-4+ 2013 data base.

3. Results and discussion

Given that commercial sand or ceramic proppants show wide variability, we have chosen to use simple alumina particles of appropriate size as a model system to allow for attribution of any effects to the CNTs rather than impurities within the proppant. The surface of the pure alumina particle is representative of commercial high alumina ceramic proppants. Typical proppant used in hydraulic fracturing stimulation have particles diameters in the range of 12 to 100 mesh (1680-149 μm) [32]. The Kumichael alumina particles used in this work have rough surfaces and particle diameters of 369 ±47 μm. Figure 2 shows the surface of the bare ceramic sphere, EDX elemental analysis of the surface shows that it is mostly composed of alumina: Al, O, and Si signals can be seen in the spectrum shown in Fig. 2.

Several microns length, multiwall carbon nanotubes (Fig. S1a) were used in this study. A multiwall carbon nanotube sample was treated under microwave (1 min 1000 Watt) in air. Intermittent light emission was observed during the process and, after microwave treatment, some areas shown a colour change from black to orange. Fig. S1b shows a SEM micrograph of the multiwall carbon nanotube after microwave treatment with some areas affected by microwave radiation showing a clear change in morphology and contrast related with the high temperatures reached.

Two approaches have been followed to modify the surfaces of the ceramic particles. In the first one, SiO$_2$ nanoparticles were synthesized by the well-known Stöber sol-gel method [31] in the presence of multiwall carbon nanotubes and ceramic particles. In this simple way, the surface of the particles was covered by 120 nm silica nanoparticles and carbon nanotubes (Fig.

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3). As Fig. 3a shows, the surface of the alumina particle is covered by silica nanoparticles. Silica and alumina ceramics have similar surface composition, being mostly terminated with hydroxyl groups and adsorbed water. In this regard, it appears that the SiO_2 nanoparticles act as anchor points and attach the MWCNT to the particle surface. Fig. 3b-d shows how carbon nanotubes are homogeneously distributed among the silica particles and are fixed to the surface by their interaction with the particles, (sample **SiO$_2$/NT/AlP**). During the condensation process of the supersaturated silicic acid to form the silica nanoparticles, some nanotubes are trapped in the SiO_2 structure and are thus fixed to the surface of the ceramic particles.
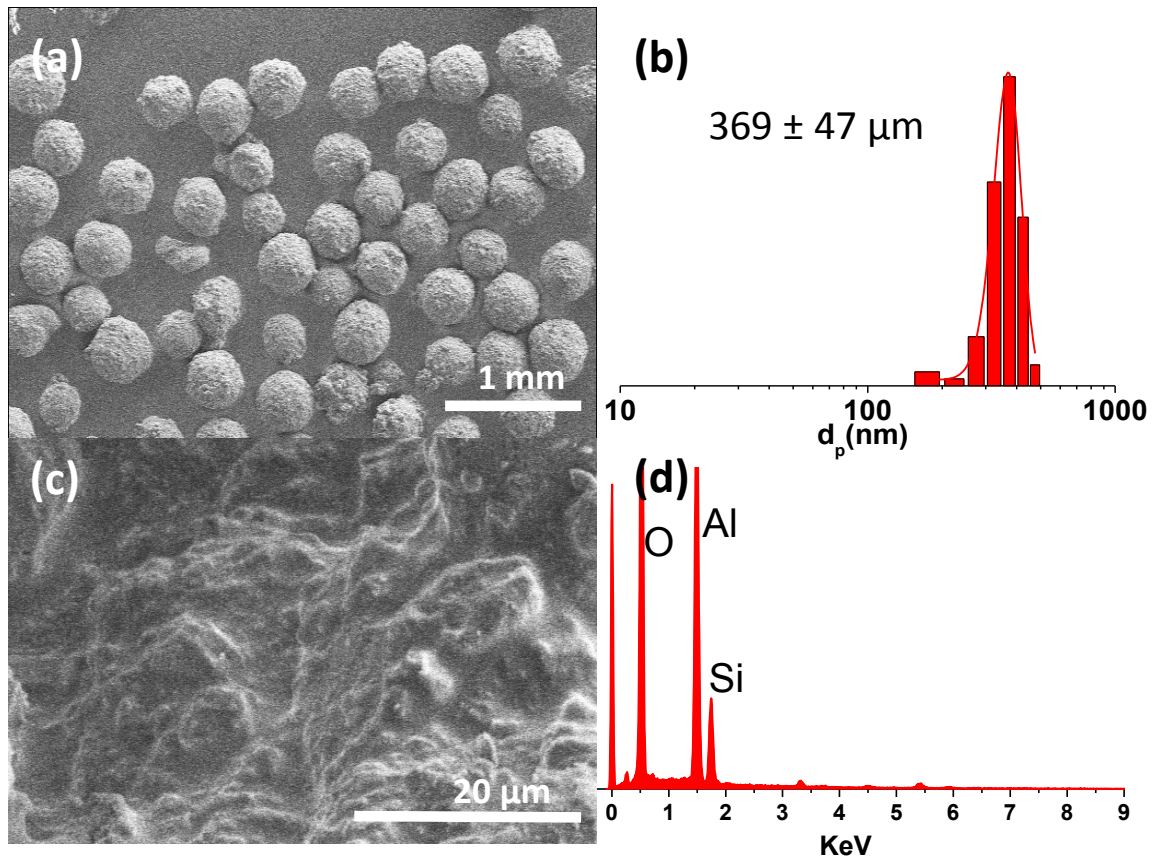

Fig. 2 - SEM micrograph of (a) Kumichael alumina ceramic particles, (b) the associated particle size distribution based in the SEM measurement of more than 100 particles, (c) a representative SEM of a bare surface of one ceramic particle, and (d) the EDX elemental analysis spectrum of the particles. (A colour version of this figure can be viewed online.)
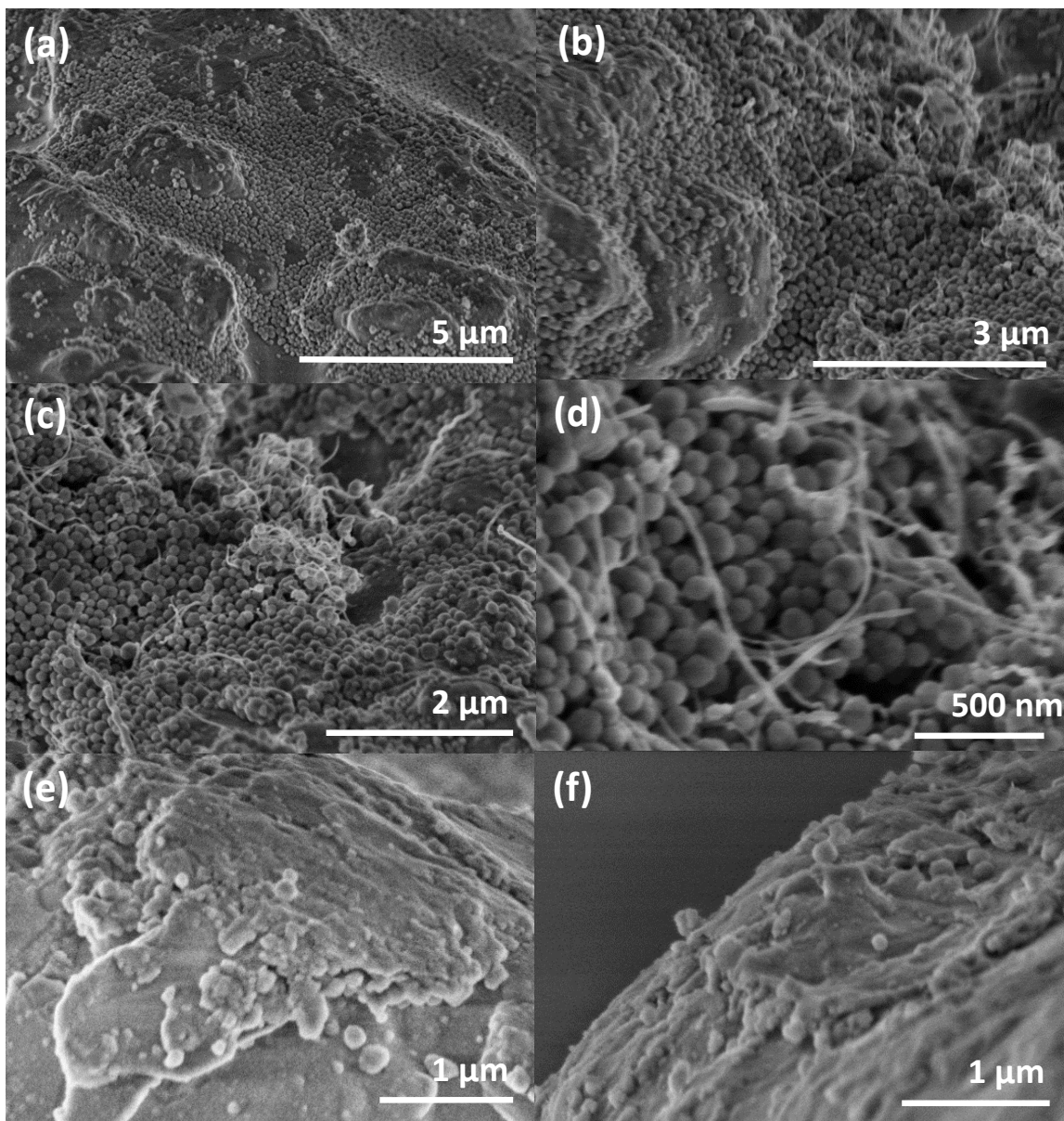
Fig. 3 - SEM micrographs of Kumichael ceramic particles (a)-(d) after their surface modification with SiO$_2$ nanoparticles and multiwall carbon nanotubes, (sample SiO$_2$/NT/AlP) and (e) and (f) after two treatments of 1 min at 1000 Watt (i.e., sample SiO$_2$/NT/AlP_MW$_2$).

In order to microwave the modified ceramic particles, they were placed in a glass vial and treated for 1 minute at 1000 Watt. After the microwave treatment, SEM images of the surface show sintered silica in the surface of the ceramic particles, (sample **SiO$_2$/NT/AlP_MW$_1$**) As can be observed in Fig. 3e and f silica plates of a few nanometers in height have been formed and

some spherical silica nanoparticles are still visible on the sintered material. Stöber silica nanoparticles were also microwaved in the same way, showing no change in their morphology (Fig. S2). Therefore, we concluded that the MWCNT absorb microwave radiation and act as localized heating points to super heat the surrounding silica and alumina. Some authors have measured the temperatures finding values over 1000 °C [24]. The localized heat that MWCNT generate under microwave radiation in the silica seems to be high enough produce a sintering processes.

The second approach to modify the surface of the ceramic particles involves the synthesis of silica coated multiwall carbon nanotube hybrid materials. Among the different ways of coating carbon nanotubes the sol-gel method is considered the most convenient because it is fast and easy [33]. Fig. 4a and b shows scanning electron micrographs of multiwall carbon nanotubes samples covered with silica (**SiO₂-NT**). It is observed that both individual carbon nanotubes and small bundles were covered with silica. Under microwave treatment, some of the silica was

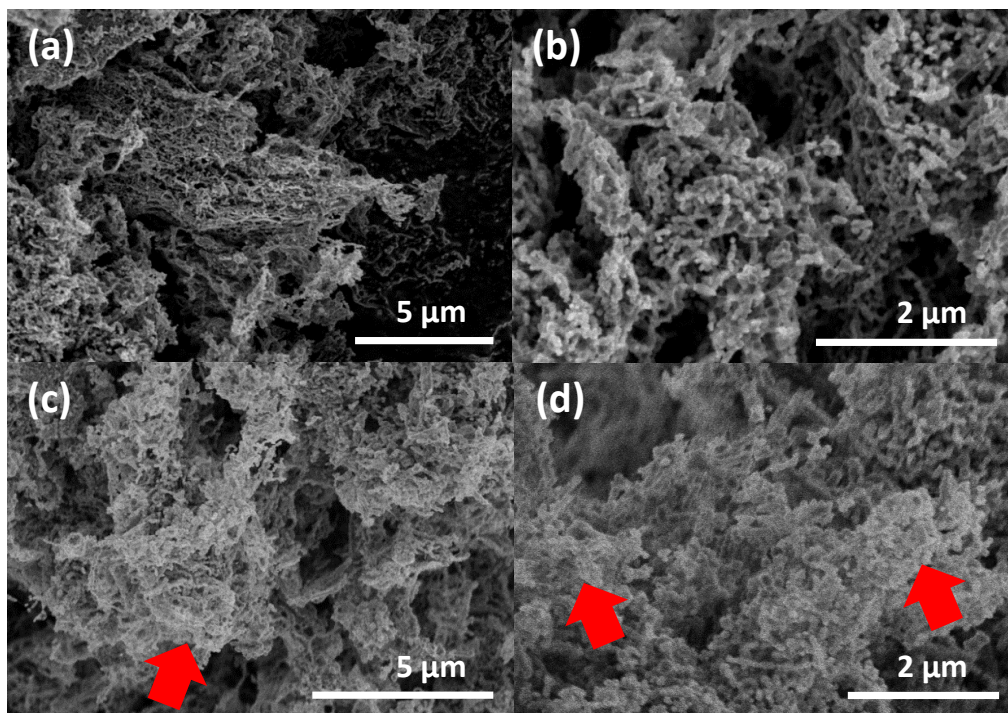**Fig. 4 - SEM micrographs of multiwall carbon nanotubes samples coated with silica (SiO₂-NT) (a, b) before and (c, d) after microwave treatment. The arrows indicate the areas were silica was melted and underwent sintering. (A colour version of this figure can be viewed online.)**

melted and underwent sintering (Fig. 4c and d). The FTIR spectra were obtained for MWCNT, SiO_2 nanoparticles, **SiO_2-NTs** before and after a microwave treatment (Fig. S3a). The absorption peak observed for Stöber nanoparticles and **SiO_2-NTs** between 1057 and 1079 cm^{-1} is related to the Si-O-Si stretching vibration and confirms the presence of silica in the hybrid materials. In addition, wide-angle X-ray powder diffraction patterns of several samples (Fig. S3b) show a broad peak around 22° related to the poorly crystalline (amorphous) silica.

Fig. 5 shows the thermogravimetric analysis of SiO_2 nanoparticles (SiO_2 NP), multiwall carbon nanotubes (NT) and hybrid materials before and after microwave treatment (**SiO_2-NT** and **SiO_2-NT_MW$_x$**, respectively). SiO_2 nanoparticles shown a first loss step below 200 °C related to the loss of adsorbed and interlayer water and a 14% weight loses at 800 °C. As can be observed in Table 2 and Fig. 5, the onset temperature and the decomposition temperature of multiwall carbon nanotubes in air are 528 °C and 579 °C, respectively. Both, onset and oxidation temperatures are shifted to higher values when the carbon nanotubes are covered with silica.
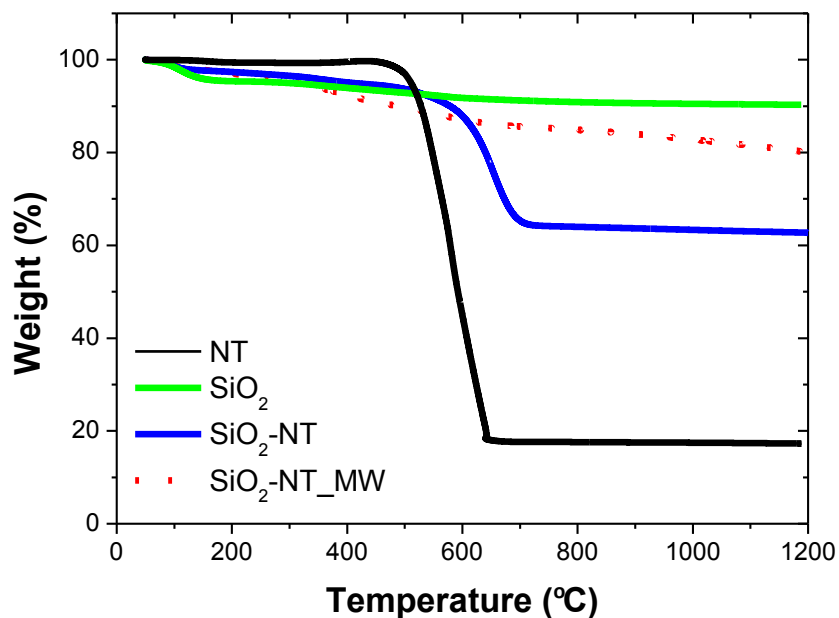

Fig. 5 - Thermogravimetric analysis of SiO_2 nanoparticles (SiO_2), multiwall carbon nanotubes (NT) and hybrid materials before and after microwave treatment (SiO_2-NT and SiO_2-NT_MW$_1$ respectively). (A colour version of this figure can be viewed online.)

Table 2. Thermogravimetric analysis of multiwall carbon nanotubes (NT), SiO$_2$ nanoparticles (SiO$_2$), and hybrid materials before and after microwave treatment (SiO$_2$-NT and SiO$_2$-NT_MW, respectively).

	Oxidation Temp. (°C)	Onset point (°C)	Wt% loss <200 °C	Wt% loss 300-800 °C	Residue @ 800 °C
NT	579	528	1%	82 %	18 %
SiO$_2$	110 / 566	-	4 %	4 %	86 %
SiO$_2$-NT	93 / 654	588	2 %	32 %	62 %
SiO$_2$-NT_MW	83/ -	-	3 %	10 %	78 %

This stabilization can be explained by protection of the CNT by the silica shell. Table 2 shows that sample **SiO$_2$-NT** had lost around 38 wt% by 800 °C. This behaviour is related to the oxidation of the amorphous carbon in the CNT sample and the generation of CO$_2$ during the thermolysis in air. The associated FTIR spectrum (Fig. S4b) shows the characteristics bands associated with the bond bending and stretching of CO$_2$ molecules (observed at 669 and 2350 cm^{-1}, respectively). In contrast, by 800 °C sample **SiO$_2$-NT_MW$_1$** shows only a 22 wt% mass loss and the weight loss relating to the carbon nanotubes oxidizing can be no longer be observed. This is because during the microwave treatment the amorphous carbon and other residues in the nanotubes have already oxidized [34].

SEM micrographs of **SiO$_2$-NT** and **SiO$_2$-NT_MW$_1$** respectively after thermogravimetric treatment under air (Fig. S5 (a and b)) show that during the thermogravimetric analysis, the carbon nanotubes are oxidized and the silica is sintered. However, well-preserved structures, similar to the ones in the original hybrid materials, can be observed in **SiO$_2$-NT_MW$_1$**. The better preservation of these structures can be explained by localized sintering of the samples under microwave radiation.

Fig. 6 shows SEM micrographs of Kumichael ceramic particles after modification with **SiO$_2$-NT** hybrid materials. Patches of the hybrid material can be observed on the surface of the particle (Fig. 6a and b). Fig. 6d shows the elemental EDX analysis of one patch, spectrum 1 shows the presence or Fe and C signals to a significantly higher extent than in the rest of the

surface. The lower spectrum (Fig. 6d) shows the Al, O and Si EDX signals from the bare surface of the particle.
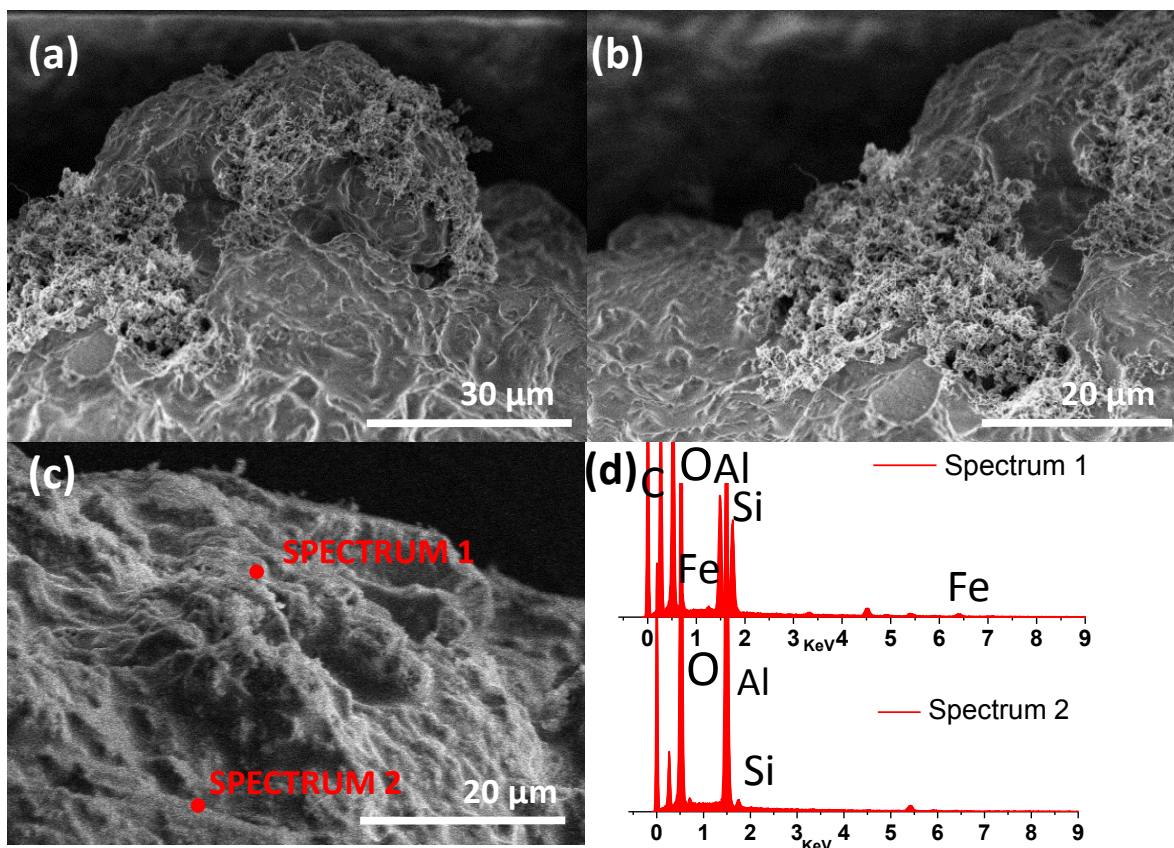

Fig. 6 - SEM micrographs of (a-c) Kumichael ceramic particles after being modified with SiO$_2$-NT hybrid materials. Patches of the hybrid material can be observed in their surface. The EDX analysis spectrum (c-d) of one patch (spectrum 1) shows the presence or Fe and C in a significant more extent than in the rest of the surface (spectrum 2). (A colour version of this figure can be viewed online.)

Fig. 7 shows that several particles in sample **SiO$_2$-NT-AlP_MW$_2$** have been effectively joined together after being irradiated with microwave radiation. After the microwave treatment **SiO$_2$-NT** patches that are in contact with two particles create sintered composite bridges. This process can be explained by the silica sintering due to the localized heating process generated by microwave treatment of the carbon nanotubes. Carbon nanotubes reach high temperatures under microwave influence [24]. Carbonaceous materials are heated directly by the action of the

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microwaves creating specific hot spots in the material [34]. In contrast, during conventional heating, the heat is transferred by conduction or convection and undesired gradients are frequently generated. In these samples, under microwave irradiation the MWCNT structures oxidize, igniting a hot CO_2 plasma, observable as an orange glow, providing extremely hot, localized energy to fuse the SiO_2 nanoparticles together, bridging the alumina microparticles. Thus, the particles can be immobilized by microwave sintering [35]. The use of porous SiO_2-MWCNT hybrid materials can be used to assist the linking of two or more proppants overcoming the reduction of the reservoir permeability caused by other particle coating methods. These materials can coat the surface of the particles partially or entirely, and can be heated before or after the proppants are placed intro the formation or fracture. As can be seen in Fig. 7 the bridges that join the particles are still keeping the porous structure of sample **SiO$_2$-NT/AlP_MW$_2$**.
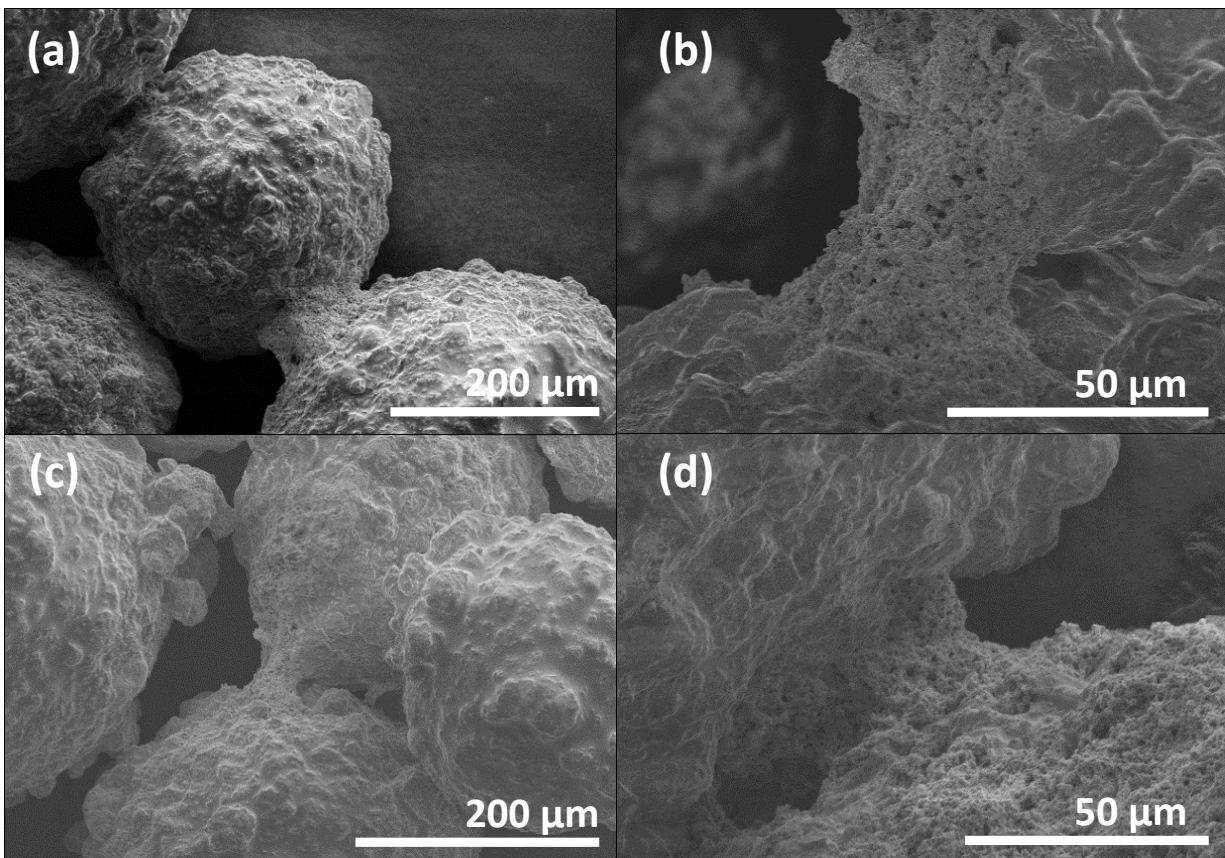

Fig. 7 - SEM micrographs of SiO$_2$-NT/AlP_MW$_2$ samples. Kumichael ceramic particles have been joined after being modified with SiO$_2$-NT hybrid materials and being treated under microwave irradiation.

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4. Conclusions

By modifying the ceramics particles surface with carbon nanotubes and silica before microwave irradiation, bridges are formed between particles beads. The use of advanced materials such as carbon nanotubes allows the use of microwaves to control the particle interaction. When silica coated carbon nanotube hybrid materials are exposed to a microwave source, the carbon nanotubes are heated and part of the silica that covers then is sintered. The main advantage of this new approach is that microwave energy can be used to control particle interaction. A microwave source can therefore be used to initiate and assist the linking of two or more proppants together overcoming problems such as flowback. Besides, the sintered material conserved its porous structure leading to less reduction of the proppant pack conductivity.

The main objective of this work was to develop surface modified ceramic particles containing high strength irreversible bonding between ceramic beads creating twins, triplets or higher-order linked proppants that does not significantly affect the fluid permeability of it. Microwave sources can be positioned and operated down well shafts using currently available technology within the oil and gas industry. Therefore, a completely new approach is described where carbon nanotubes and silica have been used to modify the proppant surface.

Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at http://dx.doi.org/xxxxxx/j.carbon.xxxxxxx.

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Graphical Abstract
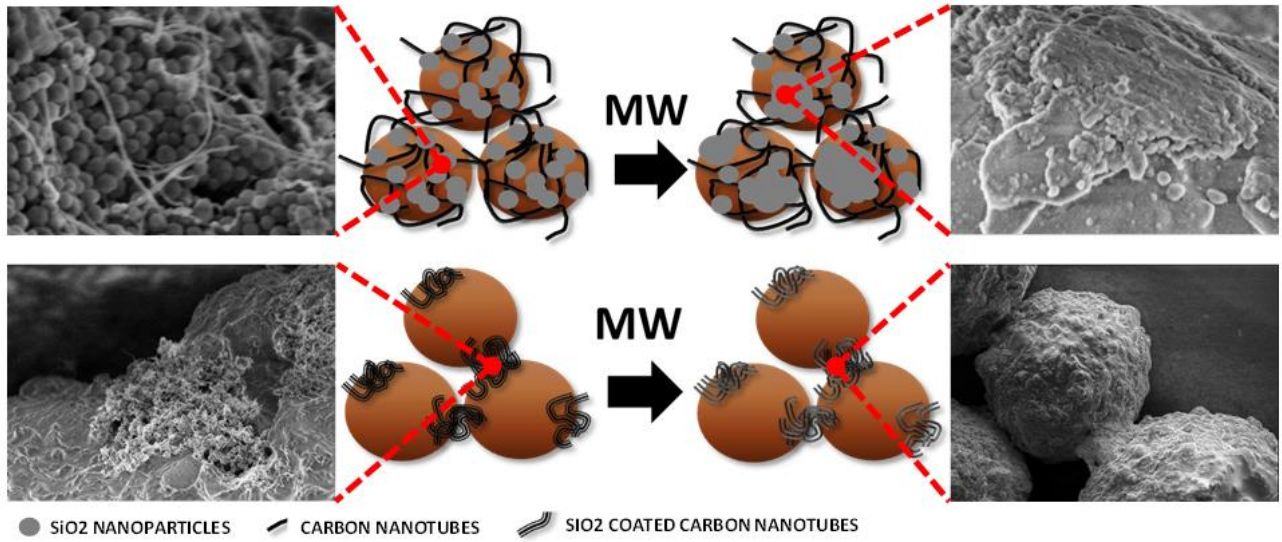
SiO2 NANOPARTICLES   CARBON NANOTUBES   SIO2 COATED CARBON NANOTUBES

A microwave cured flux for the adhesion of ceramic particles using silica coated carbon nanotubes

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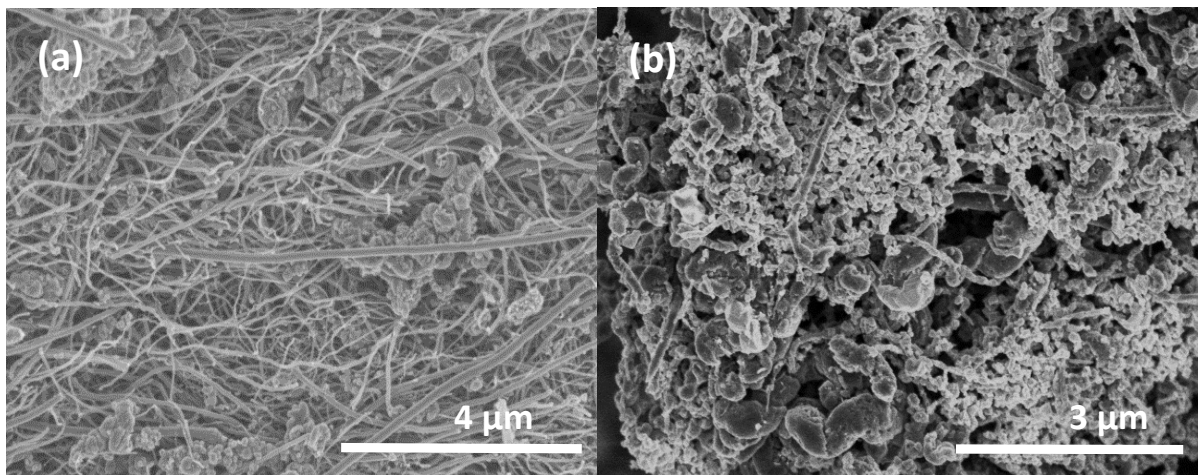
Fig. S1 - SEM micrographs of multiwall carbon nanotubes (NT) (a) before and (b) after a one min 1000 Watt microwave treatment in air.
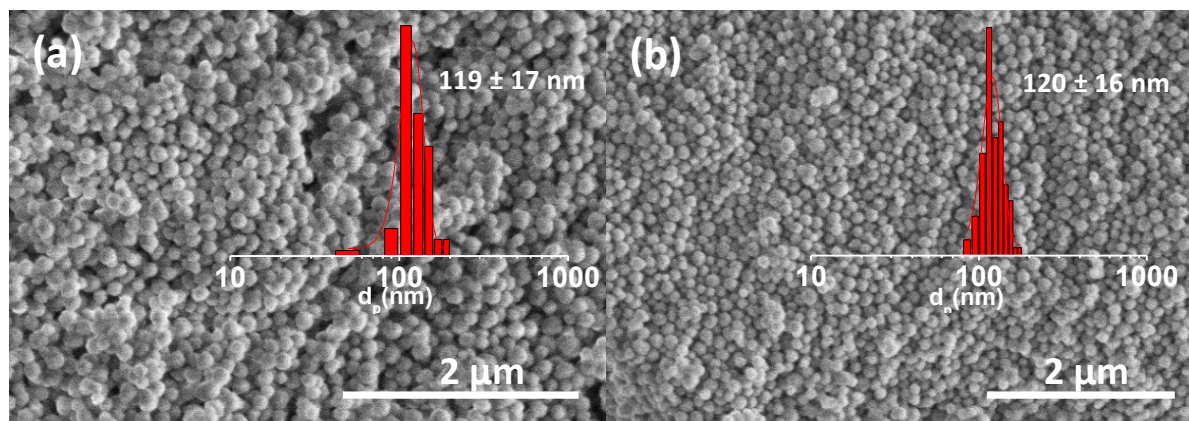

Fig. S2 - Silica nanoparticles (a) before and (b) after a microwave treatment. As can be seen the particles do not suffer any changes in their size or shape.
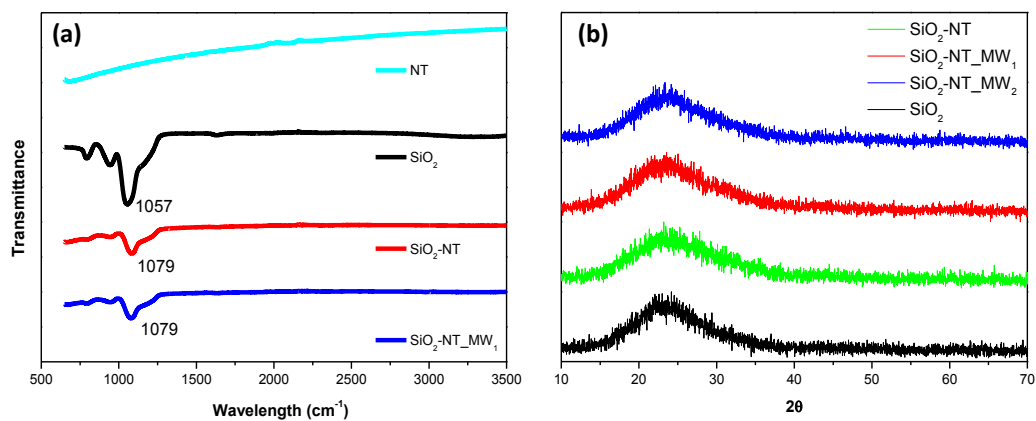
Fig. S3 - (a) FT-IR spectra of multiwall carbon nanotubes, SiO_2 nanoparticles, SiO_2-NT and SiO_2-NT-MW_1 materials and (b) XRD patterns of SiO_2, SiO_2-NT, SiO_2-NT_MW_1 and SiO_2-NT_MW_2 respectively.
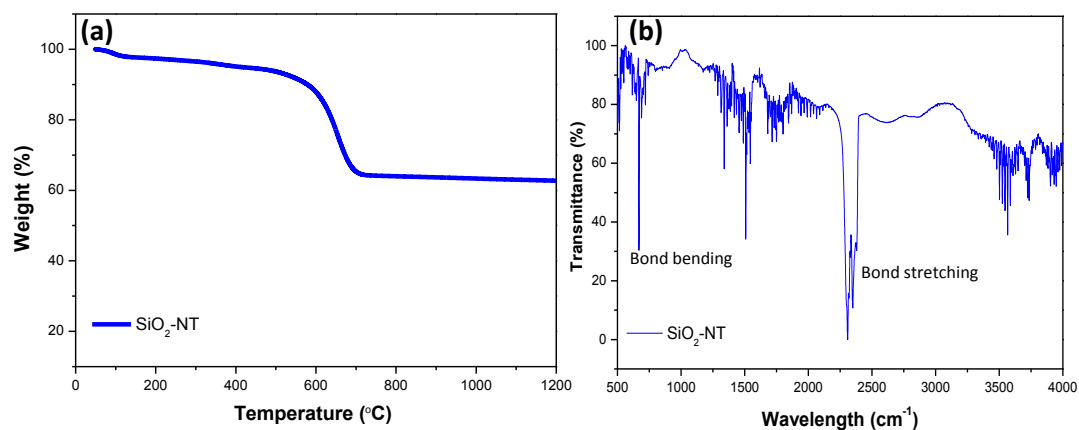

Fig. S4 - (a) Thermogravimetric analysis of SiO_2-NT. (b) FTIR transmittance spectra related with the CO_2 generated during the carbon nanotubes burning during the thermogravimetric analysis of the SiO_2-NT sample.
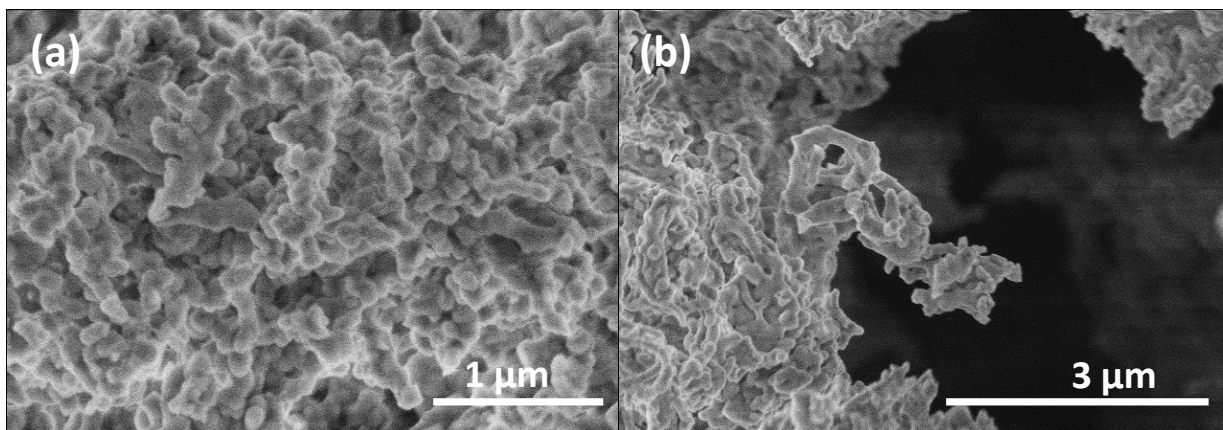
Fig. S5 - (a) SiO$_2$-NT and (b) SiO$_2$-NT_MW samples after a thermogravimetric treatment. In (b) it can be observed that the CNT original structures are still well-preserved.