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1 **Controlled structural damaging of multiwalled carbon nanotubes and graphene nanoplatelets by**
2 **oxidation for stable nanofluids with enhanced thermal conductivity**

3

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12 *Keywords: multi walled carbon nanotubes; graphene nanoplatelets; covalent functionalization;*

13 *stability; nanofluids; thermal conductivity*

14

15

16 **Abstract**

17 Because thermal conductivity of carbon nanomaterials is inevitably lowered upon
18 functionalization and functionalization is required to stabilize nanofluids, to meet the two
19 criteria of thermal conductivity enhancement and homogeneous dispersion over time is still
20 highly challenging for carbon nanomaterial based nanofluids. In this work, both multiwalled
21 carbon nanotubes and graphene nanoplatelets have been covalently functionalized with
22 different rates by refluxing in sulfuric acid/nitric acid of different concentrations (1, 3, 5 and 7
23 M). We show that a compromise can be found between thermal conductivity enhancement of
24 carbon-based nanofluids (to maximize) and carbon structure damaging through
25 functionalization (to minimize) while a stable dispersion is obtained. An in-depth

26 characterization by transmission electron microscopy, Raman spectroscopy, Fourier
27 transformed Infra-red spectroscopy, thermogravimetry analysis and thermogravimetry
28 analysis coupled to a mass spectrometer allow to evaluate both the applied functionalization
29 efficiency and the structural damage undergone by each carbon nanomaterial. From the
30 prepared nanofluids at 0.25 wt.% concentration, the best performance is achieved with
31 MWCNT treated by an acid mixture of H₂SO₄/HNO₃ (1:1 volumetric proportion) at
32 concentrations of 3 and 5 M where the thermal conductivity reaches an enhancement of 9.4 %
33 at 20 °C and a dispersion stability over 5 weeks with no change in nanofluid absorbance. We
34 have proved that the proposed approach allows to meet the two key criteria strongly desired
35 for nanofluid design, leading to nanofluids with higher performances compared to other
36 nanofluids prepared with carbon nanotubes treated with similar methods from the oxidized
37 carbon nanotube family.

38

39 **Abbreviations**

DIW	Deionized water
EG	Ethylene glycol
TC	Thermal conductivity
CNTs	Carbon nanotubes
MWCNTs	Multiwalled carbon nanotubes
GNPs	Graphene nanoplatelets
TGA	Thermogravimetry analysis
MS	Mass spectrometer
FTIR	Fourier transformed infra-red spectroscopy
UV-Visible	Ultraviolet-visible
CCF	Carboxylated carbon fragments

40

41.1. **Introduction**

42 First reported in 1995, nanofluids were born from the mankind's need of having advance heat
43 transfer fluids [1]. They are defined as conventional heat transfer fluids, generally deionized
44 water (DIW), ethylene glycol (EG) or a mixture of both (the solvent used is named base fluid),
45 containing nanoparticles or nanomaterials with one dimension lower than 100 nm [2].

46 Nowadays with the relentless increase of energy consumption, it is expected that nanofluids
47 with superior heat transfer features are foreseen to be used in the near future mostly in
48 industry engines [3] or renewable energy production systems like solar panels or electronic
49 devices [4] requiring high thermal transfer ability or dissipation rates. The nanoparticles are
50 dispersed in the base fluid with the aim of improving its overall properties, especially their
51 thermal conductivity. Generally, the higher the intrinsic thermal conductivity (TC) or the
52 specific heat capacity of the dispersed nanoparticles, the better the resulting thermal properties
53 of the nanofluid.

54 One of the main objectives in nanofluid research field is to maximize the transfer of the
55 intrinsic TC of the nanoparticles at the macroscopic scale of the nanofluid [5,6]. For this
56 purpose, a compromise has to be reached since the designed nanofluids have to follow two
57 conflicting requirements: to preserve the intrinsic thermal conductivity of the nanoparticles
58 and to achieve their good dispersion and stability within the base fluid. Indeed,
59 functionalization either covalent or non-covalent of the nanoparticles required to induce the
60 nanomaterial dispersion is known to affect the thermal performances of the nanofluids [7–10].
61 Carbon nanomaterials are widely known to possess a combination of outstanding chemical
62 and physical properties [11–14]. Besides, carbon nanotubes (CNTs) and graphene, which
63 have a remarkable thermal conductivity and chemical stability, have been the subject of many
64 studies [15–18]. By using carbon nanomaterials into nanofluids, their exceptional properties
65 can be leveraged on a larger scale, resulting in great benefits in a macroscopic context.

66 Unfortunately, carbon nanomaterials are very hydrophobic and they present a high tendency
67 to self-aggregate due to the existence of strong van der Waals forces which prevent their
68 proper dispersion in most polar liquids. Therefore, to solve this issue, a chemical modification
69 or functionalization of the carbon nanomaterial surface is compulsory. The non-covalent
70 approach, consisting of using surfactants that adsorb onto the materials surface creating a

71 coating layer and promote its dispersibility, is a simple and a widely used way to disperse
72 nanocarbons [19–21]. However, the surfactant can be an undesired contaminant as the coating
73 layer hinders nanocarbon thermal transfer and at the same time, it increases the nanofluid
74 viscosity [22,23]. Covalent functionalization helps to reduce the nanocarbon hydrophobicity
75 by attaching functional groups on the material surface [24]. This modification, if it is weakly
76 controlled, disrupts the nanoparticle structure which directly hinders its native properties,
77 being the intrinsic thermal conductivity not an exception [25]. Different types of chemical
78 treatment have yet been tested in the past for developing carbon-based nanofluids with a large
79 varieties of base fluids[19,26,27].

80 Increasing the nanoparticle content in the nanofluid in order to compensate these negative
81 effects would reflect higher TC, however it is counterproductive as the resulting viscous
82 nanofluid would require a great pumping power to flow [22,28]. Whereas for the non-covalent
83 method, reduction of the surfactant layer is prejudicial for the nanofluid stability as discussed
84 above. In an applicative perspective of nanofluids, it is challenging to match the two
85 expectations: good thermal properties and good dispersion stability. With the covalent
86 approach, to find a compromise between the oxidative power and properties preservation
87 appears as a smart strategy to follow. However, such study is delicate to deal with since
88 carbon nanomaterial chemical reactivity depends on the kind and the characteristic of the
89 employed nanocarbon and the strength of the functionalization treatment is not easy to
90 evaluate [29,30]; a multi-technique characterization strategy is here essential.

91 Besides the TC enhancement, to obtain a high performance nanofluid, the nanomaterial
92 proper dispersion and stability in the base fluid is mandatory, although this requirement is
93 weakly boarded in literature [31,32]. Therefore, control and manage the functionalization
94 degree is essential to design a material capable to fulfill the stability and TC requirements for
95 nanofluids.

96 Here, we present how to obtain highly stable water-based nanofluids prepared with both
97 oxidized CNTs and graphene and with good thermal conductivity. The behavior and the
98 chemical reactivity of the modified CNTs and graphene are compared with regards to the
99 resulting nanofluid thermal conductivity and stability over time. First, multiwalled CNTs
100 (MWCNTs) and graphene nanoplatelets (GNPs) were functionalized following a widely
101 reported functionalization treatment consisting of refluxing the MWCNT/GNP in a mixture of
102 sulfuric and nitric acid [33–35]. In this work, different molar concentrations have been used
103 so that the oxidative power could be tuned; such approach applied to the two different carbon
104 nanomaterials is seldom reported in literature. The damaging degree of the treated samples
105 was evaluated by transmission electronic microscopy (TEM) and Raman spectroscopy. In
106 addition, Fourier transformed infra-red spectroscopy (FTIR), thermogravimetry analysis
107 (TGA) and TGA coupled to a mass spectrometer (MS) served to determine the nature of the
108 introduced chemical species on the nanomaterial. Later, the functionalized nanoparticles (0.25
109 wt.%) were used to prepared nanofluids by the two-step method using DIW as base fluid. The
110 quality of the dispersion was evaluated by ultraviolet-visible (UV-Visible) spectroscopy. An
111 optimized functionalization rate of MWCNTs is found, allowing both limitation in the CNT
112 structural damage, and promoting at the same time their dispersibility and stability in the base
113 fluid, and the thermal conductivity (at 20 °C) of the nanofluids. This compromise cannot be
114 not obtained with GNP. It appears though, that for the applied oxidative method, it cannot be
115 reached here under the used range of chemical reaction strengths.

116

1172. **Materials and methods**

118 **2.1 Materials**

119 The employed starting MWCNTs were synthesized by a CCVD process which took place at
120 the Universiti Sains Malaysia facilities. As catalyst, Co-Mo and MgO were used. As

121 purification treatment, the produced tubes were stirred in nitric acid at 60 °C for 30 min to
122 remove the remaining catalyst components without introducing functional groups. The
123 resulting nanotubes possess 12 to 16 walls with an average diameter of 7 nm [36] and have a
124 length not higher than 10 µm, estimated from TEM observations.

125 In the case of graphene, pristine GNP was furnished by Sigma Aldrich France. According to
126 the manufacturer, GNPs possess an average length of 5 µm and a surface area between 120-
127 150 m²g⁻¹ and 15 to 20 layers.

128 For the oxidative treatments, sulfuric acid (H₂SO₄), nitric acid (HNO₃), hydrochloric acid
129 (HCl) and sodium hydroxide (NaOH) were purchased from Sigma Aldrich and used as
130 received.

131 **2.2 Oxidative treatments**

132 The oxidative treatment involved the two samples to be submitted into reflux with an acid
133 mixture of H₂SO₄/HNO₃, at concentrations of 1, 3, 5 and 7 M in a 1:1 volumetric proportion.
134 Initially, 300 mL of the acid mixture were poured in a 500 mL round flask. Then, 300 mg of
135 the departing sample were added. The flask was let to heat up at 110 °C in an oil bath and
136 once the reflux started, it was let for 24 h. After, the flask was retired from the oil bath and set
137 to cool down. Once room temperature was reached (RT), the product was filtered and rinsed
138 with DIW, then it was sonicated during 30 min in 150 mL of a NaOH solution at 4 M to
139 eliminate potential carboxylated carbon fragments (CCF) [37]. Then, the product was filtered
140 and 250 mL of diluted HCl were added. Finally, sample was rinsed with DIW until neutral pH
141 was reached and set to dry with the help of a freeze drier during 4 days. Each
142 functionalization treatment was replicated at least 3 times for both starting samples.

143 Nanofluids were prepared with a representative 0.25 wt.% concentration of the treated
144 MWCNT or GNP. Each sample was prepared at least twice. For all cases, DIW, without any
145 additive or surfactant, was used as base fluid. The nanoparticles were dispersed in the base

146 fluid with the help of a sonication probe (Sonics Vibra-Cell VCX750 equipped with a CV334
 147 probe) during 30 min at 20 °C in a cyclic mode (2 sec on, 1 sec off) at 300 W . To avoid
 148 heating and evaporation, the nanofluid container was put in ice bath during the sonication.
 149 Sample nomenclature is displayed in Table 1 to differentiate the type of carbon nanostructures
 150 and the oxidative treatment strength.
 151

Sample nature	Sample name	H₂SO₄/HNO₃ (1 M)	H₂SO₄/HNO₃ (3 M)	H₂SO₄/HNO₃ (5 M)	H₂SO₄/HNO₃ (7 M)
MWCNT	SNT	NT-1M	NT-3M	NT-5M	NT-7M
GNP	SG	G-1M	G-3M	G-5M	G-7M

152 **Table 1** Sample nomenclature.

153

154 **2.3 Nanomaterial characterizations**

155 For the TEM observations, the starting and oxidized nanotubes and graphene powder were
 156 dispersed in ethanol and gently sonicated in a sonication bath (Fisherbrand, Elmasonic S, 95
 157 W, 37 kHz) during 5 min. A droplet of the prepared dispersion was placed on a copper grid
 158 covered with a holey amorphous carbon film (200 mesh size). The TEM micrographs were
 159 obtained using a JEOL JEM-ARM 200F Cold FEG apparatus equipped with a spherical
 160 aberration (Cs) probe corrector working at an accelerating voltage of 80 and 200 kV for the
 161 MWCNT and GNP observations, respectively. In this work, the TEM figures were prepared
 162 with selected MWCNT and GNP images representative of each sample from a batch of ca. 40
 163 images obtained at different places randomly selected on the TEM grid for the same sample.
 164 The TGA analysis was performed with the help of a Setaram Setsys evolution 1750. The
 165 analysis was made by increasing temperature from 20°C to 900°C (5 °C/min) under

166 controlled air flow (20 mL/min). In the context MS analysis, the TGA apparatus was linked
167 with a Pfeiffer GSD 301C Vacuum PrismaStar mass spectrometer. As before, the temperature
168 was raised from 20°C to 900 °C (5 °C min⁻¹). However, in this case the analysis was
169 conducted under a helium flow (20 mL min⁻¹).

170 Micro-Raman spectroscopy was carried out with a Jobin Yvon LabRAM HR800 equipped
171 with a CCD detector cooled to -70 °C. A 633 nm laser wavelength was used as the incident
172 beam focused on the sample with a microscope through a wide length x100 objective and a
173 numerical aperture of 0.50. For each sample, at least 8 spectra were recorded from different
174 spots. For each spectrum, the background was subtracted and the maximum intensity of the D
175 and the G bands were used to calculate the D intensity over the G intensity ratio, I_D/I_G . The
176 spectra with the closest values of the average I_D/I_G was chosen to be displayed.

177 A Nicolet 6700 FT-IR (Thermo Scientific) spectrometer was used for FTIR spectrometry
178 investigations. At least 5 spectra of each sample were recorded in ATR mode (diamond
179 crystal) using 100 scans and a resolution of 2 cm⁻¹.

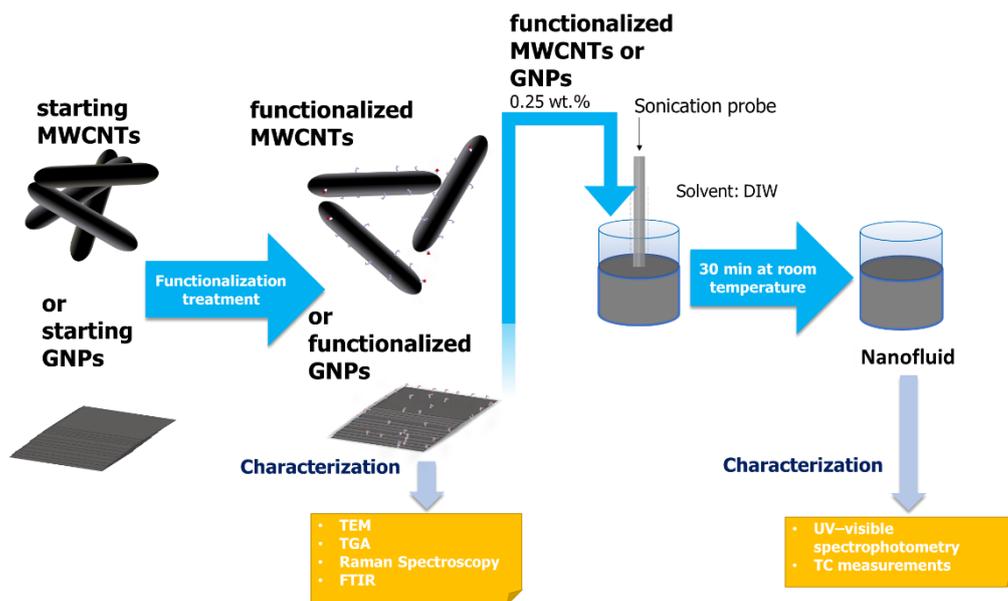
180 **2.4 Thermal conductivity measurements**

181 The thermal conductivity measurements of the prepared nanofluids were carried out in several
182 replicates at 293.15 K (20 °C) with a THW-L2 device (Thermtest Inc., Richibucto Road, NB,
183 Canada) using the transient short hot-wire method according to the ASTM D7896 standard,
184 similarly to the procedure developed in [38]. In the temperature range 283.15 to 313.15 K, the
185 experimental uncertainty of the device has been evaluated from DIW water measurement after
186 probe calibration. These data have been compared to reference values for DIW. As an
187 experimental uncertainty evidence, an average absolute deviation (AAD) around 1 % in the
188 temperature range of 283.15 to 313.15 K has been obtained. This result is similar the AAD of
189 1.1 % reported by Prado *et al.* [39] with the same device, fluid and temperature range. Each
190 thermal conductivity value reported later is an average of at least 10 measures.

191 **2.5 Nanofluid stability investigation**

192 The UV–visible spectrophotometry of the nanofluids has been carried out with a Varian
193 Cary7000 spectrophotometer in the 200–700 nm range using quartz cuvettes (28-F/Q/10) with
194 an optical path of 2 mm furnished by Jasco France. As commonly found for such absorptive
195 materials [40–42] , the nanofluids were first diluted 1:10 and the absorbance of the dispersion
196 was measured by using a double beam mode and deducting the absorbance of the base fluid
197 served as reference. Sample relative absorbance was compared at 500 nm [43,44] and
198 followed during 35 days.

199 To sum up, the principle of nanomaterials and nanofluids preparations and characterizations
200 methods are gathered in Fig. 1.



201
202 **Figure 1.** Schematic representation of the method to prepare nanofluids with oxidized
203 MWCNT and GNP. Starting samples were first functionalized and then dispersed in the base
204 fluid for the nanofluid preparation.

2063. **Results and Discussion**

207 **3.1 Morphological, structural and chemical study of the oxidized MWCNTs and GNPs**

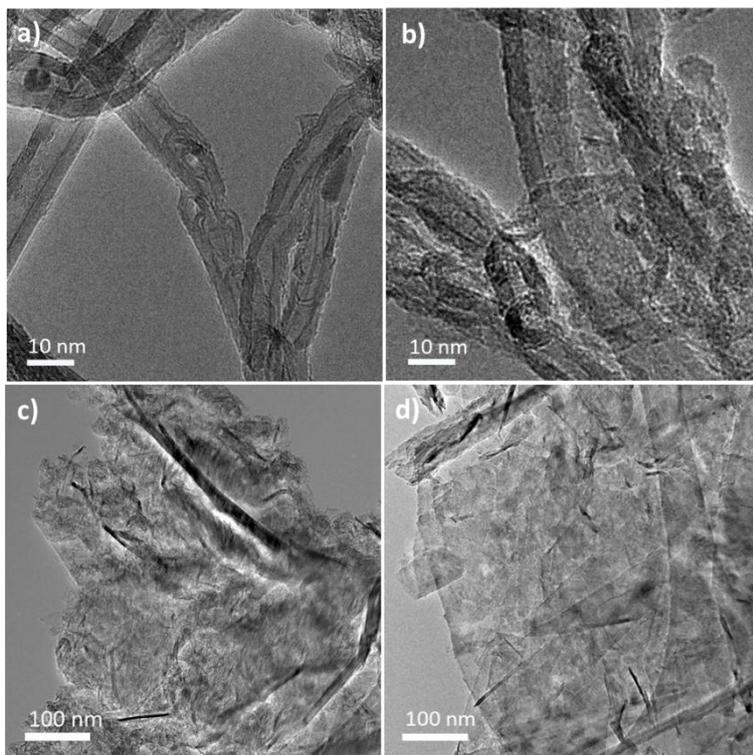
208 The TEM observations of starting MWCNTs and GNPs as well as their oxidized counterpart
209 are shown in Figure 2.

210

211

212

213



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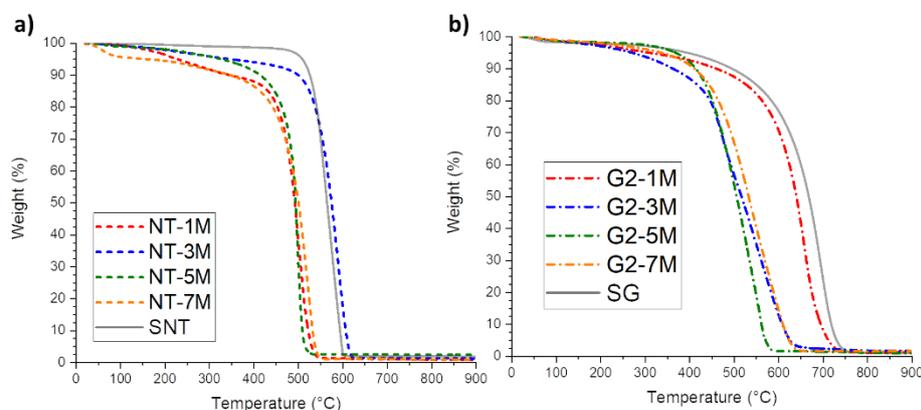
215 **Figure 2** Typical TEM micrographs of a) starting MWCNTs (SNT), b) functionalized
216 MWCNTs by $\text{H}_2\text{SO}_4/\text{HNO}_3$ at 7 M (NT-7M), c) pristine GNPs (G) and d) functionalized
217 GNPs by $\text{H}_2\text{SO}_4/\text{HNO}_3$ at 7 M (G-7M).

218

219 Some embedded tubes are noticeable in the starting MWCNTs (SNT) and functionalized
220 MWCNTs by $\text{H}_2\text{SO}_4/\text{HNO}_3$ with 7 M concentration (NT-7M) in Figs. 2a and 2b. From Figs.
221 2c and 2d, some wrinkles are typically detectable on the pristine GNPs (SG) and GNPs

222 functionalized with $\text{H}_2\text{SO}_4/\text{HNO}_3$ at 7 M (G-7M). For both GNP and MWCNT samples, the
223 carbon structure seems of good quality without visible damaging which is certainly the sign
224 that the applied treatment with $\text{H}_2\text{SO}_4/\text{HNO}_3$ at 7 M, even at high concentration, does not
225 strongly attack the carbon network and avoids formation of breaks or holes in MWCNT walls
226 and GNP layers. Both used carbon nanomaterials, MWCNT and GNP, possess a relatively
227 high number of graphene sheets in their structure, around 15 for the first and 15 to 20 for the
228 GNP (in agreement with the respective suppliers) which stabilizes them towards the applied
229 chemical attack.

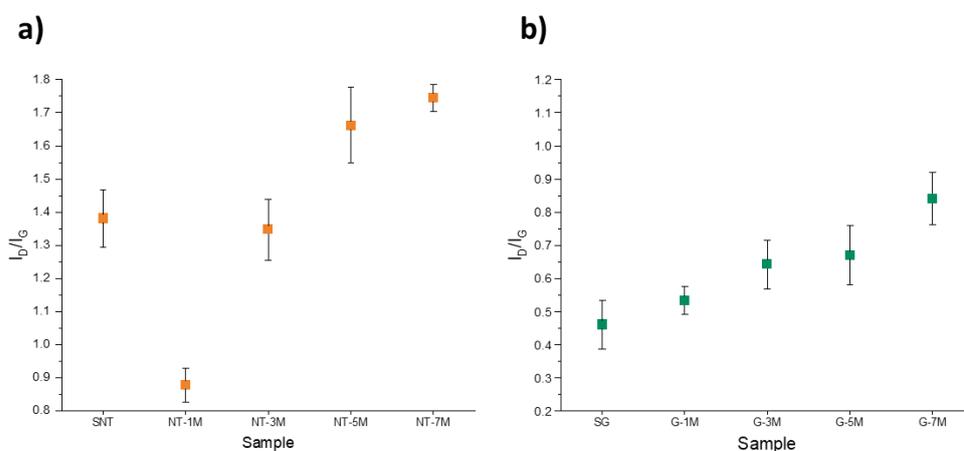
230 TGA is considered as an important technique for the nanocarbon study; the combustion
231 temperature is sensitive to their structural properties in the sense that if their structure is
232 damaged, for a similar content of inorganic impurities, the combustion temperature is
233 downshifted to lower values. Fig. 3 shows the thermograms of the starting and oxidized
234 MWCNTs and GNPs.



235
236 **Figure 3** Thermograms under dry air of a) the starting and treated MWCNTs by $\text{H}_2\text{SO}_4/\text{HNO}_3$
237 at 1, 3, 5 and 7 M (SNT, NT-1M, NT-3M, NT-5M and NT-7M) and b) the starting and
238 treated GNPs by $\text{H}_2\text{SO}_4/\text{HNO}_3$ at 1, 3, 5 and 7 M (SG, G-1M, G-3M, G-5M and G-7M).

239
240 A weak weight loss visible at around 100 °C for NT-7M is related to the moisture release by
241 the nanocarbons. For the oxidized MWCNTs, another small weight loss is detected at around

242 250 °C, it corresponds to the removal of the oxygen-containing groups [45]. For all the
 243 samples, the main weigh loss due to the carbon specie combustion is located in the 450-
 244 750 °C range. From a general observation, the burn off temperature of both the oxidized
 245 MWCNTs and GNPs is downshifted compared to that of the respective starting unoxidized
 246 carbon nanomaterial. Such behavior is commonly detected in oxidized nanocarbons and it is
 247 strongly related to their structural quality since introduction of functional groups increases *de*
 248 *facto* their structural defects [34]. After combustion, the remaining weight in starting and
 249 treated MWCNTs and GNPs is in the 1-2 wt.% range which shows the good purity of both
 250 carbon nanomaterials (Figs. 3a and 3b). The starting MWCNTs (SNT) burn at around 600 °C
 251 (Fig. 3a). A shift towards lower combustion temperatures becomes evident as sample gets
 252 oxidized at 1 M, 5 M and 7 M. Apparently, without any explanation yet, this tendency is not
 253 followed by the MWCNTs functionalized with H₂SO₄/HNO₃ at 3 M (NT-3M) which



254 decomposes in a similar temperature range than that observed for the starting MWCNTs. The
 255 combustion of the starting GNP (SG) occurs around 700°C (Fig. 3b). Nonetheless, as the
 256 GNP sample gets functionalized there is a shift of more than 100°C towards lower
 257 combustion temperature for the samples treated with the acid mixture concentration at 3, 5
 258 and 7 M (G-3M, G-5M and G-7M, respectively). This downshift is significantly smaller for
 259 the GNPs treated with the acid mixture solution at the lowest concentration (G-1M).

260

261 **Figure 4** Raman spectroscopy I_D/I_G values of a) starting and treated MWCNT samples by
262 H_2SO_4/HNO_3 at 1, 3, 5 and 7 M (SNT, NT-1M, NT-3M, NT-5M and NT-7M) and b) starting
263 and treated GNPs samples by H_2SO_4/HNO_3 at 1, 3, 5 and 7 M (SG, G-1M, G-3M, G-5M and
264 G-7M).

265

266 Raman spectroscopy is a mandatory characterization technique for carbon nanomaterials since
267 it provides information about their integrity and it can serve to probe any structural
268 modification introduced into the MWCNTs and GNPs. Typically the so called “G band”
269 (around 1590 cm^{-1}) comes from the stretching of the C-C bonds of the sp^2 network. Moreover,
270 the presence of disorder or defects in the sp^2 -hybridized carbons is shown in the so called “D
271 band” (around 1330 cm^{-1}) intensity. To have a more accurate idea of the “defects” introduced
272 in the carbon nanomaterial framework, it is often suggested to divide both bands intensity in
273 order to obtain the parameter I_D/I_G and compare it before and after oxidation. Besides, as the
274 functionalization treatment modifies the carbon atom hybridization from sp^2 to sp^3 (defect) by
275 introduction of chemical groups in the carbon network, I_D/I_G is affected. Representative
276 Raman spectra of each sample are given in Fig. S1 (Supporting Information) and their
277 corresponding I_D/I_G is displayed in Figs. 4a and 4b for the MWCNTs and GNPs, respectively.
278 As expected for both cases, an increase in acid concentration during the oxidation treatment
279 leads to a corresponding increase in the I_D/I_G [29], being the highest for the samples treated
280 with the acid mixture at 7 M, *i.e.* $1.75 (\pm 0.04)$ for MWCNT (NT-7M) and similarly for GNP
281 treated with the acid mixture at 7 M (G-7M), as an I_D/I_G of 0.84 ± 0.08 is obtained. For the
282 MWCNTs treated with the acid mixture at 5 M and 3 M I_D/I_G values of 1.66 ± 0.11 and $1.35 \pm$
283 0.09 were found (Fig. 4a). The MWCNTs treated with H_2SO_4/HNO_3 with 1 M (NT-1M)
284 displays a particular behavior since its I_D/I_G is lower than that of the starting MWCNTs. It has

285 been reported that this behavior is due to some kind of “cleaning effect” attributed to the
 286 removal of a thin disordered carbon layer at the MWCNT surface [46]; this effect is probably
 287 overcompensate by the introduction of defects due to functionalization when the acid
 288 treatment is strengthened. It should be noted that such effect is far less pronounced for
 289 graphene since this latter leads to a less pronounced resonant effect in Raman spectroscopy
 290 than CNTs [47]. In the case of the graphene samples, by lowering the oxidation strength,
 291 lower I_D/I_G values of 0.67 ± 0.09 , 0.64 ± 0.07 and 0.53 ± 0.04 corresponding to samples
 292 treated by the H_2SO_4/HNO_3 mixture at 5 M (G-5M), 3 M (G-3M) and 1 M (G-1M) were
 293 found.

294 TGA-MS under inert atmosphere (helium) was also performed over the starting and oxidized
 295 MWCNTs and GNPs. If successful, the H_2SO_4/HNO_3 treatment will anchor oxygen-
 296 containing functional groups which will decompose and produce CO (m/z 28) and CO_2 (m/z
 297 44) detected by the MS as temperature rises. The recorded weight loss and the corresponding
 298 MS signal for each oxidized MWCNTs and GNPs are given in Figs. S2 and S3 (Supporting
 299 Information), respectively. The temperature at which these CO/ CO_2 species are detected can
 300 be assigned to specific functional groups as gathered in Table 2 [48].

301

302 **Table 2** Assignment and quantification in wt.% of the oxygen containing functional groups
 303 detected at the MWCNT and GNP surface after oxidation by the acid mixture H_2SO_4/HNO_3 at
 304 1, 3, 5 and 7 M concentration from TGA coupled with MS.

Sample	Detected m/z	Functional group identified	Weight loss temperature (°C)	Weight loss (%)
NT-1M	28	ether	750	0.38
NT-3M	44, 28	carboxylic	200-300	1.29

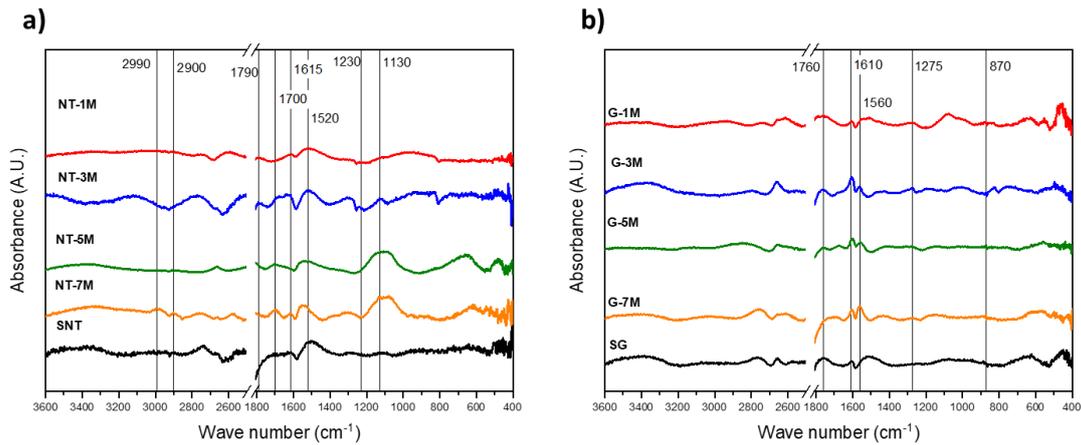
	44, 28	anhydride	600-700	0.86
NT-5M	44, 28	carboxylic	200-300	1.62
	44, 28	anhydride	600-700	1.51
	28	ether	720	0.62
	28	quinone	850	0.65
NT-7M	44, 28	carboxylic	200-300	1.84
	44, 28	anhydride	600-700	2.04
	28	ether	720	0.97
	28	quinone	850	0.48
G-1M	44,28	lactone	450	0.94
G-3M	44, 28	lactone	450	1.36
G-5M	44, 28	carboxylic	200-300	1.01
	28	quinone	700-850	2.59
G-7M	28	quinone	850	2.08

305

306 For the treated MWCNTs with the acid mixture at 3, 5 and 7 M (NT-3M, NT-5M and NT-7M
307 respectively) and GNPs treated with 5 M of the acid mixture (G-5M), CO₂ (as the parent
308 specie with CO as fragment) detected in the low temperature range; *i.e.* 200-300 °C, are
309 assigned to carboxylic group species at around 1-2 % for the above samples. The GNPs
310 oxidized with low strength (G-1M and G-3M) exhibit the presence of lactone (~450 °C)
311 whose content increases with acid concentration (0.94 and 1.36 wt.% for G-1M and G-3M,
312 respectively). At higher temperature, in the 600-700 °C domain, anhydride is evidenced from
313 the observed CO₂/CO signal for the MWCNTs treated with 3, 5, 7 M of H₂SO₄/HNO₃; their
314 content increases gradually as the treatment is strenghten (0.86, 1.51, 2.04 wt.% for 3, 5, 7 M,

315 respectively). From the detection of CO at 700 °C, a small amount of ether (less than 1 wt.%)
316 can be identified on most of the oxidized MWCNTs. For the highest used concentrations (5
317 and 7 M), quinone is detected (~850 °C) for NT-5M, NT-7M, G-5M and G-7M at a higher
318 amount for GNPs (more than 2 wt.%) than MWCNTs (around 0.5 wt.%).

319 FTIR was performed over the starting and oxidized samples to identify the nature of the
320 functional groups present at the material surface. The presence of oxygen-containing groups
321 that will promote the MWCNTs and GNPs hydrophilic character is expected [33]. From the
322 employed functionalization method, these groups contain mainly C-O, COOH and C=O
323 bonds [34]. Fig. 5 shows FTIR spectra of the raw and oxidized MWCNTs and GNPs. As
324 expected, the characteristic black bone (C=C) stretching vibration of carbonaceous materials
325 appears in both starting and functionalized samples, it is displayed at $\approx 1520\text{ cm}^{-1}$ and at 1560
326 cm^{-1} for the CNTs and the GNPs in Figs. 5a and 5b, respectively. The C-O and C=O signals
327 (expected from the grafted oxygen-containing groups) are observed for the samples oxidized
328 with the highest acid mixture concentrations, *i.e.* 5 and 7 M (NT-5M, NT-7M, G-5M, and G-
329 7M). Generally, for the CNTs, the absorption peaks observed at 1130 and 1230 cm^{-1} are
330 attributed to C-O stretching of carboxylic acid and alcohol groups, respectively. At the same
331 time the absorption peaks located between 1615 and 1790 cm^{-1} , characteristic of C=O
332 stretching, can be attributed to the presence of carboxylic acid and quinone groups [35,49–51].
333 For the GNP samples, the spectra present the characteristic signal of C-O stretching notably in
334 the 870 - 1275 cm^{-1} range and the presence of C=O, attributed to carboxylic specimens, at 1610
335 and 1760 cm^{-1} (Fig. 5b) [49,52]. Presence of oxygen containing groups for both MWCNTs
336 and GPNs is then clearly evidenced by FTIR. These results are in agreement with most of the
337 types of oxygen-containing functional group found by TG-MS (Table 2).



338

339 **Figure 5** FTIR spectra of a) starting and treated MWCNTs by H_2SO_4/HNO_3 at 1, 3, 5 and 7 M
 340 (SNT, NT-1M, NT-3M, NT-5M and NT-7M) and b) starting and treated GNPs by
 341 H_2SO_4/HNO_3 at 1, 3, 5 and 7 M (SG, G-1M, G-3M, G-5M and G-7M).

342

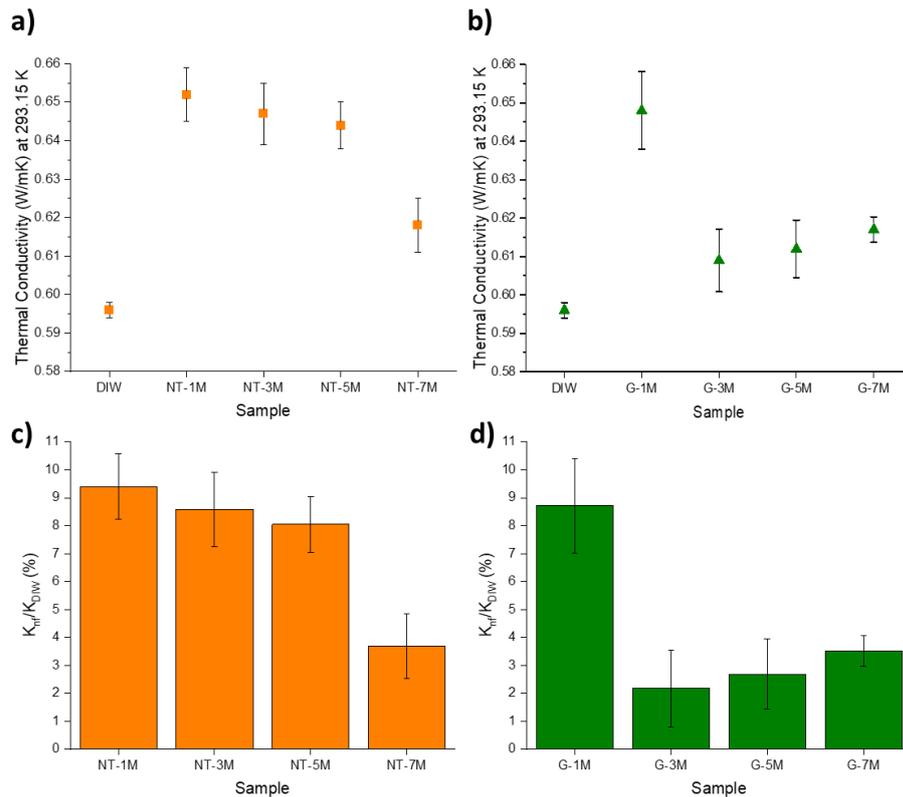
343 The applied characterization analysis shows that oxidation was promoted in different
 344 proportion among both samples. Yet, it is evident that different degrees of structural damages
 345 may have occurred in the treated MWCNTs and GNPs. Besides, as reactivity differs among
 346 different nanocarbons depending on their amount of pre-existing defects [53], morphology,
 347 curvature [54], etc., MWCNT and GNP react differently to the same functionalization force
 348 making the compromise between dispersion ability and preservation of the intrinsic physical
 349 properties difficult to predict. In the following, both dispersion stability and TC measurements
 350 have been investigated to find the optimized degree of oxidation to apply in order to prepare
 351 efficient and stable nanofluids for heat transfer applications.

352

353 **3.2 Thermal conductivity vs. stability of MWCNT and GNP based nanofluids**

354 The TC of the prepared nanofluids, measured at 293.15 K (20 °C), are presented in Fig. 6 for
 355 MWCNT and GNP (Figs. 6a and 6b, respectively). The functionalized MWCNT- and GNP-
 356 based nanofluids present TC values higher than that of water as the base fluid. In both cases,
 357 significantly higher TC values are measured for the samples treated with the lowest acid

358 mixture concentration; *i.e.* at 1 M (NT-1M and G-1M). For MWCNTs (Fig. 6a), by taking
359 into account the measurement uncertainty, TC remains in the same range around $0.65 \text{ Wm}^{-1}\text{K}^{-1}$
360 ¹ until the acid concentration of 5 M and TC diminishes significantly down to around 0.62
361 $\text{Wm}^{-1}\text{K}^{-1}$ for the sample treated with the acid mixture of concentration 7 M. This tendency is
362 obviously observed for the calculated TC enhancements going from 9 % for samples NT-1M,
363 NT-3M and NT-5M down to 4 % for NT-7M. For the GNP-based nanofluids, a similar
364 behavior showing a decrease of the TC values (from 0.65 down to $0.61 \text{ Wm}^{-1}\text{K}^{-1}$) and
365 enhancements (from 9 down to 3 %) is observed with a clear shift towards the lowest
366 oxidative force. These results reveal a strong dependency between TC enhancements and the
367 used $\text{H}_2\text{SO}_4/\text{HNO}_3$ concentration employed for chemical oxidation of the carbon
368 nanomaterials. This dependency can be explained by the oxidation mechanism as it involves
369 the disruption of the nanocarbons native structure as functionalization involves the attack and
370 reaction of oxidants with the carbon-to-carbon bonds, causing sp^2 hybridized carbon atoms to
371 break down into sp^3 carbon atoms. This process creates additional defects, facilitating the
372 incorporation of functional groups onto the MWCNT and GNP surface and subsequently,
373 increasing the defect populations leading to the loss of their intrinsic properties. This can
374 explain why the extent of defect increment is linked to the acid concentration used during the
375 functionalization process [35,55].



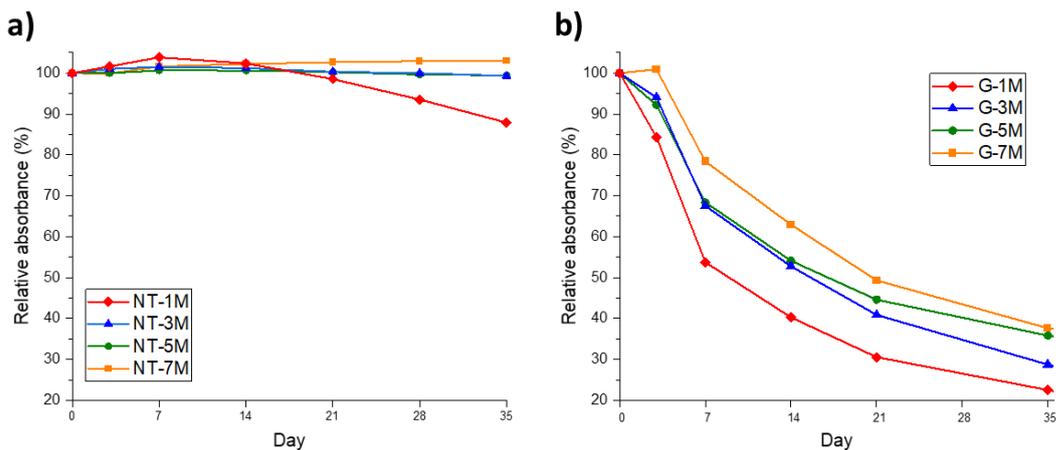
376

377 **Figure 6** TC measurements of nanofluids (a and b) and TC enhancements (c and d) with
 378 respect to the base fluid prepared with a) and c) the treated MWCNTs by H₂SO₄/HNO₃ at 1, 3,
 379 5 and 7 M (NT-1M, NT-3M, NT-5M and NT-7M) and b) and d) the treated GNPs by
 380 H₂SO₄/HNO₃ at 1, 3, 5 and 7 M (G-1M, G-3M, G-5M and G-7M).

381

382 The stability of the prepared nanofluids was further followed by means of UV-visible
 383 absorbance spectroscopy. According to the Beer-lambert law, a dispersion UV absorbance is
 384 proportional to its concentration. Normally, during destabilization, the carbon nanomaterials
 385 will aggregate slowly and sediment, leading to less particles being in suspension, therefore the
 386 higher the absorbance over time the better the stability [56]. Another commonly observed
 387 phenomenon for carbon nanomaterials leads to a slight increment of absorbance during
 388 dispersion settling. This behavior is consequence of nanocarbon flocculation-inducive
 389 attractive forces at the first stage of dispersion destabilization leading the nanoparticles to
 390 self-aggregate; these aggregates remaining in suspension for a while before the sedimentation

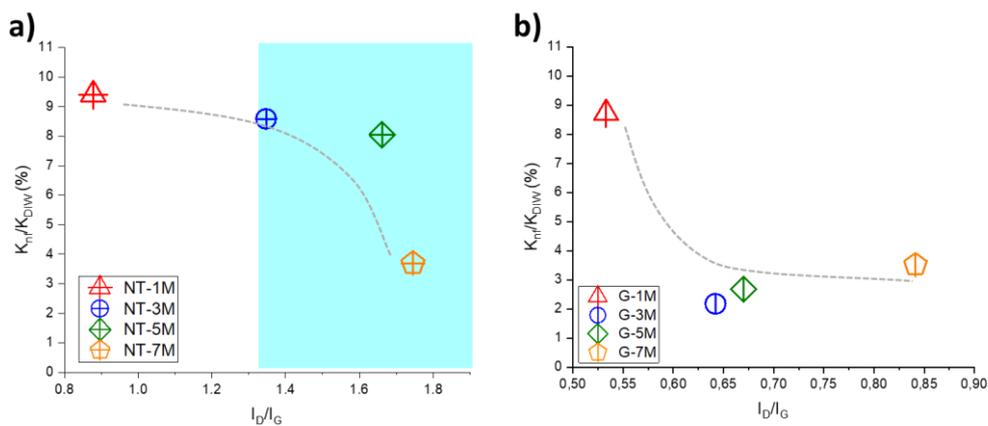
391 step [57,58]. The relative nanofluids absorbance during a 35 day-period is displayed in Figure
392 7. Contrasting behaviors can be observed between the oxidized MWCNT- and GNP- based
393 nanofluids (Figs. 7a and 7b, respectively). The nanofluids prepared with the MWCNTs
394 functionalized with H_2SO_4/HNO_3 at 7 M (NT-7M) remained stable after 35 days with a
395 relative increase in absorbance of 2 %. Likewise, nanofluids containing the MWCNTs treated
396 with an acidic mixture concentration at 3 and 5 M (NT-3M and NT-5M) show an absorbance
397 decrease of only 1 %. For the nanofluid prepared with the MWCNTs treated with the lowest
398 acid mixture concentration (NT-1M), a slight increase in absorbance (around 5 %) is observed
399 during the first 3 to 7 days and it presents a relative absorbance decrease of 20 % after the 35
400 days. As expected, the carbon nanomaterials treated with the highest functionalization rate
401 show a better endurance to sedimentation. For the GNP based nanofluids (Fig. 7b), an
402 important decay in the absorbance over time is rapidly seen since the early days of settling.
403 After 35 days, the nanofluids containing the GNPs treated with H_2SO_4/HNO_3 at 5 and 7 M
404 (G-5M and G-7M) present only 40 % of their initial relative absorbance. The GNP based
405 nanofluid treated with the 7 M acid mixture (G-7M) presents a small relative absorbance
406 increment during the first days similarly to what it was observed for sample NT-1M. The
407 relative absorbance drop becomes more pronounced for two nanofluids with the GNPs
408 functionalized with the lowest acid concentration (G-3M and G-1M) with a relative
409 absorbance of 30 and 20 %, respectively. Again here, the more oxidized the sample, the better
410 the stability improvement, being however not good for all the studied GNP based nanofluids.



411 **Figure 7** Relative absorbance over 35 days of the nanofluids (diluted 1:10) prepared with a)
 412 the treated MWCNTs by H₂SO₄/HNO₃ at 1, 3, 5 and 7 M (NT-1M, NT-3M, NT-5M and NT-
 413 7M) and b) the treated GNPs by H₂SO₄/HNO₃ at 1, 3, 5 and (7 M , G-1M, G-3M, G-5M and
 414 G-7M).
 415

416
 417 By observing TC and stability of the eight studied nanofluids (Figs. 6 and 7), it is clear that
 418 the MWCNTs oxidized with H₂SO₄/HNO₃ at 3 and 5 M concentrations (NT-3M and NT-5M
 419 respectively) present the best compromise between the nanofluids two main requirements.
 420 This compromise for the MWCNTs cannot be achieved with the GNPs showing a lack of
 421 stability for all the used conditions for the applied chemical modification. As it was stated
 422 before, the different reactivity between MWCNT and GNP would result in different nanofluid
 423 performances. Furthermore, even if the functionalization seems efficient on GNP (significant
 424 increase in I_D/I_G), the functionalization level seems not sufficient to counterbalance the
 425 aggregation forces, explaining the poor stability of the oxidized GNPs, even at the highest
 426 used acid mixture concentration (G-7M). Possibly for the GNP, the TC enhancement window
 427 and the carbon structure damaging do not concur, making impossible to find the desired
 428 compromise for this kind of carbon nanomaterial and this kind of functionalization approach.
 429 Evolution of the nanofluids TC increment as a function of the I_D/I_G which is sensitive to
 430 damaging (amount of defects) of the chemically modified MWCNTs and GNPs is shown in

431 Figs. 8a and 8b, respectively (the gray plotted line serves as a visual guide). For the oxidized
 432 MWCNTs, as the number of defects increases in the carbon network due to the strength of the
 433 oxidation treatment, the TC increment is roughly maintained with a slight decrease and drops
 434 rapidly above a certain degree of defects introduced in the carbon nanomaterials. From the
 435 results obtained above, the I_D/I_G range where the carbon nanomaterial dispersion is stable is
 436 displayed as visual guidance (in blue). Remarkably is the fact that the TC increment drop is
 437 not located at the beginning of the stable dispersion zone, suggesting that samples located in
 438 between (NT-3M and NT-5M) are capable to fulfill both stability and TC requirements for the
 439 prepared nanofluid. For the oxidized GNPs, a similar TC increment drop is observed but with
 440 a strongest sensitivity to the oxidation treatment conditions (Fig. 8b). Contrary to a
 441 continuous process, the observed interplay between TC enhancement and defect amount in the
 442 carbon network suggests the existence of a threshold above which the phonon pathway is
 443 broken and beyond which TC suddenly drops. This finding evidences the best compromise to
 444 be found by maximizing the sample stability and at the same time limiting the carbon
 445 structure damaged by the chemical treatments.



446
 447 **Figure 8** Nanofluid TC increment vs. Raman spectroscopy I_D/I_G values of a) the treated
 448 MWCNTs by H_2SO_4/HNO_3 at 1, 3, 5 and 7 M (NT-1M, NT-3M, NT-5M and NT-7M) and b)
 449 the treated GNPs by H_2SO_4/HNO_3 at 1, 3, 5 and 7 M (G-1M, G-3M, G-5M and G-7M).

450

451 **3.3 Thermal conductivity performances of the prepared MWCNT and GNP nanofluids**

452 With the aim to compare the efficiency between the nanofluids prepared here with oxidized
 453 MWCNTs and GNPs, a TC performance parameter, namely P_{TC} , derivative from Pavía *et al.*
 454 [31] is considered. This parameter allows to compare the efficiency of nanofluids prepared
 455 with different nanoparticles by considering the nanofluid TC enhancement divided by the
 456 amount of the employed nanomaterial used to prepare the nanofluid. In this work, the P_{TC}
 457 parameter is calculated with the TC enhancement reported at 20 °C and divided by
 458 temperature (in °C) as described in Eq.1:

$$P_{TC} = \frac{TC_e}{C_{NP} \cdot T_m} \quad (\text{Eq.1})$$

460
 461 where TC_e is the measured thermal conductivity enhancement with respect to the base fluid at
 462 20 °C, C_{NP} is the nanoparticle concentration (wt. %) of the employed nanocarbon and T_m is
 463 the temperature (°C) of the TC measurements [31].

464 Initially, the P_{TC} was calculated applying Eq. 1 for the 8 prepared nanofluids. The results are
 465 gathered in Table 3 below.

466
 467 **Table 3** Functionalized MWCNT- and GNP-based nanofluid preparation conditions, TC
 468 enhancements with respect to base fluid and the calculated TC parameter, P_{TC} .

Functionalization method conditions	Sample	Thermal conductivity	
		TC enhancement	P_{TC} (% increment/ wt. % per °C)
300 mL H ₂ SO ₄ :HNO ₃ , 1:1 v/v at 1 M reflux during 24 h	NT-1M	9.4	1.88
	G-1M	8.72	1.74
300 mL H ₂ SO ₄ :HNO ₃ , 1:1 v/v	NT-3M	8.58	1.72

at 3 M reflux during 24 h	G-3M	2.18	0.44
300 mL H ₂ SO ₄ :HNO ₃ , 1:1 v/v	NT-5M	8.05	1.61
at 5 M reflux during 24 h	G-5M	2.68	0.54
300 mL H ₂ SO ₄ :HNO ₃ , 1:1 v/v	NT-7M	3.69	0.74
at 7 M reflux during 24 h	G-7M	3.52	0.70

469

470 P_{TC} values obtained for the two nanocarbons treated with the lowest functionalization force
471 (H₂SO₄/HNO₃ at 1 M) are in the same range (Table 3). However, as the acid concentration
472 increases, a different impact on MWCNT and GNP TC performances appears. With G-3M
473 and G-5M, P_{TC} values were less than half of those obtained for MWCNTs at same treatment.
474 At 7 M, similar values of P_{TC} were found for both oxidized MWCNTs and GNPs (NT-7M and
475 G-7M).

476 As the treated MWCNT based nanofluids in this study exhibited superior stability over time
477 and TC performances (TC enhancement and P_{TC}), they were compared with analogous
478 samples treated under similar conditions, *i.e.* acid treated MWCNTs whose TC is reported in
479 literature Previous works used for comparison purpose are gathered in Table 4. The CNT
480 concentration influence in the nanofluid TC enhancement not always result in high P_{TC} values
481 as already been discussed in literature [31]. Additionally, nanofluids prepared with oxidized
482 MWCNTs by the acid mixture of H₂SO₄ and HNO₃ in literature present a P_{TC} (% of TC
483 increment per wt.% of CNT per °C) in the 0.3-7 range. From a detailed analysis of Table 4, it
484 could be inferred that oxidizing MWCNTs by the H₂SO₄/HNO₃ mixture results, in general, in
485 CNTs with good thermal properties that are later reflected in good nanofluids TC
486 enhancements. By comparing the applied functionalization methods, it seems that oxidizing
487 the CNTs with mild conditions (relatively low acid concentrations, shortest stirring/refluxing
488 times, etc.) does not necessarily result in high P_{TC} values (and neither for strong conditions, as

489 expected). Interestingly, for some nanofluids prepared under practically the same
490 circumstances and with similar MWCNT concentrations, contrasting P_{TC} values were found.
491 In the works of Ghozatloo *et al.* [42] and Van Trinh *et al.* [59], P_{TC} values of 6.73 and 0.21
492 are obtained, respectively. Such difference might arise from the variance among the used
493 starting MWCNT geometrical characteristics and/or the preexisting defect amount that will
494 influence the functionalization degree and the CNT network disruption of the outcoming
495 species and eventually their impact on the nanofluid TC.

496 Different techniques can be used to evaluate nanofluid stability, being the most recurrent the
497 direct visual observation, UV-visible and Zeta potential. The first method is well known as a
498 purely qualitative analysis, while the last two offer a more trustful and quantitative inquiry.
499 Zeta potential measures the surface charge around the dispersed nanomaterial giving an idea
500 of the stability of colloidal dispersions at a given time. UV-visible spectroscopy performed
501 over time can provide quantitative data about nanofluid stability during long time periods. As
502 it was stated before, nanofluids must remain stable for being efficiently used as heat transfer
503 fluids in cooling systems. Stability of nanofluids over time investigated by UV-visible
504 spectroscopy was performed only in half the works gathered in Table 4, including the
505 nanofluids prepared in this article. Good stability over time has been successfully reported for
506 80 days by Farbod *et al.* [60] while Ghozatloo *et al.* [42] have followed their MWCNT based
507 nanofluid stability only during 800 min. In the work by Hussein *et al.* [61], stability is
508 mentioned to be investigated by UV-visible spectroscopy however, no clear data are given
509 over time. For the other works, only visual observations and Zeta potential measurements
510 were performed forbidding stability over time studies. The analysis of P_{TC} /nanofluid stability
511 relationship for the best P_{TC} calculated for each reported work is provided below. P_{TC} is found
512 to be quite high (6.73 % TC increment / wt. % per °C) for the MWCNT based nanofluids
513 prepared by Ghozatloo *et al.* [42] but with the nanofluid stability only followed over 800 min.

514 For the other reported highest P_{TC} values (5.87 and 5.36 TC increment / wt. % per °C from
515 refs. [61] and [62], respectively) with no investigation of the stability of the corresponding
516 prepared nanofluids. P_{TC} are found quite low (0.34 and 0.37 TC increment / wt. % per °C
517 from refs. [59] and [63], respectively). The performances of the nanofluids prepared by
518 Farbod *et al.* [60] with MWCNTs oxidized with a H_2SO_4/HNO_3 mixture show a good
519 dispersion stability over 80 days (absorption decay of 10 %) and a P_{TC} of 3 TC increment /
520 wt. % per °C which is close to the best value found in this work.

521 The P_{TC} /stability compromise found in this study for the nanofluids containing treated
522 MWCNTs is better for the MWCNTs oxidized with intermediate functionalization forces, *i.e.*
523 3 M and 5 M (NT-3M and NT-5M) among the investigated acid mixture concentration range.
524 Furthermore, the stability evaluation displays that the nanofluids prepared with NT-3M and
525 NT-5M remained stable for at least 5 weeks suggesting that both important nanofluids criteria
526 were achieved.

527 **Table 4** Functionalized MWCNT-based nanofluid preparation conditions, including MWCNT source, functionalization treatment, nanoparticle
 528 concentration, temperature used to measure TC, TC enhancement with respect to base fluid, calculated TC parameter (P_{TC}) and stability
 529 investigation including the used technique and the found stability time.

Sample nature	Functionalization method conditions	CNT conc. (wt. %)	Thermal conductivity measurements				Stability measurements		Ref
			T (°C)	TC (W/mK)	TC enhancement	P_{TC} (% increment/wt. % per °C)	Measurement technique	Measurement over time	
MWCNTs	300 mL H ₂ SO ₄ :HNO ₃ , 1:1 v/v at 1 M reflux during 24 h	0.25	RT	0.65	9.4	1.88	UV-visible absorption	35 days. Sample max. absorbance decay 20%	This work
MWCNTs	300 mL H ₂ SO ₄ :HNO ₃ , 1:1 v/v at 3 M reflux during 24 h	0.25	RT	0.64	8.58	1.72	UV-visible absorption	35 days. Sample stable, no absorbance	This work

								decay.	
MWCNTs	300 mL H ₂ SO ₄ :HNO ₃ , 1:1 v/v at 5 M reflux during 24 h	0.25	RT	0.64	8.05	1.61	UV-visible absorption	35 days. Sample stable, no absorbance decay.	This work
MWCNTs	300 mL H ₂ SO ₄ :HNO ₃ , 1:1 v/v at 7 M reflux during 24 h	0.25	RT	0.62	3.69	0.74	UV-visible absorption	35 days. Sample stable, no absorbance decay.	This work
MWCNT commercial	40 ml of pure HNO ₃ reflux during 1 h	0.4	RT	N.A.	3	0.37	Direct visual observation	2 months, no visible precipitation	[63]
MWCNT commercial	Pure H ₂ SO ₄ :HNO ₃ , 3:1 v/v sonicated during 30 min and reflux during 4 h	0.1	40	0.61	12	3	UV-visible absorption	80 days. Sample absorbance decay 10%	[60]

MWCNT commercial	Pure H ₂ SO ₄ :HNO ₃ , 3:1 v/v sonicated during 30 min and reflux during 4 h	0.25	40	0.59	10	1	UV-visible absorption	80 days. Sample absorbance decay 20%	[60]
MWCNT commercial	Pure H ₂ SO ₄ :HNO ₃ , 3:1 v/v sonicated during 30 min and reflux during 4 h	0.5	40	0.63	11	0.55	UV-visible absorption	80 days. Sample absorbance decay 30%	[60]
MWCNT commercial	40 ml Pure H ₂ SO ₄ :HNO ₃ , 3:1 v/v and reflux during 1 h	0.1	RT	0.66	10.73	5.36	Direct visual observation	N.A.	[62]
MWCNT commercial	40 ml Pure H ₂ SO ₄ :HNO ₃ , 3:1 v/v and reflux during 1 h	0.05	RT	0.61	2.34	2.34	Direct visual observation	N.A.	[62]
MWCNT commercial	Pure H ₂ SO ₄ :HNO ₃ , 3:1 v/v stirring 1h and then	0.02	RT	0.61	2.34	5.87	UV-visible absorption	N.A.	[61]

al	sonication bath during 3 h								
MWCNT commercial	Pure H ₂ SO ₄ :HNO ₃ , 3:1 v/v stirring 1h and then sonication bath during 3 h	0.05	RT	0.63	1.05	1.05	UV-visible absorption	N.A.	[61]
MWCNT commercial	Pure H ₂ SO ₄ :HNO ₃ , 3:1 v/v stirring 1h and then sonication bath during 3 h	0.08	RT	0.65	9.06	5.66	UV-visible absorption	N.A.	[61]
MWCNT commercial	Pure H ₂ SO ₄ :HNO ₃ , 3:1 v/v stirring 1h and then sonication bath during 3 h	0.1	RT	0.66	10.73	5.36	UV-visible absorption	N.A.	[61]
MWCNT commercial	Pure H ₂ SO ₄ :HNO ₃ , 3:1 v/v stirring for 100 min	0.1	25	0.71	16.83	6.73	UV-Visible transmittance	800 min. Transmittance	[42]

al								increment of 0.5 %	
MWCNT by CVD	Pure H ₂ SO ₄ :HNO ₃ , 3:1 v/v stirring for 3 h	0.16	30	0.61	1	0.21	Zeta potential	N.A.	[59]
MWCNT by CVD	Pure H ₂ SO ₄ :HNO ₃ , 3:1 v/v stirring for 5 h	0.16	30	0.62	1.65	0.34	Zeta potential	N.A.	[59]
MWCNT by CVD	Pure H ₂ SO ₄ :HNO ₃ , 3:1 v/v stirring for 7 h	0.16	30	0.61	1.16	0.24	Zeta potential	N.A.	[59]

530

531

532 **Conclusion**

533 MWCNTs and GNPs have been submitted to a functionalization treatment under
534 $\text{H}_2\text{SO}_4/\text{HNO}_3$ mixture with a gradual increase in concentration modifying that way the
535 oxidation power applied. The chemically modified MWCNTs and GNPs have been
536 investigated by means of several characterization methods so that the amount of
537 defects/functional groups in the carbon framework was followed upon the applied chemical
538 treatments. The thermal conductivity of nanofluids produced with those MWCNTs and GNPs
539 is put into perspective with the carbon nanomaterial damage and the nanofluid stability
540 studied during 35 days by means of UV-visible spectroscopy. It appears that the GNP-based
541 nanofluids suffer from a lack of stability even for the highest functionalized rate making
542 unreachable a good compromise between TC preservation and structural damaging by the
543 applied chemical functionalization treatment. For the MWCNT-based nanofluids, an
544 interesting compromise can be found. It allows i) limiting the amount of structural defects
545 introduced by the chemical treatment and consequently the decrease in nanofluid thermal
546 conductivity and ii) a remarkable stability of the oxidized MWCNT based nanofluids is
547 observed (without addition of surfactant). The difference between the GNP and MWCNT
548 performance presumably originates from different reactivity towards the oxidative force,
549 suggesting the existence of a limit for each material after which the defect introduction causes
550 a change in both stability and thermal conductivity of carbon-based nanofluids. As rarely
551 reported, this work provides the study of a coupled effect between the chemical treatment
552 applied to the carbon nanomaterial, the nanofluid stability and the TC performance. Such
553 strategy, tuning the functionalization strength allowing to optimize nanofluid TC vs. stability,
554 could be used for other functionalization treatments with the purpose of searching to
555 maximize TC even more while keeping a good stability. From such a compromise, it would
556 be interesting to apply the proposed approach to any carbon nanomaterials such as

557 nanodiamonds, nanofibers... and to move the focus towards the diminution of the
558 nanomaterial concentration. We strongly believe that such investigation will lead to more
559 research evaluating the carbon-based nanofluid stability over time in regards with TC
560 measurements which would offer a crucial step towards nanofluids for more realistic
561 performance evaluation.

562

563 **Author Contributions**

564 Experiments, methodology, nanofluid preparation, spectroscopy characterization, writing and
565 data analysis: M.P.; TEM imaging and analysis: M.E.; thermal conductivity, data analysis,
566 writing, review and editing: P.E. MWCNT synthesis supervision, project administration and
567 funding acquisition: A.R.M.; supervision project administration, funding acquisition, data
568 analyzing, methodology, writing, review and editing: B.V.

569

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578

579 **Conflicts of interest**

580 The authors are no conflicts to declare.

581

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