

**Optical characterisation of oxidised carbon nanohorn nanofluids for
direct solar energy absorption applications**

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17 **Abstract**

18 Carbon nanohorns and oxidised carbon nanohorns-based nanofluids were characterised by
19 taking one step forward. The advantage of studying oxidised carbon nanohorns is that they are
20 surfactant-free. The stability of both nanofluids was checked after a 3-month preparation
21 period at high temperature, which comes closer to real applications. Two different dynamic
22 light scattering (DLS) systems were used to measure stability at high temperature before being
23 compared. A deep optical analysis was run. An integrating sphere was attached to the classic
24 spectrophotometer to determine the scattering of nanofluids. After obtaining the
25 experimental values of the optical parameters for both nanofluids, the Kubelka-Munk Theory
26 was applied to obtain optical coefficients. Finally, the scattering albedo was calculated to
27 facilitate comparisons with the literature. Studying both nanofluid types provided us with new
28 knowledge about their potential use as direct solar absorbers in solar thermal collectors.

29

30 **Key words:** solar absorbers; carbon nanohorns; oxidised carbon nanohorns; scattering albedo;
31 high temperature stability.

32 **1. Introduction**

33 In recent years, solar thermal energy has attracted much interest given its thermal storage
34 possibilities and economic appeal [1]. Conventional solar thermal collectors transform solar
35 radiation energy into the thermal energy of the transport medium. Typical solar collectors use
36 a black surface to absorb incoming sunlight. Then this energy is transferred to water to form
37 high quality pressurised steam in a boiler/heat exchanger. Thus, in general, many transfer
38 steps (via radiation, convection, conduction and boiling) are required to follow this process
39 and convert light energy into thermal energy for a power cycle. In order to minimise
40 limitations, which result from following many energy transfer steps, some alternative concepts
41 have been addressed [2]. Of these, the idea of absorbing light inside the working fluid while
42 generating steam has been well studied [3]. Direct steam generation can make solar plants
43 more economic and more environmentally friendly, and would present fewer thermal losses
44 than conventional solar plants, which would improve the cost of energy by 11% [4]-[6].
45 Moreover, when only light is absorbed by the working fluid, efficiency is enhanced by around
46 10% compared to absorbing light on a black surface, as in typical collectors [4]-[12].

47 One proposal is to use nanofluids as working fluids to directly absorb light. Nanofluids are
48 defined as engineered colloidal suspensions of nanometric solid particles in a base fluid [13],
49 [14]. The reason for suspending these small particles is to enhance heat transfer capabilities,
50 especially thermal conductivity over the base fluid [15]-[17].

51 Among the particles utilised as part of nanofluids, single-wall carbon nanohorns (SWCNHs) [18]
52 are modest graphene sheets wrapped to form horn-shaped cones with a half-fullerene cap.
53 They are 30-50 nm long, have a variable diameter of 2-5 nm [19], and the tips of nanohorns
54 are cone-shaped with an edge of around 20° [20], [21]. SWCNHs tend to form aggregates that
55 resemble "dahlia" flowers or buds [22]. One major characteristic of SWCNHs is lack of metal

56 contamination. Consequently, their production does not need to resort to decontamination
57 processes.

58 Suspensions of SWCNH in water have also been investigated for energy applications to
59 produce black fluids for volumetric solar absorption in solar collectors [23] – [27]. As SWCNHs
60 are not effortlessly dispersible in water given the hydrophobic nature of their surface,
61 surfactants are normally used to accomplish proper stability. However, utilising surfactants
62 entails some drawbacks that can make the colloid unstable [28]– [30]. Thus another method
63 has been used to mostly oxidise SWCNH surfaces as a perfect strategic device to achieve stable
64 suspensions in water without having to resort to surfactants [31].

65 As briefly described, since there is one paper reporting the application of CNH based
66 nanofluids in a real solar collector [26] and there is still a lack of reliable and accurate
67 experimental measurements of different thermophysical properties especially of oxCNH based
68 nanofluids for this peculiar application This is even more crucial when the optical properties
69 and the stability of such nanofluids are considered. In fact, the long-term (at lab scale) stability
70 is of fundamental interest to understand the feasibility of a nanofluid in real life applications.
71 Besides, it is also very important the analysis of the effects of the operating conditions on the
72 nanofluid, especially when the temperature is considered. The aim of this paper is to study and
73 compare the stability and optical properties of SWCNH and oxidized SWCNH suspensions in
74 water in the perspective to use them as possible future direct sunlight absorbing fluid in a solar
75 thermal collector. Different measurements to ensure the potential of these nanofluids in real
76 applications were collected. These measurements are performed for two different particle
77 concentrations of each of the SWCNH samples and include particle morphology, long-term
78 dispersion stability at room temperature, particle size distribution using two equipment and
79 also for different temperatures, scattering and absorbance spectra of the four samples. By
80 virtue of the methodologies applied (e.g. double independent DLS methods) the present

- 81 database can be considered accurate and reliable and can become a reference for future
- 82 measurements carried out in other world-wide lab.

83 2. Methods

84 2.1. Synthesis of nanofluids

85 Four different nanofluids were herein synthesised and studied. The base fluid employed for
86 them all was water (Millipore, 18 MΩ cm). The difference in them lay in the type of
87 nanoparticles, the stabilisation method and the nanoparticle concentration in nanofluids.

88 One of them consisted of SWCNH suspended in water using sodium dodecyl sulphate (SDS,
89 ~99%, Sigma) as a surfactant at two different SWCNH concentrations (0.005 and 0.002 %wt).

90 The other utilised nanofluid and was also based on an aqueous suspension, but an oxidised
91 SWCNH was used to avoid resorting to surfactants, and also at two different concentrations
92 (0.005 and 0.002 %wt). These concentrations have been determined in previous works as
93 being suitable for solar nanofluids [32], [33].

94 SWCNHs were provided by Carbonium S.r.l. and were produced by a process based on the
95 rapid condensation of carbon atoms with no catalyst, but gave considerably reduced
96 production costs [34]. The morphological characterisation of nanoparticles was made by
97 Field Emission Scanning Electron Microscopy (FESEM) with a SIGMA Zeiss instrument (Carl
98 Zeiss SMT Ltd, UK).

99 Two SWCNH suspensions were prepared with concentrations of 0.005 %wt and 0.002 %wt in
100 water according to the following procedure. Firstly, 250 mL of the water solution containing
101 SDS as the surfactant (10:1 surfactant-to-nanoparticle weight ratio) were taken, after which
102 the appropriate amount of SWCNHs was dispersed in the solution via initial homogenisation in
103 an ultrasonic processor (VCX 130, Sonics & Materials), which operated at 60 kHz and 65 W for
104 10 min with a 12 mm-diameter Ti₆Al₄V alloy tip. Next the suspension was processed for 20
105 minutes in a high-pressure homogeniser (Panda, GEA Niro Soavi, Germany) operating at 1,000
106 bar.

107 By this method, dispersions were assured long-term stability as no particle settling was
108 observed over a 3-month period.

109 In order to make SWCNH suspensions stable in water without surfactants, surface oxidation
110 was prepared by using concentrated HNO_3 (68-70%, provided by Alfa Aesar) according to a
111 previously described procedure [31]. Firstly, 0.5 g SWCNH were poured into 250 mL HNO_3 . This
112 mix was magnetically stirred for 2 h at 80°C , followed by spinning in a centrifuge at room
113 temperature for 10 minutes at 8,000 rpm. Afterwards, the processed powders and acid were
114 divided into two phases to be separated by paper filtering and thoroughly washed with
115 deionised water until the filtrate reached a pH that came close to 6. Finally, the powder was
116 washed with 100 mL of ethanol (absolute anhydrous, provided by Carlo Erba, Italy) and air-
117 dried at 80°C for 2 h. The oxidised SWCNH suspensions were prepared at the 0.005 and 0.002
118 %wt concentrations by mixing the SWCNH oxidised with deionised water by the same
119 procedure used for the suspensions with the surfactant.

120 Figure 1 (a) shows the SWCNH powder's structure, while Figure 1 (b) illustrates that of the
121 oxidised SWCNH. As the figures clearly denote, the typical morphology was maintained in both
122 cases.

123 Figure 1. SEM images of the SWCNH powder (a) and oxidised SWCNH (b)

124 As already stated, the nanofluids were prepared according to what proposed by part of the
125 present authors in ref. [31]; in fact, as clearly stated in [31], the synthesis of ox SWCNH is a
126 complex process because the selection of unbalanced operating condition during the oxidation
127 process or during the sonication can alter the morphology of the CNHs. Thus, the oxSWCNH
128 nanofluids were produced following the cited reference procedure and then a set of SEM
129 images were taken to verify the morphological characteristics of the oxCNH in the colloidal
130 dispersion. The results were similar to what found in [31], confirming with the SEM images

131 that the SWCNH dispersed in the nanofluid were not damaged by the sonication during the
132 nanofluid dispersion nor the oxidation process.

133 The investigated SWCNH samples are listed in Table 1 with their corresponding label.

134 Table 1 The samples investigated in this work

Label	Particle type	Concentration (%wt.)
CNH_0.002	SWCNH	0.002
CNH_0.005	SWCNH	0.005
oxCNH_0.002	Oxidised SWCNH	0.002
oxCNH_0.005	Oxidised SWCNH	0.005

135

136 2.2. Experimental techniques

137 Two different systems were followed to measure and validate the particle size distribution in
138 nanofluids which, if repeated over time, can be related to their stability. Both used dynamic
139 light scattering (DLS) as the measuring technique and were measured at different
140 temperatures.

141 One of the devices used for measuring stability was Zetasizer Nano (Malvern Instruments),
142 which is commonly found in the literature to measure particle size distributions of nanofluids
143 by DLS. Zetasizer Nano also includes a heating system that can measure at high temperature
144 (up to 90°C), which helps evaluate stability at different temperatures. The same equipment
145 type is available at the ITC-CNR (Padova, Italy) and the Universitat Jaume I (Castellón, Spain),
146 and was used in different research stages.

147 The other system was a VASCO FLEX particle size analyser (Cordouan Technologies). This is a
148 new commercial system used to measure a nanofluid's stability. The main difference between
149 both devices is that Vasco FLEX can analyse samples outside the apparatus. As acquisition is

150 external, the temperature range within which it is possible to measure samples' particle size
151 depends only on cuvette design. In this case, this system's maximum working temperature is
152 300°C. A spectrophotometer (with an integrating sphere) was employed to measure samples'
153 different optical properties.

154 The spectrophotometer employed to measure the sample's NIR-Vis spectra was CARY 500
155 (Varian Devices), which enables the use of an integrating sphere. This system was chosen
156 because different optical parameters, such as ballistic transmittance, reflectance, and forward
157 and backward scattering, can be measured. To measure a sample's scattering, an integrating
158 sphere was attached to the spectrophotometer.

159 Ballistic transmittance is obtained (I_T) when measuring with no integrating sphere. Figure 2
160 provides a schematic of the system.

161 Figure 2. A schematic of the CARY 500 spectrophotometer with no integrating sphere

162 Three measurements were needed to obtain the whole parameters that were involved in this
163 phenomenon. If the cuvette was placed in front of the sphere at port S1, transmittance and
164 forward scattering were obtained (I_{T+FS}). If the cuvette was located at the back of the sphere at
165 port S2, there were two possibilities: not tilted and then backward scattering (I_{BS}) obtained or
166 tilted 3° to obtain reflectance plus backward scattering (I_{R+BS}). Figure 3 represents a detailed
167 scheme of the system.

168 Figure 3 A schematic of the spectrophotometer CARY 500 with integrating sphere

169 All the measurements were normalised by their corresponding reference signal (I_0), obtained
170 by directly measuring light from the source with no cuvette on the optical path; for example,
171 ballistic transmittance (T) was calculated with no sphere.

$$T = \frac{I_T}{I_0} \quad (1)$$

172 The extinction spectra can be directly calculated as:

$$Extinction = -\log_{10} \frac{I_T}{I_0} \quad (2)$$

173 The scattering spectra values were obtained, and normalised by their corresponding reference
174 signal as:

$$Scattering = \frac{I_{T+FS}}{I_0} - \frac{I_T}{I_0} + \frac{I_{BS}}{I_0} \quad (3)$$

175 The absorption spectra were calculated by subtracting scattering from the extinction spectra.

176 Finally, the data absorption (K), scattering (S), extinction (E = K+S) and scattering albedo

177 ($\omega=S/E$) coefficients were calculated by the Kubelka-Munk Theory [35] using the following

178 equations:

179

$$\frac{K}{S} = \frac{R^2 - T^2 + 1}{2R} - 1 \quad (4)$$

$$C = \sqrt{\frac{K}{S} \left(\frac{K}{S} + 2 \right)} \quad (5)$$

$$S = \frac{1}{Cd} \coth^{-1} \left(\frac{T^2 - R^2 + 1}{2RC} \right) \quad (6)$$

180 where T is transmittance, d is sample thickness and R is calculated as:

$$R = \frac{I_{R+BS}}{I_0} - \frac{I_{BS}}{I_0} \quad (7)$$

181 **3. Results and discussion**

182 **3.1 Particle size characterisation**

183 In order to test the stability of nanofluids, the particle size distribution of the four samples was
184 measured by DLS at room temperature.

185 **3.1.1 Particle size distribution**

186 The nanofluid's particle size distribution was measured daily for 1 month after it was prepared
187 at room temperature. The averaged results of the measurements taken over the 30-day period
188 are shown in Figure 4.

189 Figure 4. The averaged particle size distribution measured over 1 month for the SWCNH (left)
190 and oxidised SWCNH (right) suspensions at two different concentrations

191 Similar particle size distributions were obtained for the four nanofluid samples during the 1-
192 month period.

193 **3.1.2 Long-term stability**

194 Three months after preparing the nanofluid, the size distribution of the four samples was
195 measured again. Figure 5 shows the particle size distribution obtained by the Zetasizer Nano
196 system for the SWCNH suspension at two different concentrations, measured 3 months after
197 preparation at room temperature.

198 Figure 5. The particle size distribution for the SWCNH (left) and oxidised SWCNH (right)
199 suspensions at two different concentrations, measured 3 months after preparation

200 The curves in Figures 4 and 5 are centred on the same values, which confirm that
201 agglomeration was almost negligible for a 3-month period. Thus these nanofluids were stable
202 at both concentrations.

203 In addition to particle size distribution, the samples' Zaverage values over time are presented.
 204 This is an intensity-based overall average size based on a specific fit to the raw correlation
 205 function data [36].

206 Table 2. A comparison of the Zaverage results between months 1 and 3 (room temperature)

	CNH_0.002	CNH 0.005	oxCNH_0.002	oxCNH_0.005
Month 1	144	145	163	149
Month 3	132	156	154	156

207

208 When comparing the Zaverage values in Table 2 of the samples measured for 1 month after
 209 preparation (in Padova) with those measured 3 months later (in Castellón), no significant
 210 differences were observed (including the measurements taken by both devices). This result
 211 reveals that the samples remained stable over time.

212 **3.1.3 Particle size distribution with temperature**

213 After evaluating the stability of the nanofluid samples at room temperature, it was necessary
 214 to check their stability at high temperatures; that is, under conditions that come closer to
 215 those in real applications.

216 Therefore, samples were thermally treated to test if this process affected their size distribution
 217 and, therefore, their stability at high temperature. The thermal treatment was performed by
 218 introducing sealed glass tubes filled with nanofluids inside a stove (Digitronic 2005141, J.P.
 219 Selecta, S.A.) for 30 minutes at 75°C. After this thermal treatment, particle size distributions
 220 were measured by the Zetasizer Nano system at 20°C, 50°C and 75°C.

221 Figure 6 shows the Zaverage results of the thermally treated samples at different measuring
 222 temperatures. The graphs demonstrate that particle size remained almost constant when
 223 temperature varied, and only a slight Zaverage increasing trend was observed.

224 Figure 6. Zaverage variation with the temperatures of the thermally treated samples measured
 225 for a) CNH 0.002 b) CNH 0.005 c) oxCNH 0.002 and d) oxCNH 0.005

226 The Zaverage results obtained with the fresh samples and the thermally treated samples at
 227 25°C were compared in Table 3 to observe if any variation occurred after thermal treatment.

228 Table 3. The Zaverage comparison between the fresh and thermally treated samples at 25°C

	CNH_0.002	CNH_0.005	oxCNH_0.002	oxCNH_0.005
Month 3	132	155	154	156
Fresh				
Month 3	125	135	154	145
Thermally treated				

229

230 After analysing particle size and the Zaverage results, it was concluded that samples remained
 231 stable within this temperature range.

232 **3.1.4 Particle size distribution with the two DLS devices**

233 The repeatability of the particle size distributions measured at different temperatures (25°C
 234 and 75°C) by two different DLS systems (VASCO FLEX and Zetasizer Nano systems) was
 235 analysed in this section.

236 Figure 7 shows that the particle size distributions obtained for all the samples were similar for
 237 both DLS systems, with only negligible differences especially in mean size terms.

238 Figure 7. Particle size distribution measured in two DLS systems at 25°C of a) CNH 0.002 b) CNH
 239 0.005 c) oxCNH 0.002 and d) oxCNH 0.005

240 Figure 8 shows a graph for all four samples, where the particle size distributions obtained in
 241 each DLS device at 75°C were compared. Similar mean size data were observed for both DLS

242 systems at high temperature, even though slightly wider distributions were observed when the
243 oxidised samples were measured by the VASCO system.

244 Figure 8. Particle size distribution measured in two DLS systems at 75°C of a) CNH 0.002 b) CNH
245 0.005 c) oxCNH 0.002 and d) oxCNH 0.005.

246 From the stability characterisation, it was concluded that all the samples proved stable in
247 either studied circumstance: for 3 months at room temperature at 75°C and corroborated by
248 two different systems; after being thermally treated at 75°C for 30 minutes.

249

250 **3.4 Optical characterisation**

251 Given the importance of the optical properties of the studied nanofluids, the spectra of the
252 SWCNH and oxidised SWCNH samples were measured in a CARY 500 Spectrophotometer
253 (Varian Dev) from 400 to 800 nm. To minimise the effects of undesired reflections and
254 absorptions, samples were placed inside a quartz cuvette with a path length of 1 mm and a
255 planar interface. Figure 9 shows the extinction, scattering and absorption spectra from 400 to
256 800 nm of the SWCNH nanofluids at different weight nanoparticle concentrations

257 Figure 9 a,b) Extinction, c,d) scattering and e,f) absorbance spectra for the SWCNH (left) and
258 oxidised SWCNH (right) water suspensions at different concentrations.

259 It is worth noting the positive effect of SWCNH as direct sunlight absorbers for both
260 concentrations in relation to the base fluid (water). In the extinction spectra, a 665% increase
261 within the 400-800 nm range was obtained for the lowest concentrate *versus* pure water,
262 while the highest concentrate presented an 860% improvement for the same wavelength
263 range. These results imply that extinction significantly improved with only a small amount of
264 nanoparticles (0.002 %wt).

265 Once again, substantial enhancement in extinction terms was achieved when the oxidised
266 SWCNH were added to water. By comparing the enhancements accomplished with the
267 oxidised SWCNH with those of the analogous SWCNH concentrations, the results of the
268 oxidised ones were lower, but still considerable.

269 The most remarkable aspect was that the scattering (Figures 9, c and d) contribution remained
270 constant within the whole wavelength range for both nanofluids, at around 0.1 a.u. This value
271 was similar in both cases because scattering mostly depends on nanoparticle size and shape.

272 The averaged values of the scattering measurements for each sample within the 400-800 nm
273 range are shown in Table 4.

274 Table 4. The averages of the scattering results for the four samples

275

276

	0.002 %wt.	0.005 %wt.
CNH	0.11	0.12
oxCNH	0.07	0.09

277

278 Table 4 and Figure 9 reveal that for the SWCNH nanoparticles within the 400-800 nm range,
279 scattering represented around 30% of extinction, increased slightly with nanoparticle
280 concentration and their contribution remained constant within this whole wavelength range.
281 This agrees with the literature [20],[24], which also indicates that the scattering of the SWCNH
282 and oxidised SWCNH remain constant within a certain wavelength range.

283 The absorbance spectra of the four samples are shown in Figure 9 (e, f). Higher dependences
284 were obtained in these spectra in relation to nanoparticle concentration, and constant
285 behaviour was also observed within the measured wavelength range.

286 Apart from the different spectra, the extinction, scattering, absorption and scattering albedo
287 coefficients were also calculated by the Kubelka-Munk Theory. These values are shown in
288 Figure 10 according to the wavelength for the different measured nanofluids.

289 Figure 10. a) Scattering coefficient b) Absorption coefficient c) Extinction coefficient and d)
290 Scattering albedo coefficients for the four measured nanofluids

291 As with the different spectra, nanoparticle load and type (oxidised and non-oxidised) more
292 strongly influenced absorption than the scattering coefficient. A reduction in relation to
293 wavelength was observed for these two coefficients.

294 The constant scattering albedo coefficient values within this wavelength range are shown in
295 Figure 10 d). For the different measured nanofluids, these values varied from 10-15%, which
296 coincides with the bibliography for such nanoparticles [23],[37],[38].

297 It can be concluded that, even with small concentrations, the higher the concentration, the
298 greater absorbance and scattering become. Finally, these results highlight the major
299 improvement that nanoparticles confer absorption, which make such nanofluids very
300 interesting candidates as direct sunlight absorbers.

301 **4. Conclusions**

302 Four water-based nanofluids with two different concentrations of SWCNH and oxidised
303 SWCNH were synthesised and evaluated herein as possible direct sunlight-absorbing fluids by
304 measuring their stability and optical properties.

305 In order to measure the stability of nanofluids at different temperatures, two DLS systems
306 were used. One of the systems is frequently found in the literature, Zetasizer Nano, while the
307 other one is a new external system that is suitable for high-temperature measurements.

308 Stability over 3 months was evaluated at room temperature with Zetasizer Nano, with good
309 results. Afterwards, samples were thermally treated at 75°C for 30 minutes, and their size
310 distribution was measured again. As the results were similar to those obtained with the fresh
311 samples, it can be concluded that the thermal treatment that goes up to 75°C does not affect
312 their stability.

313 Particle size distributions were measured from 25°C to 75°C in both DLS devices. The
314 concordance obtained between both systems' results ensures the repeatability of this
315 measurement. Moreover, samples presented good stability with temperature when
316 considering a similar size particle distribution at different temperatures.

317 Regarding optical properties, an integrating sphere was used to measure the scattering
318 phenomena produced by nanoparticles to isolate this effect from absorbance.

319 An increment from 665% to 860% in extinction within the 400-800 nm range was obtained for
320 nanofluids in relation to their base fluid. This significant improvement was obtained even for
321 low nanoparticle concentrations.

322 For both nanofluid types, the higher the concentration, the greater the absorbance and
323 scattering spectra became. Moreover, the same trend was observed for their corresponding
324 Kubelka-Munk coefficients. In line with the literature, constant scattering albedo ranging

325 values between 10-15% were found along the whole wavelength range from 400 to 800 nm for
326 all the nanofluids measured herein.

327 Given their stability and optical properties, the SWCNH and oxidised SWCNH water-based
328 nanofluids can be good candidates as direct sunlight absorber fluids. The highlighted
329 advantages of oxidised nanofluids are that they present higher absorbance values and do not
330 need surfactants to be stable, which provides a more environmentally friendly nanofluid.

331

332 **Abbreviations**

333	Dynamic Light Scattering	(DLS)
334	Single-Wall Carbon Nanohorns	(SWCNHs)
335	Sodiumdodecylsulphate	(SDS)
336	Field Emission Scanning Electron Microscopy	(FESEM)
337	Carbon nanohorns	(CNH)
338	Oxidized carbon nanohorns	(ox_CNH)

339

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353 **Competing interests**

354 The authors declare that they have no competing interests.

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