



HAL
open science

Silver/reduced graphene oxide nanocomposite materials synthesized via a green molecular level mixing

Jean-François Silvain, Benjamin Thomas, Loïc Constantin, Maël Pontoreau, Yongfeng Lu, Jean-Luc Grosseau-Poussard, Guillaume Lacombe

► **To cite this version:**

Jean-François Silvain, Benjamin Thomas, Loïc Constantin, Maël Pontoreau, Yongfeng Lu, et al.. Silver/reduced graphene oxide nanocomposite materials synthesized via a green molecular level mixing. Journal of Composite Materials, 2023, 57 (4), pp.1-10. 10.1177/00219983231152102 . hal-04002764

HAL Id: hal-04002764

<https://hal.science/hal-04002764>

Submitted on 23 Feb 2023

HAL is a multi-disciplinary open access archive for the deposit and dissemination of scientific research documents, whether they are published or not. The documents may come from teaching and research institutions in France or abroad, or from public or private research centers.

L'archive ouverte pluridisciplinaire **HAL**, est destinée au dépôt et à la diffusion de documents scientifiques de niveau recherche, publiés ou non, émanant des établissements d'enseignement et de recherche français ou étrangers, des laboratoires publics ou privés.

Silver/Reduced Graphene Oxide Nanocomposite Materials Synthesized Via a Green Molecular Level Mixing

Jean-François Silvain^{1,2*}, Benjamin Thomas¹, Loïc Constantin^{1,2}, Maël Pontoreau¹, Yongfeng Lu²,
Jean-Luc Grosseau-Poussard³ and Guillaume Lacombe⁴

¹ Univ. Bordeaux, CNRS, Bordeaux INP, ICMCB, UMR 5026, 33600 Pessac, France

² Department of Electrical and Computer Engineering, University of Nebraska-Lincoln, Lincoln, NE 68588-0511, USA

³ LaSIE UMR-CNRS 7356, Pole Science et Technologie, Université de La Rochelle, Av. M. Crépeau, 17042 La Rochelle Cedex, France

⁴ Composite Innovation SAS., Parc scientifique Unitec 1, 2 all du doyen Georges brus, 33600 Pessac, France.

* Correspondance : jean-francois.silvain@icmcb.cnrs.fr

Abstract: The fabrication of nano reinforced metal matrix composites (MMCs) is scientifically essential to further upgrade the thermal, electrical, and mechanical properties of current MMCs. Here, we present a green molecular mixing (MLM) of silver (Ag) and graphene (G) to overcome these challenges. Experimental results show that the green MLM allows to homogeneously mix 3 vol.% of G as observed with traditional MLM while adding a control on the oxidation steps. Metal and GO reductions can be precisely control by varying the solution temperature. Highly thermal conductivity and strong elastic modulus nanocomposites are fabricated making it an eco-friendlier mixing process.

Keywords: Composite; Ag; Graphene; Powder metallurgy; Microstructure

27 Introduction

28 The high thermal conductivity (TC) of silver (Ag, 429 W/m.K) makes it a predominant material for
29 electronic applications. However, Ag suffers from low mechanical properties thus, withdrawing its
30 prospective applications. A common way to promote its mechanical properties is to fabricate metal
31 matrix composites (MMCs). The fabrication of Ag composites is often made via a metallurgic powder
32 route owing to its simplicity, cost-effectiveness, net shaping, and ability to manufacture anisotropic
33 materials [1]. Oxides and graphite reinforcement have been extensively studied to enhancement the
34 mechanical and thermal properties of Ag matrix. However, it was reported that the addition of oxides
35 lowers the thermal conductivity (TC) [1–5] while the presence of graphite degrades the mechanical
36 properties [1, 6–8].

37 Therefore, the creation of multifunctional composed of nano-carbon reinforcement such as graphene
38 (G) or reduced graphite oxide (rGO) may fulfill these unmet needs [9–15]. Nonetheless, the size
39 difference between the matrix powder (i.e., micrometer, Ag) and the carbon reinforcement (i.e.,
40 nanometer, G, rGO) cause several issues during the mixing step and heterogeneous mixture are often
41 observed. Naturally, aggregation of the nano-reinforcement led to severe degradation of the resulting
42 nanocomposites' mechanical and thermal properties [12, 13, 16]. Hence, the mixing appears to be a
43 crucial step to manufacture functional Ag-based nanocomposites.

44 Mechanical mixing e.g., balling or wet mixing have been extensively used to form homogeneous
45 mixture of micro and nano composites [17–22]. However, mechanical mixing is a harsh process where
46 heating, deformation, crystallization, and perception co-occurs leading to the degradation of the
47 graphene [16, 19, 20, 22–24]. Molecular level mixing (MLM) was recently introduced as a alternative
48 mixing method to homogeneously mix G-rGO and metal matrix powders [12, 13, 25–27]. The MLM
49 approach consists of forming a colloidal suspension of graphene oxide (GO) in an aqueous solution
50 with metal salt precursors. After precipitation and reduction, a homogeneous dispersion of rGO in
51 metal powder is obtained [12, 13, 26–28]. Although the promising results observed with the MLM,
52 this method require the use of hydrazine as the reducing agent making the MLM hard to scale up
53 due to the environment and health concerns [12, 13, 26–28].

54 In this work, we developed a green MLM process to fabricate Ag/rGO using ascorbic acid (AA)
55 instead of hydrazine. AA is known as a green harmless chemical component for the environment and
56 health [29–31]. In addition, the used AA enables to tailor the MLM process as compared to
57 conventional MLM. Especially, the metal and GO reductions can be separated and precisely control
58 by only varying the solution temperature. It is demonstrated that for an rGO concentration below 3
59 vol.% monodisperse Ag particles are synthesized with a uniform dispersion of nano-reinforcements.
60 Additionally, the reduction rate of GO using AA and hydrazine had been monitored by Raman
61 spectroscopy and X-ray diffraction (XRD). It is shown that both reducing agents conduct to the same

62 reduction rate, making AA an excellent substitute to the hydrazine. Then, nanocomposites were
63 fabricated by hot pressing using the synthesized powders via the green MLM. It is shown that 1 vol.%
64 of rGO in the Ag matrix lead to a 16% increase of the elastic modulus with no degradation of the Ag's
65 TC (395 W/m.K). The research results demonstrated that substitution of hydrazine by AA allows
66 developing a green MLM process and add a control on the metal and GO reduction. Therefore, the
67 developed green MLM process enables can be easily scale up.

69 **Methods**

70 *Synthesis of nano-composite powders*

71 Ag and reduced rGO were synthesized via a green MLM process. For that, a Ag nitrate solution (Alfa
72 Aesar, ACS, 99.9+ %) and graphite oxide (Knano Co., Ltd., China) were reduced using L+ ascorbic
73 acid (AA, Acros Organics, 99%). The average lateral size and thickness of the graphite oxide are 5 μm
74 and 5 nm, respectively. The green MLM process is the following (a). First, a desired amount of
75 graphite oxide was added to 100 ml of deionized water to a concentration comprise between 5.4 10^{-2}
76 g/l and 5.6 10^{-1} g/l to obtain a concentration of rGO in the composite powder from 0.25 to 5 vol.%.
77 Then, the solution was then mixed with a magnetic stirrer for 5 min and placed in a tip sonicator for
78 1 h (Bandelin SONOPULS®) with a pulse width, frequency, and power of 0.1 s, 1 Hz and 100 W
79 respectively, to prevent reinforcement deterioration and heating. Once the solution turn into a brown
80 color, the suspension was diluted with AA to reach a GO concentration between 6.8 10^{-3} g/l to 1.4 10^{-1}
81 g/l. After a maturation step of 1 h, an aqueous solution of Ag nitrate ($c = 2.35 \cdot 10^{-1}$ mol/l) was quickly
82 added to the GO suspension. Once the Ag reduction by AA was completed (~ 5 min), the Ag / GO
83 suspension was heated to 90 °C for 1 h; reduction of GO occurred by the excess of AA in solution (c
84 $= 7.8 \cdot 10^{-2}$ mol/l). Then, the Ag+rGO mixture was filtrated and washed three times with 100 ml
85 deionized water and three times with 50 ml ethanol. Finally, the composite mixture was air-dried in
86 an oven at 60 °C for 24 h. In order to evaluate the reducing power of ascorbic acid towards GO,
87 reference powder was synthesized using hydrazine hydrate as reducing agent. The synthesis
88 conditions of this powder are identical to the previous ones but the hydrazine hydrate was
89 substituted to ascorbic acid (in the same concentrations).

90 *Fabrication of Ag/rGO nanocomposites*

91 The densification of the nanocomposite powders was carried out by hot pressing under primary
92 vacuum ($\sim 1.5 \cdot 10^{-1}$ mbar). The nanocomposite powders were placed in a 10 mm diameter graphite
93 mold and sintered under a uniaxial pressure of 60 MPa and temperature and time of 650 °C and 25
94 min respectively. The pressure was applied when the sintering temperature was reached. After
95 sintering, the composite materials were machined and polished for characterizations.

96 *Characterization*

97 The reduced GO by AA and hydrazine was characterized by XRD (PANalytical X'pert PRO MPD ®,
 98 Cu-K α) and Raman spectroscopy (Horiba spectrometer, $\lambda = 532$ nm, 10 mW). Powder XRD
 99 diffractograms were acquired from $2\theta = [3^\circ - 38^\circ]$ with a scanning speed of 0.15°/min. The density of
 100 the composite materials was measured using the Archimedes method (Sartorius Analytic® balance
 101 ($d = 0.1$ mg)). A scanning electron microscope (SEM, Tescan VEGA ®) was used to characterize the
 102 morphology of the composite powders and fractures of the bulk composite materials. Microstructural
 103 characterization was carried out by electron backscatter diffraction (EBSD, EDAX®, probe size 330
 104 nm, and step of 0.1 μm). The microstructure of the nanocomposites was revealed by electro-etching
 105 in 100 g/l citric aqueous acid solution for 10 to 20 s with a DC voltage and an intensity of 6 V and 0.5
 106 A, respectively. The deep etching was performed using the same electro-etched parameters but using
 107 0.65 wt.% nitric acid solution as the electrolyte for 1 min.

108 The thermal diffusivity (TD) of the materials was measured by the laser flash method (NETZSCH
 109 LFA 457®, MicroFlash) on composites cylinders of 10 mm and 6 mm in diameter with a thickness of
 110 5 mm at 70 °C. A graphite film was spray (KONTAKT CHEMIE graphite 33® aerosol) on the
 111 samples before measurement to reduce the laser back reflection. The TD was converted into TC
 112 using the following equation [32]:

$$k(T)=a(T)\times C_p(T)\times \rho(T) \quad (1)$$

113 where k is the TC (W/m.K), a is the TD (mm^2/s), ρ the density, and C_p the heat capacity (J/Kg.K) of
 114 the sample. The C_p of rGO, and Ag, used in this work, are the following: $C_p(\text{rGO}) = 836$ J.Kg⁻¹.K⁻¹
 115 $C_p(\text{Ag}) = 237$ J.Kg⁻¹.K⁻¹ at 70 °C.

116 Hardness and apparent elastic modulus of materials were measured by micro-hardness
 117 measurement in the transverse direction. An indentation force of 1 N, a charging and discharging
 118 speed of 500 mN/min, and a pause time of 20 s was used for all samples. Oliver and Pharr's theory
 119 [33]. [34], was used to derive the elastic modulus from the load/discharge curves of the tested
 120 composite materials.

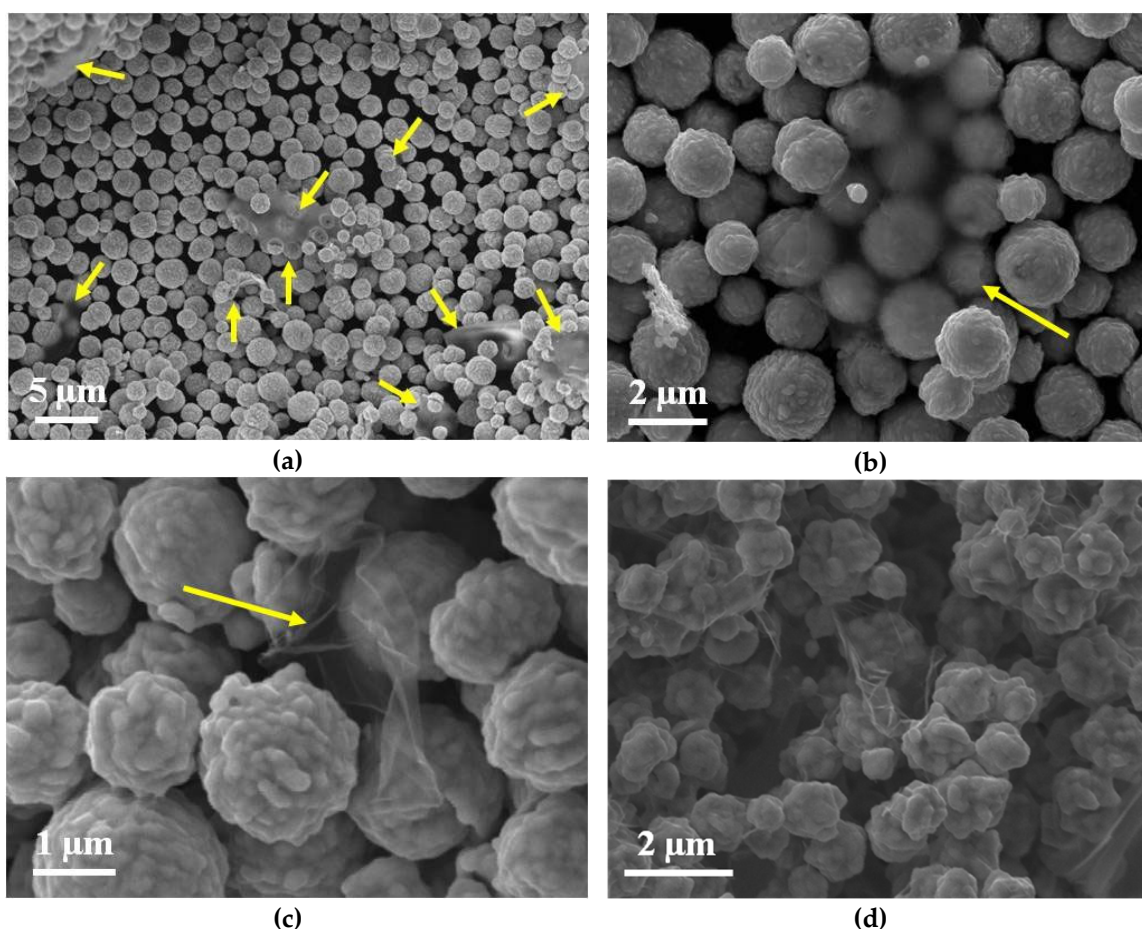
121

122 **Results & Discussion**

123 This section may be divided by subheadings. It should provide a concise and precise description of
 124 the experimental results, their interpretation as well as the experimental conclusions that can be
 125 drawn.

126 *Green molecule mixing of silver and reduced graphene oxide*

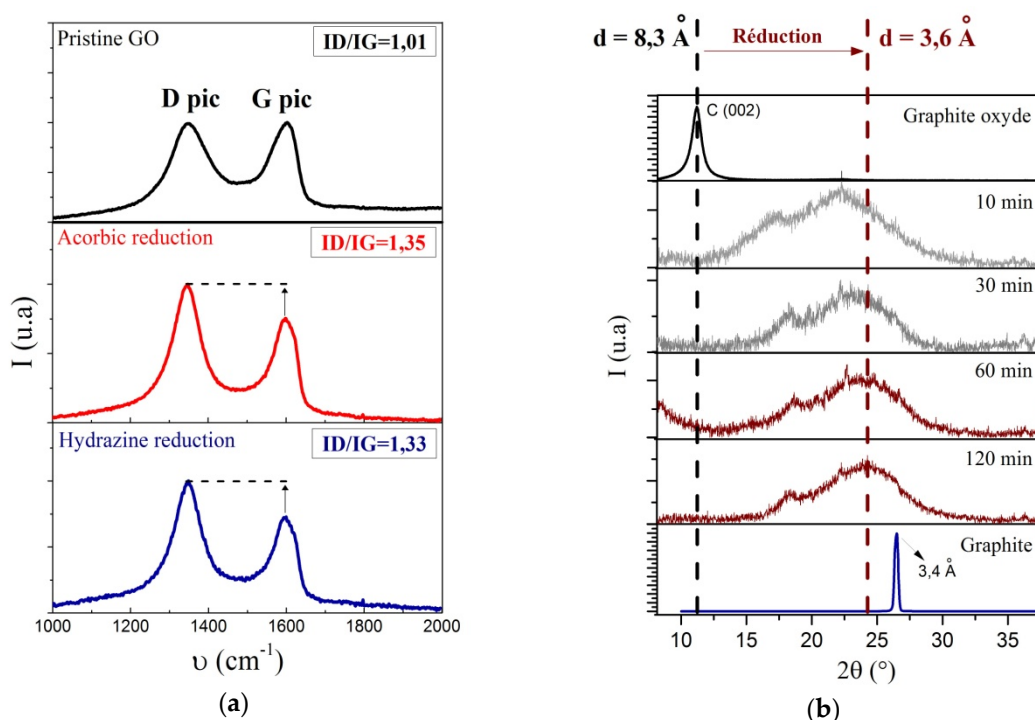
127 The size difference between the Ag particles and the GO nano reinforcement makes the mixing of
 128 these two components an essential step to produce nanocomposites. A green MLM process was
 129 developed by using AA to obtain a homogeneous powder mixture at GO concentration ranging from
 130 0.1 to 5 vol.%. The substitution of hydrazine by AA enables us to work with a green component but
 131 also to separate the precipitation/reduction of Ag particles and GO Figure 1 presents the SEM
 132 micrographs of the Ag/rGO composite powders for different rGO concentrations. It can be observed
 133 that the nucleation and growth of Ag in the aqueous suspension conducts to monodisperse particles
 134 (~2 μm) for an rGO concentration up to 3 vol.% (Figure 1 (a) to (c)).



135 **Figure 1.** SEM micrographs (SE, E = 5 KV) of the Ag/rGO nano-composite powder at different rGO
 136 concentration: (a) 0.5 vol.%; (b) and (c) 1 vol.%; and (d) 5 vol.%. Yellow arrows show rGO nano-
 137 reinforcements.

138
 139 For higher concentration (i.e., 5 vol.%), the Ag particle size decreases down to 1 μm and presents a
 140 less spherical shape (Figure 1 (d)) in comparison with Ag particles fabricated with smaller rGO
 141 concentration (1 vol.% in Figure 1 (b)). One explanation of this evolution is linked to the nucleation
 142 rate of Ag at high GO concentration. When the GO concentration becomes important, heterogeneous
 143 nucleation of Ag on GO becomes predominant over homogenous nucleation. Also, the Ag reduction
 144 by AA is an auto-catalytic reaction, which means that a higher amount of Ag nucleus increases the

145 reaction rate. Both effects can explain the morphology change of the Ag particles with rGO
 146 concentration. Once, the Ag particles precipitated, the aqueous suspension was heated to 90 °C for 1
 147 h to induce the GO reduction. As can be seen in Figure 1 (a) to (c) a concentration comprises between
 148 0.5 to 1 % .vol allows a homogenous dispersion of the nano-reinforcements in the Ag matrix (yellow
 149 arrows). However, above 1 vol.% of rGO, a network of interconnected rGO sheets surround the Ag
 150 particles Figure 1 (d).
 151 The effect of GO reduction using hydrazine or ascorbic acid has been studied by Raman spectroscopy
 152 Figure 2 (a) displays the Raman spectrum of the as-received GO and rGO reduced by AA or
 153 hydrazine, respectively.



154 **Figure 2.** (a) Raman spectrum of pristine GO provided by KNANO® (black curve), rGO reduced by
 155 ascorbic acid at 90 °C for 1 h (red curve) and rGO reduced by hydrazine (blue curve) and (b)
 156 diffractograms of pristine GO (black curve), GO reduced by ascorbic acid at 90 °C for 10, 30, 60 and
 157 120 min (grey and red curves) and graphite (blue curve).

158 On each spectrum, a D-band is observed at a wavenumber of 1350 cm^{-1} , which is related to defect or
 159 disorder in the carbon structure (sp^3 carbon) and a G-band at 1580 cm^{-1} which results from order
 160 graphite (sp^2 carbon) [35]. Due to the fact that the intensity of the I_D peak in related to “number” of
 161 defect (sp^3 carbon) and the I_G peak to the number of order carbon (sp^2 carbon) the I_D/I_G ratio is
 162 commonly used to evaluate the quality of the reduction of GO (the higher the ratio the higher the
 163 quality of the graphite). It can be observed that the I_D/I_G ratio is 1.01 for GO and increase after GO
 164 reduction to 1.34.

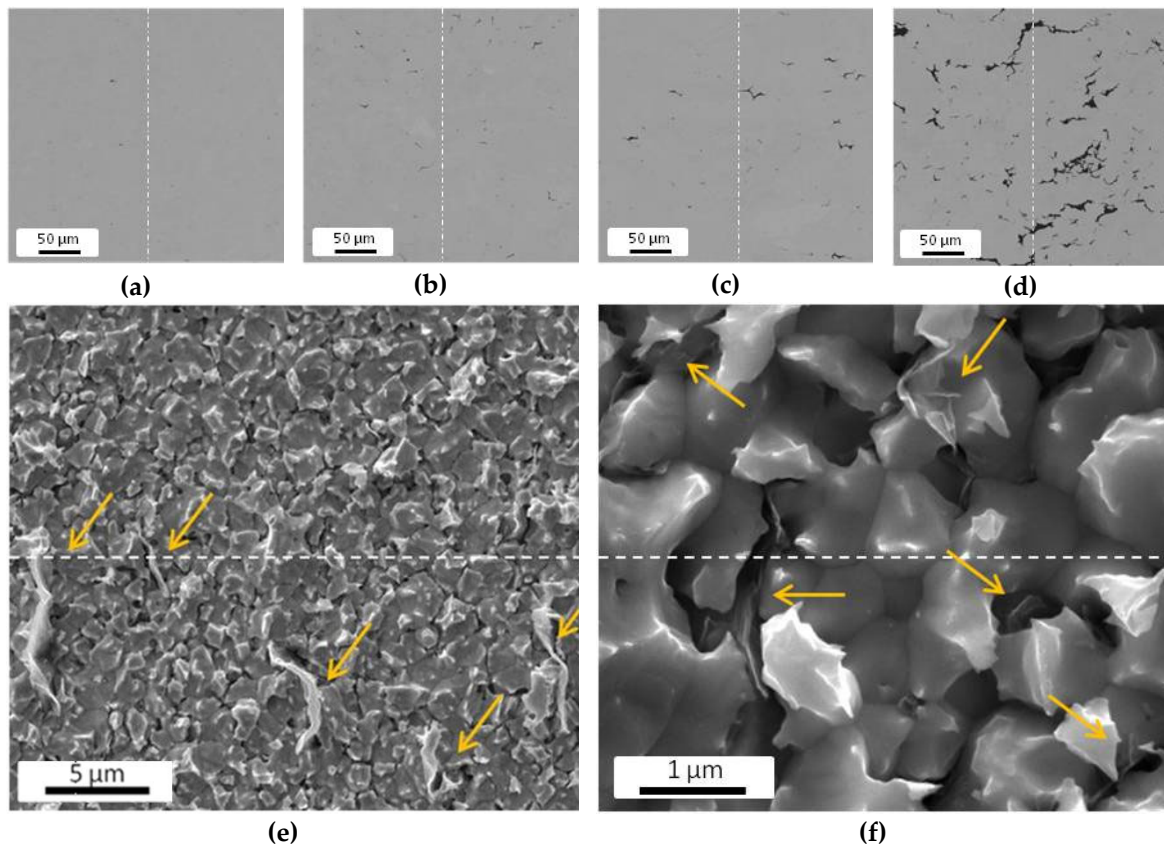
165 The same increase was reported in previous work on the chemical reduction of GO [30, 31, 36, 37].
 166 The I_D/I_G increases resulted from a decrease in the average size of Csp^2 domains [38, 39] and to an

167 increase in the distance between the C_{sp^3} defect domains [39]. Moreover, the I_b/I_G ratio of the rGO
168 reduced by either ascorbic acid or hydrazine are equivalent implying similar reduction level, as
169 reported in other studies [30, 31, 36, 37]. Furthermore, the GO reduction rate by AA was monitored
170 by measuring the inter-layer distance via XRD at different times. Figure 2 (b) presents the
171 diffractograms of the GO, the rGO from 10 to 120 min at 90 °C and the graphite. The diffractogram of
172 the as-received GO shows a peak at $2\theta = 11^\circ$ and has an interlayer distance of 8.3 Å. The rGO has a
173 diffraction peak around $2\theta = 22.5$ to 24° depending on the reduction time, which corresponds to the
174 (002) plane of the hexagonal carbon structure. Note that the low signal-to-noise ratio observed on the
175 rGO is due to the presence of only a few G layers after the exfoliation steps. The interlayer distance
176 measured on the GO rapidly decrease from 8.3 Å down to 4.2 Å after only 10 min of reduction (i.e.,
177 2θ shift toward high angles), then slowly decreases to 3.6 Å after 60 min. No change was observed
178 after 120 min of reduction which implies that 60 min is the optimal reduction time. The diffractogram
179 of pure graphite shows a diffraction peak at $2\theta = 26^\circ$, which corresponds to an interlayer distance of
180 3.4 Å. The disparity between the graphite and rGO interlayer distance can be explained by the fact
181 that the reduction of GO is never completed, and some residual oxygen will remain on it, thus
182 inducing a variation on the interlayer distance. These results are comparable with the one obtained
183 for a conventional MLM using hydrazine as reported by others [44]–[46], [50]–[52], and demonstrate
184 that AA is a suitable reducing agent to form rGO by a green MLM process.

185 *Fabrication of Ag/rGO nanocomposites*

186 After the green MLM process, the Ag/rGO composites powders were consolidated by hot pressing at
187 625 °C for 25 min and with a pressure of 60 MPa. No evolution of the composite material density is
188 observed for a rGO concentration between 0 to 5 vol.% with a density of about 98.5%.

189 The nanocomposites were cut and polished for SEM analysis, as present in Figure 3(a) to (d). The
190 microstructure analysis reveals that the concentration of agglomerate increases in respect to the
191 concentration of rGO in the materials. Besides, composites synthesis by hot pressing often results in
192 a preferential orientation of the reinforcement perpendicular to the compression axis [40–42]. The
193 same tendency is observed here, as shown in Figure 3 (e). The SEM micrographs after deep etching
194 demonstrate a preferred orientation of the rGO agglomerates perpendicular to the compression axis.
195 Nonetheless, as shown in Figure 3 (f), individual rGO sheets are located at the Ag grain boundary
196 and therefore have the same orientation as the boundaries.

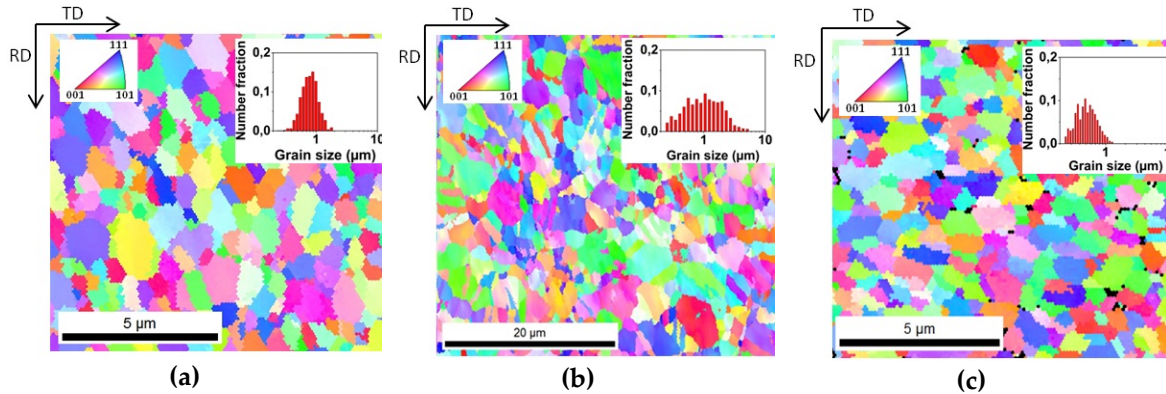


197 **Figure 3.** SEM micrographs (SE, E = 10 kV) of the cross-section of Ag/rGO composite material loaded
 198 to (a) 0.25 vol.%, (b) 0.5 vol.%, (c) 2 vol.%, (d) 5 vol.% in rGO and (e)-(f) SEM micrograph (SE, E = 5
 199 KV) of the cross-section of an Ag/rGO composite material with 2.5 vol.% rGO concentration. The
 200 white axis corresponds to the compression axis of material, the yellow arrows correspond to (e) rGO
 201 micro agglomerates and (f) individualized rGO sheets.

202 The presence of nano reinforcements in the matrix may influence the Ag grain growth and their
 203 orientations, which could affect the thermal and especially the mechanical properties. The influence
 204 of rGO sheets on the microstructure of Ag was investigated by EBSD on pure Ag and Ag containing
 205 0.5 and 2.5 vol.% of rGO. Figure 4 (a) displays the EBSD image of the pure Ag sample.

206 It can be seen that the Ag grains have an ellipsoidal shape and are randomly oriented with an average
 207 size of about 1.2 μm . Also, the size disparity is comprised of 0.1 to 2 μm . The addition of 0.5 vol.% of
 208 rGO does not influence the average size (1.18 μm), but a more significant size disparity is observed
 209 and comprise between 0.1 to 5 μm . An rGO concentration greater than 1% conducts to a decrease of
 210 the average grains size of 0.5 μm with a homogenous grains size disparity (Figure 4 (c)). The evolution
 211 of the Ag microstructure at a low rGO concentration (i.e., 0.25 and 0.5 vol.%) can be explained by two
 212 phenomena. First, due to a preferential recrystallization of Ag grains around the rGO, known as the
 213 particles simulated nucleation effect (PSN) [43–45]. Then, during the cooling stage the Ag matrix
 214 undergoes deformations which are induced by a coefficient of thermal expansion mismatch between
 215 Ag and rGO. Both effects individually or combined, could explain the grains size evolution at low
 216 rGO concentration. At higher rGO concentrations, above 1 vol.%, the refinement of the Ag

217 microstructure can be induced by a recrystallization delay due to a small distance between rGO
 218 agglomerates and defined at the Zener effect [43]. Besides, the large amount of rGO, located at the
 219 grain boundary between Ag grains, will limit the growth of the Ag grains by surface diffusion, and
 220 a finer microstructure is observed.

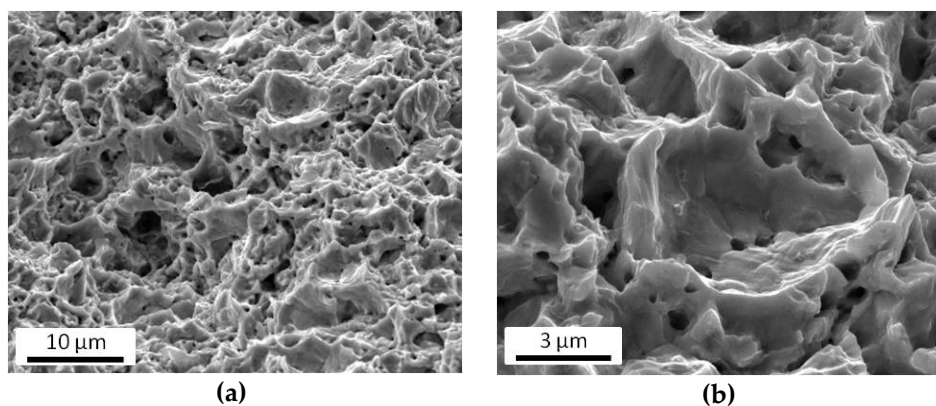


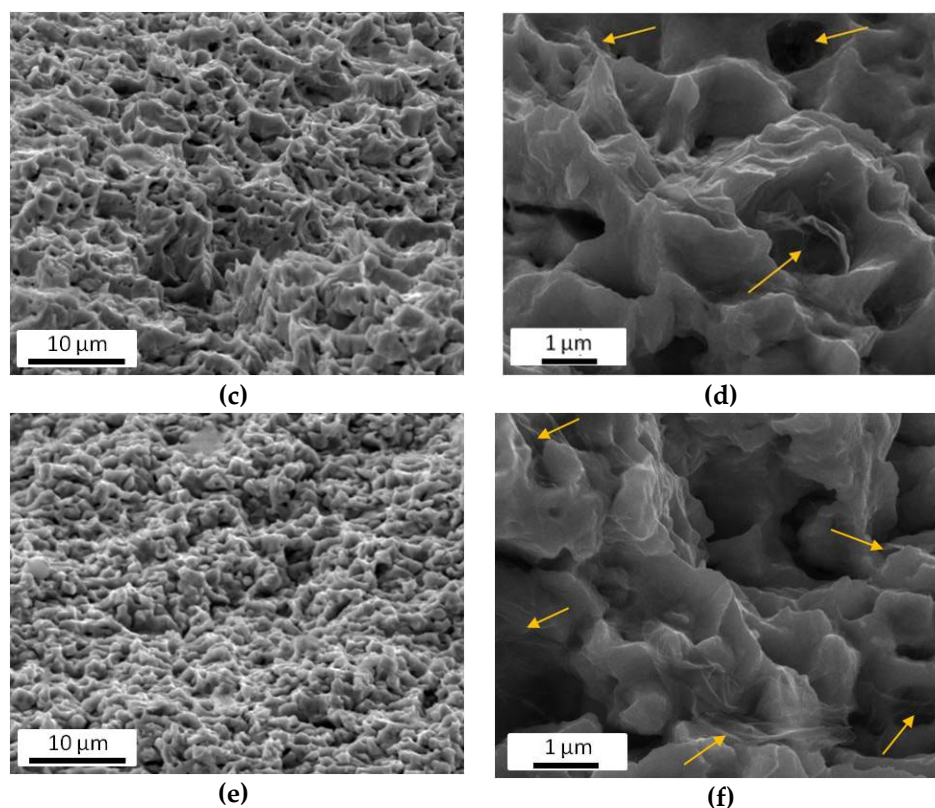
221 **Figure 4.** Inverse pole figure mapping and associated grain size of (a) pure Ag produced by MLM
 222 and composite material Ag/rGO concentrated at (b) 0.5 vol.% and (c) 2.5 vol.%.

223 *Mechanical and thermal properties of Ag/rGO nanocomposites*

224 To go further, the mechanical properties of the Ag/rGO nanocomposites were investigated at
 225 different rGO concentrations. First, the fracture behaviors of nanocomposites were studied for an
 226 rGO composition comprise between 0.5 to 5 vol.%. The SEM micrographs of the fractured composite
 227 containing 0.5 vol.% of rGO show a typical transgranular fracture, which is related to ductile behavior
 228 (Figure 5 (a) and (b)). The Ag/rGO composite having 1 vol.% of rGO shows a mixture of trans and
 229 intergranular fracture, which is assimilated to an intermediate state between ductile and brittle
 230 behavior (Figure 5 (c) and (d)). At higher rGO concentration (2.5 vol.%), an intergranular fracture is
 231 observed, as shown in Figure 5 (e) and (f), which is characteristic of a brittle behavior. Additionally,
 232 rGO sheets can be observed for an rGO concentration of 1 and 2.5 vol.% and result from the
 233 intergranular fracture of the Ag.

234 Hence, the introduction of rGO in the Ag matrix affect the grains sizes and morphology of Ag and
 235 thus change the Ag fracture behavior from ductile to brittle with an intermediate state for an rGO
 236 concentration of 1 vol.%.

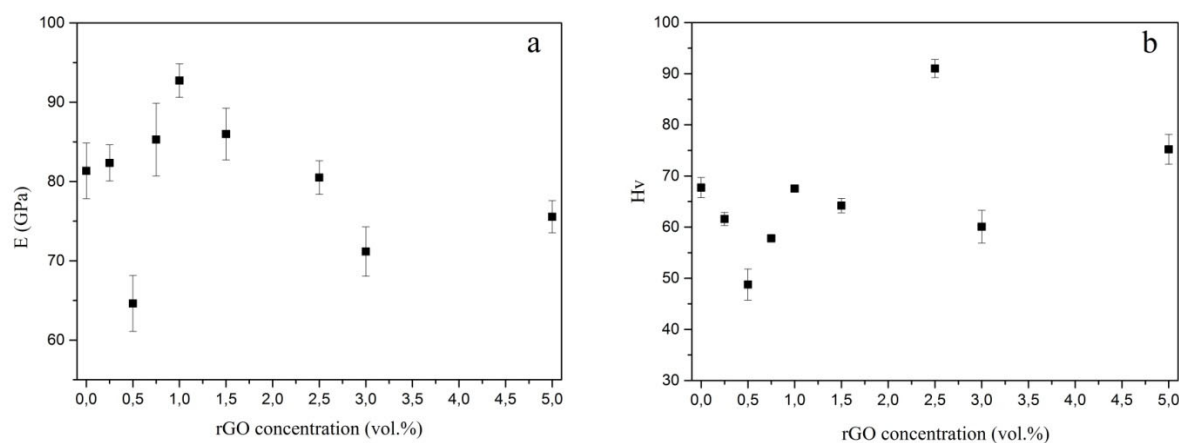




237 **Figure 5.** SEM micrographs (SE, E = 5 KV) of fracture surfaces of Ag/rGO composite materials with
 238 different rGO concentrations (a)-(b) 0.5 vol.%, (c)-(d) 1 vol.%, and (e)-(f) 2.5 vol.%. Yellow arrows
 239 show rGO nano-reinforcements.

240 Then, the apparent elastic modulus (E) and Vickers hardness (HV) were measured on pure Ag and
 241 on composite materials with an rGO concentration between 0.25 to 5 vol.% (see Figure 6). The
 242 evolution of the E shows that, for a low rGO concentration (0.25 to 0.5 vol.%), a decrease of the
 243 modulus down to 65 GPa is observed. At higher rGO concentration, the elastic modulus increases
 244 and reaches a maximum of 93 GPa and then decreases to 85 GPa for rGO concentration of 1 vol.%
 245 and 5 vol.%, respectively.

246 Moreover, the hardness of the nanocomposite follows similar trend for low concentrations comprises
 247 between 0.25 to 0.5 vol.% (decreased of HV) but differs for higher concentration. A maximum of 93
 248 HV is reached at 2.5 vol.% of rGO, and then, the HV decreases as saw for the elastic modulus.



250 **Fig. 6:** Mechanical properties of Ag/rGO composite materials as a function of rGO
251 concentration **(a)** elastic modulus and **(b)** Vickers micro-hardness.

252 These results were expected based on the previous microstructural and fracture behaviors analysis.
253 As seen in the previous section, a low rGO concentration (0.1% to 0.5 vol.%) induced preferential
254 recrystallization of the Ag grains around the rGO, which led to a broad distribution of Ag grains and
255 a softening of the matrix. At higher concentration (0.75 to 1 vol.%), a homogenous and fine Ag
256 microstructure was observed with the presence of rGO sheets in Ag grains and grain boundaries. The
257 rGO sheets, located at the Ag grain boundaries, inhibit the boundary diffusion phenomena necessary
258 for the recrystallization of the Ag matrix and harder the materials. On the other hand, the rGO located
259 inside the grains promotes the elastic modulus by inducing a load transfer from the matrix to the
260 rGO. However, when the reinforcement concentration becomes too important (> 2.5 vol.%), a large
261 number of rGO agglomerates formed in the matrix and degrade the mechanical properties.[9, 13, 17,
262 21].

263 It must be mentioned that the elastic modulus reaches its maximum value for an rGO concentration
264 of 1 vol.% (93 GPa) while the hardness is maximum for a concentration of 2.5 vol.% (91 Hv). These
265 values have to be correlated with the morphology of the fracture surfaces. Indeed, for an rGO volume
266 fraction of 2.5%, the rupture behavior, linked with granular debonding and the absence of a cup, have
267 to be associated with the decrease of the ductility and the increase of the hardness of the Ag/rGO
268 composite material, compared to pure Ag. For an rGO volume fraction of 1%, a ductile fracture
269 surface is observed associated with a cup like structure. Besides, the cup size is smaller than those
270 observed in materials with a lower concentration of rGO.

271 In addition, the presence of rGO sheets at the bottom of the cups (yellow arrows in Figure 5 (d)) may
272 explain the increase in the elastic modulus of the materials associated with a load transfer between
273 the matrix and the reinforcements. Thus, granular refinement of the matrix would be the main cause
274 of the increase in hardness of Ag/rGO materials, while load transfer between the matrix and the rGO
275 would be the cause of the increase in their elastic modulus. This would explain why the maximum
276 of these two parameters is not reached for the same rGO concentration. It should also be noted that
277 the maximum hardness of 91 HV is obtained for a concentration of 2.5 vol.% of rGO, which is close
278 to the optimal rGO volume fraction reported *Hao and al.* [9] with a hardness of 76 Hv at 2.3 vol.%
279 rGO.

280 Additionally to the mechanical measurements, the thermal properties of Ag/rGO nanocomposite
281 were studied in the longitudinal and transverse directions. It can be observed that for a low rGO
282 concentration (0.1 to 1 vol.%) the longitudinal TC is close to pure Ag with a value of 395 W/m.K but
283 the transversal TC decreases down to 375 W/m.K. The decrease of the transverse TC is may be

284 associated with the alignment, during the HP process, of the rGO perpendicular to the compression
285 axis, leading to the fabrication of an anisotropic composite. At higher rGO concentration (> 1 vol.%),
286 the TC decreases linearly with respect to the amount of rGO and the TC anisotropy increases. As seen
287 before, the number of agglomerates increases when the rGO concentration increases and these
288 agglomerates are oriented perpendicularly to the compression axis of the materials. In this case, the
289 heat transfer in the composite is governed between the Ag matrix and the rGO agglomerates resulting
290 from degradation of the thermal properties.

291

292 **Conclusions**

293 In this paper, a green MLM process is developed to synthesize Ag/rGO nanocomposites. It has been
294 demonstrated that the substitution of hydrazine by AA allows obtaining the same experimental
295 results in terms of reduction rate and mixture homogeneity. Also, the used of AA enables us to
296 separate the Ag and rGO reduction/precipitation by merely varying the solution temperature (i.e.,
297 ambient to 90 °C). The synthesized Ag powders by green MLM appeared to be spherical and
298 monodispersed for a GO concentration below 3 vol.%.

299 The fabrication of Ag/rGO composite by hot pressing led to dense composite materials with
300 homogenous dispersion of the nano-reinforcement for an rGO concentration lower than 1 vol.%. The
301 fracture behavior of Ag can be tailored from a ductile to brittle fracture depending on the amount of
302 rGO in the matrix. Besides, the preferential orientation of the nano-reinforcement conducts to an
303 improvement of the elastic modulus up to 16% while being as hard as pure Ag. Also, it was shown
304 that the TC of the Ag/rGO containing 1 vol.% of rGO is almost not affected in the longitudinal
305 direction compare to pure Ag with a value of 395 W/m.K.

306 The process developed in this work has the potential to be used on a large scale and reduced the
307 environmental impact of toxic chemical components. The fabrication of nanocomposites by green
308 MLM followed by hot pressing enables to tailor the mechanical properties and fracture behavior of
309 Ag/rGO composite materials without degrading the high TC of Ag.

310

311 **Data available statement:** The datasets generated during and/or analyzed during the current study
312 are available from the corresponding author on reasonable request.

313

314 **Conflicts of Interest:** The authors declare no conflict of interest. The funders had no role in the design
315 of the study; in the collection, analyses, or interpretation of data; in the writing of the manuscript, or
316 in the decision to publish the results.

318 **References**

- 319 1. Joshi PB, Ramakrishnan P (2004) Materials for electrical and electronic contacts : processing,
320 properties, and applications. Science Publishers
- 321 2. Lin Z, Liu S, Sun X, et al (2014) The effects of citric acid on the synthesis and performance of
322 silver-tin oxide electrical contact materials. *J Alloys Compd* 588:30–35.
323 <https://doi.org/10.1016/j.jallcom.2013.10.222>
- 324 3. Jiang Y, Liu SH, Chen JL, et al (2015) Preparation of rod-like SnO₂ powder and its application
325 in Ag-SnO₂ electrical contact materials. *Mater Res Innov* 19:S152–S156.
326 <https://doi.org/10.1179/1432891715Z.0000000001535>
- 327 4. Ćosović V, Ćosović A, Talijan N, et al (2013) Improving dispersion of SnO₂ nanoparticles in
328 Ag-SnO₂ electrical contact materials using template method. *J Alloys Compd* 567:33–39.
329 <https://doi.org/10.1016/j.jallcom.2013.03.094>
- 330 5. Guzmán D, Muñoz P, Aguilar C, et al (2014) Synthesis of Ag–ZnO powders by means of a
331 mechanochemical process. *Appl Phys A Mater Sci Process* 117:871–875.
332 <https://doi.org/10.1007/s00339-014-8447-7>
- 333 6. Rehani BR, Joshi PB, Kaushik VK (2009) Nanostructured silver-graphite electrical contact
334 materials processed by mechanical milling. *Indian J Eng Mater Sci* 16:281–287
- 335 7. Pietrzak K, Gładki A, Frydman K, Wójcik-grzybek D (2016) Electrical properties of Ag-C and
336 Cu-C contact materials. *Electron Mater* T.44:4–10
- 337 8. Borkowski P, Walczuk E (2010) Electrical properties of Ag-C contact materials containing
338 different allotropes of carbon. In: *Electrical Contacts, Proceedings of the Annual Holm*
339 *Conference on Electrical Contacts*
- 340 9. Hao X, Wang X, Zhou S, et al (2018) Microstructure and properties of silver matrix composites
341 reinforced with Ag-doped graphene. *Mater Chem Phys* 215:327–331.
342 <https://doi.org/10.1016/j.matchemphys.2018.05.036>
- 343 10. Hsieh C-C, Liu W-R (2017) Synthesis and characterization of nitrogen-doped graphene
344 nanosheets/copper composite film for thermal dissipation. *Carbon N Y* 118:1–7.
345 <https://doi.org/10.1016/J.CARBON.2017.03.025>
- 346 11. Chu K, Wang X, Wang F, et al (2018) Largely enhanced thermal conductivity of
347 graphene/copper composites with highly aligned graphene network. *Carbon N Y* 127:102–
348 112. <https://doi.org/10.1016/j.carbon.2017.10.099>
- 349 12. Hu Z, Tong G, Lin D, et al (2016) Graphene-reinforced metal matrix nanocomposites - A
350 review. *Mater Sci Technol (United Kingdom)* 32:930–953.
351 <https://doi.org/10.1080/02670836.2015.1104018>

- 352 13. Nieto A, Bisht A, Lahiri D, et al (2017) Graphene reinforced metal and ceramic matrix
353 composites: a review. *Int Mater Rev* 62:241–302.
354 <https://doi.org/10.1080/09506608.2016.1219481>
- 355 14. Che H, Xie H, Liang S, et al (2014) Highly enhanced mechanical properties in Cu matrix
356 composites reinforced with graphene decorated metallic nanoparticles. *J Mater Sci* 49:3725–
357 3731. <https://doi.org/10.1007/s10853-014-8082-x>
- 358 15. Tang Y, Yang X, Wang R, Li M (2014) Enhancement of the mechanical properties of graphene-
359 copper composites with graphene-nickel hybrids. *Mater Sci Eng A* 599:247–254.
360 <https://doi.org/10.1016/j.msea.2014.01.061>
- 361 16. Shao Z, Jiang Y, Jiang X, et al (2018) Recent Developments Concerning the Dispersion Methods
362 and Mechanisms of Graphene. *Coatings* 8:33. <https://doi.org/10.3390/coatings8010033>
- 363 17. Gao X, Yue H, Guo E, et al (2016) Mechanical properties and thermal conductivity of graphene
364 reinforced copper matrix composites. *Powder Technol* 301:601–607.
365 <https://doi.org/10.1016/j.powtec.2016.06.045>
- 366 18. Rashad M, Pan FS, Asif M, Ullah A (2014) Improved mechanical properties of magnesium-
367 graphene composites with copper-graphene hybrids. *Mater Sci Technol* 31:1452–1461.
368 <https://doi.org/10.1179/1743284714y.0000000726>
- 369 19. Yue H, Yao L, Gao X, et al (2017) Effect of ball-milling and graphene contents on the
370 mechanical properties and fracture mechanisms of graphene nanosheets reinforced copper
371 matrix composites. *J Alloys Compd* 691:755–762. <https://doi.org/10.1016/j.jallcom.2016.08.303>
- 372 20. Pérez-Bustamante R, Bolaños-Morales D, Bonilla-Martínez J, et al (2015) Microstructural and
373 hardness behavior of graphene-nanoplatelets/aluminum composites synthesized by
374 mechanical alloying. *J Alloys Compd* 615:S578–S582.
375 <https://doi.org/10.1016/j.jallcom.2014.01.225>
- 376 21. Saboori A, Pavese M, Badini C, Fino P (2018) A novel Cu-GNPs nanocomposite with improved
377 thermal and mechanical properties. *Acta Metall Sin (English Lett)* 31:148–152.
378 <https://doi.org/10.1007/s40195-017-0643-y>
- 379 22. Bastwros M, Zhu C, Kim G-Y, et al (2014) Effect of ball milling on graphene reinforced Al6061
380 composite fabricated by semi-solid sintering. *Compos Part B Eng* 60:111–118.
381 <https://doi.org/10.1016/j.compositesb.2013.12.043>
- 382 23. Ghosh G, Olson GB (2002) The isotropic shear modulus of multicomponent Fe-base solid
383 solutions. *Acta Mater* 50:2655–2675. [https://doi.org/10.1016/S1359-6454\(02\)00096-4](https://doi.org/10.1016/S1359-6454(02)00096-4)
- 384 24. Huang YY, Terentjev EM (2012) Dispersion of carbon nanotubes: Mixing, sonication,
385 stabilization, and composite properties. *Polymers (Basel)* 4:275–295.
386 <https://doi.org/10.3390/polym4010275>

- 387 25. Kumar HGP, Xavior MA (2014) Graphene Reinforced Metal Matrix Composite (GRMMC): A
388 Review. *Procedia Eng* 97:1033–1040. <https://doi.org/10.1016/j.proeng.2014.12.381>
- 389 26. Hwang J, Jeon S, Kim T-S, et al (2013) Enhanced Mechanical Properties of Graphene/Copper
390 Nanocomposites Using a Molecular-Level Mixing Process. *Adv Mater* 25:6724–6729.
391 <https://doi.org/10.1002/adma.201302495>
- 392 27. Pengpeng Wang, Zhijun Wei, Minhua Shen, Hui Pan, Jun Fu LC (2017) In-situ Synthesized
393 Silver-graphene Nanocomposite with Enhanced Electrical and Mechanical Properties. *IEEE*
394 *Holm Conf Electr Contacts*. <https://doi.org/10.1088/1742-6596/240/1/012128>
- 395 28. Lee B, Koo MY, Jin SH, et al (2014) Simultaneous strengthening and toughening of reduced
396 graphene oxide/alumina composites fabricated by molecular-level mixing process. *Carbon N*
397 *Y* 78:212–219. <https://doi.org/10.1016/j.carbon.2014.06.074>
- 398 29. Ickecan D, Zan R, Nezir S (2017) Eco-Friendly Synthesis and Characterization of Reduced
399 Graphene Oxide. *J Phys Conf Ser* 902:6426–6432. <https://doi.org/10.1088/1742-6596/902/1/012027>
- 401 30. Zhang J, Yang H, Shen G, et al (2010) Reduction of graphene oxide via l -ascorbic acid. *Chem*
402 *Commun* 46:1112–1114. <https://doi.org/10.1039/B917705A>
- 403 31. Fernández-Merino MJ, Guardia L, Paredes JI, et al (2010) Vitamin C Is an Ideal Substitute for
404 Hydrazine in the Reduction of Graphene Oxide Suspensions. *J Phys Chem C* 114:6426–6432.
405 <https://doi.org/10.1021/jp100603h>
- 406 32. Lightfoot EN, Bird RB, E. Stewart WE (1960) *Transport Phenomena*. John Wiley & Sons, Ltd
- 407 33. Oliver WC, Pharr GM (1992) An improved technique for determining hardness and elastic
408 modulus using load and displacement sensing indentation experiments. *J Mater Res* 7:
- 409 34. Oliver WC (2004) Measurement of hardness and elastic modulus by instrumented
410 indentation : Advances in understanding and refinements to methodology
- 411 35. Johra FT, Lee JW, Jung WG (2014) Facile and safe graphene preparation on solution based
412 platform. *J Ind Eng Chem* 20:2883–2887. <https://doi.org/10.1016/j.jiec.2013.11.022>
- 413 36. De Silva KKH, Huang H-H, Yoshimura M (2018) Progress of reduction of graphene oxide by
414 ascorbic acid. *Appl Surf Sci* 447:338–346. <https://doi.org/10.1016/J.APSUSC.2018.03.243>
- 415 37. Zainuddin MF, Him NRN, Othman NH, et al (2017) Review on effects of hydrazine hydrate
416 and L-ascorbic acid on electrical conductivity of graphene. p 090004
- 417 38. Pei S, Cheng HM (2012) The reduction of graphene oxide. *Carbon N Y* 50:3210–3228.
418 <https://doi.org/10.1016/j.carbon.2011.11.010>
- 419 39. Lucchese MM, Stavale F, Ferreira EHM, et al (2010) Quantifying ion-induced defects and

- 420 Raman relaxation length in graphene. *Carbon* N Y 48:1592–1597.
421 <https://doi.org/10.1016/j.carbon.2009.12.057>
- 422 40. Chamroune N, Mereib D, Delange F, et al (2018) Effect of flake powder metallurgy on thermal
423 conductivity of graphite flakes reinforced aluminum matrix composites. *J Mater Sci* 53:8180–
424 8192. <https://doi.org/10.1007/s10853-018-2139-1>
- 425 41. Oddone V, Boerner B, Reich S (2017) Composites of aluminum alloy and magnesium alloy
426 with graphite showing low thermal expansion and high specific thermal conductivity. *Sci*
427 *Technol Adv Mater* 18:180–186. <https://doi.org/10.1080/14686996.2017.1286222>
- 428 42. Firkowska I, Boden A, Boerner B, Reich S (2015) The Origin of High Thermal Conductivity
429 and Ultralow Thermal Expansion in Copper–Graphite Composites. *Nano Lett* 15:4745–4751.
430 <https://doi.org/10.1021/acs.nanolett.5b01664>
- 431 43. Humphreys FJ, Hatherly M (2004) *Recrystallization and related annealing phenomena*.
432 Elsevier
- 433 44. Humphreys FJ (1977) The nucleation of recrystallization at second phase particles in deformed
434 aluminium. *Acta Metall* 25:1323–1344. [https://doi.org/10.1016/0001-6160\(77\)90109-2](https://doi.org/10.1016/0001-6160(77)90109-2)
- 435 45. Porter JR, Humphreys FJ (1979) Nucleation of recrystallization at second-phase particles in
436 deformed copper alloys. *Met Sci* 13:83–88. <https://doi.org/10.1179/msc.1979.13.2.83>
- 437