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1 *In situ* decoration of laser-scribed graphene with
2 TiO₂ nanoparticles for scalable high-performance
3 micro-supercapacitors

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17 ABSTRACT

18 Graphene-based miniaturized supercapacitors, obtained via laser conversion of suitable
19 precursors, have been attracting recent attention for the production of energy storage
20 small-scale devices. In this work, a one-pot synthesis of TiO₂ nanoparticles embedded in
21 porous graphene-based electrodes has been obtained with the LightScribe[®] technology, by
22 converting the precursor materials through the absorption of a DVD burner infrared laser
23 light. Enhanced electrochemical performance of devices has been achieved thanks to the
24 combination of faradic surface reactions, arising from metal oxide nanoparticles, with the
25 conventional electrochemical double layer capacitance, arising from porous graphene.
26 Micro-supercapacitors, consisting of TiO₂-graphene electrodes, have been tested by
27 investigating two hydrogel polymer electrolytes, based on polyvinyl alcohol/H₃PO₄ and
28 polyvinyl alcohol/H₂SO₄, respectively. Specific areal capacitance up to 9.9 mF/cm² are
29 obtained in TiO₂-graphene devices, corresponding to a volumetric capacitance of 13 F/cm³
30 and doubling the pristine graphene-based device results. The micro-supercapacitors
31 achieved specific areal energy and specific areal power of 0.22 μWh/cm² and 39 μW/cm²,
32 along with a cyclability greater than 3000 cycles. These high-performance results suggest
33 laser-scribed TiO₂-graphene nanostructures as remarkable candidates in micro-
34 supercapacitors for environment-friendly, large-scale and low-cost applications.

35

36 KEYWORDS

37 graphene, TiO₂, micro-supercapacitors, hydrogel polymer electrolyte, LightScribe[®]
38 technology

39

40 1. INTRODUCTION

41 The increasing demand of micro power sources and small-scale energy storage devices has
42 recently moved the attention to miniaturization. Micro power modules are required in devices
43 such as sensors, portable and wearable electronics, radio frequency identification (RFID), or
44 biomedical implants. These systems need self-powered wireless devices, which can work
45 independently of an external power source. Supercapacitors (also called electrochemical
46 double layer capacitors, EDLCs) can satisfy this requirement, thanks to their high specific
47 power and their up to millions long life cycles [1–4].

48 In particular, the recent interest has been focused on miniaturized supercapacitors, also called
49 micro-supercapacitors (MSCs), employed as power sources or energy storage harvesting
50 units in microelectronic devices. Their total footprint area is in the range of square
51 millimetre/centimetre, while their electrochemical performance in terms of energy and power
52 densities is in the micro-scale. The first architecture of MSCs consists of a sandwich
53 configuration, with film electrodes (less than 10 μm thick) facing each other and a solid
54 electrolyte placed between them. However, in order to increase energy and power densities, a
55 planar interdigitated arrangement is preferred, consisting of micro-electrodes in an in-plane
56 configuration, instead of a vertical stack. The distance between the electrodes can be
57 controlled and reduced, reaching small ion diffusion pathway from the electrolyte to the
58 electrode; in addition, the increased accessibility of the electrodes sides ensures the use of
59 their entire surface [1,5,6]. Gel electrolytes are usually used in interdigitated MSCs to reduce
60 the electrolyte leakage and achieve better packaging of the devices [5,7,8].

61 As in conventional supercapacitors, essential features of the electrodes are high specific
62 surface area with a hierarchical pore structure and good electrical conductivity [4,9–12].
63 Meeting these requirements, graphene-based systems, containing mono- or few-layers of

64 carbon atoms arranged in a honeycomb lattice, are currently explored as electrode materials
65 in MSCs [12–14]. Furthermore, combining graphene with electroactive species is a promising
66 attempt to enhance the electrochemical performance of supercapacitors, by introducing
67 faradic surface effects in the storage mechanism, in addition to the electrostatic charge
68 accumulation [15–18]. Transition metal oxides or hydroxides, such as manganese oxides
69 [19], iron oxides [20], nickel oxides or hydroxides [21] and titanium dioxide [22] are
70 currently explored, due to their multiple oxidation states, which can introduce redox
71 contributions in the storage mechanism. The combination of these materials with graphene
72 ensure a good electrical conductivity in the electrode.

73 Impressive results have been recently achieved in producing interdigitated graphene-based
74 micro-electrodes using the laser light, through cost-effective techniques [23,24].
75 Carbonaceous precursor materials (such as graphite and graphene oxides) [25–29] or
76 commercial polymers (such as polyimide and poly(ether ether ketone)) [25,30–34] are
77 converted into electroactive materials by means of laser photoreduction. Different laser
78 sources have been already examined, in continuous and pulsed mode, from the UV to the
79 infrared range, to induce photothermal and/or photochemical reduction of carbon-based
80 precursors into conductive graphene-based materials [25–35]. Graphite oxide (GO) can be
81 easily converted into porous graphene-based products, thanks to the removal of oxygen
82 containing groups, changing the electrical properties of the material from insulating to
83 conductive. Infrared lasers of DVD burner drives, using the LightScribe[®] technology, are
84 currently encouraged, since the production of hundreds of interdigitated electrodes can be
85 achieved in less than one hour [27,36,37]. The technique has been recently explored to realize
86 graphene-based electrodes with a straightforward process, starting from graphite oxide
87 aqueous dispersion, realizing low-cost MSCs with remarkable electrochemical properties
88 [27]. Furthermore, the performance of these devices can be improved by combining faradic

89 systems with graphene-based materials. Redox effects are obtained from iron oxide, cobalt
90 oxide, molybdenum oxide [17], molybdenum disulfide [38] or titanium dioxide nanoparticles
91 [39]. Among them, titanium dioxide (TiO₂), besides providing faradic effects, is considered a
92 promising source to produce composite materials with graphene, thanks to its high thermal
93 and chemical stability, low cost and low toxicity [22,39–44].

94 This work exploited a novel graphene-based composite material obtained by LightScribe[®]
95 technique, with the simultaneous synthesis of TiO₂ nanoparticles (NPs) decorating the porous
96 defective graphene structure. The LightScribe[®] writing process both converts suitable
97 precursors into the active material and directly prints the electrodes ready for assembling the
98 electrochemical device. This novel one-pot synthesis route demonstrated to be particularly
99 effective to disperse TiO₂ NPs at the nanoscale, anchoring them to the graphene defects. To
100 the best of our knowledge, a similar approach has not been investigated yet so far. In fact,
101 several different techniques have been used to produce TiO₂-graphene composite materials,
102 such as sol-gel method, solvothermal reactions or microwave-assisted routes. However, the
103 synthesis of the combined materials often requires a multi-steps process, which first consists
104 in graphene production, followed by the decoration with NPs. In some cases, the materials
105 are only physically mixed, leading to phase segregation and NPs agglomeration, rather than
106 promoting a combined material [22,39,41–44]. Our obtained composite nanostructure is
107 competitive as electrode material, as displays both faradic and physical electrochemical
108 storage capacity, hence improving the electrochemical performance of the same pristine
109 graphene material without TiO₂ NPs.

110 High-performance MSCs have been produced with interdigitated electrodes and hydrogel
111 polymer electrolytes in a planar configuration. Interdigitated patterns have been achieved on
112 a proper DVD coating, based on an aqueous dispersion containing GO and titanium(IV)

113 isopropoxide, thanks to the photothermal process induced by the absorption of the infrared
114 laser light. The process gives rise to the conversion of precursors into an electroactive and
115 conductive composite material. The combination of the porous Laser-Scribed Graphite Oxide
116 (LSGO) structure with a widespread decoration of anatase TiO₂ NPs in the electrode
117 materials resulted in enhanced electrochemical properties compared to pristine graphene-
118 based devices. Two hydrogel polymers based on polyvinyl alcohol (PVA)/H₃PO₄ and
119 polyvinyl alcohol (PVA)/H₂SO₄ have been compared, achieving high-performance with
120 specific areal capacitance up to 9.9 and 6.8 mF/cm², respectively. TiO₂ NPs decorating
121 LSGO structures (henceforth called TiO₂-LSGO) obtained with the LightScribe[®] technology
122 can be encouraged as remarkable material in MSCs for large-scale and low-cost production.

123

124 2. MATERIALS AND METHODS

125 2.1 Production of laser-scribed micro-supercapacitors

126 MSCs have been obtained through the LightScribe[®] technique in an interdigitated planar
127 configuration [27]. The one-pot formation of TiO₂ NPs onto LSGO patterns has been
128 achieved by means of the infrared laser of a LightScribe[®] DVD burner to produce the
129 electrodes.

130 Graphite oxide and titanium(IV) isopropoxide have been used as precursor materials to be
131 converted by the laser irradiation. GO obtained with Hummers' method [45] has been
132 employed, due to its good solubility in water. Water as solvent in the preparation of the laser-
133 scribed disc has been preferred to toxic, high-boiling temperature, organic solvents, typically
134 employed to suspend graphene. An aqueous dispersion (2 mg/ml) of GO (GO-V50, Standard
135 Graphene) has been sonicated for 8 h (30 min rest every 30 min of sonication to avoid

136 heating effects). Then, titanium(IV) isopropoxide (TTIP, 97%, Sigma-Aldrich Co.) has been
137 added in a TTIP:GO weight ratio 1.2:1, to obtain a final TiO₂:C molar ratio 1:8
138 (corresponding to a mass ratio of 0.8:1) [46]. The dispersion has been further sonicated for 30
139 min and stirred for 3 h, under Ar atmosphere. In order to decrease the TTIP hydrolysis
140 reaction rate, the pH of the dispersion has been controlled to neutrality. The laser-scribed disc
141 has been prepared by drop-casting 5 ml of the dispersion on a polyethylene terephthalate
142 (PET) disc (0.1 mm thick) and let it dry overnight under N₂ atmosphere, forming a film ~10
143 μm thick. The TTIP-GO-coated PET disc, glued to the surface of a LightScribe[®] DVD disc,
144 has been subjected to the LightScribe[®] process by the DVD burner infrared laser ($\lambda=788$ nm).
145 Interdigitated patterns are obtained using the LightScribe[®] *Nero CoverDesigner* software with
146 a typical writing time of about 20 min and 3 repetitions of the laser-scribing process, to fully
147 convert the precursors into TiO₂ NPs and LSGO [47]. Both electrodes of MSCs consist of
148 TiO₂-LSGO patterns, while unconverted parts between them prevent electrical contact of the
149 electrodes. Cu strips glued to the electrodes using silver paint were used as current collectors
150 in the device. The borders of the interdigitated area have been covered with Teflon[®] tape, to
151 separate the contacts from the electrolyte. Two hydrogel polymer electrolytes, consisting of
152 an aqueous solution of H₂O:acid:PVA (Sigma-Aldrich Co.) in the mass ratio 10:1:1, have
153 been tested, using H₃PO₄ and H₂SO₄ as acids, respectively [33]. The hydrogel polymer
154 electrolytes have been prepared starting from concentrated acid and deionized Milli-Q water,
155 which have been mixed with PVA powder under continuous stirring. The solution has been
156 heated to about 85 °C until it became clear. The gel-electrolyte has been drop-cast onto the
157 surface of the interdigitated area and let it dry overnight to eliminate water excess. To
158 investigate the effect of TiO₂ NPs on the devices, MSCs without TiO₂ have been prepared
159 following the same experimental procedure, using pristine GO aqueous dispersion.

160 2.2 Material characterization

161 The micro-structure of TiO₂-LSGO material has been examined by scanning transmission
162 electron microscopy (STEM) and high-resolution imaging (HRTEM) using a field emission
163 JEM-2200FS microscope (JEOL Ltd., Japan), equipped with a Schottky gun working at 200
164 kV (point resolution 0.19 nm), an in-column energy filter (Ω -type), a CCD high resolution
165 camera, STEM detectors and an energy dispersive X-ray spectrometer (EDS). The material
166 has been scratched from the interdigitated patterns of the laser-scribed surface obtained by
167 the LightScribe[®] process, dispersed in isopropanol and deposited onto holey carbon films on
168 copper grids. Simulation of the HRTEM image has been performed with the JEMS software
169 [48], using Bloch waves dynamical calculation (50 reflections), quasi-parallel illumination
170 (0.6 mrad) at 200 kV, 70 nm defocus, and a crystal thickness of 6 nm as inferred from the
171 diameter of the titania nanoparticle in HRTEM. 1% of noise was added to better reproduce
172 the noise in the experiment. Electron energy loss (EEL) spectra have been acquired on a
173 Thermo Fischer Scientific Talos F200S in imaging mode (TEM) from a group of particles, to
174 assure high signal to noise ratio due to the large collection angle. A Richardson–Lucy
175 deconvolution with a low-loss spectrum has been done to reduce the contribution of multiple
176 scattering and improve energy resolution, by following the indications in section 2.4 in [49].

177 Powder X-ray diffraction (PXRD) has been carried out on a small amount of TiO₂-LSGO
178 material scratched from the PET substrate and sealed in a 0.5 mm diameter glass capillary.
179 The measurement has been performed with a Bruker D8 Discover diffractometer, operating
180 in Debye Scherrer geometry, equipped with copper anode (Cu-K α) and a Rayonix MX225
181 2D area detector.

182 Micro-Raman spectroscopy has been performed with a Horiba LabRam micro-spectrometer
183 (HORIBA Scientific, Kyoto, Japan), equipped with an Olympus microscope (Olympus,

184 Tokyo, Japan), using a 50x objective, in a backscattering geometry. The 473.1 nm line of a
185 frequency-doubled Nd:YAG laser has been used as excitation, with a spectral resolution of
186 $\sim 2 \text{ cm}^{-1}$. To avoid heating effects, density filters have been used to reduce the laser power on
187 the sample. The analysis has been performed on the TiO₂-LSGO material of the interdigitated
188 patterns on the laser-scribed disc. Acquisitions have been recorded with typical exposure of
189 20-60 s, repeated 6 times for each measurement. The data analysis has been performed by the
190 *LabSpec 5* built-in software.

191 X-Ray Photoelectron Spectroscopy (XPS) analysis has been carried out directly on the laser-
192 scribed surface, which have been supported on a carbon tape (UHV compatible), using a
193 UHV apparatus equipped with an X-ray source (Mg K_α photon at 1253.6 eV), while
194 photoelectrons have been analyzed through a VSW HA100 hemispherical analyzer with a
195 total energy resolution of 0.86 eV. Core level binding energies (BEs) have been normalized
196 using as reference the Au 4f_{7/2} core level signal at 84.0 eV, acquired from a sputtered Au
197 foil.

198 Electrical measurements have been performed on LSGO material on the laser-scribed surface.
199 The electrical resistance has been measured by four-point probes method. The measurements
200 have been carried out using a Keithley 6221 DC and AC current source and a Keithley 2182A
201 Nanovoltmeter. The four probes consisted of aligned electrodes with golden tip.

202 The specific surface area (SSA) of LSGO material has been estimated by the physisorption of
203 a common dye, methylene blue (MB), from the porous material, with UV-Visible
204 spectrophotometry [37]. After a proper calibration to correlate the absorbance and the dye
205 concentration, the amount of MB absorbed by LSGO has been evaluated. To perform the
206 analysis, the material ($\sim 3 \text{ mg}$) has been removed from the laser-scribed surface obtained by
207 the LightScribe[®] process, dispersed in a MB aqueous solution, whose initial concentration

208 was known, and stirred overnight. After centrifugation, the absorbance of the supernatant has
209 been measured using a Jasco V-550 UV-Visible spectrophotometer to evaluate the variation
210 of the MB concentration compared to the initial one.

211

212 **2.3 Electrochemical characterization**

213 The electrochemical performance of the electrodes and the devices have been tested with
214 two- and three-electrode cell arrangement cyclic voltammetry (CV) at room temperature,
215 respectively, with a Keithley Series 2400 Sourcemeter. In the three-electrode CV, the
216 electrochemical characterization of the electrodes has been performed using either H₃PO₄ 1
217 M or H₂SO₄ 1 M aqueous electrolyte, an Ag/AgCl reference electrode and Pt counter
218 electrode. The operating voltage range has been set between 0 and 1.0 V vs Ag/AgCl,
219 applying a linear potential sweep with scan rates from 1 mV/s to 50 mV/s. The mean specific
220 current ($\langle I \rangle_s$) has been plotted as a function of the scan rate (ν), in order to highlight the
221 faradic contribution in the presence of redox peaks. It is known that for a capacitive process
222 the current is proportional to ν , while for faradic reactions it is proportional to $\nu^{1/2}$ [50,51].

223 Two electrode CV for the electrochemical characterization of the devices has been carried out
224 using either PVA/H₃PO₄ and PVA/H₂SO₄ hydrogel electrolytes, applying a linear potential
225 sweep with scan rates of 1, 5 and 10 mV/s. The optimal operating voltage window for cyclic
226 voltammetry measurements has been identified between 0 and 0.8 V. Galvanostatic charge-
227 discharge measurements (GCD) have been performed at room temperature, with a Landt
228 CT2001A testing system by means of charge and discharge cycles at a fixed current, between
229 0 V and 0.8 V. Ten charge/discharge cycles have been tested at specific areal currents of 5,
230 10, 25, 50 and 100 $\mu\text{A}/\text{cm}^2$. Specific areal capacitance C_{SP} (mF/cm^2) of the material has been

231 calculated from the total capacitance C of the MSC, using the footprint area A_{AM} of the active
232 material of both electrodes:

$$233 \quad C_{SP} = 4 \frac{C}{A_{AM}}$$

234 Specific areal energy E_{SP} ($\mu\text{Wh}/\text{cm}^2$) of the electrode material in the MSC has been evaluated
235 by:

$$236 \quad E_{SP} = \frac{CU_{max}^2}{2A_{AM}3600}$$

237 where U_{max} is the maximum region of electrochemical stability [52]. For each discharge
238 cycle, the specific areal power P_{SP} has been obtained as the ratio between the specific areal
239 energy (E_{SP}) and the total discharge time. The capacitance retention of the devices has been
240 evaluated as the ratio of the specific areal capacitance at each cycle to the specific areal
241 capacitance achieved in the first one, over at least 3000 cycles at $5 \mu\text{A}/\text{cm}^2$. For each cycle,
242 the Coulombic efficiency η_C is given by:

$$243 \quad \eta_C = \frac{C_d}{C_c}$$

244 where C_d and C_c are the discharge and charge capacitance, respectively.

245 The energy efficiency η_E has been also calculated for each of the 3000 cycles at $5 \mu\text{A}/\text{cm}^2$,
246 given by the ratio between the energy during discharge and the energy during charge [53].

247

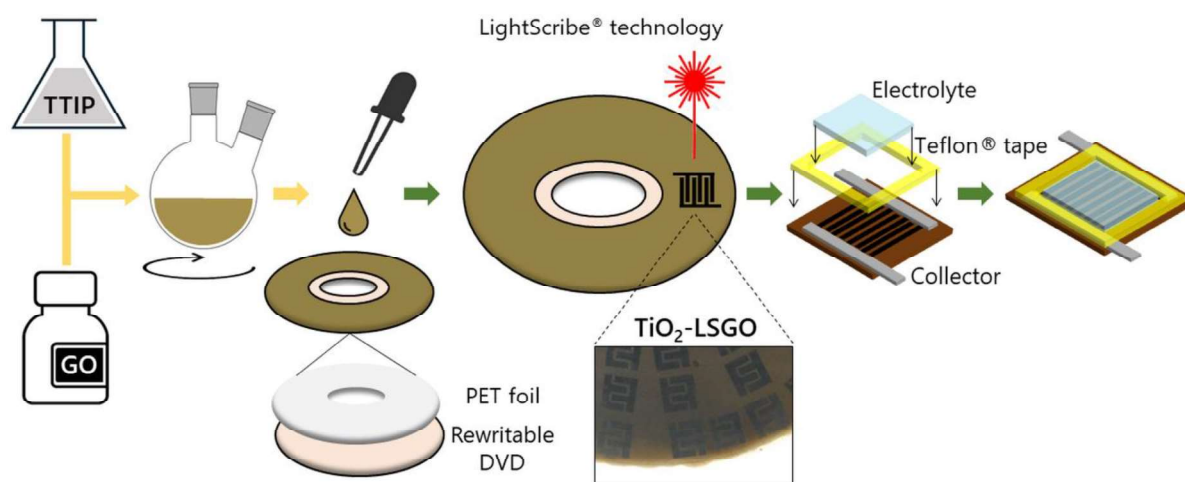
248 3. RESULTS

249 MSCs, either TiO_2 -LSGO and LSGO, have been obtained by the LightScribe[®] technique in
250 the planar configuration [27]. The scheme of the one-pot synthesis of TiO_2 -LSGO and the

251 production of MSCs has been sketched in Figure 1 and the picture of a section of the laser-
252 scribed disc is shown in the inset of Figure 1.

253 A detail of the micro-structure of the laser-scribed patterns is shown in the Supplementary
254 Material in Figure S1.

255

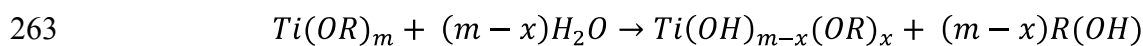


256

257 **Figure 1.** Scheme of the laser-scribed disc and MSCs production. The first steps (highlighted by
258 yellow arrows) have been performed under inert atmosphere. *Inset:* image of the laser-scribed disc
259 section.

260

261 In the process, the reactions of TTIP hydrolysis and condensation can be described by the
262 equation:

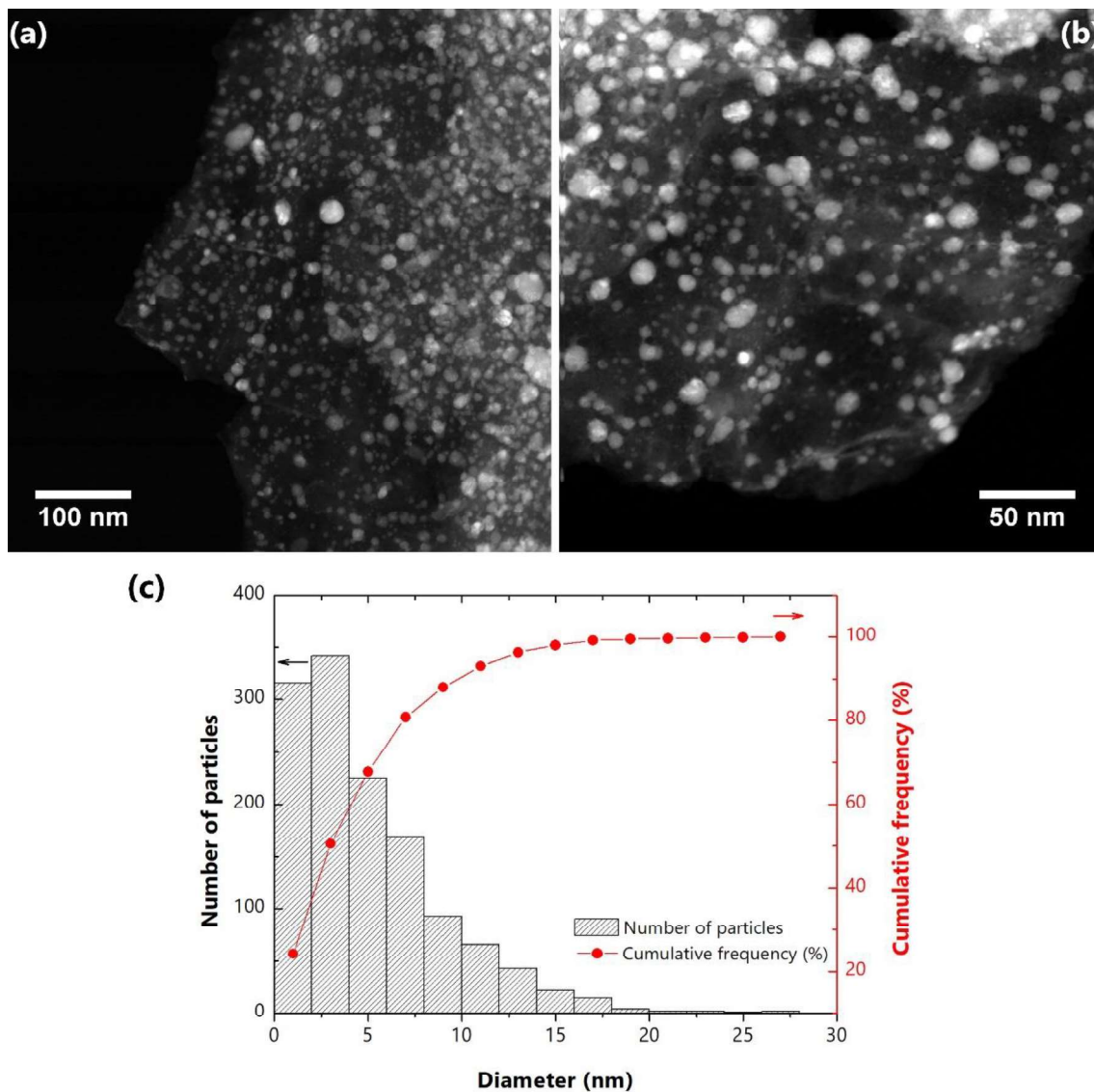


264 where R is the $CH(CH_3)_2$ group, replaced with hydroxyl group during the hydrolysis reaction.

265 Then, the hydroxyl groups condense with each other, eliminating water or isopropanol

266 molecules.

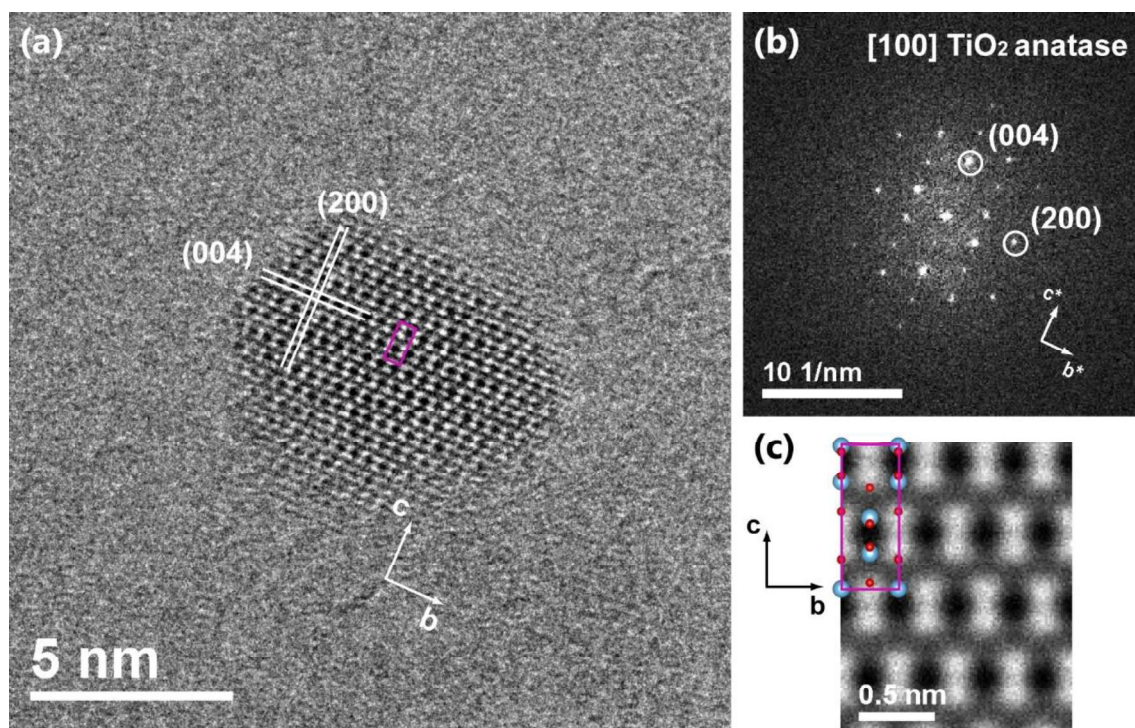
267 During the laser photoreduction, a photothermal process occurred, as expected for infrared
268 laser wavelengths [23,54]. The absorption of the infrared light can produce locally high
269 temperatures ($>10^3$ °C), which promote TiO₂ crystallization. Besides, the temperature
270 increase breaks the C-OOH and C=O bonds present in GO, which occur with gas release. The
271 irradiated material results in a higher relative content of carbon compared to the precursor,
272 due to the deoxygenation during the laser-scribing process. The conversion of GO into LSGO
273 produce a porous material with a SSA of 180 ± 20 m²/g (Figure S2 in Supplementary
274 Material), a value comparable with that observed for similar graphene-related materials [55].
275 LSGO material is also characterized by an increase in the electrical conductivity of five
276 orders of magnitude to $\sigma\sim 1.1$ S/cm (Table S1 in Supplementary Material).



278

279 **Figure 2.** (a) and (b) STEM images of TiO₂-LSGO material collected at different magnification; (c)
 280 TiO₂ diameter size distribution (in gray) and cumulative frequency curve (in red) of TiO₂-LSGO.

281



282

283 **Figure 3.** (a) HRTEM image of a TiO₂ nanoparticle of ~6 nm diameter; (b) FFT of the HRTEM
 284 image; (c). Image simulation from TiO₂ anatase at 6 nm thickness. In the model, Ti atoms are light-
 285 blue and O atoms are red. The image contrast is in good agreement with the experiment, confirming
 286 the anatase (tetragonal) structure of the nanoparticle. The (200) and (004) planes are highlighted in (a)
 287 for clarity. The tetragonal cell is highlighted in purple in (a) and (c).

288

289 A widespread decoration of TiO₂-LSGO with TiO₂ NPs without agglomeration can be
 290 observed in the dark-field STEM image in Figure 2a and 2b, covering the whole graphene-
 291 based matrix (the NPs appear bright in the image, while the LSGO is darker). From a
 292 statistical analysis performed on about 1300 particles, the TiO₂ nanoparticle size distribution,
 293 while not entirely homogeneous, reveals that 90% of NPs diameter is under 10 nm, with an
 294 average of 3 nm (Figure 2c). Quasi-spherical shaped NPs are dominating, as shown in the
 295 HRTEM image of Figure 3a, and their structure is compatible with anatase TiO₂ (space group
 296 n.141, I4₁/amd), as revealed for instance by the presence of (200) and (004) reflections
 297 (Figure 3b) and confirmed by image simulation (Figure 3c). The EEL spectra from Ti-L_{2,3}
 298 and O-K edges (reported in the Figure S3) agree with the spectra from nanostructured anatase

299 [56], in particular regarding the asymmetry of the e_g peak of the Ti-L₃ edge (rutile has the
300 opposite asymmetry of the e_g peak).

301 Anatase is confirmed as the main TiO₂ crystalline phase also by PXRD analysis, with its most
302 intense (101) reflection, occurring at $2\theta=25.3^\circ$. PXRD results are shown in the
303 Supplementary Material (Figure S4).

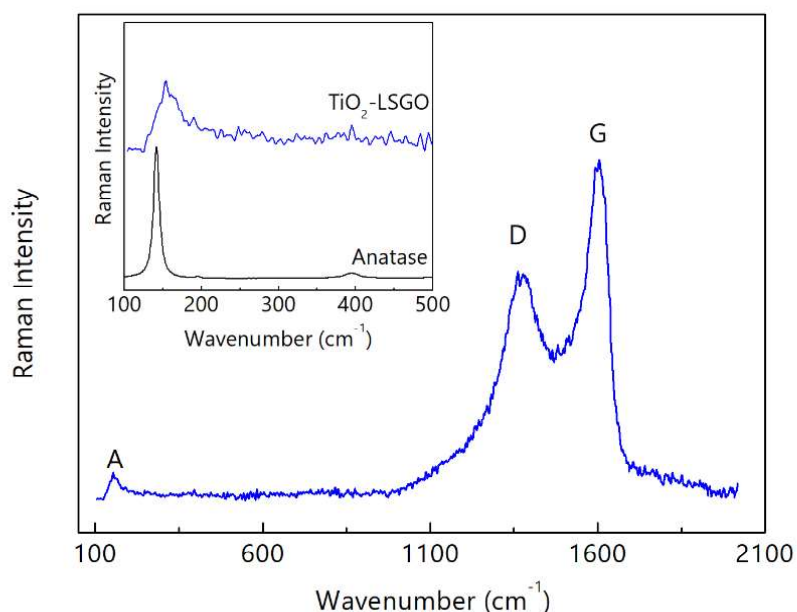
304 The elemental composition of TiO₂-LSGO material performed by EDS analysis shows that
305 the Ti:C atomic ratio is 1:6, in good agreement with the expected molar ratio (TiO₂:C=1:8)
306 (Table S2).

307

308 **3.2 Raman spectroscopy**

309 The decoration of LSGO with TiO₂ anatase NPs is proved by the Raman analysis of TiO₂-
310 LSGO, as shown in Figure 4. The presence of anatase TiO₂ is confirmed by the main E_g
311 anatase vibrational mode in the Raman spectrum at $\sim 155\text{ cm}^{-1}$, expanded in the inset of
312 Figure 4. The peak is shifted and broadened compared to the crystalline anatase signal, as
313 expected for nanoparticle sizes under $\sim 20\text{ nm}$. According to the phonon confinement effect,
314 in the case of finite size crystals, the main anatase peak is a convolution of many
315 contributions, following the phonon dispersion curve, instead of a single sharp Lorentzian, as
316 for ideal crystalline anatase. The observed peak position at $\sim 155\text{ cm}^{-1}$, shifted from the 143 cm^{-1}
317 of the crystalline reference, suggests the presence of $\sim 5\text{ nm}$ size NPs, as predicted by the
318 phonon confinement model [57]. The one-pot formation of the TiO₂-LSGO combined
319 material is highlighted by the presence of the typical D and G bands of carbon-based
320 materials, along with the anatase feature (Figure 4). The G band, related to the E_{2g} phonon
321 mode of the sp^2 domains in graphitic materials, and the D band, arising from structural

322 defects in disordered samples, are observed at $\sim 1370\text{ cm}^{-1}$ and $\sim 1600\text{ cm}^{-1}$, respectively [58].
323 The broadening of D and G band compared to ordered crystalline materials confirms the
324 highly defective structure of LSGO [59].



325

326 **Figure 4.** Raman spectrum of TiO₂-LSGO with the most intense anatase E_g vibrational mode (A) and
327 characteristic graphene-based materials bands (D and G). *Inset:* the main anatase peak in TiO₂-LSGO
328 spectrum (in blue) is expanded and compared with the reference crystalline anatase spectrum (in
329 black).

330

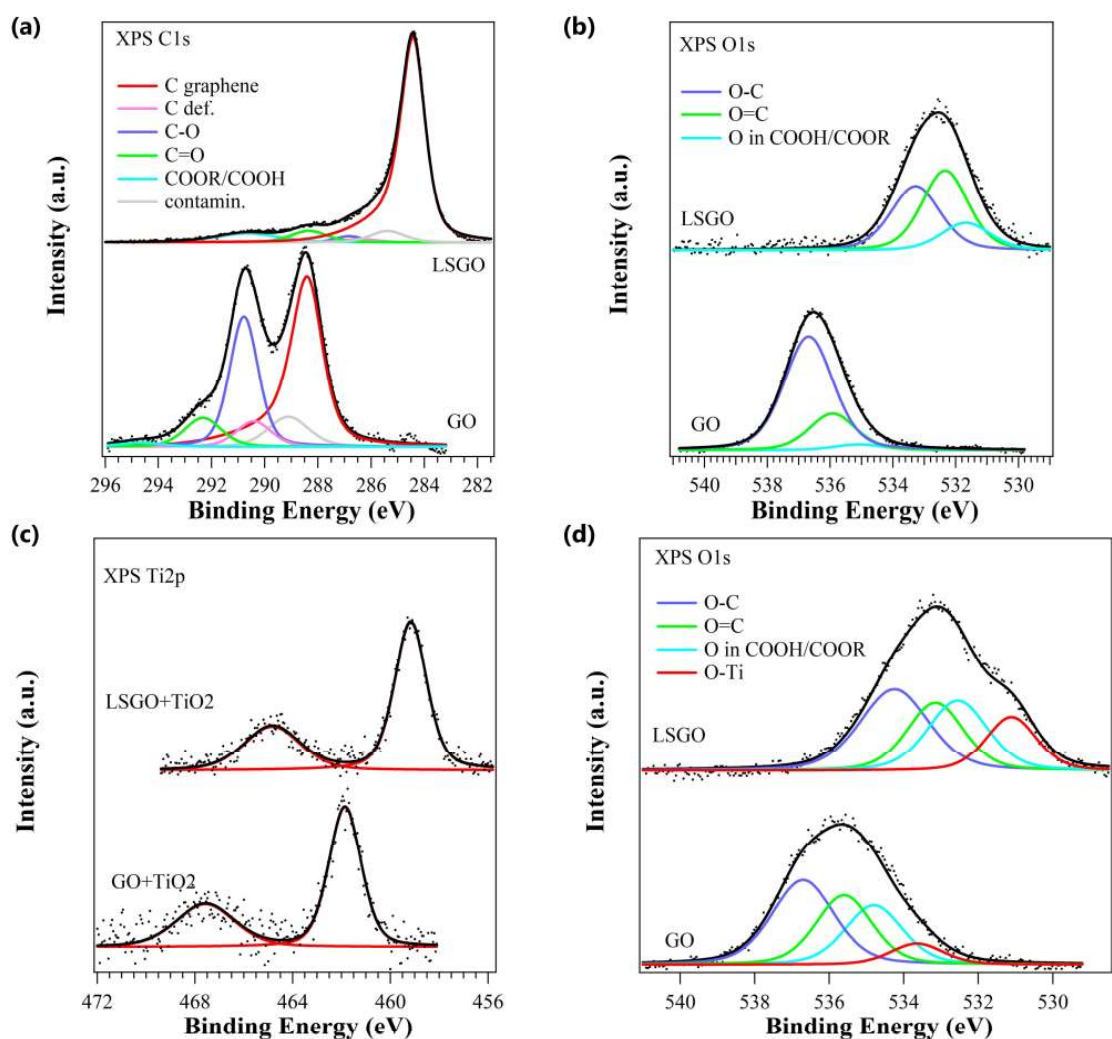
331 3.3 X-ray Photoelectron Spectroscopy

332 XPS core level spectra of C1s and O1s for GO and LSGO samples are shown in Figure 5a
333 and 5b. In GO main peaks are positioned at higher BE than expected, about +4 eV, due to
334 charging phenomena already evidenced in samples of GO [26]. After laser treatment, this
335 charge shift is no more detected and the peak positions are aligned to the expected standards
336 [60]. In C1s core level (Figure 5a), we can assign the peak at 288.4 eV to the graphene
337 emission (C=C-C bonds), while the other main feature at 290.8 eV is due to C-O bonds.
338 Other peaks are present and related to C=O, COOH/COOR, defects in the graphene structure

339 and contaminants (Table S3). O1s core level (Figure 5b) shows the corresponding oxidized
340 carbon species. The laser treatment completely changes the surface chemical properties, as
341 shown in LSGO spectra. The C/O stoichiometry ratio increase from 2.3 to 15.2, suggesting a
342 significant oxygen loss. In C1s core level, all oxygen related peaks decrease in intensity and
343 the graphene main component at 284.4 eV is sharper (Table S3). O1s core level (Figure 5b)
344 follows the same trend, with suppression of the O-C components and absence of charge shift.

345 XPS core level spectra of Ti2p and O1s core levels for GO and LSGO sample with TiO₂
346 nanoparticles are shown in Figure 5c and 5d. Charge shift is present for GO samples and
347 suppressed for LSGO, in which the Ti2p_{3/2} peak position is 459.2 eV compatible with Ti⁴⁺
348 oxidized species. Ti2p is a single, narrow peak (FWHM of Ti2p_{3/2} is 1.6 eV in both spectra),
349 characterized by the well-known Ti_{3/2} and Ti_{1/2} spin-orbit splitting, without any further
350 contribution from low valence Ti species and the corresponding O1s contribution has a BE
351 distance of (71.8±0.1) eV [61]. The O/Ti ratio is 2.0±0.05, thus indicating the presence of
352 stoichiometric TiO₂ nanoparticles in both samples.

353



354

355 **Figure 5.** XPS spectra of (a) C1s and (b) O1s core levels of GO and LSGO; (c) Ti2p and (d) O1s core
 356 levels of GO and LSGO samples, with TiO₂ nanoparticles. All spectra are normalized to peak height
 357 and background subtracted.

358

359 The residual oxygen atoms bonded to carbon network after the laser treatment, as detected by
 360 XPS analysis, are expected to contribute to the lower value of conductivity of LSGO as
 361 compared to pure graphene. In addition, the presence of defects in LSGO, related to its
 362 wrinkled structure, as observed in STEM image in Figure 2a, contributes to limit the
 363 electrical conductivity. On the other hand, the defective structure of LSGO is beneficial for
 364 the growth of small sized TiO₂ nanoparticles. The simultaneous crystallization of TiO₂ NPs

365 and conversion of GO into LSGO have been promoted by the local increase in temperature,
366 because of the absorption of laser radiation by graphite oxide.

367

368 **3.4 TiO₂-LSGO and LSGO MSCs electrochemical performance**

369 CV has been performed in a three-electrode cell arrangement to characterize LSGO and
370 TiO₂-LSGO materials before assembling the devices. The results are shown in the
371 Supplementary Material.

372 The electrochemical properties of the laser-scribed MSCs have been evaluated with two
373 different hydrogel polymer electrolytes, namely PVA/H₃PO₄ and PVA/H₂SO₄. Since the best
374 electrochemical performance has been obtained with the PVA/H₃PO₄-based electrolyte, these
375 results will be discussed here, while those obtained with PVA/H₂SO₄-based electrolyte are
376 reported in the Supplementary Material.

377 The electrochemical behaviour of the TiO₂-LSGO composite material consists of two
378 contributions: the first one has a capacitive origin, typical of EDLCs and it is due to the
379 electrostatic charge accumulation at the electrode-electrolyte interface on porous conductive
380 electrodes, as expected for graphene-based materials. The second one arises from surface
381 faradic processes and originates from the electron transfer, occurring during charge and
382 discharge cycles with the redox-active TiO₂ NPs [62].

383 The results on MSCs with PVA/H₃PO₄ hydrogel polymer electrolyte are shown in Figures 6,
384 7 and 8. Both EDLC and faradic effects are observable in the CV curves of TiO₂-LSGO
385 MSCs (Figure 6a). Faradic contribution has been confirmed by the three-electrode cell
386 arrangement CV results, shown in the Supplementary Material (Figures S5 and S6) [51]. In
387 contrast, LSGO MSCs show only the capacitive behaviour, with a nearly rectangular CV

388 curve (Figure 6b). When TiO₂ NPs are combined with LSGO (TiO₂-LSGO), an enlargement
389 in the area of CV curves and a slight deviation from the rectangular shape are observed. We
390 can exclude that this behaviour is due to an electronic leakage, possibly arising from the
391 unconverted GO regions. In that case, we would expect the same effect also in LSGO MSCs,
392 which has not been observed. Thus, the deviation from the rectangular shape can be ascribed
393 to a faradic effect. The enlargement of the area of CV curves in TiO₂-LSGO compared to
394 LSGO MSCs suggests an increase in specific areal capacitance, since at equal scan rate
395 (dV/dt) the specific areal capacitance is proportional to the integral area of the curve. In
396 particular, as depicted from the comparison at 1 mV/s in Figure 6c, redox processes seem to
397 occur at ~0.2 V in TiO₂-LSGO. The better performance at lower scan rates suggests that the
398 faradic contribution is characterized by a different process time scale compared to the EDLC
399 capacitance.

400 The combined behaviour of TiO₂-LSGO MSCs is also confirmed by galvanostatic charge and
401 discharge measurements, as shown in Figure 7. Triangular-shaped charge and discharge
402 curves are achieved by LSGO MSCs at different current densities (Figure 7b), suggesting a
403 purely electrostatic charge storage. A slight deviation from the ideal trend is obtained at the
404 lowest specific areal current (5 μA/cm²), suggesting that also LSGO can give a contribution,
405 while small, to the faradic behaviour. Residual oxygen (not removed by the LightScribe[®]
406 process) in carbonyl functional groups reacts with H⁺ of the electrolyte in acidic solutions
407 [62,63]. In TiO₂-LSGO MSCs, charge and discharge curves show a pronounced deviation
408 from the triangular shape (Figure 7a). Further contribution to the faradic system is attributed
409 to the presence of TiO₂ NPs.

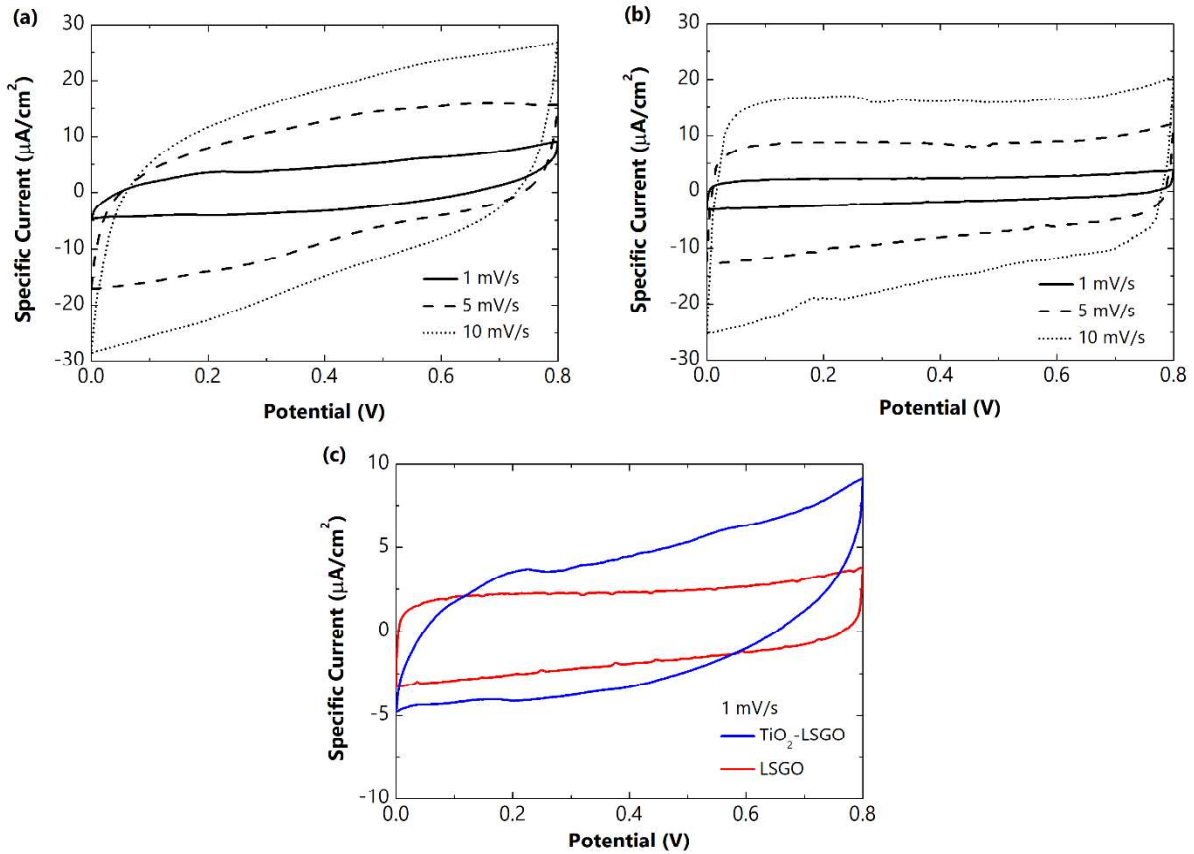
410 Specific areal capacitance, as obtained from the slope of the galvanostatic curves (GCD) is
411 shown in Figure 8a, at each current density. In TiO₂-LSGO MSCs, the highest specific areal

412 capacitance amounts at 9.9 mF/cm^2 at a current density of $5 \text{ } \mu\text{A/cm}^2$, more than twice the
413 value for LSGO MSCs (4.6 mF/cm^2), at the same current density. These results prove a clear
414 increase of performance of these MSCs, compared to other laser-scribed graphene-based
415 devices (Table S4).

416 As current density is greater, the discrepancy in specific areal capacitance between the
417 devices is reduced, and comparable values are obtained at $50 \text{ } \mu\text{A/cm}^2$. Specific areal energy
418 achieved maximum values of $0.22 \text{ } \mu\text{Wh/cm}^2$ in TiO_2 -LSGO MSCs, at $5 \text{ } \mu\text{A/cm}^2$ (specific
419 areal energy values at each current density are reported in Figure S7). Specific areal energy
420 vs specific areal power is shown in a Ragone plot in Figure 8b. Higher specific areal energy
421 is generally achieved in TiO_2 -LSGO devices, while specific areal power is comparable in
422 both LSGO and TiO_2 -LSGO devices.

423 Remarkable cycling stability is achieved in TiO_2 -LSGO MSCs. The capacitance retentions
424 over 3000 cycles are compared in Figure 8c. TiO_2 -LSGO MSCs show an 81% retention of
425 the initial specific areal capacitance, showing a better overall trend than LSGO MSCs value
426 (72%). Fluctuations observed in the LSGO devices are related to the low current level, close
427 to the instrument sensitivity and more affected by noise. To compare TiO_2 -LSGO and LSGO
428 MSCs with a comparable specific areal current, the current level for LSGO is lower due to
429 the smaller mass of the active material of the device. The mean Coulombic efficiency over
430 3000 cycles is $>98\%$ for both MSCs (Figure S8). The energy efficiency after 3000 cycle is
431 about 70% (Figure S8).

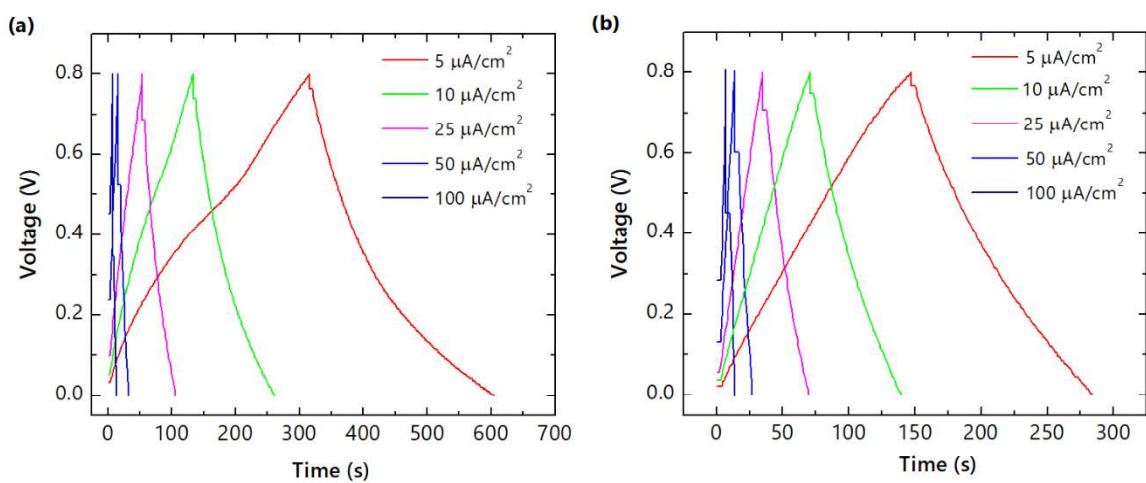
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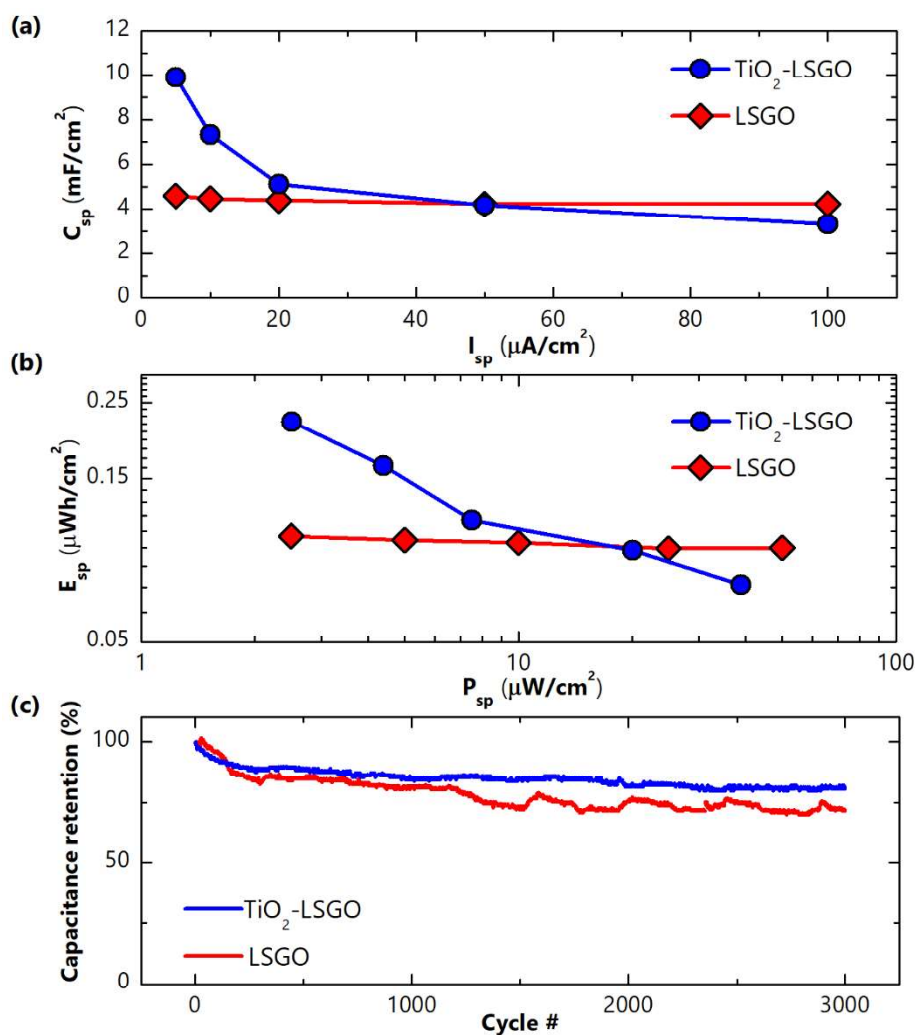
434 **Figure 6.** Cyclic voltammetry curves of laser-scribed MSCs with PVA/H₃PO₄ gel electrolyte: (a)
 435 TiO₂-LSGO and (b) LSGO curves at different scan rates; (c) TiO₂-LSGO and LSGO curves at the rate
 436 of 1 mV/s.

437



438

439 **Figure 7.** Galvanostatic charge and discharge curves at different specific areal currents of (a)
 440 TiO₂-LSGO and (b) LSGO MSCs with PVA/H₃PO₄ gel electrolyte.



441

442 **Figure 8.** (a) Specific areal capacitance and (b) Ragone plot achieved for TiO₂-LSGO and LSGO
 443 MSCs with PVA/H₃PO₄ gel electrolyte at different specific areal currents. Values are averaged on 10
 444 cycles at each specific areal current. (c) Capacitance retention over 3000 charge and discharge cycles
 445 at 5 μ A/cm².

446

447 The results on MSCs with PVA/H₂SO₄ hydrogel polymer electrolyte are discussed in the
 448 Supplementary Material and shown in Figures S9-S14. Similar electrochemical behaviour has
 449 been observed in the MSCs, as for the PVA/H₃PO₄ hydrogel electrolyte. The increase in the
 450 performance has been confirmed for TiO₂-LSGO MSCs, compared to LSGO MSCs (highest
 451 specific areal capacitance amounting at 6.8 mF/cm² and 5.6 mF/cm² at a current density of 5
 452 μ A/cm² for TiO₂-LSGO and LSGO, respectively). A remarkable cycling stability has been
 453 achieved also in PVA/H₂SO₄ devices (capacitance retention >80% after 3000 cycles).

454 4. DISCUSSION

455 The electrochemical results on TiO₂-LSGO and LSGO MSCs show an increase in the
456 performance in the presence of anatase TiO₂ nanoparticles in the electrodes, compared to the
457 LSGO devices. The enhancement is achieved for both the hydrogel polymer electrolytes
458 tested, based on PVA/H₃PO₄ and PVA/H₂SO₄.

459 In LSGO devices, a typical EDLC behaviour is observed, both from the rectangular shape of
460 CV curves and from the linear voltage dependence on time in the GCD curves. In TiO₂-
461 LSGO devices, both capacitive and pseudocapacitive effects are achieved. Anatase
462 nanoparticles are expected to introduce redox contributions in the charge storage mechanism
463 [41,42]. This effect is here confirmed both in the cyclic voltammetry curves and from the
464 galvanostatic charge and discharge measurements. In CV curves, the integral area is enlarged
465 in TiO₂-LSGO. In addition, at low scan rates (Figure 6c), redox peaks contributing to the
466 increase in specific areal capacitance are also observed in MSCs with both the electrolytes.
467 Regarding GCD investigation, the higher specific areal capacitance is confirmed by the slope
468 of galvanostatic curves. Specific areal energy is higher than that in LSGO devices, especially
469 at low current density, as observed for the specific areal capacitance. Remarkably, the TiO₂-
470 LSGO devices exhibit excellent cycling stability in retaining the specific areal capacitance for
471 more than 3000 cycles.

472 TiO₂ in anatase phase has been reported to lead to a higher increase in capacitance compared
473 to the other TiO₂ polymorphs, i.e. rutile, which is instead considered as a better source of
474 cycle stability in supercapacitors [41]. Here, as TiO₂ nanoparticles consist of anatase, a good
475 specific areal capacitance is proved and a great stability is additionally achieved.

476 Regarding the hydrogel polymer electrolytes, good performance has been observed with two
477 different electrolytes, confirming the appropriate use of electrolytes based on acidic

478 conductive substances. It has been proved that a quick diffusion of H^+ from the electrolytes
479 (here, from H_3PO_4 and H_2SO_4 solutions) can easily occur into graphene-based electrodes
480 pores [5]. Comparing the gel electrolytes, the PVA/ H_3PO_4 -based TiO_2 -LSGO micro-
481 supercapacitors give rise to an overall higher improvement in the electrochemical
482 performance than PVA/ H_2SO_4 -based TiO_2 -LSGO devices.

483 It is well known that transition metal oxides, such as TiO_2 , can introduce redox effects in the
484 charge storage mechanism, achieving a higher amount of charge stored in supercapacitors.
485 The EDLC-like behaviour can be combined to the redox contribution [22,41,64,65]. In TiO_2 ,
486 the contribution to the charge storage can be ascribed to two synergic mechanisms. The first
487 consists of the intercalation and de-intercalation of cations from the electrolyte (H^+ in the
488 electrolytes tested here) into the electrode, occurring during the charge and the discharge of
489 the supercapacitor, while the second one involves surface adsorption, according to [41]:



491 Both mechanisms are reported to determine the change in the oxidation state of Ti, from Ti^{4+}
492 to Ti^{3+} with reduction and oxidation reactions, as confirmed from redox peaks in cyclic
493 voltammetry curves in three-electrode cell arrangement (Figures S5 and S9). This process is
494 likely to occur only in one of the two electrodes of the MSC, typically the negatively
495 polarised one (the behaviour of the other electrode is assumed to be purely capacitive), and
496 should not depend on the electrolyte used, as far as acidic electrolytes are concerned.

497 The higher performance achieved with the PVA/ H_3PO_4 -based electrolyte can be ascribed to
498 the larger amount of available H^+ ions than in PVA/ H_2SO_4 -based one, keeping the same
499 concentration [66]. In addition, the solvated ionic radius of $(PO_4)^{3-}$ is slightly smaller than
500 that of $(SO_4)^{2-}$, facilitating its insertion in the porous cavities of LSGO [67]. Furthermore,

501 ionic conductivity of H₃PO₄ aqueous electrolyte is higher than that of H₂SO₄ one, being
502 beneficial for the device performance [68]. The synergistic effect of these factors is expected
503 to contribute to a higher electrochemical performance in PVA/H₃PO₄-based MSCs. Overall,
504 the results on TiO₂-LSGO combined material, consisting of a widespread distribution of
505 anatase TiO₂ nanoparticles over graphene-based material, show competitive properties
506 compared to other graphene-based electrodes (Table S4, Figures S15 and S16) and
507 demonstrate the remarkable electrochemical performance of the MSCs.

508

509 5. CONCLUSION

510 In summary, the production of the TiO₂-LSGO combined material has been successfully
511 achieved through the one-pot synthesis of TiO₂ anatase nanoparticles onto Laser-Scribed
512 Graphite Oxide by the LightScribe[®] technique, using a low-cost and scalable method. The
513 local increase in temperature as a result of the absorption of the DVD burner infrared laser
514 radiation by GO promotes both the nanoparticles crystallization and the conversion of GO
515 into graphene-based material. An extensive spread of anatase NPs has been obtained onto the
516 porous LSGO surface.

517 The TiO₂-LSGO combined material, arranged into interdigitated patterns obtained by the
518 LightScribe[®] process, has been used as electrode material of planar MSCs, which have been
519 tested with two hydrogel polymer electrolytes, based on PVA/H₃PO₄ and PVA/H₂SO₄,
520 respectively. Nanocrystalline TiO₂ combined with LSGO gives rise to a considerable increase
521 in the electrochemical performance, compared to the pristine LSGO. The enhanced results
522 obtained with the TiO₂-LSGO MSCs have been ascribed to the combined behaviour of the
523 electrode material, including faradic effects due to redox contributions (arising from TiO₂
524 NPs) and capacitive storage mechanisms (arising from LSGO). Specific areal capacitance up

525 to 9.9 and 6.8 mF/cm² has been achieved in TiO₂-LSGO MSCs with PVA/H₃PO₄ and
526 PVA/H₂SO₄ polymer hydrogel electrolytes, respectively. Improvement in the specific areal
527 energy has also been obtained in TiO₂-LSGO MSCs (0.22 μWh/cm² and of 0.15 μWh/cm² for
528 the two electrolytes, respectively). Cycling stability has been maintained for thousands of
529 cycles.

530 The impressive electrochemical performance of TiO₂-LSGO devices reveals that the one-pot
531 formation of TiO₂ nanoparticles onto laser-scribed graphene structures by the LightScribe®
532 technique can be a successful strategy to produce cost-effective, low-toxicity and large-scale
533 micro-supercapacitors with competitive electrochemical performance for energy storage.

534

535 CREDIT AUTHORSHIP CONTRIBUTION STATEMENT

536 **Laura Fornasini:** writing – original draft, validation, formal analysis, investigation,
537 visualization, **Silvio Scaravonati:** validation, formal analysis, investigation, visualization,
538 **Giacomo Magnani:** validation, investigation, **Alberto Morengi:** investigation, **Michele**
539 **Sidoli:** investigation, **Danilo Bersani:** conceptualization, supervision, **Giovanni Bertoni:**
540 investigation, formal analysis, **Lucrezia Aversa:** investigation, formal analysis, **Roberto**
541 **Verucchi:** investigation, formal analysis, **Mauro Riccò:** conceptualization, **Pier Paolo**
542 **Lottici:** visualization, **Daniele Pontiroli:** conceptualization, methodology, writing – original
543 draft, visualization, supervision, project administration.

544

545 DECLARATION OF COMPETING INTEREST

546 The authors declare that they have no known competing financial interests or personal
547 relationships that could have appeared to influence the work reported in this paper.

548

549 APPENDIX A. SUPPLEMENTARY MATERIAL

550 Supplementary Material includes micro-structure of the laser-scribed material; specific
551 surface area of LSGO; electrical resistance and conductivity of GO and LSGO; EEL
552 spectroscopy; EDS analysis; powder X-ray diffraction; XPS lineshape analysis on GO and
553 LSGO; comparison among different micro-supercapacitors with laser-scribed graphene-based
554 electrodes; supplementary electrochemical results of TiO₂-LSGO and LSGO MSCs with
555 PVA/H₃PO₄-based electrolyte; three-electrode cell cyclic voltammetry; electrochemical
556 results of TiO₂-LSGO and LSGO MSCs with PVA/H₂SO₄-based electrolyte; Ragone plot
557 comparison among this work MSCs and other graphene-based energy storage devices.

558

559

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