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Original

Fast Rare Events in Exit Times Distributions of Jump Processes / Vezzani, A.; Burioni, R. - In: PHYSICAL REVIEW LETTERS. - ISSN 0031-9007. - 132:18(2024). [10.1103/PhysRevLett.132.187101]

Availability: This version is available at: 11381/2991833 since: 2025-01-14T13:47:01Z

Publisher: American Physical Society

Published DOI:10.1103/PhysRevLett.132.187101

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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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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 light. Enhanced electrochemical performance of devices has been achieved thanks to the 23 24 combination of faradic surface reactions, arising from metal oxide nanoparticles, with the conventional electrochemical double layer capacitance, arising from porous graphene. 25 26 Micro-supercapacitors, consisting of TiO₂-graphene electrodes, have been tested by 27 investigating two hydrogel polymer electrolytes, based on polyvinyl alcohol/H₃PO₄ and polyvinyl alcohol/H₂SO₄, respectively. Specific areal capacitance up to 9.9 mF/cm² are 28 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 achieved specific areal energy and specific areal power of 0.22 μ Wh/cm² and 39 μ W/cm², 31 along with a cyclability greater than 3000 cycles. These high-performance results suggest 32 33 laser-scribed TiO₂-graphene nanostructures as remarkable candidates in micro-34 supercapacitors for environment-friendly, large-scale and low-cost applications.

36 KEYWORDS

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

40 1. INTRODUCTION

The increasing demand of micro power sources and small-scale energy storage devices has recently moved the attention to miniaturization. Micro power modules are required in devices such as sensors, portable and wearable electronics, radio frequency identification (RFID), or biomedical implants. These systems need self-powered wireless devices, which can work independently of an external power source. Supercapacitors (also called electrochemical double layer capacitors, EDLCs) can satisfy this requirement, thanks to their high specific 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 micro-supercapacitors (MSCs), employed as power sources or energy storage harvesting 49 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].

As in conventional supercapacitors, essential features of the electrodes are high specific
surface area with a hierarchical pore structure and good electrical conductivity [4,9–12].
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 in MSCs [12–14]. Furthermore, combining graphene with electroactive species is a promising 65 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 conductive. Infrared lasers of DVD burner drives, using the LightScribe® technology, are 83 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

systems with graphene-based materials. Redox effects are obtained from iron oxide, cobalt oxide, molybdenum oxide [17], molybdenum disulfide [38] or titanium dioxide nanoparticles [39]. Among them, titanium dioxide (TiO₂), besides providing faradic effects, is considered a promising source to produce composite materials with graphene, thanks to its high thermal 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 defective graphene structure. The LightScribe[®] writing process both converts suitable 96 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 promoting a combined material [22,39,41-44]. Our obtained composite nanostructure is 106 107 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.

High-performance MSCs have been produced with interdigitated electrodes and hydrogel polymer electrolytes in a planar configuration. Interdigitated patterns have been achieved on 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 graphenebased devices. Two hydrogel polymers based on polyvinyl alcohol (PVA)/H₃PO₄ and 118 119 polyvinyl alcohol (PVA)/H₂SO₄ have been compared, achieving high-performance with specific areal capacitance up to 9.9 and 6.8 mF/cm², respectively. TiO₂ NPs decorating 120 LSGO structures (henceforth called TiO₂-LSGO) obtained with the LightScribe[®] technology 121 122 can be encouraged as remarkable material in MSCs for large-scale and low-cost production.

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4 2. MATERIALS AND METHODS

125 2.1 Production of laser-scribed micro-supercapacitors

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

Graphite oxide and titanium(IV) isopropoxide have been used as precursor materials to be converted by the laser irradiation. GO obtained with Hummers' method [45] has been employed, due to its good solubility in water. Water as solvent in the preparation of the laserscribed disc has been preferred to toxic, high-boiling temperature, organic solvents, typically employed to suspend graphene. An aqueous dispersion (2 mg/ml) of GO (GO-V50, Standard 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 (corresponding to a mass ratio of 0.8:1) [46]. The dispersion has been further sonicated for 30 138 139 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 µm thick. The TTIP-GO-coated PET disc, glued to the surface of a LightScribe[®] DVD disc, 143 has been subjected to the LightScribe[®] process by the DVD burner infrared laser (λ =788 nm). 144 145 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 in the device. The borders of the interdigitated area have been covered with Teflon[®] tape, to 150 151 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 surface of the interdigitated area and let it dry overnight to eliminate water excess. To 157 158 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

The micro-structure of TiO2-LSGO material has been examined by scanning transmission 161 162 electron microscopy (STEM) and high-resolution imaging (HRTEM) using a field emission JEM-2200FS microscope (JEOL Ltd., Japan), equipped with a Schottky gun working at 200 163 164 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 copper grids. Simulation of the HRTEM image has been performed with the JEMS software 168 169 [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,

Tokyo, Japan), using a 50x objective, in a backscattering geometry. The 473.1 nm line of a frequency-doubled Nd:YAG laser has been used as excitation, with a spectral resolution of $\sim 2 \text{ cm}^{-1}$. To avoid heating effects, density filters have been used to reduce the laser power on the sample. The analysis has been performed on the TiO₂-LSGO material of the interdigitated patterns on the laser-scribed disc. Acquisitions have been recorded with typical exposure of 20-60 s, repeated 6 times for each measurement. The data analysis has been performed by the *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 $_{\alpha}$ 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 4f7/2 core level signal at 84.0 eV, acquired from a sputtered Au 197 foil.

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

The specific surface area (SSA) of LSGO material has been estimated by the physisorption of a common dye, methylene blue (MB), from the porous material, with UV-Visible spectrophotometry [37]. After a proper calibration to correlate the absorbance and the dye concentration, the amount of MB absorbed by LSGO has been evaluated. To perform the analysis, the material (\sim 3 mg) has been removed from the laser-scribed surface obtained by the LightScribe[®] process, dispersed in a MB aqueous solution, whose initial concentration was known, and stirred overnight. After centrifugation, the absorbance of the surnatant has
been measured using a Jasco V-550 UV-Visible spectrophotometer to evaluate the variation
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 (v), in order to highlight the 221 faradic contribution in the presence of redox peaks. It is known that for a capacitive process the current is proportional to v, while for faradic reactions it is proportional to $v^{1/2}$ [50,51]. 222

223 Two electrode CV for the electrochemical characterization of the devices has been carried out using either PVA/H₃PO₄ and PVA/H₂SO₄ hydrogel electrolytes, applying a linear potential 224 225 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 μ A/cm². Specific areal capacitance C_{SP} (mF/cm²) of the material has been calculated from the total capacitance *C* of the MSC, using the footprint area A_{AM} of the active material of both electrodes:

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

234 Specific areal energy E_{SP} (μ Wh/cm²) of the electrode material in the MSC has been evaluated 235 by:

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

where U_{max} is the maximum region of electrochemical stability [52]. For each discharge cycle, the specific areal power P_{SP} has been obtained as the ratio between the specific areal energy (E_{SP}) and the total discharge time. The capacitance retention of the devices has been evaluated as the ratio of the specific areal capacitance at each cycle to the specific areal capacitance achieved in the first one, over at least 3000 cycles at 5 μ A/cm². For each cycle, the Coulombic efficiency η_C is given by:

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

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 μ A/cm²,

given by the ratio between the energy during discharge and the energy during charge [53].

247

MSCs, either TiO₂-LSGO and LSGO, have been obtained by the LightScribe[®] technique in the planar configuration [27]. The scheme of the one-pot synthesis of TiO₂-LSGO and the

- 251 production of MSCs has been sketched in Figure 1 and the picture of a section of the laser252 scribed disc is shown in the inset of Figure 1.
- A detail of the micro-structure of the laser-scribed patterns is shown in the SupplementaryMaterial in Figure S1.



256

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

260

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

263
$$Ti(OR)_m + (m-x)H_2O \to Ti(OH)_{m-x}(OR)_x + (m-x)R(OH)$$

where *R* is the $CH(CH_3)_2$ group, replaced with hydroxyl group during the hydrolysis reaction. Then, the hydroxyl groups condense with each other, eliminating water or isopropanol 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 temperatures (>10³ °C), which promote TiO₂ crystallization. Besides, the temperature 269 270 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 σ ~1.1 S/cm (Table S1 in Supplementary Material).



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



Figure 3. (a) HRTEM image of a TiO_2 nanoparticle of ~6 nm diameter; (b) FFT of the HRTEM image; (c). Image simulation from TiO_2 anatase at 6 nm thickness. In the model, Ti atoms are lightblue and O atoms are red. The image contrast is in good agreement with the experiment, confirming the anatase (tetragonal) structure of the nanoparticle. The (200) and (004) planes are highlighted in (a) for clarity. The tetragonal cell is highlighted in purple in (a) and (c).

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 $Ti-L_{2,3}$ and O-K edges (reported in the Figure S3) agree with the spectra from nanostructured anatase 298

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

Anatase is confirmed as the main TiO_2 crystalline phase also by PXRD analysis, with its most intense (101) reflection, occurring at 20=25.3°. PXRD results are shown in the Supplementary Material (Figure S4).

The elemental composition of TiO₂-LSGO material performed by EDS analysis shows that the Ti:C atomic ratio is 1:6, in good agreement with the expected molar ratio (TiO₂:C=1:8) (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-LSGO, as shown in Figure 4. The presence of anatase TiO_2 is confirmed by the main E_g 310 anatase vibrational mode in the Raman spectrum at ~155 cm⁻¹, expanded in the inset of 311 312 Figure 4. The peak is shifted and broadened compared to the crystalline anatase signal, as expected for nanoparticle sizes under ~20 nm. According to the phonon confinement effect, 313 in the case of finite size crystals, the main anatase peak is a convolution of many 314 contributions, following the phonon dispersion curve, instead of a single sharp Lorentzian, as 315 for ideal crystalline anatase. The observed peak position at ~155 cm⁻¹, shifted from the 143 316 cm⁻¹ of the crystalline reference, suggests the presence of ~5 nm size NPs, as predicted by the 317 318 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 materials, along with the anatase feature (Figure 4). The G band, related to the E_{2g} phonon 320 mode of the sp² domains in graphitic materials, and the D band, arising from structural 321

- defects in disordered samples, are observed at ~1370 cm⁻¹ and ~1600 cm⁻¹, respectively [58].
- 323 The broadening of D and G band compared to ordered crystalline materials confirms the
- highly defective structure of LSGO [59].



Figure 4. Raman spectrum of TiO_2 -LSGO with the most intense anatase E_g vibrational mode (A) and characteristic graphene-based materials bands (D and G). *Inset:* the main anatase peak in TiO₂-LSGO spectrum (in blue) is expanded and compared with the reference crystalline anatase spectrum (in 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 and contaminants (Table S3). O1s core level (Figure 5b) shows the corresponding oxidized
carbon species. The laser treatment completely changes the surface chemical properties, as
shown in LSGO spectra. The C/O stoichiometry ratio increase from 2.3 to 15.2, suggesting a
significant oxygen loss. In C1s core level, all oxygen related peaks decrease in intensity and
the graphene main component at 284.4 eV is sharper (Table S3). O1s core level (Figure 5b)
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 nanoparticles are shown in Figure 5c and 5d. Charge shift is present for GO samples and 346 suppressed for LSGO, in which the Ti2p_{3/2} peak position is 459.2 eV compatible with Ti⁴⁺ 347 348 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 stoichiometric TiO₂ nanoparticles in both samples. 352



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

354

The residual oxygen atoms bonded to carbon network after the laser treatment, as detected by XPS analysis, are expected to contribute to the lower value of conductivity of LSGO as compared to pure graphene. In addition, the presence of defects in LSGO, related to its wrinkled structure, as observed in STEM image in Figure 2a, contributes to limit the electrical conductivity. On the other hand, the defective structure of LSGO is beneficial for the growth of small sized TiO₂ nanoparticles. The simultaneous crystallization of TiO₂ NPs and conversion of GO into LSGO have been promoted by the local increase in temperature,
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.

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

The electrochemical behaviour of the TiO_2 -LSGO composite material consists of two contributions: the first one has a capacitive origin, typical of EDLCs and it is due to the electrostatic charge accumulation at the electrode-electrolyte interface on porous conductive electrodes, as expected for graphene-based materials. The second one arises from surface faradic processes and originates from the electron transfer, occurring during charge and discharge cycles with the redox-active TiO_2 NPs [62].

The results on MSCs with PVA/H₃PO₄ hydrogel polymer electrolyte are shown in Figures 6, 7 and 8. Both EDLC and faradic effects are observable in the CV curves of TiO₂-LSGO MSCs (Figure 6a). Faradic contribution has been confirmed by the three-electrode cell arrangement CV results, shown in the Supplementary Material (Figures S5 and S6) [51]. In 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 μ A/cm²), suggesting that also LSGO can give a contribution, while small, to the faradic behaviour. Residual oxygen (not removed by the LightScribe[®] 405 process) in carbonyl functional groups reacts with H⁺ of the electrolyte in acidic solutions 406 [62,63]. In TiO₂-LSGO MSCs, charge and discharge curves show a pronounced deviation 407 408 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/cm² at a current density of 5 μ A/cm², more than twice the 413 value for LSGO MSCs (4.6 mF/cm²), 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).

As current density is greater, the discrepancy in specific areal capacitance between the devices is reduced, and comparable values are obtained at 50 μ A/cm². Specific areal energy achieved maximum values of 0.22 μ Wh/cm² in TiO₂-LSGO MSCs, at 5 μ A/cm² (specific areal energy values at each current density are reported in Figure S7). Specific areal energy vs specific areal power is shown in a Ragone plot in Figure 8b. Higher specific areal energy is generally achieved in TiO₂-LSGO devices, while specific areal power is comparable in both LSGO and TiO₂-LSGO devices.

423 Remarkable cycling stability is achieved in TiO₂-LSGO MSCs. The capacitance retentions 424 over 3000 cycles are compared in Figure 8c. TiO2-LSGO MSCs show an 81% retention of 425 the initial specific areal capacitance, showing a better overall trend than LSGO MSCs value (72%). Fluctuations observed in the LSGO devices are related to the low current level, close 426 427 to the instrument sensitivity and more affected by noise. To compare TiO₂-LSGO and LSGO MSCs with a comparable specific areal current, the current level for LSGO is lower due to 428 429 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).



433

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



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



442 **Figure 8. (a)** Specific areal capacitance and **(b)** Ragone plot achieved for TiO₂-LSGO and LSGO 443 MSCs with PVA/H_3PO_4 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

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

The electrochemical results on TiO_2 -LSGO and LSGO MSCs show an increase in the performance in the presence of anatase TiO_2 nanoparticles in the electrodes, compared to the LSGO devices. The enhancement is achieved for both the hydrogel polymer electrolytes 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 TiO_2 in anatase phase has been reported to lead to a higher increase in capacitance compared 473 to the other TiO_2 polymorphs, i.e. rutile, which is instead considered as a better source of 474 cycle stability in supercapacitors [41]. Here, as TiO_2 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 two477 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 H₃PO₄ and H₂SO₄ solutions) can easily occur into graphene-based electrodes
480 pores [5]. Comparing the gel electrolytes, the PVA/H₃PO₄-based TiO₂-LSGO micro481 supercapacitors give rise to an overall higher improvement in the electrochemical
482 performance than PVA/H₂SO₄-based TiO₂-LSGO devices.

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

490
$$(TiO_2)_{surface} + H_3O^+ + e^- \leftrightarrow (TiO_2^-H_3O^+)_{surface}$$

Both mechanisms are reported to determine the change in the oxidation state of Ti, from Ti⁴⁺ to Ti³⁺ with reduction and oxidation reactions, as confirmed from redox peaks in cyclic voltammetry curves in three-electrode cell arrangement (Figures S5 and S9). This process is likely to occur only in one of the two electrodes of the MSC, typically the negatively polarised one (the behaviour of the other electrode is assumed to be purely capacitive), and should not depend on the electrolyte used, as far as acidic electrolytes are concerned.

The higher performance achieved with the PVA/H₃PO₄-based electrolyte can be ascribed to the larger amount of available H⁺ ions than in PVA/H₂SO₄-based one, keeping the same concentration [66]. In addition, the solvated ionic radius of $(PO_4)^{3-}$ is slightly smaller than that of $(SO_4)^{2-}$, facilitating its insertion in the porous cavities of LSGO [67]. Furthermore, ionic conductivity of H_3PO_4 aqueous electrolyte is higher than that of H_2SO_4 one, being beneficial for the device performance [68]. The synergistic effect of these factors is expected to contribute to a higher electrochemical performance in PVA/H₃PO₄-based MSCs. Overall, the results on TiO₂-LSGO combined material, consisting of a widespread distribution of anatase TiO₂ nanoparticles over graphene-based material, show competitive properties compared to other graphene-based electrodes (Table S4, Figures S15 and S16) and demonstrate the remarkable electrochemical performance of the MSCs.

508

509 5. CONCLUSION

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

517 The TiO₂-LSGO combined material, arranged into interdigitated patterns obtained by the LightScribe[®] process, has been used as electrode material of planar MSCs, which have been 518 519 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 to 9.9 and 6.8 mF/cm² has been achieved in TiO₂-LSGO MSCs with PVA/H₃PO₄ and PVA/H₂SO₄ polymer hydrogel electrolytes, respectively. Improvement in the specific areal energy has also been obtained in TiO₂-LSGO MSCs (0.22 μ Wh/cm² and of 0.15 μ Wh/cm² for the two electrolytes, respectively). Cycling stability has been maintained for thousands of cycles.

The impressive electrochemical performance of TiO_2 -LSGO devices reveals that the one-pot formation of TiO_2 nanoparticles onto laser-scribed graphene structures by the LightScribe[®] technique can be a successful strategy to produce cost-effective, low-toxicity and large-scale 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, visualization, Silvio Scaravonati: validation, formal analysis, investigation, visualization, 537 538 Giacomo Magnani: validation, investigation, Alberto Morenghi: 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.

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.

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