

A perspective on laser-induced graphene for micro-supercapacitor application

Original

A perspective on laser-induced graphene for micro-supercapacitor application / Zaccagnini, P.; Lamberti, A.. - In: APPLIED PHYSICS LETTERS. - ISSN 0003-6951. - ELETTRONICO. - 120:10(2022), p. 100501. [10.1063/5.0078707]

Availability:

This version is available at: 11583/2965742 since: 2022-06-07T13:24:12Z

Publisher:

American Institute of Physics Inc.

Published

DOI:10.1063/5.0078707

Terms of use:

This article is made available under terms and conditions as specified in the corresponding bibliographic description in the repository

Publisher copyright

(Article begins on next page)

A perspective on laser-induced graphene for micro-supercapacitor application

Cite as: Appl. Phys. Lett. **120**, 100501 (2022); <https://doi.org/10.1063/5.0078707>

Submitted: 15 November 2021 • Accepted: 01 March 2022 • Published Online: 11 March 2022

 Pietro Zaccagnini and  Andrea Lamberti



View Online



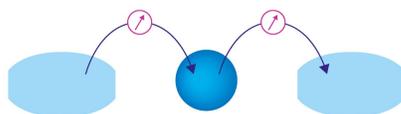
Export Citation



CrossMark

Webinar

Interfaces: how they make or break a nanodevice



March 29th – Register now



Zurich Instruments



A perspective on laser-induced graphene for micro-supercapacitor application

Cite as: Appl. Phys. Lett. **120**, 100501 (2022); doi: [10.1063/5.0078707](https://doi.org/10.1063/5.0078707)

Submitted: 15 November 2021 · Accepted: 1 March 2022 ·

Published Online: 11 March 2022



View Online



Export Citation



CrossMark

Pietro Zaccagnini^{1,2}  and Andrea Lamberti^{1,2,a)} 

AFFILIATIONS

¹Politecnico di Torino, Dipartimento di Scienza Applicata e Tecnologia (DISAT), Corso Duca Degli Abruzzi, 24, 10129 Torino, Italy

²Istituto Italiano di Tecnologia, Center for Sustainable Future Technologies, Via Livorno 60, 10140 Torino, Italy

^{a)}Author to whom correspondence should be addressed: andrea.lamberti@polito.it

ABSTRACT

Due to its unique features, laser-induced graphene (LIG) can be considered as disruptive technology for creating a few-layer graphene-based film that received much attention in the field of flexible electronics. Among all, energy storage, catalysis, sensing, and separation are the main applications that have been investigated in recent years with large improvements in the respective device performance. In particular, miniaturized supercapacitor—usually called a micro-supercapacitor (μ SC)—is the most investigated field in which LIG can strongly provide outstanding results concerning the state of the art simplification of the fabrication procedure and intrinsically allowing the flexibility of the device. However, many open points still limit the possible full exploitation of this technology in the energy storage sector. This paper provides a concise overview of the LIG application in μ SCs suggesting where the community should direct efforts to enhance the results together with associated challenges.

Published under an exclusive license by AIP Publishing. <https://doi.org/10.1063/5.0078707>

The discovery of graphene by mechanical exfoliation in 2004 has had a great impact in the fields of chemistry, physics, and materials science due to its unique structure and excellent properties such as great electrical and thermal conductivity and flawless quantum tunneling.¹ Chemical vapor deposition (CVD), crystal epitaxy on insulating single crystal silicon carbide (SiC) surfaces, and oxidation-reduction processes have allowed significant progress to be made in the creation of single-layer graphene.² However, cost reduction and environmental impact still need to be addressed together with the issue of scalability.³ In this regard, the so-called family of few-layers graphene (FLG) materials has been under the spotlight through the easier synthesis procedure.⁴ This kind of material is often derived from wet chemical routes that allow faster processes with high yield. Moreover, in most cases, FLGs result in porous 3D arrangements, which are highly desirable in the fields of energy storage, catalysis, sensing, and separation.⁵

Laser ablation of polymers has been reported since 1982. It is possible to move from surface modification to material ablation by tuning laser parameters, i.e., by adjusting the dose. In fact, at low laser doses, it is possible to slightly alter rugosity impinging on properties such as wettability and adhesion. By increasing the dose, it is possible to obtain conversion and ablation. The conversion of polymers to a different solid-state does not always occur due to the chemistry of the polymer. There is no apparent agreement in the literature as to

whether the process is photothermal or photochemical, although a photothermal model has been developed for polyimide (PI). Some model-based studies suggest that a photothermal reaction is the most likely since the temperature developed with laser pulses in short exposure times provides enough energy to let volatile species leave the monomer, which rearranges itself in a different aggregate.⁶

In 2014, Lin *et al.* reported for the first time the production of porous 3D multilayer graphene by direct laser writing of a PI substrate.⁷ The formation of LIG was demonstrated relying on a photothermal process in which sp³ carbon atoms in the polymer rearrange in an sp² structure. It is possible to obtain a porous structure composed of FLG walls thanks to the evolution of volatile compounds deriving from broken atomic bonds.

Simple design, environmental friendliness, programmable compositions, and controllable morphologies are among the main benefits of LIG over traditional graphene. LIG can provide good porosity, flexibility, and mechanical toughness as well as outstanding electrical and thermal conductivity.⁸ All these advantages of LIG open up a smart approach to manufacturing graphene-based energy storage devices (ESDs). Because of the increased surface area, the material proves to be suitable for supercapacitors (SCs), where the storage mechanism is limited to the electrode–electrolyte interface without any bulk contribution either in the solid or liquid phase. In this context, SCs are

divided into two categories: electrical double-layer capacitors (EDLCs) and pseudocapacitors. The difference between the two categories is determined by their storage mechanism. In the case of EDLCs, the accumulation occurs under electrostatic interactions of ions in the electrolyte with electronic charges, and in pseudocapacitors, fast and reversible redox reactions are the main contributors to capacitance.

SCs are electrochemical ESDs complementary to rechargeable batteries in terms of energy and power densities.⁹ Moreover, they exhibit an extremely long lifetime, as no intercalation is occurring, higher safety, and a wide operative temperature range. To satisfy the power requirement of the portable electronics and to allow a higher degree of integration with microelectronics, research has pushed for SCs miniaturization resulting in the so-called micro-supercapacitors (μ SCs).¹⁰

Traditionally, μ SCs were fabricated starting from microtechnology approaches such as silicon micromachining and thin film deposition and patterning. The interdigitated structure of the electrodes allows for a planar design, in which traditional SC materials can also be combined to achieve a symmetrical or asymmetrical configuration.¹¹ The direct laser writing approach introduced an important leap forward since the common microtechnology methods require long

and complex processes. LIG can push this advancement further by greatly simplifying the manufacturing steps and introducing a dependence on the laser parameters of the electrochemical performance of the electrodes.¹² However, some issues are still open in the optimization of the LIG electrodes for μ SC fabrication. The main problems result from the impact of the laser parameters on the LIG properties, the restricted mechanical properties of PI, the relatively high resistance, the relatively low surface area of LIG compared to common SC materials, and the design of the μ SC itself.

The paragraphs that follow review the recent outcomes obtained by this research team on LIG and provide Perspectives for improvement of LIG-based devices. Figure 1 shows a diagram of the research focus of this working group.

In the previous work,¹² we showed that by tuning laser parameters it is possible to control the morphology, elemental composition, and electrical properties of LIG. Many morphologies were achieved from a more porous network to needle-like or fiber-shaped LIG.^{12,13} XPS measurements proved that graphitization happens in all morphological cases. Furthermore, the measurements showed that it is possible to control the content of pyrrolic nitrogen, which can cause pseudocapacitance contribution to the material.¹² This is an example

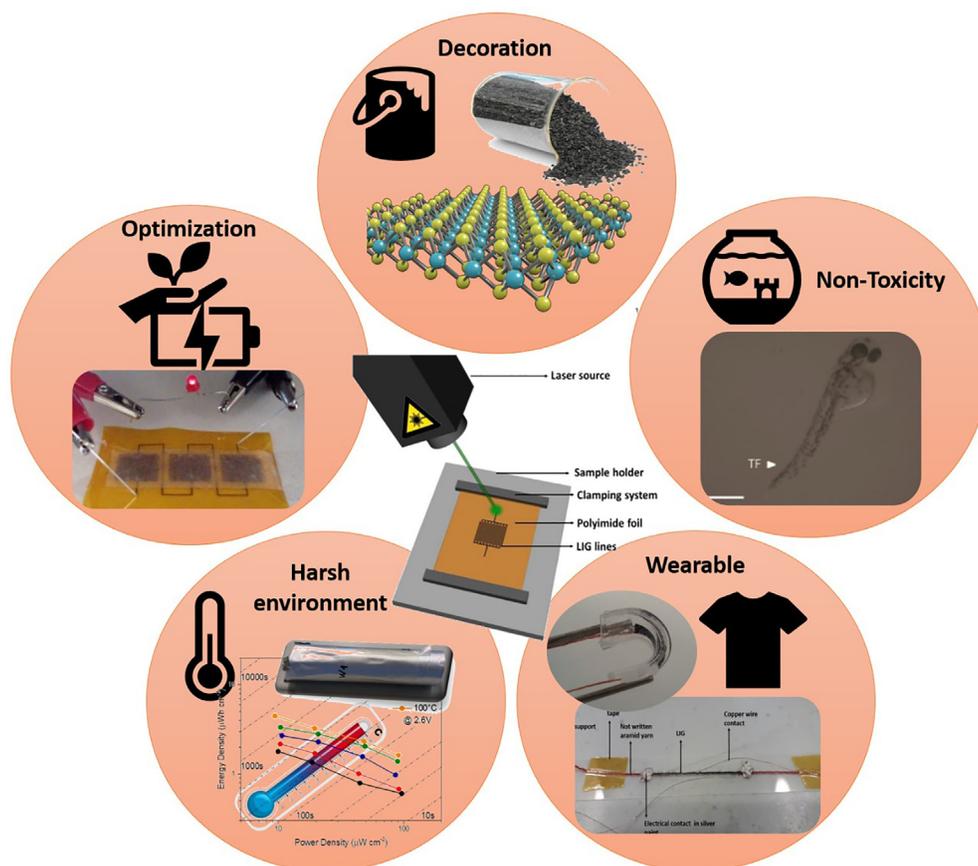


FIG. 1. Optimization strategies and application fields of LIG from the tuning of the laser parameters for sustainable micro-supercapacitors to the decoration with carbon or pseudocapacitive materials to enhance the energy storage performance. From the assessment of biocompatibility for the implantable device to the characteristics of flexibility and resistance to high temperatures that allow the use of LIG for wearable devices and applications in harsh environments.

of the versatility of laser scribing technology in producing electrodes for ESD applications.

Pseudocapacitive materials can provide a fast faradic contribution to capacity. Metal oxides and dichalcogenides with pseudocapacitive properties were used to decorate the surface of LIG to increase its specific capacity.^{14,15} This class of materials presents an electrical response typical of capacitors. This research team developed the one-pot synthesis of a pseudocapacitive LIG-based device. A MoS₂ dispersion was spin-coated on the PI substrate and exposed to laser radiation. The conversion process allowed LIG decoration with MoS₂. XPS measurements confirmed the results of this process since the 2D material features (20–100 nm) were not discernable from LIG features under electron microscopy. Device measurements were performed in an aqueous polymer electrolyte composed of 1M NaCl in a PVP matrix. As a result of its higher storage capabilities, the device also proved that it was able to directly store charges arriving from a harvesting source such as a third-generation solar cell.¹⁵

The increase of the EDL storage mechanism was also investigated by this research team. The deposition of EDLC materials, such as activated carbons, is a challenge for fabrication of μ SCs. This class of materials can be produced on top of compatible substrates via pyrolysis and subsequent chemical activation, although PI does not meet the requirements for such processes. This team proposed a fast process to increase the performance of LIG-based EDLC devices in terms of specific capacitance and energy. An activated carbon (AC) based slurry was prepared in dimethyl sulfoxide (DMSO) together with carbon black (CB) and polyvinylidene fluoride (PVDF). CB and PVDF were exploited to improve, respectively, conductivity and adhesion between LIG and AC particles. The as-prepared active material was loaded on LIG via vacuum infiltration. With this procedure, the performance of the device improved remarkably. To ease the infiltration process, LIG wettability was increased through nitric acid activation.¹⁶ Following this approach, we achieved the highest EDL capacitance obtained so far in μ SCs using LIG electrodes as current collectors.

LIG produced by our workgroup proved to be biocompatible thanks to the zebrafish model. Zebrafish (*Danio rerio*) tests are increasingly used as alternative model systems due to their high-throughput screening. Their convenience is due to the 70% homology with human genes, and they are widely used to test chemical and drug compatibility. Tests on LIG showed that the Zebra fish model had no impact on movement or cardiac activities. This is a remarkable result if compared to nanomaterials such as graphene, graphene oxide (GO), and others, making LIG a suitable candidate for implantable μ SCs and biological applications.¹⁷

Materials and processes for micro and nanofabrication have been optimized for rigid electronics. Flexible and stretchable electronics are emerging classes of devices that aim to achieve conformity and deformability while ideally preserving electrical properties and performance under mechanical deformation. Moreover, the manufacture of micro ESDs requires numerous steps. Despite PI flexibility and its advantages as a widely employed material in electronics, this polymer is not stretchable. In this framework, our research focused on transferring or producing LIG on different substrates that are more stretchable than PI. The objective was to introduce LIG into stretchable electronics and wearable devices. One of the first attempts we developed involved transferring LIG onto polydimethylsiloxane (PDMS). PDMS

is a well-known elastomer, biocompatible, and its modulus of elasticity can be tuned according to the degree of polymerization of the siloxane-based monomers. LIG was transferred to a soft PDMS substrate using the scotch tape-like transferring method. The results were promising since the quasi-solid device cycled in both high bent and stretched conditions.¹⁸

PDMS was also tried as a substrate material for LIG production because of the presence of carbon in the methyl groups. It was possible to convert the substrate into a carbonaceous conductive material, but the yield was low because of the low carbon content. Moreover, the conductivity was not remarkable since also some byproducts, such as silica and silicon carbide particles, were produced during this conversion process. Consequently, we improved the carbon content in the PDMS matrix. Two composite materials were produced: PDMS mixed with powdered PI and PDMS mixed with triethylene glycol (TEG). Both composite materials showed softer mechanical properties compared to PI and could be stretched. Moreover, good adhesive properties were preserved with respect to bare PDMS. The yield of conversion was increased as expected, and the production of a graphene-based material was demonstrated through Raman spectroscopy and transmission electron microscopy (TEM). In both cases, the PDMS conversion into silicon-based particles was lowered, and the material conductivity was increased with respect to LIG produced directly on PDMS. An advantage of this approach is that the thickness of the substrate can be adjusted, i.e., adapted to other substrates to allow the conversion process without causing strong deformations of the substrate. This advantage allowed us to convert the designed areas without any damage to the devices. Both devices were tested under mechanical stress conditions and showed no deviations from their original capacitive behavior. In both cases, LIGs produced were hydrophobic.¹⁹

Another polymeric substrate was studied as a precursor for LIG: sulfonated poly (ether ether ketone) (SPEEK).²⁰ SPEEK is a well-known functional polymer used for the production of ion exchange membranes (IEMs), and its aromatic repeating unit fulfills the requirements for LIG production. It was easily converted to LIG without further processing. XPS, Raman, and TEM analyses demonstrated the effective conversion into an FLG structure. A μ SC was fabricated by exploiting SPEEK as a separator and a solid-state electrolyte. In an aqueous environment, the device showed a remarkable specific capacitance for an exotic polymer differing from PI. In this case, some traces of S doping may have enhanced the capacitive behavior of the device. Future research could use this result as a basis to further investigate functional materials to achieve micro ESDs constituted by a limited number of substances.

Producing LIG-based devices directly on polymeric fibers was investigated with a view to increasing the level of integration of micro-devices into textiles for wearable applications. Aramid yarns were subject to femtosecond pulsed laser radiation. A more focused laser process allowed the preservation of the structural integrity of the yarn while the LIG pattern showed very good conduction properties resulting in device integration directly into weft and warp.²¹

Finally, the applicability of LIG μ SCs in harsh environments, such as high temperatures, was demonstrated. Because of the thermal properties of PI, LIG, and ionic liquids (IL), supercapacitors can be allowed to operate at high temperatures. A device based on 1-butyl-1-methylpyrrolidinium bis(trifluoromethylsulfonyl)imide, [PYR14][TFSI],

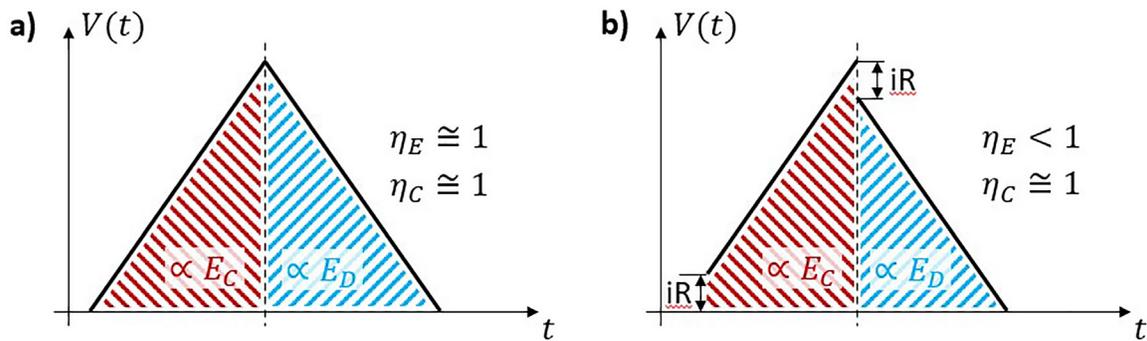


FIG. 2. Energy efficiency interpretation in galvanostatic experiments. In (a), the ideal case of a lossless device with maximized efficiencies. In (b), the effect of losses (iR -drop) on the energy efficiency.

IL was studied at constant voltage up to 100 °C, limited by the thermal stability of the pouch cell packaging material. Device stability was observed, together with an increase in storage performance in terms of specific energy and capacitance.²²

Much work has been carried out to investigate the LIG formation mechanism and the tunability of its properties to enlarge its applicability. However, we believe that research on μ SCs and LIG-based μ SCs should be more focused on the optimization of the architectures to improve the electrochemical performance of the devices. Charge balancing and minimization of Ohmic losses are fundamental strategies to maximize energy and power densities. There is currently no literature on optimization of LIG-based devices that considers charge balancing and Ohmic losses, although some research is available on microfabricated μ SCs.²³ Moreover, parameters like Coulombic efficiency (η_C) and energetic efficiency (η_E) should be provided to better compare literature results, together with capacitance density evaluation and Ragone plot.

Charge balancing is an optimization procedure to let anodes and cathodes operate in their full potential window, allowing the device to exploit the maximum voltage window and, hence, maximizing the energy density.²⁴ Both in the case of symmetrical or asymmetrical electrodes (i.e., a combination of EDLCs or pseudocapacitive materials), anodes and cathodes should be designed with low dissipative properties, that is, low resistive components. Impedance spectroscopy (IS) is fundamental for the direct evaluation of dissipative properties. IS allows the direct evaluation of $\text{Re}\{Z\}$, where Z is the electrochemical impedance, which is responsible for energy losses. However, an indirect evaluation of Ohmic losses can be retrieved by evaluating the energy efficiency. The energy efficiency is the quotient between discharge and charge energies, i.e., $\eta_E = E_d/E_c$. The quantity $1 - \eta_E$ can be shown to be related to the energy losses. A representative interpretation of the energy efficiency obtained from galvanostatic tests is given in Fig. 2. Figure 2(a) shows an ideal voltage response characterized by maximized efficiencies, while in Fig. 2(b) is shown the effect of Ohmic losses due to the iR -drop on the voltage response with a consequent decrease in the energetic efficiency. However, iR -drop is not the only influence on η_E but also the overall voltage profile which is related to the device chemistry.

Energy must be evaluated by integrating instantaneous power over the integration period to guarantee correct reporting of η_E , that is

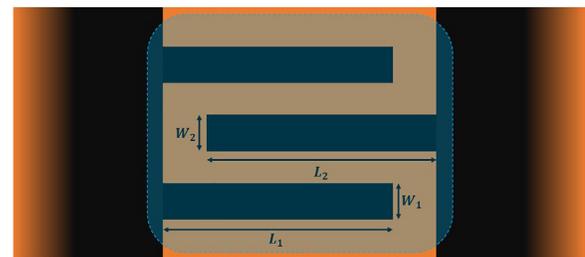
$$E = \frac{1}{\Delta t} \int_t^{t+\Delta t} v(t)i(t) dt,$$

with Δt being the charging or discharging period.

One of the main issues of LIG is the relatively low electrical conductivity. In the literature, the electrical conductivity of LIG is evaluated indirectly through square resistance (R_{sq}) measurements. This parameter is influenced by the thickness of the sample, and its value can be lowered, in principle, by increasing the laser dose and considering the laser depth of the field.

The other advantage of thickening the LIG layer is the enhancement of the charge accumulation. However, the overall LIG electrode resistance can be further reduced by properly accessing the entire electrode, i.e., research should strive to find a way to produce LIG directly on a metal current collector. This manufacturing procedure is simpler with other types of active materials such as those that can be grown electrochemically. A further possibility to reduce Ohmic losses is the optimization of the electrodes interdigitation. The r parameter reported in Fig. 3 offers various degrees of freedom for that purpose. LIG digit distances and aspect ratios can be tuned to minimize dispersions and balance electrode charges as well.

In addition, the electrolyte and properties of the LIG surface must be optimized to improve wettability, thereby reducing the interfacial resistivity. Among electrolytes, high voltage systems like ILs or novel organic salts must be tested.²⁵ Most of the literature is focused on aqueous electrolytes, but the operating voltage is limited. ILs and



$$r = \frac{A_1}{A_2} = \frac{m L_1 W_1}{n L_2 W_2}, \quad m = \begin{cases} n \\ n + 1 \end{cases}$$

FIG. 3. An expression for the areal ratio: six parameters can be finely tuned to perform areal balancing: lengths, L , widths, W , and number of digits, n and m .

organic electrolyte systems offer several common advantages such as a relatively high operating voltage window. ILs offer the further advantage of high thermal stability, low volatility, and flammability increasing device safety. In the recent decade, they have been widely explored for SCs; thus, ILs can be studied for μ SC applications.²⁶

In conclusion, it is known in the literature that possible μ SC device topologies concerning 2D, i.e., relatively thin, electrodes are coplanar and parallel plates. To date, LIG-based μ SCs have been developed in the coplanar configuration, limiting the device specific performance per footprint area.²⁷ Based on the research developments achieved and foreseen, we also expect that LIG will be exploited as an electrode material for efficient, high fabrication yield μ SCs for electronics.

AUTHOR DECLARATIONS

Conflict of Interest

The authors have no conflicts to disclose.

DATA AVAILABILITY

Data sharing is not applicable to this article as no new data were created or analyzed in this study.

REFERENCES

- ¹K. S. Novoselov, D. Jiang, F. Schedin, T. J. Booth, V. V. Khotkevich, S. V. Morozov, and A. K. Geim, *Proc. Natl. Acad. Sci. U. S. A.* **102**, 10451 (2005); M. I. Katsnelson, *Mater. Today* **10**, 20 (2007).
- ²Y. Zhang, L. Zhang, and C. Zhou, *Acc. Chem. Res.* **46**, 2329 (2013); N. Mishra, J. Boeckl, N. Motta, and F. Iacopi, *Phys. Status Solidi A* **213**, 2277 (2016).
- ³M. Yi and Z. Shen, *J. Mater. Chem. A* **3**, 11700 (2015).
- ⁴C. Faugeras, A. Nerrire, M. Potemski, A. Mahmood, E. Dujardin, C. Berger, and W. A. De Heer, *Appl. Phys. Lett.* **92**, 011914 (2008); U. Stöberl, U. Wurstbauer, W. Wegscheider, D. Weiss, and J. Eroms, *Appl. Phys. Lett.* **93**, 051906 (2008); T. Sattar, *Top. Curr. Chem.* **377**, 10 (2019).
- ⁵Z. Sun, S. Fang, and Y. H. Hu, *Chem. Rev.* **120**, 10336 (2020); Z. Wang, H. Gao, Q. Zhang, Y. Liu, J. Chen, and Z. Guo, *Small* **15**, 1803858 (2019); N. R. A. Mohd Shah, R. Mohamad Yunus, N. N. Rosman, W. Y. Wong, K. Arifin, and L. Jeffery Minggu, *Int. J. Hydrogen Energy* **46**, 9324 (2021).
- ⁶N. Bityurin, B. S. Luk'yanchuk, M. H. Hong, and T. C. Chong, *Chem. Rev.* **103**, 519 (2003).
- ⁷J. Lin, Z. Peng, Y. Liu, F. Ruiz-Zepeda, R. Ye, E. L. G. Samuel, M. J. Yacamán, B. I. Yakobson, and J. M. Tour, *Nat. Commun.* **5**, 5714 (2014).
- ⁸R. Ye, D. K. James, and J. M. Tour, *Acc. Chem. Res.* **51**, 1609 (2018).
- ⁹Poonam, K. Sharma, A. Arora, and S. K. Tripathi, *J. Energy Storage* **21**, 801 (2019).
- ¹⁰M. Beidaghi and Y. Gogotsi, *Energy Environ. Sci.* **7**, 867 (2014).
- ¹¹J. Wang, F. Li, F. Zhu, and O. G. Schmidt, *Small Methods* **3**, 1800367 (2019); S. Mojtahedi, M. Serrapede, A. Lamberti, C. F. Pirri, E. Heydari-Bafrooei, M. Molaei, and M. Karimipour, *Electrochim. Acta* **390**, 138856 (2021); A. Rafique, U. Zubair, M. Serrapede, M. Fontana, S. Bianco, P. Rivolo, C. F. Pirri, and A. Lamberti, *Nanomaterials* **10**(6), 1084 (2020); M. Serrapede, A. Rafique, M. Fontana, A. Zine, P. Rivolo, S. Bianco, L. Chetibi, E. Tresso, and A. Lamberti, *Carbon* **144**, 91 (2019).
- ¹²A. Lamberti, F. Perrucci, M. Caprioli, M. Serrapede, M. Fontana, S. Bianco, S. Ferrero, and E. Tresso, *Nanotechnology* **28**, 174002 (2017).
- ¹³L. X. Duy, Z. Peng, Y. Li, J. Zhang, Y. Ji, and J. M. Tour, *Carbon* **126**, 472 (2018).
- ¹⁴L. Li, J. Zhang, Z. Peng, Y. Li, C. Gao, Y. Ji, R. Ye, N. D. Kim, Q. Zhong, Y. Yang, H. Fei, G. Ruan, and J. M. Tour, *Adv. Mater.* **28**, 838 (2016).
- ¹⁵F. Clerici, M. Fontana, S. Bianco, M. Serrapede, F. Perrucci, S. Ferrero, E. Tresso, and A. Lamberti, *ACS Appl. Mater. Interfaces* **8**, 10459 (2016).
- ¹⁶A. S. Marco Reina, G. Auxilia, M. Fontana, F. Bella, S. Ferrero, and A. Lamberti, *Adv. Sustainable Syst.* **6**, 2100228 (2021).
- ¹⁷M. d'Amora, A. Lamberti, M. Fontana, and S. Giordani, *J. Phys. Mater.* **3**, 034008 (2020).
- ¹⁸A. Lamberti, F. Clerici, M. Fontana, and L. Scaltrito, *Adv. Energy Mater.* **6**, 1600050 (2016).
- ¹⁹M. Parmeggiani, P. Zaccagnini, S. Stassi, M. Fontana, S. Bianco, C. Nicosia, C. F. Pirri, and A. Lamberti, *ACS Appl. Mater. Interfaces* **11**, 33221 (2019); P. Zaccagnini, C. Ballin, M. Fontana, M. Parmeggiani, S. Bianco, S. Stassi, A. Pedico, S. Ferrero, and A. Lamberti, *Adv. Mater. Interfaces* **8**, 2101046 (2021).
- ²⁰A. Lamberti, M. Serrapede, G. Ferraro, M. Fontana, F. Perrucci, S. Bianco, A. Chiolerio, and S. Bocchini, *2D Mater.* **4**, 035012 (2017).
- ²¹M. Parmeggiani, S. Stassi, M. Fontana, S. Bianco, F. Catania, L. Scaltrito, and A. Lamberti, *Smart Mater. Struct.* **30**, 105007 (2021).
- ²²P. Zaccagnini, D. di Giovanni, M. G. Gomez, S. Passerini, A. Varzi, and A. Lamberti, *Electrochim. Acta* **357**, 136838 (2020).
- ²³B. Asbani, K. Robert, P. Roussel, T. Brousse, and C. Lethien, *Energy Storage Mater.* **37**, 207 (2021).
- ²⁴S. Pohlmann, R. S. Kühnel, T. A. Centeno, and A. Balducci, *ChemElectroChem* **1**, 1301 (2014).
- ²⁵L. Köps, F. A. Kreth, A. Bothe, and A. Balducci, *Energy Storage Mater.* **44**, 66 (2022).
- ²⁶A. Brandt, S. Pohlmann, A. Varzi, A. Balducci, and S. Passerini, *MRS Bull.* **38**, 554 (2013); C. Zhong, Y. Deng, W. Hu, J. Qiao, L. Zhang, and J. Zhang, *Chem. Soc. Rev.* **44**, 7484 (2015).
- ²⁷C. Lethien, J. Le Bideau, and T. Brousse, *Energy Environ. Sci.* **12**, 96 (2019).