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Laser-Carbonization – A Powerful Tool for Micro-Fabrication of Patterned Electronic Carbons

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Fabricating electronic devices from natural, renewable resources is a common goal in engineering and materials science. In this regard, carbon is of special significance due to its biocompatibility combined with electrical conductivity and electrochemical stability. In microelectronics, however, carbon's device application is often inhibited by tedious and expensive preparation processes and a lack of control over processing and material parameters. Laser-assisted carbonization is emerging as a tool for the precise and selective synthesis of functional carbon-based materials for flexible device applications. In contrast to conventional carbonization via in-furnace pyrolysis, laser-carbonization is induced photo-thermally and occurs on the time-scale of milliseconds. By careful selection of the precursors and process parameters, the properties of this so-called laser-patterned carbon (LP-C) such as porosity, surface polarity, functional groups, degree of graphitization, charge-carrier structure, etc. can be tuned. In this critical review, a common perspective is generated on laser-carbonization in the context of general carbonization strategies, fundamentals of laser-induced materials processing, and flexible electronic applications, like electrodes for sensors, electrocatalysts, energy storage, or antennas. An attempt is made to have equal emphasis on material processing and application aspects such that this emerging technology can be optimally positioned in the broader context of carbon-based microfabrication.

1. Introduction

Device fabrication via laser-patterning of carbon is a new and valuable addition to both carbon technology and microfabrication. This technique has already been employed for a variety of

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applications, but there is still plenty of scope for further research owing to i) the availability of a wide range of lasers and advancements in high-power lasers technology, and ii) the availability of various carbonizable precursors that can yield graphitizing and non-graphitizing carbon, and iii) rapidly growing flexible device industry that demands inexpensive, biocompatible, and stable materials.

Carbon has been synthetically prepared for several decades to produce carbon filaments, graphite for electrodes, glasslike carbon, activated carbon, and carbon black in the scale of a few milligrams to hundreds of kilograms.^[1-3] Polymeric carbon-based micro- and nano-device fabrication is greatly inspired by these industrial carbon manufacturing processes, which entirely rely on high-temperature furnaces for the carbon-conversion of organic precursors.^[4] These energy-intensive furnaces require multiple high-temperature components, leakage-free gas connections, and highly specialized manpower. Consequently, the majority of synthetic carbon materials remain expensive. Most of the efforts toward reducing the cost

of synthetic carbon have been focused on modifying the precursors, for example, by minimizing the unsaturated bonds and oxygen content in them, incorporating catalysts, or performing stabilization steps prior to carbonization.^[5–7] It is only in the last two decades that the heat-treatment process itself has been tweaked by introducing the use of lasers as a replacement for the furnaces.

This new process of carbonization has proven that polymers can be converted into carbon in a single step via laserinduced pyrolysis, and that such carbon materials are useable in a wide range of micro-scale device applications.^[8–10] Unlike traditional heat-treatment, laser-induced carbonization (simply: lasercarbonization), takes place very rapidly. It is typically carried out under ambient conditions, that is, without ensuring an oxygenfree environment. A plasma-like substance known as a plume is generated during the process, which may additionally contribute to the pyrolysis of the polymer.^[10] Evidently, the mechanism of laser-carbonization and hence the properties of laser-carbonized materials, differ from the carbons prepared in a furnace.

This emerging technology offers great potential for industrial manufacturing owing to a much lower cost and scalability. But to achieve this goal, it is essential to understand the chemistry ADVANCED SCIENCE NEWS ______ ADVANCED MATERIALS

of the laser-carbonization process as well as the prevailing challenges and future prospects. As of now, only a handful of polymers in combination with specific laser parameters have been explored for laser-carbonization, which is only a very small fraction of the available range of carbon precursors. There is a need to borrow the know-how from industrial and academic carbon science and integrate it with laser materials processing to exploit the full potential of this niche technology. While a number of applications using laser-carbonized materials have already been established, there are still several unanswered questions, for example,

- What are the effective reaction temperatures and what type of cooling mechanism takes place during laser carbonization?
- Can the temperatures generated in this process be further increased or modulated? If yes, would this enhance the purity of the material?
- What is the influence of this rapid yet high-energy heating process on the microstructure of resulting carbon?
- What is the influence of the precursors on the microstructure and surface functionalities?
- What is the role of the plume during the carbonization process?
- Can a non-graphitizing carbon be converted into graphite by taking advantage of this plasma-assisted process?
- Where does LP-C stand in comparison with other carbon materials?
- Which functionalities of LP-C are suitable for devices and how can one maximize the benefits of this new form of carbon in micro-fabrication?

In this review article, an attempt is made to answer some of these questions based on the available literature. For example, properties of laser-carbonized materials derived from different polymers may help the reader directly deduce or extrapolate useful information about the expected behavior from a material of their interest. Findings from different investigations on the mechanism of laser-carbonization could explain the general characteristics and parameter-specific aspects of this process. Successful applications of this material can provide insight into plausible process improvements, both immediate and long-term. We also provide a comprehensive collection of different application areas that have already utilized LP-C with an emphasis on, electrocatalytic devices, sensors, antenna-related devices, and energy storage devices. While there are some excellent review articles already present on this topic, [11-19] to our knowledge they are mostly application-specific. A broader perspective on positioning LP-C among other advanced carbon materials used in similar applications is yet to be presented. All-in-all, we believe that there is a compelling need to i) converge the knowledge-base generated from different application areas of LP-C, ii) understand LP-C obtained from different precursors from a mechanistic viewpoint, and iii) integrate the fundamental principles of laser physics and carbonization in order to enable tailoring of LP-C's properties for innovative applications. The goal is to provide a common platform for experts from different research fields that would lead to an exchange of ideas and pave the way for this futuristic multidisciplinary technology.

1.1. The Complexity of Carbonization

1.1.1. Processes and Microstructure

Carbonization is the process of converting organic compounds into carbon-rich materials via a controlled, oxygen-free heat treatment (via pyrolysis). This process is responsible for the formation of coals, graphite, diamonds, and petrochemicals from natural organic precursors under the Earth's crust. While these "deep carbon" materials evolve under high-pressure high-temperature conditions over millions of years, during artificial carbonization such conditions are mimicked with carefully chosen process parameters.^[20] The natural formation of different types of carbonaceous materials indicates that there are certain factors that promote the formation of specific carbon allotropes. For example, small flakes of graphite co-exist with coal in the coal seams, but the entire coal doesn't convert into graphite despite similar tectonic and environmental conditions. The reserves of petrochemicals contain cokes, coals, and various liquid and gaseous hydrocarbon materials at the same location without converting into one-another. Despite the fact that graphite is thermodynamically the most stable carbon allotrope, numerous metastable forms of carbon exist in nature for thousands of years. Evidently, the type of precursor, in addition to the temperature and pressure conditions plays an important role in determining the chemistry and microstructure of the final carbon product. This principle has been used for over a century for the purpose of synthetic carbon production. The carbon technology today is a result of a long journey, full of planned and serendipitous discoveries, which enabled us to manufacture a variety of goods composed of only elemental carbon, but in many different forms. A few examples that completely changed our understanding of carbon include the inventions of glassy carbon, Kish graphite, fullerenes, carbynes, and even some raw materials such as needle coke and advanced petroleum pitches. The list continues to grow.

While most aspects of carbonization unearthed during the last 100 years have been focused on precursor modification, the recent advancements in carbon technology are based on exploring new heat-treatment pathways. Heat-treatment is the key to converting organic material into carbon. This is essentially performed in the absence of oxygen which leads to pyrolysis (bond cleavage without burning) in a hydrocarbon, followed by C-C bond formation, thus resulting in a solid carbon residue.^[4,21] The heat-treatment temperature, heating rate, and presence of surrounding gases and applied pressure can cause significant differences in the microstructure of carbon, even derived from the same starting material.^[22,23] Temperature can be as high as 3000 °C in the heat-treatment processes aimed at producing graphite (commonly known as graphitization).^[24] The process needs to be slow in order to remove all heteroatoms from the mixture and ensure the ordering of the crystal structure.^[22] The bond-cleavage between carbon and heteroatoms, followed by C-C bond formation is an extremely complex combination of multiple reactions, which may or may not be interconnected.^[25] For example, some compounds produced by pyrolysis of a polymer may be unstable organic fragments that can trigger another reaction within the same reaction mixture.^[26] Such fragments can undergo further fragmentation or combine with another chemical or radical available for reaction. Volatile materials can

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which either stay or leave the reaction container, depending upon the conditions provided to them. The rates and orders of all of the aforementioned reactions can be different and often influenced by one another. Needless to say, it is hard to decipher all chemical changes occurring during pyrolysis at any given point in time.

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Pyrolysis is dominant up to 700 °C in the case of most solid polymers subject to heat-treatment. Above 700 °C, the C-C bond formation prevails. This part is equally complex and mostly dictated by the carbon fragments formed during pyrolysis.^[27] In some cases, there are sheet-like structures formed from the beginning itself (e.g., during pyrolysis of poly vinyl chloride), while some polymers may convert into curved structures including fullerenes, due to the presence of a large amount of non-sixmembered rings.^[28]

Carbonaceous materials containing a high fraction of layers with plenty of hexagons can be converted into polycrystalline graphite when heated >2500 °C. These are called "graphitizing carbons". On the other hand, carbon containing highly curved fragments and a significant fraction of non-six-membered rings cannot be converted into graphite, irrespective of the heat-treatment temperature. Such materials are known as nongraphitizing carbons. Transmission electron micrographs showing the differences in the microstructures of a graphitizing and a non-graphitizing carbon are presented in Figure 1 A and B, respectively. In a recent study on the microstructure of a nongraphitizing carbon by Sharma et al.^[28] the presence of $\approx 7\%$ spherical fullerenes (mainly C₆₀) along with larger carbon fragments and stacked carbon layers in non-graphitizing carbons was confirmed via small-angle neutron scattering. This microstructural model proposed by the authors is shown in Figure 1C. On a close observation, one can see that in addition to fullerenes, the material contains some relatively flat-tacked sheets as well as curved carbon structures of variable sizes. All these structures are chemically bonded in order to yield a uniform bulk material. Notably, any continuous material (i.e., which does not contain freely moving, discrete nano-scale structures), is not recognized as a nanomaterial, even if its constituting units may have nano-scale dimensions.

Generally, graphitizing carbons pass through a so-called liquid crystal phase (mesophase^[29] at intermediate temperatures (see phase diagram of carbon). In these intermediate phases, graphitic domains (crystallites) of different extensions are found. Descriptors of these phases are the stacking thickness (L_c) and crystallite diameter (L_a) of the graphitic domains, and their defect density.^[30,31] Among the most prominent structural defects are vacancies, five- or seven rings (Stone-Wales) defects, edge sites, deformations, or heteroatoms.^[32]

Like other polymeric carbon materials, carbon produced from laser-induced pyrolysis of different polymers features variations in crystallinity and surface functional groups. In Section 3, we have listed some precursors and the properties of the carbon derived from these polymers. Polyimide (PI) sheets have been most commonly used as precursors in laser-carbonization. The reasons could be many. For instance, PIs (particularly KaptonTM) are well-known for yielding graphitizing carbon,^[33] polyimides are already popular in sensors and bioelectronic medicine owing to their excellent biocompatibility,^[34,35] PIs yield a reasonably



Figure 1. Transmission electron micrographs showing the microstructural of A) non-graphitizing carbon and B) a graphitizing carbon, as observed at 900 °C during their carbonization (in situ). C) Latest microstructural model of non-graphitizing carbon which confirms up to 7% closed fullerene fraction. Scale bar in the right-bottom corner of (A,B): 5 nm (1 column). Reproduced with permission.^[28] Copyright 2022, Elsevier.

high fraction of carbon with industrial CO₂ lasers that are commonly available, etc.^[18] The carbon obtained by laser-pyrolysis of PI is known to contain impurities as we go down the film.^[10] While the carbon content in the top-most layer of this film can be >95%, the bottom-most layer is often only \approx 80% carbon. This is attributed to the unidirectional energy input by the laser. It is also possible that some tarry pyrolysis byproducts redeposit on the film. Pyridinic and pyrrolic N-rings are commonly observed iPI-derived LP-C (denoted as LC-PI in this manuscript).^[36] In some recent reports, these so-called impurities have been utilized as functionalities, as they indeed increase the polarity of the carbons, thus increasing the chemical activity and reactivity of this material. Polymers other than PI as well as other precursors are also reviewed in this article. While they may also contain impurities, their chemical functionalities are not the same. For example, if the precursor polymer itself does not contain any nitrogen (e.g., lignin), there are no N-containing groups on the resulting carbon surface. Such polymers undergo a different pyrolysis mechanism and also feature differences in terms of crystallinity and other associated properties. Similar to other carbon materials, some polymers may yield graphitizing while others may yield non-graphitizing carbon. Such studies are currently limited.



Figure 2. Illustration of the hierarchical porous structure of bulk porous carbons and substrate-supported porous carbons film.[37]

1.2. Structure Engineering

1.2.1. Pore Engineering

As the process of carbonization is accompanied by decomposition reactions, that is, creating gaseous leaving groups, every carbonization reaction comes with a mass loss of the material. Thereby, either the material undergoes dimensional shrinkage or there is porosity generated during carbonization. For many applications, porosity is an advantage as the porosity brings a high surface area to the material. Due to their intrinsic lightweight and high surface area, such materials are used in technologies such as filtration, separation, construction, energy storage, catalyst supports, etc. The production and tuning of specifically porous carbon materials have become a separate field of materials science and engineering.

The most prominent example of porous carbon materials is activated carbons^[37]These are porous carbon materials that have been further "activated" via physical or chemical methods to increase their microporosity as well as induce desirable surface functional groups. A typical feature of porous carbons is a hierarchical (fractal-like) porosity where the pores are hierarchically arranged spanning pore scales from macro over meso to micropores reaching specific surface areas of up to 3000 m² g⁻¹ (Figure 2). This structure makes the entire surface area of the porous materials accessible for liquid or gaseous adsorptive. Such highly light-weight carbons are often referred to as carbon aerogels or carbon foams, with reference to their solid state porous morphology dispersed in a gas.[38]

Besides physical and chemical activation, a number of strategies to modify the porosity in carbons have been developed. A common technique is the addition of porogens or templating agents, where pre-organization, growth, or alignment of the carbon phase is achieved using structure-directing agents (SDA) with specific geometries.^[39] Thereby, control over the pore structure and the textural properties is gained. The templating approaches are categorized into three groups: soft-, hard-, and salttemplating (Figure 3).

Structure formation via soft-templating is typically achieved by the ordered assembly of carbon precursors supported by am-

phiphilic compounds such as surfactants or polymers.^[40] The handling of soft templates is delicate for the synthesis of carbon materials.^[41] Universally, strong interactions (e.g., hydrogenbonding) between the carbon precursor and the SDA are required to prevent phase separation. A requirement to the carbon precursor is an ability to crosslink and form a precursor "backbone" with higher thermal stability than the SDA to facilitate the removal of the SDA prior to carbonization. Many synthesis routes for mesoporous carbons using soft-templating methods have been developed.[39]

Hard-templating (also-called nanocasting) is a method where rigid templates (nanoparticles) are impregnated into the precursor during carbonization.^[41] The carbonization occurs around the sacrificial hard-templates and afterward, the template is chemically removed (Figure 3).

Salt-templating is another method for the engineering of the pore structure in carbon materials.^[42] Typically, non-carbonizable inorganic salts are homogeneously blended with the carbon precursors. Upon heating, the salt melts and mixes with the carbon precursors or the carbon precursors dissolve into the molten salt phase. At high enough temperatures, carbonization occurs in a sol-gel mechanism. After carbonization, the remaining salt phase is removed by washing with H₂O.

1.2.2. Composition and Surface Engineering

Another important feature of carbons besides their physical surface structure is their chemical surface properties since in any interface application, the surface functionalities play an important role. As carbons are typically derived from oxygenated hydrocarbons as precursors, a high degree of oxygenation of the surface is observed. Noteworthy, the presence of defects and dangling bonds obtained in low temperature (<1000 °C) carbonized materials also affect the surface properties and facilitate the adsorption of or reaction with environmental oxygen. Depending on the precursors and the involved reactions during the carbonization process, different surface oxide groups evolve (Figure 4). Among them are acidic groups, such as carboxylic acids, phenols, and lactols, or basic groups like anhydrides, quinones, ketones, or ethers.^[43] Moreover, the amount of oxygen on the surface of a carbon material influences the surface polarity. This, in turn, has an impact on the sorption behavior of adsorptive (analytes or reactants) to the surface of the adsorbent (carbon material). The adsorption characteristics of gases of different polarity, for example, N₂, SO₂, CH₃OH, and H₂O, show a clear dependence on the type and number of oxygen-containing functional groups.^[44] Most N-containing carbons (NC) obtained from the carbonization of polymers contain N inside the lattice as well as surface groups/impurities, as illustrated in Figure 5.



Figure 3. Schematic illustration of the hard- and soft-templating approach.







Figure 4. Hypothetical schemes summarizing the most important surface oxide groups in carbons.^[49]

The functional groups and the surface polarity also influence the wettability of carbon materials.^[45–47] Carbon in its purest form (graphite or diamond) is generally hydrophobic, but porous carbons obtained by carbonization (e.g., 700 °C) of various synthetic and natural polymers contain hydroxyl, carbonyl, and carboxylic groups on their surface making them hydrophilic.^[47,48]

Besides oxygenation, any other functionalities that form covalent bonds with carbon, such as boron (B), nitrogen (N), Phosphorus (P), sulfur (S), etc., can change the structure and the properties of the carbons.^[50–56] For example, nitrogen can be incorporated into the bulk and surface structure of carbons. The addition of such heteroatoms is carried out to tune the properties of carbon for various applications, namely electrochemical and sensing applications.

N-containing carbons are of special interest to the carbon community as N in carbon (graphitic N) renders the material with n-type electronic behavior. Nitrogen in carbon can be in the form of i) doping (pyrrolic N, pyridinic N, graphitic N).[57-59] ii) surface functional groups (amine, amide, nitro, cyano, and nitrogen oxide),^[60,61] and /or iii) stable compounds like carbon nitrides^[62,63] as illustrated in Figure 5. Specific incorporation of N into porous carbon materials is also achieved by co-pyrolysis with small reactive nitrogen-rich precursors like urea, melamine, or nucleobases at temperatures lower than 1000 °C.[50,64] Another common route for the synthesis of NCs is the pyrolysis of carbon precursors in a reductive ammonia atmosphere. Typical nitrogen contents of such NCs range between 1 and 10 at.%. The binding and the chemical configuration of the nitrogen groups in the carbons depend on the synthesis (carbonization) temperature. Typically a decrease in the nitrogen content is observed with increasing temperatures.^[65] The temperature range between 700 and 1000 °C is characteristic of the largest changes in nitrogen content and configuration.[66]

Heteroatom functionalities not only change the surface structure of carbons but also influence electrical conductivity, electrochemical properties, and environmental stability. Apart from these three main elements, carbon lattices containing sulfur, phosphorus, selenium, etc. have been synthesized for various applications. A review article by Wang et al. may be referred for further details.^[67]

1.3. Alternative Carbonization Methods

A recent review article on sustainable materials stated that "the development of synthesis processes with lower energy penalties coupled with the search for sustainable, greener catalysts (i.e., catalytic graphitization) and reducing agents (for graphene production) are challenges that need to be overcome".^[68] It describes the paradox of carbon materials. On one hand, carbon materials are considered sustainable alternatives. On the other hand, the high-energy demand of their synthesis and their processing to achieve reproducible standards in device performance are still major drawbacks for their widespread application. Common approaches toward lowering production costs are reducing the carbonization temperatures or the energy input.

An alternative method toward lowering the reaction temperatures and using milder conditions in general, is hydrothermal carbonization, which has been extensively investigated in the past decade.^[69,70] It generally describes the carbonization of typically water-soluble precursors in the presence of water at temperatures between 150 and 350 °C.

Another alternative heating process that can be utilized for direct on-substrate carbonization is the so-called rapid thermal processing (RTP). As a heat source, a number of high-power halogen lamps are used. Thereby, very fast heating rates of up to 400 K s⁻¹ and cooling rates of 50 K s⁻¹ can be achieved.^[71] RTP is mainly used for the synthesis of single- or few-layer graphene on catalytic surfaces.^[72,73] However, the energy-inefficiency of conventional carbon preparation routes (pyrolysis) prompts for the study of RTP as an alternative direct processing method of porous carbon.

1.4. Carbon Materials for Devices

Carbon materials used in electronic applications can be broadly divided into two types: carbon nanomaterials and bulk carbons. Here the term "bulk" does not indicate a several-kilogram production scale, but rather the fact that the material is continuous and does not exhibit the properties shown by its individual nanounits. It features a structural continuity in all dimensions, unlike discrete nano-scale units, which have well-defined borders.

While various alternative carbonization methods have their own advantages, scalable fabrication of micro- and nano-scale devices demands compatibility with commonly available microfabrication and packaging processes. Miniaturized carbon devices are fabricated either via bottom-up fabrication processes such as 2D and 3D printing of carbon nanomaterials (graphene, CNT, CNF, etc.)^[74-76] or using top-down approaches where lithographically patterned polymer structures are converted into carbon in a furnace.^[4,77,78] Carbon fibers, mats, or bundles inserted into a glass capillary have also been used for making a variety of sensors and biomedical devices.^[34,79] The advantage of the topdown process is the high purity of carbon, because no binder, surfactants, or any foreign chemicals are present that may lead to a compromise in material's functionalities. Printing processes, however, offer a much greater choice of substrate materials including flexible polymers. Laser-assisted carbonization combines these two aspects. It does not contain foreign materials, but at the same time, it is essentially designed for flexible substrates as the substrate itself converts into carbon. The material obtained







Figure 5. Schematic representation of different possibilities for nitrogen to be present in bulk and nanoscale carbons. N-doped CNT, Reproduced with permission.^[58] Copyright 2015, Elsevier. N-doped graphene, Reproduced with permission.^[59] Copyright 2009, American Chemical Society.

in this process is a continuous film of carbon with a high inherent porosity and heteroatom-containing functional groups. Unlike nanomaterials such as graphene and CNTs, LP-C does not require any binders because it is a bulk form of carbon that already has interconnectivity at a large scale. Laser patterning enables nearly any design that can be computer controlled, which makes this process more device-friendly compared to lithographic processes based on expensive cleanroom equipment. A comparison of properties relevant to the electronic device application of LP-C and other bulk solid carbons as well as micro/nano-scale carbons is given in **Table 1**. Note that these are representative properties that depend upon the manufacturing process used.

2. Laser-Processing of Materials - Fundamentals

2.1. Beam-Material Interactions

Laser-processing of materials is a complex field with many different aspects. Several challenges of material processing have been solved by using lasers as a processing tool. Nowadays, lasers are commonly used in industrial materials processing for different purposes. The processes enabled by lasers can be categorized into the vaporization of material (cutting, drilling, or piercing) melting of materials (welding), or microstructural optimization (patterning or finishing).^[99] In this section, a general overview of the main aspects of materials processing with significance to lasercarbonization will be given.

Different models describing the beam-materials interactions have been discussed. Some fundamental aspects are commonly

described as depicted in **Figure 6**: A laser beam provides sufficient energy to evaporate material to form a keyhole. Around the keyhole, the material may be molten (melt pool). The energy impact causes plastic deformation to the surrounding



Figure 6. Illustration of some common beam-material interactions.^[99]

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Carbon materials*	Fabrication method	$\sigma \otimes RT [S cm^{-1}]$	YM [MPa]	SSA [m ² g ⁻¹]	Ref.
Graphite	Commercial: Graphite grade JP932	104	11.5×10^{3}	_	[80]
Graphene	Mechanical/chemical exfoliation of graphite	10^2-10^3 (theoretical). pprox 2700 (experimental)	10 ⁶	≈2629	[81–83]
MWCNT	Arc discharge/CVD	2×10^4 (Single tube)	$3.70 imes10^{6}$ (Single tube)	64.8	[84–86]
Electrospun carbon fibers	Electrospinning + carbonization (1000 °C)	2.5 × 10 ³	$228 \times 10^{\ 3}$	<0.7 (Can be increased on activation)	[87–89]
Vapor-grown carbon fibers	CVD (1100 °C)	$\approx 8 \times 10^3$	237×10^{3}	2.73	[90–92]
Glassy carbon (Bulk solid)	Commercial (Polycarbon USA / Hochtemperatur-Werkstoffe GmbH, Germany)	2 × 10 ²	$20-40 \times 10^{3}$	-	[93,94]
Polymeric carbon (micro/nano patterned)	Photo patterning + carbonization (900 °C)	$pprox 4 imes 10^2$ (nanowires)	25.27×10^3 (micropillars)	-	[23,95]
Activated carbon	Carbonization + activation	25.13 × 10 ⁻³	35–55 × 10³ (PAC/starch composite)	≈1200	[96,97]
LP-C	IR laser irradiation	10–30	1.02	200–300	[10,36,98]

Table 1. Comparison of the properties of LP-C with other bulk (crystalline and disordered) solid forms of carbons.

modulus; SSA: specific surface area; CVD: chemical vapor deposition; PAC: powdered activated carbon.

material. Within the keyhole, the laser beam undergoes multiple reflections and is eventually (re)absorbed. Above the keyhole, a plasma plume consisting of ejected material and gases is present.

Mechanistically, laser-carbonization may be described with the same principle models. Similar to general observations during materials laser-processing, tentatively, the processes occurring during laser-carbonization may be divided into three steps: Absorption of the high energy of the laser beam causes evaporation of the precursor materials forming the keyhole. From there, the process gets very complex. Competing processes such as melting, bond dissociation, plasma absorption, and high gas pressure occur simultaneously. The evaporated material most likely consists of ionic carbon clusters or a colloidal carbon plasma. The complexity of the process and the consideration of all reaction parameters and materials properties makes modeling the processes occurring during laser-carbonization highly challenging.

Due to this complexity, processing materials with laser beams requires solid knowledge of the underlying beam-matter interactions. It is known from industrial materials processing that every material shows a different response to the impact of a laser beam due to its materials characteristics. Primarily, the direct laser beam-materials interactions need to be considered, that is, primary light-matter interactions such as absorptivity and reflectivity. These two parameters depend on the materials and surface properties and define the so-called laser coupling according to Equation (1).

$$P = \alpha P_A + \beta P_R$$

$$\alpha + \beta = 1$$
(1)

P is the incident laser power, P_A is the portion of power absorbed and P_R is the portion reflected, while α and β are the absorptivity or reflectivity, respectively. Several examples of the interplay between materials parameters (e.g., aluminum, stainless steel, etc.) and laser irradiation are given in the literature.^[100] The same principle applies to organic or carbon precursor films. However, as laser-carbonization has been scarcely investigated mechanistically, comprehensive databases are still lacking.

Once absorbed, the thermal properties of the materials, such as heat capacity and heat conductivity are decisive for the energy conversion and transport within the material. Moreover, intrinsic materials properties like melting point and evaporation point are essential. For example, a low melting point leads to a strongly different heat dissipation during the reaction due to enthalpic effects during melting.

Finally, gases or volatile species evolving during the laser beam-induced reactions form a colloidal plasma that interacts with the laser beam and reacts with the product material. Therefore, evaporation rates, the density of the evaporated products, their reactivity, and their interaction with the laser beam need to be considered. All these parameters also apply to carbonization reactions.

In this regard, the reaction atmosphere is another critical parameter, especially in carbonization reactions. Despite the fast reaction rates induced by the laser, the reaction is largely dependent on the presence of reactive gases such as oxygen, ammonia, or hydrogen in the atmosphere.

To summarize, the characteristics of the key material that are essential to understand or tune a reaction are:

- 1) absorptivity/reflectivity of the laser beam (reflectivity very low in organic materials)
- 2) thermal properties heat capacity and heat conductivity
- 3) melting point and evaporation point
- 4) interaction with the products (absorption, reflection, e.g. plasma, gases, dust, or melt)
- 5) reaction atmosphere







Figure 7. A) Schematic illustration of the working principle of a processing laser; B) Sketch illustrating the difference between vector and bitmap mode.

2.2. Laser Parameters

In most materials, the high photonic energy density is absorbed and converted to heat. Therefore, lasers are considered an alternative localized heat source. An illustration of a typical standard laser setup is given in Figure 7A. A laser source generates a beam with a tunable intensity which is directed along a mirror system and a focusing lens to the workpiece. The position and speed of the laser beam are controlled by a moveable x-y axis while the focal distance and focal length are controlled by the specifications of the focusing lens and a movable specimen stage. These laser setups are operated either in the vector mode or in the bitmap mode. In the former, the x-y-control follows the lines or paths in a vector graphic while in the image mode a bitmap with a certain resolution, given in dots per inch (dpi), is rastered (Figure 7B). The bitmap mode is generally applicable for scanning (converting) larger areas (engraving). However, higher precision in the patterns and power control is achieved in the vector mode. When using the vector mode to carbonize larger areas, the line separation needs to be defined (Figure 7B). Noteworthy, the interaction cross-section is dependent on the material's specific absorption at the laser energy and the thermal diffusivity, therefore the line separation varies with the material in the primary film.

Similar to conventional heating methods, the temperature of the laser-induced carbonization reaction is adjusted by the energy input which is a direct result of the power density and the reaction time, that is, the time the laser beam resides on a spot. In comparison to conventional furnace heating a laser-induced reaction is extremely fast, that is, occurring on the time scale of milliseconds. To understand heat induction, some fundamental aspects distinguishing laser heating from conventional joule heating need to be considered. For the sake of the conciseness of this text, a laser should just be simply viewed as a source of bundled photonic energy.^[101] Lasers are among the energy sources with the highest power density. The high power densities in a laser beam are a result of the condensation of photons of a certain wavelength. These properties, the power density, and the wavelength are the two main criteria that are relevant for (carbon-)materials processing. The power density depends on the beam diameter (spot size) in the focus of the laser. The beam diameter is determined by the focusing lens and the wavelength of the laser.^[100] For example, a 1 W laser that is focused to a spot size of 0.2 mm results in a power density of 3200 W cm⁻² according to Equation (2).

$$\frac{1 W}{\pi \cdot (0.01 \text{ cm})^2}$$
 (2)

In materials processing, the fluence (energy density) is provided as a figure of merit. As a universal value, the fluence, that is, the energy delivered per unit area is a direct result of the laser power and the spot size (the focus). The laser fluence F, is adjusted by setting the incident power P and the scanning speed v (**Figure 8**A). The fluence is given as either lineal F_L or areal F_A in J cm⁻¹ or J cm⁻², respectively. The values are determined directly from the preset output power, the scanning speed, and the focal diameter (spot size) according to Equations (3) or (4).^[100]

$$F_L = \frac{P}{v} \tag{3}$$

$$F_A = \frac{P}{v \cdot d} \tag{4}$$

Thereby, precise and reproducible fluence values for the area of a laser-carbonized line on a primary film are given (Figure 8B).

Notably, the effective energy distribution is also dependent on the beam profile with either Gaussian or non-Gaussian (flattop) intensity distributions (Figure 8C). The profile of the beam largely influences the energy density distribution delivered to the workpiece (precursor film). For Gaussian beams, often the peak energy density is provided as it is significantly higher than the average energy density.^[77] Moreover, techniques to produce lineshaped beams with cylindrical lenses are sometimes used to expose a larger focus to the workpiece.

The effective output power (incident power) is determined directly with a power meter prior to processing since each laser system has its own specifications. In many commercial laser setups, the output power is generically given in % of the maximum power. However, the real output power often scales non-linearly with the user settings as it is dependent on the repetition rate or scanning speed.

The scanning speed enters directly into the equation of the exposed energy density and is therefore a primary parameter.







Figure 9. Absorption spectra of an organic precursor for laser-carbonization (CA/U(300)^[103] in the (A) UV/vis/NIR and (B) MIR regions.

Moreover, it defines the reaction time. Therefore, the scanning speed should be viewed as a parameter with an individual impact on the processing. In turn, the exposure time is important when considering material characteristics such as heat capacity and heat conductivity, and the reactivity of the primary material.

The wavelength depends on the laser source and its active medium and ranges from the ultraviolet (100-380 nm) over the visible (380-780 nm) and the near-infrared (780-3000 nm) to the mid-infrared (3-50 µm). An overview of laser sources commonly used in materials processing is given in the fundamental literature.^[102] Notably, CO₂-lasers are the most widely used type in materials processing, in general, and for carbonization reactions, in particular. It is available for different power ranges from the microwatt (mW) to the megawatt (MW) regime, making it the work-horse in materials processing. With regard to CO₂lasers, significant power fluctuations in the low energy regime are typical for direct current (DC)-pumped laser sources. Since laser-carbonization is conducted in the low output power regime between 0.1-5 W, radiofrequency (RF) laser sources are the preferred choice, as these provide a higher laser beam stability in the low power regime. Reactions in the material, especially when using long wavelengths lasers, are induced by the so-called photothermal effect: Photonic energy is absorbed by the material and transformed into lattice vibrations. This effect is dominant at long-wavelength excitation. Upon excitation, for example, in the infrared (CO₂-lasers), specific molecular bond vibrations may be directly excited when in resonance (Figure 9). The absorptivity of short wavelengths (e.g., ultraviolet light) by organic materials or semiconductors is generally higher than for long wavelength because the photonic excitation energy in the UV is in the resonant range of chemical bond energies and is thus able to directly induce bond dissociation (photolysis). Additionally, shorter wavelengths are generally stronger absorbed due to the plasmonic resonance of most materials at higher energies. Moreover, in short wavelengths of excitation, nonlinear optical effects like multiphoton absorption have to be taken into account.

The spot size, or more specifically the beam diameter, is determined by the characteristics of the focusing lens and the laser wavelength. Although the effective focal diameter strongly depends on the laser optics, shorter wavelengths can be generally focused on smaller spot sizes, which is an advantage for miniaturization in small-scale materials synthesis. However, also the response (absorptivity, reactivity) of the materials is largely dependent on the wavelengths. Some materials are transparent or show a high reflectivity for certain wavelengths.

Another non-negligible beam property that should be considered is the operation mode of the laser, that is, continuous wave (CW) or pulsed mode. Especially for the latter, the energy per pulse is an important criterion for the product properties. Typical repetition rates in pulsed lasers range between Hz and GHz depending on the type of laser. For example, a beam propagation speed of 500 ms mm⁻¹ (2 mm s⁻¹) and a pulse repetition rate of 1000 Hz, would result in 500 pulses mm⁻¹. Changing the propagation speed to 50 ms mm⁻¹ gives 50 pulses per mm. This may have a significant impact on the product properties. In many commercial engraving setups, the repetition rate is given either in pulses per distance (e.g., per inch: PPI) or pulses per time (e.g., per second in Hz).

To summarize, the most important beam properties (laser parameters) that account for laser-induced materials processing in general, and laser-carbonization, in particular, are:

- 1) photon-energy/wavelength of the laser
- 2) incident power
- 3) processing speed
- 4) pulse sequence, repetition rate
- 5) spot size and focal position

Systematic mechanistic studies based on a statistical range of laser-carbonized materials and process parameters are still scarce. A comprehensive model for laser-carbonization based on different precursor materials and laser setups would certainly help to understand the principal mechanisms and gain control over the material's properties. In the next section, a survey of individual mechanistic studies on laser-carbonization will be given.





Figure 10. Outline of the application fields of conventionally carbonized materials and potential application fields of laser-patterned carbons.

3. Laser-Carbonization – Review

3.1. Overview

The fundamentals described in Section 1 demonstrate the complexity of carbonization and introduce some of the most essential tuning knobs for the selective modification of the properties of carbonized materials. In film-based or flexible electronics, their application is often hindered by their processing limitations due to their general insolubility and delicate surface chemistry. Laser-carbonization is an upcoming alternative for producing electronic or electrochemical electrodes by the versatile and precise (photonic) heat source and synthesis on the spot of application. Many everyday applications rely on small amounts of film-based materials, such as electrodes in batteries, sensors, or catalytic surfaces (Figure 10). In these cases, direct on-chip fabrication techniques are an advantage over classical bulk synthesis reducing the use of solvents and reagents and avoiding tedious post-processing procedures. Consequently, the sub-field of using lasers to synthesize carbon patterns for film-based applications has been established in materials science in recent years.

However, this approach also bears challenges, which require fundamental investigations. A major challenge is precise control over the reaction conditions and laser parameters that define the rapid energy impact. The unidirectional energy input and the limited penetration depth of the laser beam lead to structural and chemical gradients within the product film. In the production of laser-carbonized materials for direct use in their respective applications, some precautions regarding the properties of the substrate have to be taken into account (see Section 2).

A variety of starting materials and precursors have been identified (**Table 2**). These are referred to as primary films (**Figure 11**). In all cases, organic starting materials were converted into functional solid-state materials with increased carbon content. Therefore, the term laser-induced carbonization or simply lasercarbonization is an appropriate description of all processes in the surveyed studies. The term carbon laser-patterning (CLaP) may be used to describe the general process of "writing" carbon patterns with a laser beam. The resulting functional carbonized films will be generally referred to as laser-patterned carbon (LP- C) or laser-carbonized films. The material itself, regardless of the pattern or structure, is referred to as laser-carbonized material (LCM), a general term for composite materials that were produced in presence of additives or reactants. In the case of specifically addressing particular properties, for instance, intrinsic functionalization or composite materials, variations such as laser-pattered nitrogen-doped carbon (LP-NC) or specific precursors, for example, laser-carbonized polyimides (LC-PI) is used.

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Among the best-studied materials are LC-PI and laser-reduced graphene oxide (LR-GO). The common terminology used in literature for the former is laser-induced graphene (LIG). PIs are very specific due to their intrinsic material properties, namely extraordinary thermal stability and duroplastic properties, that is, without a melting point. Even more so, LR-GO is a special case, as the laser-induced reaction of GO is considered a deoxygenation or a reduction rather than a classic carbonization.

The first reports on the laser-induced structural modification of organic materials (PI) appeared in the 1980s.^[104,105] Throughout the following decade's publications, the topic appeared sparingly and mostly with a focus on investigating the laser-induced decomposition of polymers for materials processing.^[106-111] The potential of the general method to specifically apply carbonized patterns has been recognized with the rise of interest in carbon-based printed and flexible electronics during the 2010s (Figure 12).^[112] Especially, the utilization of so-called LC-PI and LR-GO in flexible electronic devices inspired the research on direct laser-writing or laser-patterning of carbon films. Several review articles on laser-carbonization / laser-reduction of PI or GO exist.^[11,12,14,15,112-115] Additionally, laser-assisted carbonization of other polymers, for example, Parylene C^[116] and Polyaramids^[117] has also been reported. Apart from carbonizing pure polymeric films, laser processing has been extended to the self-assembly and ordering of block co-polymers and their hybrids to generate highly porous hierarchical structures.^[118-120] In most of these processes, laser parameters below the carbonization threshold are applied. Interestingly, when the block-copolymer is irradiated with the laser above its carbonization threshold, high-surfacearea porous carbon patterns similar to those obtained from PI are achieved. Further studies on the laser-carbonization of blockcopolymers shall reveal the mechanistic aspects and properties of this variation of LP-C.^[121]

The research in the field experienced a great acceleration more than ten years ago after the publication of the first reports on using lasers to reduce primary films of GO.^[125,126] In these studies LR-GO films were obtained either in the form of stacked few-layer graphene or as 3D-graphene foams^[122,127] This discovery fell into a period where extensive research on the fundamental properties of graphenes and their processing methods was conducted.^[128] A few years later in 2014, the first modern report on laser-induced carbonization from commercial PI films sparked interest in the scientific elucidation of the laser-carbonization process,^[123] although, the first reports on laser-carbonization of PI date back to 1983.^[129,130] Originally, an argon laser was used to convert PI into a conductive structure. During that time the carbonization of PI was broadly investigated.^[131,132] In 2016, laser-induced carbonization has also been suggested as an alternative strategy to induce the carbonization of polyacrylonitrile (PAN) fiber mats.^[124] The latter demonstrates several limitations of laser-induced

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				Laser p	arameters				Surface			
Precursors	۶ [nm]	v [mm s ⁻¹]	P [W]	z	f [Hz]	d [um]	F _A [] cm ⁻²]	atm	groups/properties of the resulting carbon	Target of study	Remarks	Ref
					0	eneral applic.	ations and me	chanistic studi	ies			
Cellulose (Fiber)	10 600	40	N	I	I	40	I	amb.	-C=COH, -COOH Conductivity: 60 mS cm ⁻¹	Laser-induced graphitization	Graphitization in presence of Na in the cellulose	[140]
Cellulose (Fiber)	522	0.25	0.2	192 fs	63 M	1.6	I	amb.	Conductivity: 6.9 S cm ⁻¹	Laser-induced graphitization	Graphitization using defocus method at a defocus distance of 100 um	[141]
O	800	I	0	100 fs	× L	170	0.035	I	-C-C-, -C-O, -C=O Resistance: 0.7 kΩ sq ⁻¹ for the 20.1 nm thick LrGO film	Optoelectronics	Laser carbonized rGO transferred to PET substrate to obtain a flexible device	[114]
Wood, coconut, potatoes, cardboard	10 600 9300 1060	150	I	I	I	I	I	N22	I	Mechanism	Multiple lasering using defocus method	[142]
Wood/leaves	10 600	10	0.8	I	I	I	I	amb.	Resistance: 10 Ω sq ^{-1}	Flexible electronics	I	[143]
Citric acid + urea	10 600				× F	170		amb.		Flexible electronics	Pre-carbonization of molecular precursors	[103]
glucose/cytosine / citric acid + urea	10 600	3.33 2.65 6.85	1.05	I	<u>メ</u> 「	170	185 233 90	amb. / N ₂	Extinction coefficient (a) 943 cm ⁻¹ 0.21 L (g cm) ⁻¹ 0.28 L (g cm) ⁻¹ 0.56 L (g cm) ⁻¹	Microstructure/extinction coefficients/laser parameters	Pre-carbonization of molecular precursors / N-doping	[144]
0	780	0.005	0.013	70 fs	50 M	2	0.0083	I	I	Mechanism	Study of conversion of sp ³ to sp ² carbon and removal of oxygen functional groups	[145]
CO	790	I	0.003	120 fs	80 M	I	I	I	−C=C-, −C−O, -C=O Resistance: 7.8 and 2.1 MΩ	Electronic microdevice	GO coated on a glass slide before laser irradiation	[122]
CO	1064 532 355 266	-	I	6 ns	30	5 k	0.38 0.15 0.085 0.05	I	-C=C-, -C-C-, -C-O, -C=O	Mechanism	I	[146]
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				Laser p	arameters				Surface			
Precursors	۲ [nm]	v [mm s ⁻¹]	P [W]	τ	f [Hz]	[mn] p	F _A [] cm ⁻²]	atm	groups/properties of the resulting carbon	Target of study	Remarks	Ref
Polybenzimidazole/ DMSO	335	100	-	1	3372.8	20	0.006-0.045	amb.	C-N,C=N,C-S,-SO ₄	Doping	S- and N-doped graphene	[147]
PAN fiber mat	968 998	spot	800	1	I	30 k	1	Z2	Surface area: 140 m² g ⁻¹	Mechanism	Higher surface area compared to thermally carbonized carbon fiber mats	[124]
Polyaramid	10 600	130 320	m	I	* -	120	1	amb	Conductivity: 45.22 ± 10.68 S cm ^{−2}	Antibacterial coatings	Bacteria immobilization after Cu electroplating on carbon	[קוו]
Polyaramid	10 600	OL	60	I	I	I	1	I	-C=0, -C-C-, -C-N	Multi	Laser-induced graphene fibers reinforced Kevlar composites	[148]
Lignosulfonate	10 600	I	1	I	1	- Electric	- -	apacitors	Resistance: 3.8 Ω sq ⁻¹	Flexible electronics	Laser carbonization of printed lignin-based ink	[149]
Lignin Films	10 600	I	I	1	I	100	1		Surface area: 338 m² g ⁻¹	mEDLC	Laser-patterned lignin is transferred to the PVA substrate by a lignin lift-off process	[150]
Lignin/PI	10 600	80	I	I	I	1	1	I	Hydrophobic surface -C=C-, -C-OH, -C-OOH, O and S co-doped	mEDLC	Lignin slurry coated on LC-Pl electrodes followed by second carbonization	[151]
Ы	10 600 9300	I	60	I	6k	I	>40	amb	Resistance: 100 to 200	mEDLC	Laser-induced graphene fibers generated at higher fluence	[152]
Ы	10 600	85	40	I	I	I	1	I	-с=с-, -с=о, Мп-он	mEDLC	SWCUT-bridged graphene fibers decorated with MnO ₂	[153]
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				Laser p	arameters				Surface			
recursors	λ [nm]	v [mm s ⁻¹]	P [W]	1	f [Hz]	q [mm]	F_{A} [J cm ⁻²]	atm	groups/properties of the resulting carbon	Target of study	Remarks	Ref
G	1030/515	125	1	220 fs	500 k	1	1	1	Electrical conductivity: ≈10⁴ S m⁻¹	mEDLC	LR-GO transferred to the PDMS substrate to obtain a flexible device	[154]
0	780	I	I	I	I	I	I	amb.	Surface area:1520 m ² g ⁻¹	mEDLC	LR-GO transferred to PET substrate to obtain a flexible device	[127]
0	10 600	200	26.5	500 µs	٦k	line	I	N_2	-C=C-, -C-O, -C=O, -COOH	mEDLC	GO carbonized by laser on a PET substrate	[155]
Vielamin/PI	10 600	180	φ	I	20 k	I	I	amb.	C-N, C=N, N-O	Flexible supercapacitors	Nitrogen-doped laser carbon materials derived from melamine/ polyimide	[156]
-	522	0.14	I	500 fs	I	м	I	amb.	Surface area: 101.7 m ² g ⁻¹	mEDLC	Solid state supercapacitor with polyvinyl alcohol- phosphoric acid (PVA-H ₃ PO ₄) electrolyte.	[157]
citric acid + urea	10 600	I	I	I	I	I	I	N ₂ / O ₂	phase angle of –84°, RC time constant of 0.29 ms	mEDLC	High-frequency response	[158]
GO/citric acid + urea	10 600	I	I	I	I	I	I	amb.	phase angle of -84.3°, RC time constant of 7.6 ms 214 F g ⁻¹ at 10 mV s ⁻¹	mEDLC	Defects in GO were reduced in presence of carbon nanodots	[159]
AN	10 600	1	I	I	× -	170	63 117	amb.	low charge transfer resistance	mEDLC	Direct carbonization of PAN in presence of MWCNTs as IR-absorbers	[160]
0		I	I	I	I	I	I	amb.	178 F g ⁻¹ , high cycling performance	mEDLC	+ Ferrocene	[113]
citric acid + urea	10 600	I	I	I	I	I	I	amb.	relaxation time of 3.44 ms	Supercapacitors	First report on molecular precursors/effect of	[191]
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Table 2. (Continued).

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				Laser pi	arameters				Surface			
Precursors	λ [nm]	v [mm s ⁻¹]	P [W]	r	f [Hz]	[mu] b	F _A [] cm ⁻²]	atm	groups/properues or the resulting carbon	Target of study	Remarks	Ref
al/H ₃ PO ₄	10 600		1	1	1	1	1	amb.	C-N, C-P	Supercapacitors	N and P co-doped laser carbon has 13 times capacity higher than non-doped materials	[162]
Id/dd	10 600	100	59	I	I	I	I	amb.	C-P, P-O, C-N	Supercapacitors	Phosphorus-doped porous graphene	[163]
AA/ H ₃ BO ₃ /PI	10 600	68	8.	14 µs	<u>х</u>	0001	I	amb.	B-N, C-N, BCO ₂ , BC ₂	mEDLC	Boron-doped laser-induced graphene, dissolving H ₃ BO ₃ into PPA solution as a boron-doped precursor	[54]
-	800	-	0.08	35 fs	1 k 80 M	00	I	I	I	mEDLC	Carbon lines with various widths written by point-to-line carbonization strategy	[164]
-	10 600	150	٥	I	20 k	220	I	I	Foam-like topography	mEDLC	Carbon transferred onto the PDMS substrate	[165]
_	10 600	I	4.8	14 µs	I	I	I	amb.	I	mEDLC	Supercapacitors with PVA/H ₂ SO ₄ electrolyte.	[166]
_	405	I	0.27	I	I	I	I	Ar	-C=C, -C-N, Amide groups Resistance: 65 Ω sq ⁻¹	mEDLC/photodetector	Supercapacitors for on-chip, self-powered photodetection system	[167]
-	405	I	0.22	1	1	ε	I	amb.	Hydrophobic surface R = 220 Ω or 400 Ω sq ⁻¹	mEDLC	Air plasma treatment to convert the carbon surface to hydrophilic	[168]
-	10 600	1	4.8	I	I	1	I	amb.	1	mEDLC	Electrodeposition of pseudocapacitive materials on LP-C	[169]
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Table 2. (Continued).

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				Laser p	arameters				Surface			
Precursors	λ [nm]	v [mm s ⁻¹]	P [W]	τ	f [Hz]	[mn] p	F _A [] cm ⁻²]	atm	groups/properties of the resulting carbon	Target of study	Remarks	Ref
MoS ₂ /PI	10 600		6.5	1	I	I	1	amb	C-S/C=C, C-O/C-S and C =O	Micro supercapacitors	MoS ₂ nanoparticles embedded in the LP-C to improve wetting properties	[170]
PI/PDMS	I	I	I	15 µs	I	I	I	I	P-0, C=C, C-C, C-0, C=0	Micro supercapacitor arrays	ZnP nanosheets anchored on 3D laser-induced graphene foams through a shadow mask	[ודו]
MnO ₂ /PI	I	12	15	I	I	I	1	amb	Mn-O-Mn, Mn-O-H, C-C, C-O, C = O, O-C = O	Micro supercapacitors	MnO ₂ nanoparticles evenly embedded in highly conductive LP-C	[172]
MnO _x /Cotton cloth	10 600	50	1–2.5	1	I	1	- Flortroratalvsi	amb	Mn-0, C-0/C-0-C, C = 0	Bio-based micro-supercapacitors	Laser-induced graphene/MnOx electrode on cotton cloth	[173]
Citric acid + urea	10 600	14.1	1.02	I	٦k	170	43	amb	catalytically iron oxide species	ORR catalyst	+Fe(NO ₃) ₃	[174]
Pt/Ni/Fe doped PI	10 600	I	I	I	I	I	I	H_2/Ar	. 1	Electrocatalyst support	HER and OER catalyst	[175]
Mood	10 600	150	8.6	1	1	1000	1	Ar/H ₂	-C=C-, -C-O, -C=O, -C-OOH	Electrocatalytic support	Electrodeposition of PANI on the wood-derived carbon	[6]
ā	10 600	5%	3%	I	I		1	I	-C=C-, -C-O, -C=O, -C-OOH	OER/ORR electrocatalyst	Laser-induced graphene was oxidized by oxygen plasma treatment	[176]
ā	10 600	5.55	2	I	I	400	9.6	amb	-C=C-, -C-O, -C=O, -C-OOH, -C-N	OER electrocatalyst	Porous carbon film acts as an OER catalyst while obviating the need for a substrate	[36]
CF ₃ -PI/SO ₂ -PI/PI	10 600	1	I	1	I	1	505130 I	amb	C-N, C-S, C-F	E-chem. sensing of dopamine	N, F, and S-doped graphene derived from polymer-doped PI	[177]

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				Laser p	oarameters				Surface	
Precursors	γ [nm]	v [mm s ⁻¹]	P [W]	τ	f [Hz]	[mn] p	F _A [] cm ⁻²]	atm	groups/properties of the resulting carbon	Target of study
H ₃ BO ₃ /PI	10 600	166	1.6	1	1.2 k	I	I	amb	C–N, C=N, BC ₃ , BC ₂ O	Bactericidal application
Polyaniline/PI	10 600	1400	7.5	I	I	I	I	amb	Polyaniline doped carbon	pH Sensor
Heteroatom doped PI	10 600	500	12.5	I	I	I	I	I	I	Biosensor
citric acid + urea	10 600	17.6	1.0	I	Ч Г	170	33	amb	Hall coefficient: +0.099 ± 0.043 cm³ C ^{−1}	Humidity sensors
citric acid + urea	10 600	10.2	1.37	I	× L	170	79	amb	Surface area: up to ≈400 m² g ^{−1}	VOC sensors
citric acid + urea	10 600	10.2	1.02	I	<i>メ</i> 「	170	59	amb	Surface area: up to ≈700 m² g ⁻¹	VOC sensors
citric acid + urea	10 600	6.85	1.05	I	<u>х</u> Г	170	06	amb	Different film thickness	Motion and pressure sensors
adenine/glucose	10 600	5.3	1.12 1.07	I	* -	170	124	amb/ N ₂ / O2	Imidazolic / pyrrolic nitrogen and oxygen functionalities	CO ₂ sensor
Ā	10 600	180	I	I	I	I	I	I	Surface area: 350 m² g ⁻¹ high thermal conductivity	Gas sensors

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Ref

Remarks

[178]

N, B doped

graphene shows

laser-induced

peroxidase-like

high

activities

[671]

Direct spraying of

polyaniline on

laser carbon

material

[77]

Electrochemical

sensing of

dopamine

[180]

Electronic properties

[181]

+(NH₄)₆Mo₇O₂₄

measurements

/ Hall

(for Schottkyjunctions) / +Nal

(as a porogen)

[174]

+Zn(NO₃)₂ /+ZnO (as hard

templates)

[182]

cross-sectional

Detailed

microscopic

electronic properties

analysis /

[183]

cross-sectional

detailed

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composite gas

sensor

[184]

Fabrication of LIG/cement

analysis + glucose as foaming agent

microscopic

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Table 2. (Continued).		Precursors	ā	ā	Paper (cardboard)	ī	ā	ā	ā	ā	Ы
		۸ [mm]	405	10 600	532	355	450	1030	10 600	10 600	1030
		ر. s mm ا		1.6	15	1	8.5	1.0	127	9	0.5
		۲ [w]	0.16	0.57	0.4	2.5	0.5	0.6	0.3	5.6	0.23

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				Laser pa	Irameters				Surface			
Precursors	λ [nm]	v [mm s ⁻¹]	P [W]	τ	f [Hz]	d [um]	F_{A} [] cm ⁻²]	atm	the resulting carbon	Target of study	Remarks	Ref
L.	405		0.16	>2 us	1	1	1	1	Resistance: 108 Ω sq ⁻¹	Humidity sensor	Laser writing performed in situ while recording SEM images	[185]
d	10 600	1.6	0.57	357 us	I	100	I	I	Surface area: 6.83 m² g ^{− 1}	Gas sensors	Three-line electrode for ammonia sensing	[186]
Paper (cardboard)	532	15	0.4	I	I	18	I	I	-C=C, -C-O, -C=O	Multi-sensors	Conductive carbon films	[138]
d	355	1	2.5	I	30 k	400	7.4	amb	Sheet resistance: 65	Strain sensors	Patterned carbon transferred to PDMS	[781]
Ы	450	8.5	0.5	I	I	100	I		I	Acoustic sensors	Carbon patterns capable of detecting and generating sound	[188]
Id	1030	1.0	0.6	I	I	I	I		I	Biosensors	The device coated with gold, r-GO, and polyaniline for flavor sensing	[681]
ā	10 600	127	0.3	I	I	I	I	amb	Foam-like topography	Biosensors	Monitor living cells by impedance measurement	[061]
ā	10 600	59	5.6	I	I	180	2.3	amb/N ₂	-C=C-,-C-OH, -C-OOH, pyrrolic, pyridinic, amide Conductivity: 10 S cm ⁻¹	Biosensors	Enzymatic pH-based urea sensors	[01]
Id	1030 532	0.5	0.23 0.08	400 fs	120 k	S	S	amb	Hydrophobic surface, <40 Ω sq ⁻¹	Biosensor	bisphenol A detection in river water	[161]
Cellulose	10 600	15	2.4	I	I	I	I	amb	–OH, –CH, C=C, C–H Resistance: 2–12.2 kΩ	Force sensors	Amorphous carbon films with high porosity	[192]
Lignin/PVA/urea film	10 600	I	I	I	I	I	1	amb	-C=C, -C=O, -C-N, -COOH groups Resistance: 2.8 Ω sq ⁻¹	Biosensors	Glucose detection from sweat	[193]
												6000000

ADVANCED MATERIALS **ADVANC**

Table 2. (Continued).

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Precursors λ [mi] v [mm s ⁻¹] P [W] P1 tube 10 600 15.3 0.85 Polyaramid 10 600 130 3 Block copolymer hybrid 10 600 - - PI - 40% 35% PI - - 0.15- PI - - 0.15-		f [Hz] 20 k - コ k	d [um] 62.7 120	F _A [] cm ⁻²]	atm	groups/properties of the resulting carbon	Target of study	Remarks	
Pl tube 10 600 15.3 0.85 Polyaramid 10 600 130 3 Block copolymer hybrid 10 600 - - Pl - 40% 35% Pl - 10 600 80 Pl - 40% 35%		20 k	62 <i>.7</i> 120 -			•	•		Ref
Polyaranid 10 600 130 3 Block copolymer hybrid 10 600 - - Pl - 40% 35% Pl - 40% 35% Pl - - - Pl - 0.015 - Pl - - 0.15	m Ι	÷ .	120		1	1	Strain sensors	3D Tubular Sensing System	[194]
Block cooplymer hybrid 10 600 - - thin films - 40% 35% Pl - 40% 35% Pl - - 40% Pl - 0.0 11% Pl - 0.15- 0.4	1	1	I	I	amb	-C=C-, -C-OOH,- C=O, Cu ₂ O groups	Biosensor	Cu/CuO/Laser- induced carbon composites for glucose detection	[195]
PI - 40% 35% PI 10600 80 11% PI - 0.15- 0.4					amb	-C-C-' -C=0' -C-0	Gas sensor	pluronic F127 Pluronic F127 copolymer with resold hybrid thin films was laser carbonized to form foam-like structures	[[2]
PI 10600 80 11%	-	1	I	I	amb	1	Pressure sensors	MoS ₂ nanoparticles embedded in 3D LP-C foam to increase sensitivity.	[196]
PI - 0.15- 0.4	- %	1	I	1	1	1	Pressure sensors	r-GO coated cloth layers were stacked between two LIG and connected to an external circuit	[761]
			I	I	I	-C=C-, -C-C-, -C-O-, -C=O, Cu _{2p}	Non-enzymatic glucose sensors	Cu nanoparticles anchored in LP-C by selected area electroless deposition	[861]
PI 10.5%	0.5%	1	I	1	1	the sheet resistance of ≈25 Ω cm ^{−1}	Non-enzymatic glucose sensors	LP-C layers were coated with Au and Ni by electroless deposition and used as the working electrode	[661]

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		Laser p	arameters				Surface			
v [mm s	[M] P [W]	τ	f [Hz]	[mn] p	F _A [] cm ⁻²]	atm	groups/properties of the resulting carbon	Target of study	Remarks	Ref
75/25	0 0.25/9	-/sri	-/00/	20/75	-1	amb	C=C, C-OH, C-N, C-O, C=O O-C=O, $\pi-\pi$ satellite, pyrridinic N, amide, pyrrolic N, quatemary N, aliphatic O=C, aromatic O=C, C-O-C, C-OH	Biosensors	Porous 3D-like graphene films for electrochemical sensing of Doparmine	[200]
0.28	3.2	1	I	≈150	- Antenna relatec	ampa	the sheet resistance of 5.8 Ω sq ⁻¹	Biosensors	Electrochemically deposited Au or Ag nanoparticles/laser- scribed graphene for electrochemical sensing of uric acid and doparnine	[102]
I	ε	I	I	I	I	amb	C-0, C=0, 0-C=0	Antenna-based strain sensors	Flexible LP-C layer on Cu tape, for wireless human motion monitoring	[202]
55	-	I	50	1	1	amb	Side-to-side total resistance ≈1 kΩ	Antennas	Realizing 3D-printed elements as an Ultrahigh (UHF) radiofrequency identification (RFID) application using LP-C	[203]
100	6	I	I	I	I	amb	The sheet resistance of $62~\Omega~cm^{-1}$	Antennas	Antenna for S-band wearable	[204]

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Table 2. (Continued).

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				Laser pa	rameters				Surface			
Precursors	λ [nm]	v [mm s ⁻¹]	P [W]	1	f [Hz]	q [mm]	F _A [] cm ⁻²]	atm	the resulting carbon	Target of study	Remarks	Ref
PES and PES-MoS ₂ membranes	1	-	1.5–5	1	1	1	1	amb	CS, CC Sheet resistance of 5-26 Ω sq ⁻¹	Polygon monopole antennas	Laser-induced graphene/2D transition metal dichalcogenides heterostructures	[205]
09	445	0.28	0.5	1	1	I	I.	Ar	Surface resistivity of 100 Ω sq ⁻¹	Antenna sensor	Laser direct writing for GO-coated Cu-carbon hybrid materials toward humidity sensors	[206]
Ы	355	I	17	10 ps	I	26	I	amb	Sheet resistance: 50 Ω sq ⁻¹	Antenna sensor	Self-powered wireless direction senor	[207]
CNT/Quartz	450	I	0.5-2	1	1	I	1	amb	Surface resistance: 4 Ω	Ultra-wideband antenna	Antennae with ultrawide bandwidth performance between 3.4 and 14 GHz	[208]
Graphene papers	I	I	I	I	I	I	I	amb	Electrical Conductivity: 4.20 × 10 ⁵ S m ⁻¹	Antennas	Graphene papers formed by compression of graphene nano pellets	[209]
ā	1	10%	16%	1	1	1	1	amb	Sheet resistance: 1.2 ± 0.06 Ω cm ^{−1}	Antenna and rectenna	Ag nanoparticle/LP-C stretchable rectennas to harvest RF energies with low-power sensors	[2 10]

Table 2. (Continued).



Figure 11. Illustration of the laser-carbonization / laser-patterning process and the dependencies of LP-C on the properties of the primary film and the reaction conditions.

carbonization. For example, the cyclization reaction is too slow to be induced by the rapid temperature increase of the laser beam as it is limited by the diffusion of O₂. To achieve effective carbonization, the heating rate by the laser was finely adjusted to $\approx 50~{\rm K~s^{-1}}$. Second, the absorption of the infrared laser beam (968 and 998 nm) in the PAN precursor needed to be enhanced by impregnation with IR absorbers (graphene nanoplatelets).

The laser-induced carbonization of other polymers as starting materials for efficient laser-carbonization, such as polysulfones, were also reported.^[133] Around the same time as the revival article on LC-PI appeared, the laser-induced carbonization of polyfluorene was reported.^[134] Another prominent precursor for laser-induced degradation is poly-dimethylsiloxane (PDMS) which converts into silicon carbide structures upon laser irradiation.^[135–137] In the past few years, the approach of laser-carbonization has been applied to other natural polymeric materials, such as cellulose, wood, paper, or coconut fibers directly.^[9,138,139]

Direct carbonization of molecular starting materials has not been reported. Generally, the high energy impact of the laser beam causes the evaporation of volatile molecular species and prevents the effective formation of a carbon network. In a report in 2018, the thermal conversion of molecular precursors into so-called carbon nanodots (CND), which is considered a precarbonized or a pre-condensed intermediate was reported. After pre-carbonization (300 °C), organic materials are less volatile and, additionally, the energetically unfavorable dehydration reactions are completed. Laser-treatment of such pre-carbonized products leads to conductive porous carbon films similar to LC-PI.

3.2. Properties and Process Parameters

3.2.1. General Properties

Generally, laser-carbonization affords carbon films with a hierarchical porous morphology as depicted in **Figure 13**C–E. Depending on the composition, the physical and chemical properties of the primary film, and the reaction conditions, different chemical



Figure 12. Timeline of laser-patterned carbons showing some examples of modern kick-off studies on the topic of laser-carbonization. A) "Writing" conductive patterns of graphene into graphene oxide primary films with a 790 nm femtosecond laser in 2010; Reproduced with permission.^[122] Copyright 2010, Elsevier; B) "Writing" conductive patterns of LC-PI into commercial PI primary films with a 10.6 μm CO₂-laser in 2014; Reproduced with permission.^[123] Copyright 2014, Springer Nature; C) Laser-induced carbonization of carbon nano-fabrics based on PAN; Reproduced with permission.^[124] Copyright 2016, ACS.



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Figure 13. A) Schematic illustration of the properties of LP-C (mechanical (B), structural (C), chemical (D), electronic (E)) in dependence on the composition and properties of the primary film, the substrate, and the reaction conditions (A).

and structural properties, like porosity, surface area, local crystallinity, and morphology are obtained.

The resulting mechanical properties are dependent on the degree of carbonization and the structural properties, but also on the substrate properties (Figure 13B).^[182] In fact, the LP-C / substrate interactions are a critical component of the overall mechanical performance. LP-C derived from PI is reported to exhibit \approx 100% retention of its electrochemical performance up to a bending radius of 25 mm.^[157] Similar results were reported in a study in which, two LC-PI films were stacked together to form a single device.^[166] LP-C neural electrodes derived from Parylene-C showed excellent adherence to the metal contact pads after adhesion tests.^[116] Based on the results presented in these studies the general structural and chemical functionalities are largely retained upon mechanical deformation, at least regarding bending. Although flexibility in terms of stretching is limited (<3%) due to the inherent brittleness of the LP-C film.^[182] This makes LP- Cs applicable in a range of flexible electronic and electrochemical applications, but not universally applicable in flexible devices.

A general observation in LP-C is the formation of a structural and chemical gradient across the film (Figure 13) due to the effective reaction temperature gradient induced by the unidirectional energy impact of the laser beam (**Figure 14**).^[10,182] The chemical composition and the chemical surface properties, like functional groups, active sites, and composite structures are mainly dependent on the type of precursor, additional reactants, and the reaction atmosphere (Figure 13D).^[180] The principle electronic structure of LP-Cs, that is, conductivity, charge carrier properties and electronic band-gap depends on mainly the precursors and the reaction conditions.^[181] The latter is also decisive for the degree of carbonization or graphitization, which influences the conductivity (Figure 13E). Moreover, additives or reactants are used to implement heterostructures (nanoparticles) into the LP-C, by which electronic heterojunctions are incorporated.^[183]



Figure 14. Addressing structural and mechanical properties of LP-C.^[182] A) Optical cross-sectional micrograph of an LP-C film supported on a PET substrate; B) Cross-sectional high-angle annular dark-field-STEM overview of LP-C film (PET substrate on bottom cropped, some pores appear black due to insufficient infiltration, web of Lacey TEM support film superimposed, epoxy at constant grey value); C) Corresponding electron energy loss spectroscopy elemental maps of C, N, and O taken from the dashed area. D) Bonding analysis of the same region (blue: pure graphitic carbon, red: amorphous pore walls, yellow: pockets, white/black: resin; E) Representative selected-area electron diffraction patterns from the upper and lower regions of the LP-C film where the atomic-resolution micrographs were recorded.^[182] Reproduced (Adapted) with permission.^[182] Copyright 2021, Springer Nature.

3.2.2. Chemical Structure – Heteroatoms – Functional Groups

Non-metal-heteroatom-doping of LP-C is a common strategy to enhance their electrochemical performance and has a potential application in low-cost and flexible energy storage devices. For example, during laser processing of polyimide (PI), impurities in the form of amide groups are often observed in the material.^[10] Han et al. developed a one-step strategy to fabricate nitrogendoped LC-PI by introducing melamine into the polyamide acid (PAA) as a nitrogen-rich doped starting solution.^[156] Tour's group demonstrated boron-doping of LC-PI by impregnating PI sheets with an H₃BO₃, resulting in a three-fold increase in their capacitance.^[54] Furthermore, the hetero-doped LP-Cs exhibit a high peroxidase-like activity in bactericidal applications^[178] and electrochemical sensitivity for bio-neuromodulator molecules (like dopamine).^[177]

LP-Cs synthesized from PI as precursors using a UV-laser were doped with nitrogen and sulfur by using polybenzimidazole as the N source and DMSO as the S source.^[106] Alternatively, Rahimi et al. sprayed polyaniline directly on the LP-C to form a polymer-doped carbon film to enhance the mechanical properties of electrochemical pH sensors.^[179] A comprehensive cross-sectional analysis based on high-resolution transmission electron microscopy coupled with electron energy loss spectroscopy demonstrates the gradual decrease in heteroatom content across the film (Figure 14).^[182]

3.2.3. Process Parameters

The properties of LP-Cs such as morphology, crystallinity, surface area, conductivity, etc. are largely dependent on the reaction parameters. Especially the laser parameters like wavelength (λ), incident power (*P*), scanning speed (v), fluence (*E*), pulse duration (τ), pulse frequency or repetition rate (*f*), spot size (*d*), and beam shape were in the center of several studies. Other reaction parameters like reaction atmosphere and pressure are also critical. Moreover, the properties of the precursor materials, like extinction coefficients, composition, heat conductivity, and heat capacity as well as the reactivity of the precursor films are important to consider. Some insights into the decomposition mechanism of the precursor films were also obtained by analyzing the composition of the ejected material or gases during laser-carbonization. In the following paragraphs, the influence of these parameters on the properties of the LCMs are briefly described.

A first comprehensive mechanistic study on the lasercarbonization of PI was published in 1985, in which several process components, such as laser wavelength, fluence, or the composition of the ejected materials were individually studied.^[105] In principle, laser-carbonization, although performed with UV or visible lasers, followed a photo-thermal rather than a photochemical mechanism which was confirmed by a sharp reaction threshold in the excitation energy. In other words, the initially induced electronic absorption leads to a rapid transformation into vibrational heating of the precursor film and subsequently a temperature-catalyzed carbonization reaction.

Extinction Coefficients: The absorbance of the incident beam by the film is critical for the efficient transformation of photonic into thermal energy. The thermochemical decomposition of PI

primary films with particular emphasis on the light-matter interactions and the extinction coefficients have been investigated in an exemplary study in 2019.^[10] According to this study, the extinction of the laser beam in the PI film follows the Beer-Lambert law. The extinction coefficients are typically determined at the laser excitation energy (10.6 μ m \triangleq 943 cm⁻¹) by Fourier-transform infrared spectroscopy. This is the resonant energy range of C-H and C-H₂ vibrations. However, plasmonic absorption of particulate or polymeric precursors is also present in this energy regime. It has been demonstrated that different precursors show characteristic reaction responses to the laser parameters like incident power and scanning speed.^[144] Moreover, a correlation of the obtained electric conductivity to the extinction coefficients at the excitation wavelength was found. The addition of high-temperature inert IR absorbers such as graphene nanoplatelets or carbon nanotubes helps to increase photonic absorption and heat dissipation within the primary film.^[124,160]

Ejected Material: The type and properties of the ejected material during laser impact onto PI were first qualitatively analyzed by gas chromatography–mass spectrometry.^[105] Besides soot (colloidal carbon plasma) that evolves during the laser-carbonization, typical pyrolysis reaction products such as H₂O, CO₂, and CO were observed as trace amounts of hydrocarbons. The soot recondenses to form a carbon-like material, which deposits at the cooler zones. The formation of soot is effectively suppressed in the presence of O₂ as a combustion accelerator.

Composition and Additives: The extinction coefficients and other materials properties such as heat capacity and heat conductivity but also reactivity depend on the chemical properties and the composition of the primary films. Additives play an important role in the laser-carbonization process as they change both the chemical and the physical properties of the primary film. For example, a study in which cellulose nanofibers (CeNF) were carbonized with a 10.6 μ m laser showed efficient conversion only in the presence of sodium as a counter ion in the CeNF.^[140] It was argued, that sodium lowers the activation energy of the dehydration step during carbonization. It is, however, more likely that sodium transforms into sodium oxide during laser-carbonization and induces a carbothermic reduction, which catalyzes carbonization.

Effective carbonization of a variety of precursor materials (filter paper, cloth, and other cellulose-based materials) was enabled by previous heat pretreatment, for instance, exposure to a propane torch.^[142] Thereby, the precursor materials were partly carbonized (charred, pre-carbonized) into amorphous carbon. The materials with an amorphous carbon surface absorbed enough laser energy to be fully carbonized. Such a pretreatment as an essential step was confirmed in other studies.^[103,211] Furthermore, it illustrates the effect of product absorption during laser-carbonization.

Porogens or templating agents are commonly used to modify the structure and morphology of carbons. Sodium halides are particularly well suited as porogenic agents for laser-carbonization. During laser-carbonization temperatures >1500 °C are induced. The melting point of the sodium-halide salts is between 661 and 802 °C. However, in this temperature regime oxidation and carbothermic reactions occur. Sodium iodide (NaI) was employed to increase the specific surface areas of the LP-C. An increase in electronic conductivity and surface area corroborates a



Figure 15. Addressing structural properties of LP-C; Upper: Carbon lines written with laser power of 180 to 200 mW (scale bar: 100 μm); Lower: Carbon lines written with 30 mW starting from carbonized points (scale bar: 100 μm); Right: Schematic of the point-to-line strategy; Reproduced with permission.^[164] Copyright 2021, Wiley.

deeper penetration of the laser beam into the film in the presence of NaI. A hard-templating effect based on carbothermic reduction of ZnO was utilized for increasing the microporosity of LP-Cs.^[39,174] Nanoparticle impregnation or functionalization can be simply achieved by the addition of respective metal salts to the primary inks. For example, LP-C was decorated or impregnated with iron oxide or metallic molybdenum carbide nanoparticles.^[181,212]

Fluence, Incident Power, and Scanning Speed: In most studies, the primary laser settings like power *P* (W), scanning speed *v* (mm s⁻¹), or fluence *F* (J cm⁻²) have been optimized. According to several studies, the efficiency of laser-carbonization is predominantly dependent on the fluence *F* exposed to the precursor film and is usually given as areal F_A in J cm⁻².^[100] Depending on the laser source, the laser parameters are optimized for fluence values in the range between 0.01–200 J cm⁻² (Table 2). The divergent range of these values is attributed to inconsistencies in the methods of determination and varying laser technology.

Specific investigations on the influence of the laser parameters on the structural properties of LR-GO prepared with a 10.6 μ m laser were included in a study from Tran et al.^[155] A threshold fluence was necessary to induce sufficient laser reduction, which again points to a photo-thermal rather than a photo-chemical mechanism. In a study from Wan et al. a 780 nm laser operating at 50 MHz (70 fs) the power was varied between 3 and 13 mW and a clear dependence of the degree of carbonization on the laser power was found.^[145] In a more recent study, the scanning speed and output power were screened and correlated into matrices showing the effectiveness of laser-carbonization in dependence of output power and scanning speed.^[177]

An interesting phenomenon demonstrating the influence and limitations of the precursor film in terms of heat capacitance and heat conductivity was described recently by Guo et al.^[164] In this study, PI was carbonized with an 800 nm femtosecond laser. An initial carbonization point with fluence above the threshold was set and all subsequent carbonization lines starting from this point were "written" at fluences three times lower than the fluence threshold for bare PI (**Figure 15**). Generally, **lower** and **up**-

per threshold values for effective laser-carbonization or ablation, respectively, are found in several studies summarized in **Table 3**.

The laser fluence is principally a measure of the reaction temperature and has thus a significant influence on the properties of the LP-C films. For example, the decomposition temperature of PI (commercial Kapton) is \approx 500 °C in air and decomposes almost exclusively to CO₂ and CO.^[216]The energy threshold could be a measure of the decomposition temperature. The fluence range within the lower and upper thresholds determines the effective temperature window. Within this window, the film composition, morphology, and electronic properties are directly dependent on the fluence. For example, the porosity of LC-PI shows significant differences depending on the fluence.^[10] Also for GO, the reduction efficiency is clearly dependent on the laser fluence. The lower carbonization fluence threshold of GO may be correlated to the

 $\ensuremath{\textbf{Table 3.}}$ Overview of the threshold values of the laser fluence found in different studies.

Precursor	Wavelength [nm]	Fluence (lower threshold) [J cm ⁻²]	Fluence (upper threshold) [J cm ⁻²]	Ref.
GO	243	0.010		[11]
GO	243	0.006		[213]
GO	248	0.07		[214]
GO	266		0.050	[145]
GO	355		0.085	[145]
GO	532		0.15	[145]
GO	1064		0.38	[145]
PI	248	0.027		[105]
PI	308	0.070		[105]
PI	351	0.12		[105]
PI	800	0.9		[164]
PI	10 600	1.3		[10]
PI	405	83.4		[215]
		(single pulse)		





Figure 16. A) Image visualizing the influence of the focus of the effectively irradiated area; Reproduced with permission.^[142] Copyright 2018, ACS. B) Image visualizing the difference between CW and pulsed laser modes, the pulse duration, and repetition rate. Reproduced with permission.^[155] Copyright 2018, ACS.

threshold temperature of 200–230 $^{\circ}\text{C}$ for the reduction of GO obtained in reference experiments. $^{[114,146,145]}$

The laser scanning speed is a particular parameter that correlates with the reaction kinetics of the specific carbonization reaction of the precursors.^[155,177,144]

Wavelength and Resolution: Systematic studies on the effect of the laser wavelength to the reduction of GO show that deoxy-genation is more effective in the short wavelengths region toward the UV while the reduction to the sp²-carbon lattice is more effective at longer wavelengths. These insights enable differentiation between photochemical and thermochemical effects.^[145]

Although, in the early investigations on the laser-carbonization mechanism of PI short UV-lasers (248, 308, and 351 nm) were used, the most commonly used laser source for laser-carbonization of PI is the CO₂ laser ($\lambda = 10.6 \mu$ m). Other wavelengths such as 405 nm are increasingly used due to the higher achievable patterning resolutions. The resolution of LC-PI has been improved from ≈ 100 to $\approx 12 \mu$ m and even 6.5 μ m.^[164,215] A comparison of these studies clearly shows that the effective power/fluence threshold is largely dependent on the wavelength of the laser.

Focus and Beam Shape: The effective reaction temperature is varied with the fluence, which peaks in the focus of the laser beam. The effective fluence exposed to the precursor film can be reduced by defocusing the laser beam. Chyan et al. demonstrated that defocusing of a 10.6 µm laser has a strong influence on the properties of LP-Cs from different precursors, such as PI, Kevlar, cardboard, etc. (**Figure 16A**).^[142] The overlapping regions of the individual laser lines thus experienced multiple exposures which enhanced the electrical sheet conductivity of the product films.

Besides the beam profile, the beam shape is a variable in the laser-carbonization process. To improve the throughput of laser-carbonization a line-beam CO₂ laser reduction process of GO was investigated.^[155] To this end, a cylindrical lens was employed to achieve an effective line shape of 3.9 × 0.23 mm². Parameters such as pulse duration and repetition rate of the 10.6 µm laser were finely adjusted to meet the optimum requirements of the laser reduction, with the pulse-to-pulse pitch being the effective critical parameter.

Repetition Rate / Pulse Duration: Pulsed lasers are frequently used for laser carbonization. Their characteristics are defined by pulse frequency (repetition rate) and pulse duration (Figure 16B). Both parameters were shown to have an influence on the properties of the LP-Cs. Pulsed laser beams show decisive advan-

tages in terms of power control over continuous wave (CW) operated lasers^[155]To test this effect, the pulse duration and repetition rate of a CW CO₂-laser were modulated by a beam chopper and studied toward the performance of LR-GO in EDLCs (Figure 16B).^[155] It was found that the beam modulation from 100 to 1 kHz resulted in a better laser-reduction efficiency as indicated by an improved capacitance. The laser-reduction mechanism of GO was systematically studied in 2014 and optimized for the application of LR-GO films as electrodes in transparent organic photovoltaics.^[114] Moreover, the number of pulses of a 248 nm KrF laser showed a significant influence on the efficiency of the laser reduction, especially in terms of charge-carrier mobility. A 405 nm fiber-coupled laser integrated into a scanning electron microscope (SEM) chamber allowed for the in situ investigation of the laser-carbonization process of PI.^[215] The results provide insights into the reaction kinetics of PI.

Reaction Atmosphere: The presence of O_2 during lasercarbonization was initially found to play no direct role in the reaction rate or the ablation process.^[105] However, later it was found that the reaction atmosphere has a significant influence on the surface properties of the carbonized film. Differences appear mainly in the oxygen content on the surface, which is significantly higher in the presence of oxygen.^[183] Subsequently, the surface polarity is much higher which was confirmed by contact angle measurements.^[10,217] In general, the presence of O_2 promotes the combustion reaction at high reaction temperatures. Due to a more complete combustion reaction, the remaining carbon shows a higher degree of graphitization which is reflected in lower defect and disorder-related signals (D, D3, and D4) in the Raman spectrum.^[10]

Substrates: Depending on the targeted application, the choice of substrate is critical. The penetration depth of the laser energy is limited by the absorptivity (extinction coefficients), heat conductivity, and heat capacity of the primary film. The remaining thermal energy arriving at the substrate is either absorbed by, reflected from, or dissipated through the substrate (see Section 2). Similar to the primary film, the fate of the thermal energy is quantified by absorptivity, heat conductivity, and heat capacity of the substrate. The absorbed thermal energy is either dissipated across the substrate or leads to reactions of the substrate itself, such as physical melting, evaporation, or reactions (carbonization). In reverse, the heat dissipation within the primary film also depends on the same physical properties of the substrate, that is, more heat is generated within the primary film when reflective substrates are used. On the other hand, thermally conductive

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Material	Thermal conductivity [W (m K) ⁻¹]	Heat capacity [J (g K) ⁻¹]	Absorptivity @ 10.6 μm [%]	Melting point [°C]	Boiling point [°C]	Electrically conductive
Al	237	0.90	\approx 3 (reflective)	660		1
PET	0.24	1.03	High	264	≈350	
Graphite	≈400	0.70		3600		\checkmark
Si-wafer	149	0.71	Reflective	1410	3260	
Glass	0.8	0.75	High	≈1500	≈2200	
Cu	401	0.39	\approx 2 (reflective)	1084		\checkmark
Stainless steel	16	0.49	\approx 11 (reflective)	1510		\checkmark
PI (Kapton)	0.75	1.09	≈92	-	≈520	

Table 4. Overview of some properties of the substrates used. The values for absorptivity are taken from a comparative study.[11]

substrates may absorb the thermal energy and dissipate it. Therefore, the intrinsic thermal properties of the substrate influence the carbonization and the properties of the primary film.^[103]

The primary film formation and interaction (bonding) with the substrate also depend on the surface tension (hydrophilicity) of the substrate. Decisive is the interfacial tension, between ink and substrate. Substrates may be grouped into different categories according to their properties: electronically conductive, mechanically flexible, or stretchable (**Table 4**). Polyethylene terephthalate (PET) as a substrate melts at the interface and merges into the LP-C, which supports the stability of flexible electronics.^[174]

3.3. Applications – Sensors, Energy Storage, Electrocatalysis, Antennas – Literature review

3.3.1. Overview

The electrically conductive carbon materials obtained from lasercarbonization are generally useful for application in film-based flexible electronics and are listed in Table 2. Conductive porous carbon materials generally offer many advantages, but there is always a trade-off between porosity and electrical conductivity. Moreover, many applications rely on large interface materials and the interaction of gaseous or liquid media with the electronic surface or specific active sites on the surface of the materials. As described in the previous sections, LP-C exhibits an intrinsic porosity along with a conductive graphitic structure, which makes it suitable for applications as electrodes. Its surface functionalities are easily tunable and it can often be used with little to no interface engineering. Four areas of application have been distinguished as particularly suitable test beds for LP-Cs, namely electric double-layer capacitors (EDLCs), electrocatalysis, sensors, and antenna-related applications (Figure 17). In this section, we collect and discuss reports from these fields of application.

3.3.2. LP-C in Electric Double-Layer Capacitors

Literature Review: Among the most widely studied applications of high-surface-area carbons in flexible electronics are EDLCs. EDLCs are devices where energy storage is achieved through electrostatic charge deposition at the electrode/electrolyte interface.^[218] The charge stored at the biased

electrode surfaces and the proximate layer with an equivalent counter ion population continuously increases with the potential difference between the two, limited only by the standard electrochemical potentials of the electrolyte ions and/or the stable voltage range of the electrolyte solvent. Therefore, for high-performance EDLCs, high surface areas with a hierarchical porous structure are preferred. Such requirements are generally fulfilled in LCMs.^[219] In light of future flexible and wearable electronics as well as on-chip fabrication of electronic devices, particular focus was laid on the development of so-called micro-EDLCs (mEDLC). mEDLCs are mostly developed in a planar fashion in order to be integrated onto different substrates in form of inplane interdigitated electrodes (Figure 17A). For further reading on the operation principles, device performance parameters, engineering, and limitations one of the plenty of review articles on the topic is recommended.^[220,221]



Figure 17. Overview of the most prominent fields of application for lasercarbonized materials: Electrochemical sensors, electrochemical energy storage, antenna-related devices, and electrocatalytic devices.



Α





Figure 18. Addressing structural properties of LP-C; A) Cross-sectional SEM image of GO (left) and laser-reduced GO (right); Reproduced with permission.^[127,222] Copyright 2012, AAA Science. B) Cross-sectional SEM image of a PI substrate with both sides laser-treated to form LC-PI (laserinduced graphene – LIG) and top-view SEM image of the LC-PI films showing a porous 3D network; Reproduced with permission.^[166] Copyright 2015, ACS. C) Illustration of the laser-induced reduction of GO and laser-reduced carbonization of PI and the resulting morphological properties of the film and its impact on properties (SSA, Capacitance).

Laser-carbonization is a direct synthesis method suitable for the fabrication of porous carbon electrodes on both rigid and flexible substrates.^[154,168,169] In 2015, it was demonstrated, that LC-PI, processed with a 10.6 µm CO₂-laser from commercial Kapton tapes show a high electrochemical performance in both vertically stacked and in-plane arrangement (Figure 18A).^[166] To test and improve the mechanical flexibility, LC-PI was transferred to a stretchable PDMS substrate and showed only little impact on the performance in the bent or in the stretched state.^[165] It has been shown, that the capacitive performance of LC-PIbased mEDLCs can be significantly improved by conducting the laser-carbonization in an inert gas atmosphere.^[142] Polymers can be directly laser-patterned/carbonized to derive electrodes, but for carbonizing nanomaterials (e.g., GO, PAN), the precursor ink/slurry has to be first coated onto a suitable rigid/flexible substrate before laser irradiation. The slow carbonization reaction of polymers like PAN was improved by integrating carbon nanotubes as additives to support the absorption of the infrared laser beam and directly laser-carbonized on a printed circuit board as substrate.^[160] For obtaining flexible EDLC electrodes, direct laser-carbonization of polymers (cellulose, PAN fiber mats, PI, etc.) is carried out, however, an extra step of pattern transfer to a flexible substrate is required for the fabrication of flexible supercapacitor electrodes based on laser-carbonized GO (Figure 18B).^[127,154,155,222] A laser-reduced rGO/ZnO composite was prepared by laser-treatment of a $Zn(NO_3)_2$ impregnated GO film.^[223] To increase the throughput of the laser-fabrication technique, a line-beam shape was utilized in a CO₂-laser to reduce GO films.^[155] LP-C electrodes can also be used in the form of a sandwich structure to increase the capacitance.^[166] Other options that increase the current density are heteroatom doping (B, Ni, Fe)^[54,175] nanomaterial bridging (CNTs),^[224] or decorating the laser-carbonized electrodes with pseudocapacitive materials such as MnO₂, MoS₂ FeOOH, or polyaniline (PANI).^[169,170,172] Micro supercapacitor arrays based on pseudocapacitive ZnP nanosheets anchored on LP-C electrodes were integrated with an Au-based triboelectric generator and graphene-based strain sensor, demonstrating a self-powered stretchable system.^[171] Pseudocapacitive graphene/ferrocene composites produced highly reversible, conductive LP-C electrodes for high-power, high-energy density EDLCs.^[113] Additionally, LP-C electrodes are also suitable for the fabrication of all-solid-state supercapacitors by direct laser writing on flexible polymers.^[157]

B

Molecule-based carbon nanodots (CNDs) were demonstrated to be versatile precursors for LP-C networks with excellent electrochemical properties. Such LP-C electrodes were first fabricated on stainless steel substrates and tested for their performance in EDLCs.^[161] By changing the reaction atmosphere between Ar or O₂ the frequency response of these EDLCs has reduced 0.29 ms for the utilization as current filters in electronic circuits.^[158] A combination of CNDs and GO leads to drastically improved electrochemical properties.^[159] In addition, stretchable microsupercapacitors, fabricated via laser patterning of MnOx/cotton cloth microelectrodes have also been reported,^[173] with a rated voltage of 60 V can light up 20 LEDs for more than 30 s.

Challenges: Obvious challenges are improving the electrochemical performance of the mEDLCs in terms of energy and power densities, cyclability, high retention upon bending, high flexibility, etc. Clearly, energy densities in energy storage devices need to be improved to meet the requirements of long-term energy storage. To be applicable in future flexible electronic devices a fundamental understanding of the surface properties and the porosity of LP-Cs is necessary. Standard characterization methods such as sorption analysis commonly fail, due to the low amounts of materials. The specifications of any device need to be adapted to the market-specific demands, as every commercial EDLC is designed for the specific demands of the intended application. For example, the capacitive frequency window is crucial for many electronic circuit applications such as AC line filtering. Therefore, universal strategies for selective tuning of the LP-C materials parameters must be a goal of current research. The applicability of LP-Cs on different substrates is another requirement. To adopt a general concept for a variety of precursors, universal strategies to apply carbon precursor films on different



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Figure 19. Addressing chemical properties of LP-C. A) Fabrication process of the laser-carbonized PI / NiFe or Co-P electrodes. Commercially available Kapton (PI) was directly laser-carbonized. Then the catalysts were electrochemically deposited on the laser-patterned carbon; B) Schematic drawing of the integrated water-splitting electrode membrane. Reproduced with permission.^[175] Copyright 2017, ACS.

substrates need to be identified. Although minimal feature sizes of only a few μ m have been achieved, miniaturization is still a challenge in most LCMs. The abovementioned examples, PI and GO have been widely investigated as precursors of LP-Cs, however, their relatively high costs may be a limiting factor for widespread application. Additionally, limited tunability in terms of surface and electronic structure is inherent.

3.3.3. LP-C in Electrocatalysis

Literature Review: In the past decades, carbon nanomaterials such as CNTs, graphene, and other waste/biomass-derived bulk carbons have been extensively studied as electrocatalyst materials or conductive supports for electrocatalysts and contributed to a fundamental understanding of electrochemical carbon-electrolyte interfaces.^[225,226] These materials exhibit very large surface areas, moderate to high electrical conductivity, and chemically reactive sites for the adsorption and desorption of reactive intermediates during catalysis. General strategies to improve the electrocatalytic activity in carbonized materials include the introduction of active sites by heteroatom doping, nanostructuring, pore engineering, surface functionalization, defect engineering, or hybridization and composite synthesis.^[225,226] For an in-depth understanding, we refer to one of the recent review articles.^[226,227]

LP-Cs has mainly been published as a catalytic support for electrochemically active species such as $Ni_xFe_y(OH)_{2x + 3y}$ (NiFe) catalyst or a combination of $Co_3(PO_4)_2$ and CoO_x (Co-P) as well as Pt nanoparticles. A full water splitting set-up was fabricated using these active materials as the electrodes supported on PI-derived LP-C (**Figure 19**).^[175] In a separate study, it was shown that laser-carbonized natural wood also serves as a support material for the electrodeposition of the aforementioned HER or OER catalysts showing similar performance.^[9] Apart from being used as catalytic support for electrochemical systems, LP-C possesses intrinsic electrocatalytic activity toward OER due to the presence of pyridinic and pyrrolic N on the surface, which acts as the active sites.^[36] N in carbon structures makes the functional groups on the LP-C surface slightly polarized, rendering it a bet-

ter electrocatalyst compared to other bulk-solid carbon materials. Additionally, LP-C is reported to show promising catalytic activity toward OER or ORR by increasing the oxygen content on the surface by plasma treatment. The oxygen-containing functional groups on the surface provide active sites, on the one hand, and reduce the activation energy by facilitating the adsorption of reaction intermediates.^[176] The type of activity centers for the catalytic reaction can be selectively modulated by the reaction conditions. Unlike most materials, LP-C can serve as both catalysts and electrodes owing to its electrical conductivity combined with Nfunctional groups. Of course, its patternability makes it directly useable in devices. In a recent report, it was shown, that the addition of Fe(NO₃)₂ before or after pre-carbonization of the citric acid/urea precursors, either the 2e⁻ or the 4e⁻ pathway in the oxygen reduction reaction is facilitated leading to either H₂O₂ or H₂O as a reaction product, respectively.^[228]

Challenges: In the light of oxidation or reduction reactions utilized in fuel cells and metal-air batteries, current scientific challenges are among others improvements in the catalytic performance of carbons and their composites. Although many carbon or carbon composite materials show a decent performance, the exact mechanisms are still unknown. Systematic mechanistic studies to derive universal principles would help to develop the field of carbon-based electrocatalysis but are largely missing. Reproducibility is another critical issue. The synthesis conditions of the carbon materials, in particular, the composite materials need to show a high experimental batch-to-batch control. This counts especially for heteroatom-doped carbons. The synthesis strategies need to come along with high economic efficiency to avoid the use of expensive fabrication methods and the use of extensive amounts of solvents.

3.3.4. LP-C in Antenna-Related Applications

Literature Review: Antennas are transducers used for wireless data transmission by converting any electrical signals to electromagnetic waves or vice-versa. Although metal-based antennas made of Cu or Ag provide the advantages of good electrical conductivity, they come with issues of oxidation, corrosion,

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and difficult disposal. Their patterning to form flexible and disposable antennas involves expensive techniques such as sputtering and etching, and additional requirements of harsh chemicals during etching, which could possibly damage the substrates on which the metals are deposited. Laser-patterning under the right conditions may provide reasonably conductive carbon patterns along with a flexible design, inexpensive manufacturing, and various substrates. LP-C has been utilized for wireless transmission of data for healthcare, structural health monitoring, and other applications,^[202-206] where the (partly) porous and electrically conductive nature of LP-C is typically exploited. For example, in a study, Mostaccio et al. found that the higher the sheet resistance of the LP-C prepared from PI, the lower the gain of the input signal.^[204] The radiative performance of LP-C as a singlelayer broadband monopole with coplanar feeding in the S-band was compared to the copper-based antenna, and it was found that the achieved gain was 7-8 dB lower when the LP-C antenna was applied over the skin. In another study by Mohamed et al., a co-planar waveguide-polygon monopole antenna comprising of a MoS₂/LP-C composite was fabricated from polyether sulfone-MoS₂ membranes coated on a glass slide, which achieved 30% gain enhancement compared to copper-based antennas.^[205] This enhancement in gain is attributed to the porous nature of LP-C films, which ultimately affects the refractive index of the material. Apart from using LP-C as the data transmitting element, LP-C antenna-based sensors have also been fabricated where LC-PI acts as both the sensing and transmitting element.^[202] The LC-PI antenna offers a gain of 1.82 dBi in the operating band (5.8 GHz) and its sensitivity to strain establishes its feasibility in real-time IoT-based sensors. The same concept of antenna-based sensing was studied on laser carbonized GO-CuO nanorod hybrid films coated on a PET substrate and GO-coated Cu-carbon hybrid antenna on PI, for direct sensing of humidity. The return loss of the signal from the antenna increased with increasing relative humidity along with a shift in resonance to lower frequencies, that was attributed to the change of dielectric constant of GO under humid conditions.[206] Antennas fabricated by laser-carbonization of graphene paper showed better stability by maintaining the conductivity and inductance up to one million cycles at various bending radii,^[209] showing a better performance than antennas based on laser-cut Cu-foil, where bendingreleasing up to 200 cycles showed a slight shift in the resonance frequency.[229]

Challenges: Attaining uniform surface porosity across the LP-C films by maintaining constant fluence is a challenge during laser processing, which ultimately affects the antenna performance of LP-C and their hybrids. Attempts to reduce the sheet resistance by proper combination of laser process parameters are also crucial for such applications. The contribution of the surface functionalities on the antenna behavior is not established to a proper extent in the reported studies. Moreover, the effect of the substrate on the properties of LP-C plays an important role, which ultimately affects the antenna behavior of the materials. Studies on LP-C derived from different substrates are required to understand the sensing mechanism of these IoT sensors. For antenna sensors, the effect of environmental conditions on LP-C during structural health monitoring needs more emphasis. For motion sensing on human skin, simulation studies need to be validated by more real-time experiments.

3.3.5. LP-C in Sensors

Literature Review: Sensors are devices for detecting and processing external stimuli. The general types of signals or stimuli are categorized into five groups: electromagnetic radiation, electromagnetic fields, temperature, mechanical, and chemical. Carbon materials have been investigated as active sensor materials mainly for the last three categories.^[230] A broad overview about carbon-based materials used in flexible electronics and sensors, in particular, is covered in a recent book on "flexible carbon-based electronics".^[231] Important assets of modern sensors are flexibility, portability, integrability.^[232,233] As a matter of course, such devices should be available at low cost and be based on sustainable materials and manufacturing processes. An ideal sensor device fulfills all requirements but in reality, each sensor device is designed to fulfill the requirements of a specific application.

Carbon nanomaterials such as graphene, CNTs, CNFs, and their hybrids^[230] and other bulk carbons such as glassy carbon^[234] and carbon fibers^[34] have been intensively investigated as active materials in sensor devices.^[235] These materials are either used in powder form or in device form after fabricating devices on rigid/ flexible substrates. Common pathways for microfabrication of carbon-based flexible devices are discussed in the review by Devi et al.^[235] As a viable alternative LP-Cs offer all the benefits like large surface area and tunable surface chemistry, scalability, and low cost. LP-C also provides the additional advantage of bendability and rollability of the sensor devices when fabricated from flexible polymers which can be further extended toward the development of wearable mechanical and chemical sensor devices. Sensors derived from other carbon materials (graphene CNTs, CNFs) require additional steps of pattern transfer or printing onto flexible substrates, post their synthesis, to facilitate a complete microdevice fabrication.^[235-237] LP-C not only offers a single-step fabrication, it even reduces the number of post-processing steps owing to its already functional large surface area. Its porous surface can indeed be further utilized to support other active nanoparticles to increase the sensitivity of the device toward the analyte, which increases its utility in sensor fabrication manifolds.^[121] To provide the reader with a direct comparison of LP-C with other carbon materials employed in device fabrication, the properties and performance of different carbon materials and LP-C are compiled in Table 5 for one particular application, neural sensing. This application was selected because of multiple reasons. First of all, a wide range of carbon materials has been used for making neural sensors. Second, some characteristic properties of LP-C such as bendability and biocompatibility are of utmost importance for these implantable sensors. And finally, the fact that neural sensors utilize the entire range of carbon's properties including electrochemical, electrical, mechanical, and bio-compatible.

LP-C derived from PI has the ability to detect sound waves through the piezoelectric effect, where the LP-C acts as a sensitive electrically resistive membrane that is able to detect vibrations in the frequency range between 100 and 40 000 Hz. It was shown, that the thickness of the membrane controls the frequency range.^[157] Porous conductive LP-C films based on citric acid/urea show a quantitative and reversible change in resistance upon bending or application of pressure in a normal loading direction. Such properties enable their application as bending or

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Table 5. Comparison of the performance of LP-C-based neural sensors with other carbon-based flexible sensors/devices fabricated via different processes.

Carbon material ^{a)}	Substrate	Fabrication process	Electrochemical stability window	Advantages	Limitations	Ref.
Glassy carbon	PI	Photolithography followed by pattern transfer	—0.8—+1.2 V pH: 7	Biocompatibility High signal-to-noise ratio compared to Pt during in vivo experiments	Expensive fabrication processes, Pattern transfer onto a flexible substrate	[238]
Graphene	Parylene-C	CVD, wet transfer of graphene. Electrode patterned by RIE	—0.6—+ 0.8 V рН: 5.5	<i>In-vivo</i> imaging of the cortical vasculature via fluorescence microscopy	The expensive fabrication process, The additional step of graphene transfer onto a flexible substrate	[239]
CNT	Self-supporting CNT film	CNT growth by CVD	–0.8–+ 1.0 V pH: 7	Wide electrochemical stability window	In vivo cytocompatibility, is a concern.	[240]
Carbon fiber	PI	Electrospinning and CF patterning by RIE.	–0.9–+ 1.1 V pH: 7.4	Wide electrochemical stability window	Expensive fabrication like electrospinning and RIE	[34]
LP-C	Parylene-C	Direct laser patterning of Parylene-C	−1–+ 1.7 V pH: 7.4	Large electrochemical stability window compared to Pt as well as other flexible carbon electrodes	Inexpensive and one-step fabrication process	[116]
Platinum	-	Sputtered Pt, diameter = 300 μ m	-0.8-+ 0.5 V pH: 7	Good electrical conductivity	Limited natural reserves and low electrochemical stability window	[238]

^{a)} Acronyms used: CVD: Chemical vapor deposition, RIE: Reactive ion etching.

mechanical pressure sensors. Strain greater than 3.3% caused the rupture of the LP-C film.^[182] Strips (2 × 30 mm) of LP-C films ($\lambda = 10.6 \mu$ m) when transferred onto elastic membranes such as PDMS or silicone (by cross-linking and peel-off technique), are reported to show a stable electric conductivity toward stretching to up to 100% longitudinal strain, with R/R_o value = 9, for bending angle of 145°.^[185] In another study, similar LP-C structures transferred onto PDMS, by a different technique, resulted in the total fracture of the device at 30% longitudinal strain.^[187] Hence pattern transfer techniques determine the interfacial forces between the LP-C structures and the substrate, which in turn determines the response to mechanical loading. Most of the mechanical sensors make use anisotropic property of laser-derived carbon.

Chemical sensors are devices for the specific detection of chemical species, thus mimicking the gustatory or olfactory senses. On the other hand, devices for the quantitative detection of biomarkers in body fluid analysis are used for medical diagnostics, like the monitoring of human vital parameters.^[241] Modern, portable, and wearable sensors become increasingly important for non-invasive medical diagnosis and physical performance optimization. Therefore, a high interest in the development of new inexpensive, and sustainable materials for modern sensors exists.^[242] New functional materials, such as hierarchical porous carbons constitute interesting alternatives for everyday-use or disposable sensor arrays.^[243-245] As outlined above, laser-carbonization is a well-suited method to produce electronically conductive porous carbon films and provide the possibility to incorporate functional sites for selective interaction with analytes.^[246] In particular, the possibility for tuning the properties of LP-C by simple modification of the precursor formulas or anchoring heteroatoms (Pt/Ni/Cu/Au) has demonstrated

a significant enhancement of the sensitivity of LP-C.^[181,198,199,247] A common strategy to tune the electronic properties of carbon materials is the integration of electronic heterojunctions, for example, Schottky barriers or p-n-junctions and thereby modulate the charge-carrier density to achieve higher response upon electronic/chemical interaction with analytes.^[248] These aspects make this process generally interesting for commercial applications. LP-C electrodes are used for chemical sensing as bare electrodes or post-functionalization for sensing various analytes. The signals are often read out by statistical principal component analysis.^[189] The principle of capacitive sensing with interdigitated LP-C based on the electroosmotic effect was also utilized for the selective sensing of Bisphenol.^[191] Another example demonstrates the quantitative detection of gaseous ammonia in a simple resistive device architecture based on LC-PI ($\lambda = 10.6 \,\mu\text{m}$).^[249] In a similar fashion gas sensors were fabricated for distinguishing gases based on their thermal conductivities by measuring the resistances of the electrodes at various gaseous environments (Figure 20A).^[184] Furthermore, LC-PI served as an electrocatalyst support for Pd nanoparticles for the selective amperometric detection of methane gas.^[250] Porous gas sensing platforms were achieved by laser carbonization of block co-polymers followed by decorating with Ag nanoparticles, such that the resistance of the device decreased after its exposure to NO₂ gas.^[121]

Direct gas sensing with LCMs by detecting adsorption events has been realized in terms of quantitative humidity response. The change in electronic resistance upon a change in humidity was used as a read-out value.^[180,215] Under a dry atmosphere, the LP-C films act as a thermometer with a linear relationship between temperature and relative variation of resistance (0.07% K⁻¹).^[180] This concept was further exploited to modulate the chemistry and morphology of LP-C to prepare resistive gas



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Figure 20. Addressing electronic and structural properties of LP-C: A) Upper panel: the optical image of the LC-PI sensor-embedded in cement, Lower panel: response of the cement-embedded device to varying molar concentrations of CO2 in He ranging from 0% to 100%; Reproduced with permission.^[184] Copyright 2019, ACS. B) Upper panel: resistive response of a molybdenum carbide containing LP-C toward exposure to different concentrations of acetone, Lower panel: scanning electron micrograph (SEM) of a molybdenum carbide containing LP-C showing a foam-like morphology and a TEM image of a fragment of the material shown in the SEM image. Reproduced with permission.^[181] Copyright 2021, Wiley.

sensors. Metallic nanoparticle impregnation leads to the formation of Schottky junctions and a drastic decrease in charge carrier density, which increases the resistive response to volatile organic compounds (VOC) (Figure 20B).^[181] A similar concept was utilized to fabricate a layered nitrogen-doped carbon film with a high content of pyrrolic or imidazolic nitrogen by laser-patterning of adenine-CNFA (ade380) for selective sensing of CO2.[183]

LP-C devices have also been utilized in the form of interdigitated electrodes for the detection of multiple input signals, for example, the detection of VOCs in human breath. In this study, LP-C devices were coated with MXene to form a flexible virtual sensor array (FVSA) which, when exposed to concentrations of various VOCs. From the broadband impedance spectra of the FVSA, eight characteristic parameters were detected which created a unique fingerprint for each VOC without a need for changing the temperature of the sensor. A systematic analysis of the characteristic parameters was carried out using machine learning algorithms to identify different types of VOCs and predict the concentrations of the target VOCs.^[251] One can always alter the surface morphology of LP-C within a single device, by tuning the laser parameters or supporting different active materials in its porous structure of the device, such that a single device can sense multiple input signals such as bending, twisting, tension, etc.^[252] The most commonly referred approach for simultaneous detection of distinct input signals is through in-plane integration of multiple sensing units^[253] and this can easily be achieved for LP-C because of the one-step manufacturing process and availability of a wide range of precursors, capable of yielding multiple LP-C sensor units in-plane. For a better understanding of multimodal sensors with decoupled sensing mechanisms, the review article by Cheng et al. can be referred.^[254]

Challenges: A general difficulty is the design of specific active sites in a sensor material that shows a sensitive response and is

broadly applicable. Challenges for the application of LP-C in sensor architectures are primarily the tuning of the surface properties, as functional groups are responsible for any kind of interaction between analytes and the active material. Thereby, the chemical adsorption characteristics can be modified. Therefore, it is of pronounced importance to identify new precursor materials for the selective integration of functional groups. Mechanistic carbonization studies are necessary to create a fundamental understanding of the sensor detection principles, that is, the analytematerial interactions and the electronic transduction. This entails a combination of mechanistic studies with the systematic tuning of the chemical composition and surface chemistry of LP-Cs. Importantly, the sensing principle based on adsorption and desorption typically proceeds at low response times. Mechanisms for improving the response times need to be identified. As outlined above, the major features of chemical, as well as mechanical sensors, are flexibility, portability, integrability, sensitivity, selectivity, accuracy, short response time, and reliability. With regard to all these assets, the engineering aspect is to improve the mechanical properties toward high flexibility and stretchability as well as optimized substrate interactions.

4. Conclusions and Roadmap

Laser-carbonization is a powerful method for the direct synthesis and utilization of functional carbonized materials in film-based or flexible electronic devices. Compared to other established carbon materials and technologies, it is relatively new. But if history is any guide, it only takes one trigger in terms of synthesis or application for carbon materials to change the course of the entire technology. For LP-C, surface functionality, particularly the role of nitrogen in its catalytic activity can provide the required impetus. The need for inexpensive and metal-free electrocatalysts







Figure 21. Historical overview and future prospects of LP-C technology.

is one major roadblock in the commercialization of fuel cell and water electrolyzer systems at present, which can be addressed by LP-C at a much lower cost. Multi-modal sensors are yet another promising application area where the one-step in-plane fabrication scheme offered by LP-C can come in handy. A schematic diagram that summarizes the historical development of LP-C and suggests some general future directions based on the authors' opinion is presented in **Figure 21**.

This critical review summarizes and contextualizes early and recent investigations in the field with a focus on fundamental chemical and physical aspects. Lessons learned from conventional furnace-carbonization (via pyrolysis) can be adapted to laser-carbonization, however, the rapid reaction conditions yield different materials properties. In combination with the insights generated in other disciplines of laser-assisted materials processing this review attempts to create a more holistic picture of the sub-processes involved in laser-carbonization.

Besides being a relatively simple fabrication and processing method for integrated functional material, it also offers access to new materials with unknown properties. The ultra-fast reaction conditions generally enable the one-step synthesis of heteroatomcontaining high-surface carbon materials with specific properties and functionalities for targeted applications. Four categories of dominant applications for such conductive porous carbon films, namely electrochemical sensors, small-scale energy storage devices, electrocatalytic electrodes, and antenna-related devices are the main focus of discussion in this review, as it allows us to draw a picture towards a common understanding. Evidently, a large gap in understanding the fundamental physical principles of laser-carbonization is still present. A thorough understanding of the underlying mechanism and influence of each process parameter would greatly help in improving the design of devices.

In fact, investigations on laser-carbonization come with several challenges, most prominently the precise characterization of the material films. The complex interplay of the many processing parameters (laser parameters, atmosphere, substrate, precursors, etc.) makes generalizations on the precursor–product relationship difficult. Especially, the analysis of the microstructure and porosity, and their correlation with the chemical and electronic properties of such small amounts of material is highly challenging. Advanced in situ characterization methods are required to create comprehensive and fundamental knowledge for the customized design of such functional material films. Such insights could create an essential database of the functionality of carbon material films for their specific applications. For example, one of the most remarkable features of LP-C is the chemical and structural gradient due to the unidirectional energy input. In many applications, for example, chemical sensors, this gradient may be a decisive advantage, as specific functional groups are retained in the LP-C films that may not be available by conventional pyrolysis. Another advantage is the relatively high reaction temperatures in the upper layers of the films by which carbon phases can be produced that would be only accessible by extreme energyconsuming fabrication processes. At this point, most of the application areas are focused on the top surface of the film, rather than exploiting the potential of the entire structure.

As outlined in this review, comprehensive systematic mechanistic studies addressing all aforementioned aspects to derive universal processing parameters are still lacking. For example, standardization on the beam-precursor interactions (wavelengths, extinction coefficients, heat conductivity, etc.) for a representative set of precursors is necessary to establish a quick method to pre-determine the general suitability of precursors. Based on the experience from decades of carbonization research, we know that each system comes with individual challenges. Therefore, the identification of common laws on the mutual dependencies between precursors, processing parameters, and the properties of the LP-Cs is needed.

Sophisticated, selective spectroscopic characterization of the individual layers would help in understanding the formation mechanism and enable the tuning of the functional properties, also in terms of correlating the surface properties with the electronic properties. This would provide important information on the micro- and macroscale and support the targeted design of simple functional carbon-based electrodes. Similarly, a systematic correlation between pore size and functional groups is necessary to understand the chemical bonding and activation of gaseous or liquid analytes. Furthermore, the specific LP-C/substrate interactions have a major influence on the film properties and device performance. To this end, alternative filmcasting strategies should be developed. Importantly, the determination of the active surface areas of such low amounts of material is still difficult to achieve with conventional sorption-isotherm analysis. Simple lab-based alternative methods are highly demanded.

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Based on such comprehensive fundamental knowledge, new concepts for the tuning of structure, morphology, and chemistry of LP-C for the improvement of their functionality in EDLCs, electrocatalyst electrodes, and sensors could be developed.

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Conflict of Interest

The authors declare no conflict of interest.

Author Contributions

M.D. dealt with conceptualization, writing of original draft, and writing of review and editing. H.W. and S.M. dealt with the conceptualization and writing of the original draft. S.S. and V.S. did conceptualization, writing of original draft, writing of review and editing, and project administration.

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- [1] (Eds.: H. Jäger, W. Frohs), Industrial Carbon and Graphite Materials, Wiley, Weinheim 2021.
- [2] (Eds.: G. Kreysa, K. Ota, R. F. Savinell), Encyclopedia of Applied Electrochemistry, Springer, New York, NY 2014.
- [3] K. Kinoshita, Carbon: Electrochemical and Physicochemical Properties, Wiley, New York, NY 1988.
- [4] S. Sharma, *Materials* **2018**, *11*, 1857.
- [5] I. Mochida, S.-H. Yoon, W. Qiao, J. Braz. Chem. Soc. 2006, 17, 1059.
- [6] Q. Mao, S. Rajabpour, M. Kowalik, A. C. T. van Duin, Carbon 2020, 159, 25.
- [7] G. M. Jenkins, K. Kawamura, Polymeric Carbons: Carbon Fibre, Glass and Char, Cambridge University Press, Cambridge 2011.
- [8] J. Liu, H. Ji, X. Lv, C. Zeng, H. Li, F. Li, B. Qu, F. Cui, Q. Zhou, Microchim. Acta 2022, 189, 54.
- [9] R. Ye, Y. Chyan, J. Zhang, Y. Li, X. Han, C. Kittrell, J. M. Tour, Adv. Mater. 2017, 29, 1702211.
- [10] E. R. Mamleyev, S. Heissler, A. Nefedov, P. G. Weidler, N. Nordin, V. V. Kudryashov, K. Länge, N. MacKinnon, S. Sharma, *npj Flexible Electron*. **2019**, *3*, 2.
- [11] W. Ma, J. Zhu, Z. Wang, W. Song, G. Cao, Mater. Today Energy 2020, 18, 100569.
- [12] R. Ye, D. K. James, J. M. Tour, R. Ye, D. K. James, M. Tour, *Adv. Mater.* 2019, *31*, 1803621.
- [13] R. Ye, D. K. James, J. M. Tour, Acc. Chem. Res. 2018, 51, 1609.
- [14] Z. Wan, N. T. Nguyen, Y. Gao, Q. Li, Sustainable Mater. Technol. 2020, 25, e00205.

- [15] L. Cheng, W. Guo, X. Cao, Y. Dou, L. Huang, Y. Song, J. Su, Z. Zeng, R. Ye, *Mater. Chem. Front.* **2021**, *5*, 4874.
- [16] E. Alhajji, F. Zhang, H. N. Alshareef, Energy Technol. 2021, 9, 2100454.
- [17] A. Kaidarova, J. Kosel, *IEEE Sens. J.* **2021**, *21*, 12426.
- [18] L. Huang, J. Su, Y. Song, R. Ye, Nano-Micro Lett. 2020, 12, 157.
- [19] J. Zhu, X. Huang, W. Song, ACS Nano **2021**, *15*, 18708.
- [20] S. Sharma, Materials 2019, 12, 774.
- [21] M. Devi, S. Rawat, S. Sharma, Oxford Open Mater. Sci. 2020, 1, itab014.
- [22] S. Sharma, R. Kamath, M. Madou, J. Anal. Appl. Pyrolysis 2014, 108, 12.
- [23] S. Sharma, A. Sharma, Y.-K. Cho, M. Madou, ACS Appl. Mater. Interfaces 2012, 4, 34.
- [24] H. Marsh, F. Rodríguez-Reinoso, in Activated Carbon, Elsevier, Amsterdam, Netherlands 2006, pp. 454–508.
- [25] G. P. Biryukova, M. V. Shablygin, N. V. Mikhailov, K. A. Andrianov, *Polym. Sci. U.S.S.R.* **1973**, *15*, 1762.
- [26] O. Senneca, M. Urciuolo, P. Bareschino, G. Diglio, F. Pepe, R. Chirone, Combust. Sci. Technol. 2016, 188, 759.
- [27] S. Sharma, C. N. Shyam Kumar, J. G. Korvink, C. Kubel, *Sci. Rep.* 2018, *8*, 16282.
- [28] S. Sharma, S. Zorzi, V. Cristiglio, R. Schweins, C. Mondelli, *Carbon* 2022, 189, 362.
- [29] "International Union of Pure and Applied Chemistry, 2008" can be found under https://iupac.org/, n.d.
- [30] D. B. Schuepfer, F. Badaczewski, J. M. Guerra-Castro, D. M. Hofmann, C. Heiliger, B. Smarsly, P. J. Klar, *Carbon* 2020, 161, 359.
- [31] K. Dasgupta, D. Sathiyamoorthy, Mater. Sci. Technol. 2013, 19, 995.
- [32] P. T. Araujo, M. Terrones, M. S. Dresselhaus, *Mater. Today* 2012, 15, 98.
- [33] P. A. Thrower, L. R. Radovic, Chemistry & Physics of Carbon, Vol. 26, Marcel Dekker, New York, NY 1999, p. 341
- [34] M. Vomero, C. Gueli, E. Zucchini, L. Fadiga, J. B. Erhardt, S. Sharma, T. Stieglitz, Adv. Mater. Technol. 2020, 5, 1900713.
- [35] C. P. Constantin, M. Aflori, R. F. Damian, R. D. Rusu, *Materials* 2019, 12, 3166.
- [36] M. Devi, C. Madan, A. Halder, S. Sharma, *Carbon Trends* 2022, 9, 100221.
- [37] IUPAC Compend. Chem. Termin. Int. Union Pure Appl. Chem. (IU-PAC), Res. Triangle Park. NC, 2008, n.d.
- [38] IUPAC Compend. Chem. Termin. Int. Union Pure Appl. Chem. (IU-PAC), Res. Triangle Park. NC, 2014. n.d.
- [39] T. Y. Ma, L. Liu, Z. Y. Yuan, Chem. Soc. Rev. 2013, 42, 3977.
- [40] L. Chuenchom, R. Kraehnert, B. M. Smarsly, Soft Matter 2012, 8, 10801.
- [41] Y. Xia, Z. Yang, R. Mokaya, Nanoscale 2010, 2, 639.
- [42] N. Fechler, T. P. Fellinger, M. Antonietti, Adv. Mater. 2013, 25, 75.
- [43] L. S. Blankenship, N. Balahmar, R. Mokaya, Nat. Commun. 2017, 8, 1545.
- [44] R. Hoffmann, S.-C. Chang, Z. H. Kafafi, R. H. Huage, W. E. Billups, J. L. Margrave, J. Am. Chem. Soc. 1992, 96, 4373.
- [45] G. Zhou, C. Xu, W. Cheng, Q. Zhang, W. Nie, J. Anal. Methods Chem. 2015, 2015, 467242.
- [46] Y. Wei, C. Q. Jia, Carbon 2015, 87, 10.
- [47] D. Dong, Y. Zhang, T. Wang, J. Wang, C. E. Romero, W. Pan, Mater. Chem. Phys. 2020, 252, 123381.
- [48] F. Liu, Z. Wang, H. Zhang, L. Jin, X. Chu, B. Gu, H. Huang, W. Yang, *Carbon* **2019**, *149*, 105.
- [49] E. Fuente, J. A. Menéndez, D. Suárez, M. A. Montes-Morán, Langmuir 2003, 19, 3505.
- [50] M. Inagaki, M. Toyoda, Y. Soneda, T. Morishita, *Carbon* 2018, 132, 104.

www.advancedsciencenews.com

- [51] W. Cermignani, T. E. Paulson, C. Onneby, C. G. Pantano, *Carbon* 1995, 33, 367.
- [52] D.-W. Wang, F. Li, Z.-G. Chen, G. Q. Lu, H.-M. Cheng, Chem. Mater. 2008, 20, 7195.
- [53] L. Yang, S. Jiang, Y. Zhao, L. Zhu, S. Chen, X. Wang, Q. Wu, J. Ma, Y. Ma, Z. Hu, Angew. Chem., Int. Ed. 2011, 50, 7132.
- [54] Z. Peng, R. Ye, J. A. Mann, D. Zakhidov, Y. Li, P. R. Smalley, J. Lin, J. M. Tour, ACS Nano 2015, 9, 5868.
- [55] J. Wu, Z. Yang, X. Li, Q. Sun, C. Jin, P. Strasser, R. Yang, J. Mater. Chem. A 2013, 1, 9889.
- [56] W. Kiciński, M. Szala, M. Bystrzejewski, Carbon 2014, 68, 1.
- [57] F. A. M. Köck, J. M. Garguilo, B. Brown, R. J. Nemanich, *Diam. Relat. Mater.* 2002, 11, 774.
- [58] O. S. G. P. Soares, R. P. Rocha, A. G. Gonçalves, J. L. Figueiredo, J. J. M. Órfão, M. F. R. Pereira, *Carbon* **2015**, *91*, 114.
- [59] D. Wei, Y. Liu, Y. Wang, H. Zhang, L. Huang, G. Yu, Nano Lett. 2009, 9, 1752.
- [60] R. J. J. Jansen, H. van Bekkum, Carbon 1995, 33, 1021.
- [61] R. Arrigo, M. Hävecker, R. Schlögl, D. S. Su, Chem. Commun. 2008, 4891.
- [62] M. Inagaki, T. Tsumura, T. Kinumoto, M. Toyoda, Carbon 2019, 141, 580.
- [63] T. S. Miller, A. B. Jorge, T. M. Suter, A. Sella, F. Corà, P. F. McMillan, Phys. Chem. Chem. Phys. 2017, 19, 15613.
- [64] A. Bagreev, S. Bashkova, T. Bandosz, J. A. Menéndez, I. Ivanenko, Y. Trasenko, Nitrogen Enriched Activated Carbons as Adsorbents and Catalysts in Desulfurization Technologies, 2004, 49, 920.
- [65] J. R. Pels, F. Kapteijn, J. A. Moulijn, Q. Zhu, K. M. Thomas, *Carbon* 1995, 33, 1641.
- [66] M. Gehring, H. Tempel, A. Merlen, R. Schierholz, R.-A. Eichel, H. Kungl, RSC Adv. 2019, 9, 27231.
- [67] H. Wang, Y. Shao, S. Mei, Y. Lu, M. Zhang, J. Sun, K. Matyjaszewski, M. Antonietti, J. Yuan, *Chem. Rev.* 2020, 120, 9363.
- [68] M. Titirici, S. G. Baird, T. D. Sparks, S. M. Yang, A. Brandt-Talbot, O. Hosseinaei, D. P. Harper, R. M. Parker, S. Vignolini, L. A. Berglund, Y. Li, H.-L. Gao, L.-B. Mao, S.-H. Yu, N. Díez, G. A. Ferrero, M. Sevilla, P. Á. Szilágyi, C. J. Stubbs, J. C. Worch, Y. Huang, C. K. Luscombe, K.-Y. Lee, H. Luo, M. J. Platts, D. Tiwari, D. Kovalevskiy, D. J. Fermin, H. Au, H. Alptekin, et al., *J. Phys.: Mater.* **2022**, *5*, 032001.
- [69] M.-M. Titirici, M. Antonietti, Chem. Soc. Rev. 2009, 39, 103.
- [70] L.-C. Dolores, P. M.-L. Juan, C. Falco, M.-M. Titirici, C.-A. Diego, in Sustainable Carbon Materials from Hydrothermal Processes, John Wiley & Sons, Hoboken, NJ, USA 2013, pp. 75–100.
- [71] V. E. Borisenko, P. J. Hesketh, in (Eds.: V. E. Borisenko, P. J. Hesketh), Springer, Boston, MA 1997, pp. 253–300.
- [72] J. Hofrichter, B. N. Szafranek, M. Otto, T. J. Echtermeyer, M. Baus, A. Majerus, V. Geringer, M. Ramsteiner, H. Kurz, *Nano Lett.* 2010, 10, 36.
- [73] J. H. Chu, J. Kwak, T.-Y. Kwon, S.-D. Park, H. Go, S. Y. Kim, K. Park, S. Kang, S.-Y. Kwon, ACS Appl. Mater. Interfaces 2012, 4, 1777.
- [74] X. Wu, F. Mu, Z. Lin, E. Jabari, F. Ahmed, F. Liravi, E. B. Secor, L. Lin, E. Toyserkani, R. Tortorich, J.-W. Choi, 2D Mater. 2019, 3, 453.
- [75] E. Jabari, F. Ahmed, F. Liravi, E. B. Secor, L. Lin, E. Toyserkani, 2D Mater. 2019, 6, 042004.
- [76] X. Wu, F. Mu, Z. Lin, Mater. Today Adv. 2021, 11, 100157.
- [77] A. Zakhurdaeva, P.-I. Dietrich, H. Hölscher, C. Koos, J. Korvink, S. Sharma, *Micromachines* 2017, 8, 285.
- [78] J. Bauer, A. Schroer, R. Schwaiger, O. Kraft, Nat. Mater. 2016, 15, 438.
- [79] S. Sharma, G. Agrawal, in *Encyclopedia of Materials: Plastics and Poly*mers, Elsevier, **2022**, pp. 681–696.
- [80] "JP932 | Enhanced Reader," n.d.
- [81] H. Murata, Y. Nakajima, N. Saitoh, N. Yoshizawa, T. Suemasu, K. Toko, Sci. Rep. 2019, 9, 4068.

- [82] Y. Zhu, S. Murali, M. D. Stoller, K. J. Ganesh, W. Cai, P. J. Ferreira, A. Pirkle, R. M. Wallace, K. A. Cychosz, M. Thommes, D. Su, E. A. Stach, R. S. Ruoff, *Science* **2011**, *332*, 1537.
- [83] D. G. Papageorgiou, I. A. Kinloch, R. J. Young, Prog. Mater. Sci. 2017, 90, 75.
- [84] T. W. Ebbesen, H. J. Lezec, H. Hiura, J. W. Bennett, H. F. Ghaemi, T. Thio, *Nature* **1996**, *382*, 54.
- [85] M. M. J. Treacy, T. W. Ebbesen, J. M. Gibson, Nature 1996, 381, 678.
- [86] J. J. Niu, J. N. Wang, Y. Jiang, L. F. Su, J. Ma, *Microporous Mesoporous Mater.* 2007, 100, 1.
- [87] Y. Wang, I. Ramos, R. Furlan, J. J. Santiago-Avilés, IEEE Trans. Nanotechnol. 2004, 3, 80.
- [88] S. A. Mirdehghan, Eng. Polym. Fibrous Mater. 2021, 1.
- [89] I. M. K. Ismail, Carbon 1987, 25, 653.
- [90] G. G. Tibbetts, G. L. Doll, D. W. Gorkiewicz, J. J. Moleski, T. A. Perry, C. J. Dasch, M. J. Balogh, *Carbon* **1993**, *31*, 1039.
- [91] J. Heremans, Carbon 1985, 23, 431.
- [92] G. G. Tibbetts, C. P. Beetz, J. Phys. D. Appl. Phys. 1987, 20, 292.
- [93] R. R. Saxena, R. H. Bragg, J. Non-Cryst. Solids 1978, 28, 45.
- [94] C. Garion, C. Garion, World J. Mech. 2014, 4, 79.
- [95] R. Mishra, B. Pramanick, A. Chatterjee, T. K. Maiti, T. K. Bhattacharyya, Proc. IEEE Sensors, IEEE, New York, NY 2018.
- [96] T. Adinaveen, J. J. Vijaya, L. J. Kennedy, Arabian. J. Sci. Eng. 2016, 41, 55.
- [97] A. Kwaśniewska, M. Świetlicki, A. Prószyński, G. Gładyszewski, Polymers 2021, 13, 4406.
- [98] P. Zaccagnini, C. Ballin, M. Fontana, M. Parmeggiani, S. Bianco, S. Stassi, A. Pedico, S. Ferrero, A. Lamberti, *Adv. Mater. Interfaces* 2021, 8, 2101046.
- [99] W. M. Steen, J. Mazumder, Laser Material Processing, 4th ed., Springer, London, 2010.
- [100] (Eds.: E. T. Akinlabi, R. M. Mahamood, S. A. Akinlabi), Advanced Manufacturing Techniques Using Laser Material Processing, IGI Global, Hershey, PA, USA 2016.
- [101] G. G. Gladush, I. Smurov, J. Chem. Inf. Model. 2011, 146, 287.
- [102] "Laser Surface Engineering –1st Edition," can be found under https://www.elsevier.com/books/laser-surface-engineering/ lawrence/978-1-78242-074-3, n.d.
- [103] S. Delacroix, H. Wang, T. Heil, V. Strauss, Adv. Electron. Mater. 2020, 6, 2000463.
- [104] J. I. Raffel, J. F. Freidin, G. H. Chapman, Appl. Phys. Lett. 1998, 42, 705.
- [105] J. H. Brannon, J. R. Lankard, A. I. Baise, F. Burns, J. Kaufman, J. Appl. Phys. 1998, 58, 2036.
- [106] M. Schumann, R. Sauerbrey, M. C. Smayling, Appl. Phys. Lett. 1998, 58, 428.
- [107] R. Srinivasan, Appl. Phys. A 1993, 56, 417.
- [108] R. Srinivasan, R. R. Hall, D. C. Allbee, Appl. Phys. Lett. 1998, 63, 3382.
- [109] T. Feurer, R. Sauerbrey, M. C. Smayling, B. J. Story, *Appl. Phys. A* 1993, 56, 275.
- [110] R. Srinivasan, R. R. Hall, W. D. Wilson, W. D. Loehle, D. C. Allbee, *Chem. Mater.* 1994, 6, 888.
- [111] E. E. Ortelli, F. Geiger, T. Lippert, J. Wei, A. Wokaun, *Macromolecules* 2000, 33, 5090.
- [112] A. Kothuru, C. Hanumanth Rao, S. B. Puneeth, M. Salve, K. Amreen, S. Goel, *IEEE Sens. J.* **2020**, *20*, 7392.
- [113] A. Borenstein, V. Strauss, M. D. Kowal, M. Yoonessi, M. Muni, M. Anderson, R. B. Kaner, J. Mater. Chem. A 2018, 6, 20463.
- [114] E. Kymakis, C. Petridis, T. D. Anthopoulos, E. Stratakis, IEEE J. Sel. Top. Quantum Electron. 2014, 20, 106.
- [115] P. Zhang, D. Wan, Z. Zhang, G. Wang, J. Hu, G. Shao, Environ. Sci.: Nano 2018, 5, 1813.
- [116] M. Vomero, A. Oliveira, D. Ashouri, M. Eickenscheidt, T. Stieglitz, *Sci. Rep.* 2018, 8, 14749.

4DVANCED MATERIALS

www.advancedsciencenews.com

- [117] E. R. Mamleyev, F. Falk, P. G. Weidler, S. Heissler, S. Wadhwa, O. Nassar, C. N. Shyam Kumar, C. Kübel, C. Wöll, M. Islam, D. Mager, J. G. Korvink, ACS Appl. Mater. Interfaces 2020, 12, 53193.
- [118] H. M. Jin, S. H. Lee, J. Y. Kim, S. W. Son, B. H. Kim, H. K. Lee, J. H. Mun, S. K. Cha, J. S. Kim, P. F. Nealey, K. J. Lee, S. O. Kim, ACS Nano 2016, 10, 3435.
- [119] K. W. Tan, B. Jung, J. G. Werner, E. R. Rhoades, M. O. Thompson, U. Wiesner, *Science* **2015**, *349*, 54.
- [120] K. W. Tan, U. Wiesner, Macromolecules 2019, 52, 395.
- [121] L. Yang, H. Ji, C. Meng, Y. Li, G. Zheng, X. Chen, G. Niu, J. Yan, Y. Xue, S. Guo, H. Cheng, ACS Appl. Mater. Interfaces 2022, 14, 17818.
- [122] Y. Zhang, L. Guo, S. Wei, Y. He, H. Xia, Q. Chen, H.-B. Sun, F.-S. Xiao, Nano Today 2010, 5, 15.
- [123] J. Lin, Z. Peng, Y. Liu, F. Ruiz-Zepeda, R. Ye, E. L. G. Samuel, M. J. Yacaman, B. I. Yakobson, J. M. Tour, *Nat. Commun.* **2014**, *5*, 5714.
- [124] D. Go, P. Lott, J. Stollenwerk, H. Thomas, M. Möller, A. J. C. Kuehne, ACS Appl. Mater. Interfaces 2016, 8, 28412.
- [125] D. A. Sokolov, K. R. Shepperd, T. M. Orlando, J. Phys. Chem. Lett. 2010, 1, 2633.
- [126] W. Gao, N. Singh, L. Song, Z. Liu, A. L. M. Reddy, L. Ci, R. Vajtai, Q. Zhang, B. Wei, P. M. Ajayan, *Nat. Nanotechnol.* **2011**, *6*, 496.
- [127] M. F. El-Kady, V. Strong, S. Dubin, R. B. Kaner, Science 2012, 335, 1326.
- [128] T. Barkan, Nat. Nanotechnol. 2019, 14, 904.
- [129] J. I. Raffel, J. F. Freidin, G. H. Chapman, Appl. Phys. Lett. 1983, 42, 705.
- [130] J. H. Brannon, J. R. Lankard, A. I. Baise, F. Burns, J. Kaufman, J. Appl. Phys. 1985, 58, 2036.
- [131] M. Inagaki, S. Harada, T. Sato, T. Nakajima, Y. Horino, K. Morita, *Carbon* **1989**, *27*, 253.
- [132] A. Bürger, E. Fitzer, M. Heym, B. Terwiesch, Carbon 1975, 13, 149.
- [133] S. P. Singh, Y. Li, J. Zhang, J. M. Tour, C. J. Arnusch, ACS Nano 2017, 12, 289.
- [134] N. Morita, Y. Shimotsuma, M. Nishi, M. Sakakura, K. Miura, K. Hirao, Appl. Phys. Lett. 2014, 105, 201104.
- [135] P. A. Atanasov, N. E. Stankova, N. N. Nedyalkov, T. R. Stoyanchov, R. G. Nikov, N. Fukata, J. W. Gerlach, D. Hirsch, B. Rauschenbach, J. Phys.: Conf. Ser. 2016, 700, 012023.
- [136] P. A. Atanasov, N. E. Stankova, N. N. Nedyalkov, N. Fukata, D. Hirsch, B. Rauschenbach, S. Amoruso, X. Wang, K. N. Kolev, E. I. Valova, J. S. Georgieva, S. A. Armyanov, *Appl. Surf. Sci.* 2016, 374, 229.
- [137] N. E. Stankova, P. A. Atanasov, R. G. Nikov, R. G. Nikov, N. N. Nedyalkov, T. R. Stoyanchov, N. Fukata, K. N. Kolev, E. I. Valova, J. S. Georgieva, S. A. Armyanov, *Appl. Surf. Sci.* 2016, 374, 96.
- [138] K. Ju, Y. Gao, T. Xiao, C. Yu, J. Tan, F. Xuan, RSC Adv. 2020, 10, 18694.
- [139] P. I. C. Claro, T. Pinheiro, S. L. Silvestre, A. C. Marques, J. Coelho, J. M. Marconcini, E. Fortunato, L. H. C. Mattoso, R. Martins, *Appl. Phys. Rev.* 2022, *9*, 041305.
- [140] S. Lee, S. Jeon, ACS Sustain, Chem. Eng. 2019, 7, 2270.
- [141] F. Morosawa, S. Hayashi, M. Terakawa, ACS Sustain, Chem. Eng. 2021, 9, 2955.
- [142] Y. Chyan, R. Ye, Y. Li, S. P. Singh, C. J. Arnusch, J. M. Tour, ACS Nano 2018, 12, 2176.
- [143] T. D. Le, S. Park, J. An, P. S. Lee, Y. Kim, Adv. Funct. Mater. 2019, 29, 1902771.
- [144] H. Wang, S. Delacroix, O. Osswald, M. Anderson, T. Heil, E. Lepre, N. Lopez-Salas, R. B. Kaner, B. Smarsly, V. Strauss, *Carbon* 2021, 176, 500.
- [145] Z. Wan, S. Wang, B. Haylock, J. Kaur, P. Tanner, D. Thiel, R. Sang, I.
 S. Cole, X. Li, M. Lobino, Q. Li, *Carbon* 2019, 141, 83.
- [146] B. S. de Lima, M. I. B. Bernardi, V. R. Mastelaro, Appl. Surf. Sci. 2020, 506, 144808.

- [147] Y. Huang, L. Zeng, C. Liu, D. Zeng, Z. Liu, X. Liu, X. Zhong, W. Guo, L. Li, Small 2018, 14, 1803143.
- [148] J. Nasser, L. Groo, L. Zhang, H. Sodano, *Carbon* 2020, 158, 146.
- [149] J. Edberg, R. Brooke, O. Hosseinaei, A. Fall, K. Wijeratne, M. Sandberg, npj Flexible Electron. 2020, 4, 17.
- [150] W. Zhang, Y. Lei, F. Ming, Q. Jiang, P. M. F. J. Costa, H. N. Alshareef, Adv. Energy Mater. 2018, 8, 1801840.
- [151] M. Yuan, F. Luo, Y. Rao, Y. Wang, J. Yu, H. Li, X. Chen, J. Power Sources 2021, 513, 230558.
- [152] L. X. Duy, Z. Peng, Y. Li, J. Zhang, Y. Ji, J. M. Tour, Carbon 2018, 126, 472.
- [153] M. Yuan, F. Luo, Y. Rao, J. Yu, Z. Wang, H. Li, X. Chen, Carbon 2021, 183, 128.
- [154] S. Park, H. Lee, Y.-J. Kim, P. S. Lee, NPG Asia Mater. 2018, 10, 959.
- [155] T. X. Tran, H. Choi, C. H. Che, J. H. Sul, I. G. Kim, S.-M. Lee, J.-H. Kim, J. Bin In, ACS Appl. Mater. Interfaces 2018, 10, 39777.
- [156] S. Han, C. Liu, N. Li, S. Zhang, Y. Song, L. Chen, M. Xi, X. Yu, W. Wang, M. Kong, Z. Wang, *CrystEngComm* **2022**, *24*, 1866.
- [157] J. Bin In, B. Hsia, J.-H. Yoo, S. Hyun, C. Carraro, R. Maboudian, C. P. Grigoropoulos, *Carbon* 2015, *83*, 144.
- [158] V. Strauss, M. Anderson, C. L. Turner, R. B. Kaner, S. Delacroix, H. Wang, T. Heil, V. Strauss, *Mater. Today Energy* **2019**, *11*, 114.
- [159] V. Strauss, M. Muni, A. Borenstein, B. Badamdorj, T. Heil, M. D. Kowal, R. Kaner, *Nanoscale* **2019**, *11*, 12712.
- [160] A. Hoffmann, P. Jiménez-Calvo, J. Bansmann, V. Strauss, A. J. C. Kuehne, Macromol. Rapid Commun. 2022, 43, 2100731.
- [161] V. Strauss, K. Marsh, M. D. Kowal, M. F. El-Kady, R. B. Kaner, Adv. Mater. 2018, 30, 1704449.
- [162] M. Khandelwal, C. Van Tran, J. Bin In, Appl. Surf. Sci. 2022, 576, 151714.
- [163] W. Yang, Y. Liu, Q. Li, J. Wei, X. Li, Y. Zhang, J. Liu, RSC Adv. 2020, 10, 23953.
- [164] H. Guo, J. Yan, L. Jiang, L. Qu, J. Yin, J. Lu, Adv. Opt. Mater. 2021, 9, 2170102.
- [165] A. Lamberti, F. Clerici, M. Fontana, L. Scaltrito, Adv. Energy Mater. 2016, 6, 1600050.
- [166] Z. Peng, J. Lin, R. Ye, E. L. G. Samuel, J. M. Tour, ACS Appl. Mater. Interfaces 2015, 7, 3414.
- [167] J. Cai, C. Lv, A. Watanabe, Nano Energy 2016, 30, 790.
- [168] J. Cai, C. Lv, A. Watanabe, J. Mater. Chem. A 2016, 4, 1671.
- [169] L. Li, J. Zhang, Z. Peng, Y. Li, C. Gao, Y. Ji, R. Ye, N. D. Kim, Q. Zhong, Y. Yang, H. Fei, G. Ruan, J. M. Tour, *Adv. Mater.* **2016**, *28*, 838.
- [170] J. Zhao, L. Gao, Z. Wang, S. Wang, R. Xu, J. Alloys Compd. 2021, 887, 161514.
- [171] C. Zhang, Z. Peng, C. Huang, B. Zhang, C. Xing, H. Chen, H. Cheng, J. Wang, S. Tang, *Nano Energy* **2021**, *81*, 105609.
- [172] R. Xu, Z. Wang, L. Gao, S. Wang, J. Zhao, Appl. Surf. Sci. 2022, 571, 151385.
- [173] L. Lu, D. Zhang, Y. Xie, W. Wang, J. Energy Storage 2022, 51, 104458.
- [174] H. Wang, P. Jiménez-Calvo, M. Hepp, M. Isaacs, I. Below-Lutz, B. Butz, V. Strauss, ACS Appl. Nano Mater. 2023, 6, 966.
- [175] J. Zhang, C. Zhang, J. Sha, H. Fei, Y. Li, J. M. Tour, ACS Appl. Mater. Interfaces 2017, 9, 26840.
- [176] J. Zhang, M. Ren, L. Wang, Y. Li, B. I. Yakobson, J. M. Tour, Adv. Mater. 2018, 30, 1707319.
- [177] K.-H. Nam, M. Abdulhafez, E. Castagnola, G. N. Tomaraei, X. T. Cui, M. Bedewy, *Carbon* **2022**, *188*, 209.
- [178] L. Chen, T. Hou, Y. Tan, C. Guo, B. Wang, L. Ge, F. Li, ACS Sustain, *Chem. Eng.* 2022, 10, 2750.
- [179] R. Rahimi, M. Ochoa, A. Tamayol, S. Khalili, A. Khademhosseini, B. Ziaie, ACS Appl. Mater. Interfaces 2017, 9, 9015.
- [180] S. Delacroix, A. Zieleniewska, A. J. Ferguson, J. L. Blackburn, S. Ronneberger, F. F. Loeffler, V. Strauss, ACS Appl. Electron. Mater. 2020, 2, 4146.

www.advancedsciencenews.com



- [181] H. Wang, S. Delacroix, A. Zieleniewska, J. Hou, N. V. Tarakina, D. Cruz, I. Lauermann, A. J. Ferguson, J. L. Blackburn, V. Strauss, Adv. Funct. Mater. 2021, 31, 2104061.
- [182] M. Hepp, H. Wang, K. Derr, S. Delacroix, S. Ronneberger, F. F. Loeffler, B. Butz, V. Strauss, *npj Flexible Electron.* 2022, 6, 3.
- [183] H. Wang, C. O. Ogolla, G. Panchal, M. Hepp, S. Delacroix, D. Cruz, D. Kojda, J. Ciston, C. Ophus, A. Knop-Gericke, K. Habicht, B. Butz, V. Strauss, *Adv. Funct. Mater.* **2022**, *32*, 2207406.
- [184] M. G. Stanford, K. Yang, Y. Chyan, C. Kittrell, J. M. Tour, ACS Nano 2019, 13, 3474.
- [185] R. Rahimi, M. Ochoa, W. Yu, B. Ziaie, ACS Appl. Mater. Interfaces 2015, 7, 4463.
- [186] D. Wu, Q. Peng, S. Wu, G. Wang, L. Deng, H. Tai, L. Wang, Y. Yang, L. Dong, Y. Zhao, J. Zhao, D. Sun, L. Lin, *Sensors* **2018**, *18*, 4405.
- [187] S. Y. Jeong, Y. W. Ma, J. U. Lee, G. J. Je, B. S. Shin, Sensors 2019, 19, 4867.
- [188] L.-Q. Tao, H. Tian, Y. Liu, Z.-Y. Ju, Y. Pang, Y.-Q. Chen, D.-Y. Wang, X.-G. Tian, J.-C. Yan, N.-Q. Deng, Y. Yang, T.-L. Ren, *Nat. Commun.* 2017, *8*, 14579.
- [189] Y. Yu, P. C. Joshi, J. Wu, A. Hu, ACS Appl. Mater. Interfaces 2018, 10, 34005.
- [190] P. Puetz, A. Behrent, A. J. Baeumner, J. Wegener, Sens. Actuators, B 2020, 321, 128443.
- [191] C. Cheng, S. Wang, J. Wu, Y. Yu, R. Li, S. Eda, J. Chen, G. Feng, B. Lawrie, A. Hu, ACS Appl. Mater. Interfaces 2016, 8, 17784.
- [192] Y. Yao, X. Duan, M. Niu, J. Luo, R. Wang, T. Liu, Cellulose 2019, 26, 7423.
- [193] Y. Lei, A. H. Alshareef, W. Zhao, S. Inal, ACS Appl. Nano Mater. 2020, 3, 1166.
- [194] X. Duan, Y. Yao, M. Niu, J. Luo, R. Wang, T. Liu, ACS Appl. Polym. Mater. 2019, 1, 2914.
- [195] E. R. Mamleyev, P. G. Weidler, A. Nefedov, D. V. Szabó, M. Islam, D. Mager, J. G. Korvink, ACS Appl. Nano Mater. 2021, 4, 13747.
- [196] D. P. Hao, R. X. Yang, N. Yi, H. Y. Cheng, Sci. China Technol. Sci. 2021, 64, 2408.
- [197] S. Y. Xia, Y. Long, Z. Huang, Y. Zi, L. Q. Tao, C. H. Li, H. Sun, J. Li, Nano Energy 2022, 96, 107099.
- [198] Y. Zhang, N. Li, Y. Xiang, D. Wang, P. Zhang, Y. Wang, S. Lu, R. Xu, J. Zhao, *Carbon* **2020**, *156*, 506.
- [199] J. Zhu, S. Liu, Z. Hu, X. Zhang, N. Yi, K. Tang, M. G. Dexheimer, X. Lian, Q. Wang, J. Yang, J. Gray, H. Cheng, *Biosens. Bioelectron.* 2021, 193, 113606.
- [200] N. F. Santos, S. O. Pereira, A. Moreira, A. V. Girão, A. F. Carvalho, A. J. S. Fernandes, F. M. Costa, Adv. Mater. Technol. 2021, 6, 2100007.
- [201] T. Beduk, J. I. De Oliveira Filho, A. Ait Lahcen, V. Mani, K. N. Salama, *Langmuir* 2021, 37, 13890.
- [202] B. Sindhu, A. Kothuru, P. Sahatiya, S. Goel, S. Nandi, IEEE Trans. Electron Devices 2021, 68, 3189.
- [203] F. P. Chietera, R. Colella, A. Verma, E. Ferraris, C. E. Corcione, C. L. Moraila-Martinez, D. Gerardo, Y. H. Acid, A. Rivadeneyra, L. Catarinucci, *IEEE J. Radio Freq. Identif.* 2022, 6, 601.
- [204] A. Mostaccio, G. Antonelli, C. Occhiuzzi, E. Martinelli, G. Marrocco, 2022, 51.
- [205] M. R. R. Abdul-Aziz, S. A. Mohassieb, N. A. Eltresy, M. M. K. Yousef, B. Anis, S. O. Abdellatif, A. S. G. Khalil, *IEEE Trans. Nanotechnol.* 2020, 19, 269.
- [206] A. Watanabe, A. Rahman, J. Cai, M. Aminuzzaman, J. Photopolym. Sci. Technol. 2020, 33, 159.
- [207] B. Xie, Y. Guo, Z. Ou, Y. Chen, M. Hou, X. Chen, J. Gao, 23rd Int. Conf. Electron. Packag. Technol. ICEPT, IEEE, New York, NY 2022.
- [208] H. Qiu, H. Liu, X. Jia, X. Liu, Y. Li, J. Feng, H. Wei, Y. Yang, T. L. Ren, RSC Adv. 2018, 8, 31331.
- [209] A. Scidà, S. Haque, E. Treossi, A. Robinson, S. Smerzi, S. Ravesi, S. Borini, V. Palermo, *Mater. Today* 2018, 21, 223.

- [210] J. Zhang, Y. Wang, R. Song, Z. Kou, D. He, Energy Environ. Mater. 2022, e12548.
- [211] M. Yadav Kumar, A. Borenstein, *Carbon* **2022**, *199*, 208.
- [212] V. Strauss, M. Anderson, C. Wang, A. Borenstein, R. B. Kaner, Small 2018, 14, 1803656.
- [213] P. Malinský, A. Macková, M. Cutroneo, J. Siegel, M. Bohačová, K. Klímova, V. Švorčík, Z. Sofer, EPJWC 2018, 167, 04010.
- [214] K. C. Yung, H. Liem, H. S. Choy, Z. C. Chen, K. H. Cheng, Z. X. Cai, J. Appl. Phys. 2013, 113, 244903.
- [215] M. G. Stanford, C. Zhang, J. D. Fowlkes, A. Hoffman, I. N. Ivanov, P. D. Rack, J. M. Tour, ACS Appl. Mater. Interfaces 2020, 12, 10902.
- [216] "DuPont Kapton thermal management materials," can be found under https://www.dupont.com/electronic-materials/kaptonthermal-management-materials.html, n.d.
- [217] Y. Li, D. X. Luong, J. Zhang, Y. R. Tarkunde, C. Kittrell, F. Sargunaraj,
 Y. Ji, C. J. Arnusch, J. M. Tour, *Adv. Mater.* 2017, *29*, 1700496.
- [218] C. Wang, V. Strauss, R. B. Kaner, Trends Chem. 2019, 1, 858.
- [219] F. Bu, W. Zhou, Y. Xu, Y. Du, C. Guan, W. Huang, npj Flexible Electron. 2020, 4, 1.
- [220] M. F. El-Kady, Y. Shao, R. B. Kaner, Nat. Rev. Mater. 2016, 1, 16033.
- [221] P. Simon, Y. Gogotsi, B. Dunn, Science 2014, 343, 1210.
- [222] M. F. El-Kady, R. B. Kaner, Nat. Commun. 2013, 4, 1475.
- [223] M. H. Amiri, N. Namdar, A. Mashayekhi, F. Ghasemi, Z. Sanaee, S. Mohajerzadeh, J. Nanopart. Res. 2016, 18, 237.
- [224] S. D. Dsouza, M. Buerkle, P. Brunet, C. Maddi, D. B. Padmanaban,
 A. Morelli, A. F. Payam, P. Maguire, D. Mariotti, V. Svrcek, *Carbon* 2021, 183, 1.
- [225] J. Wang, H. Kong, J. Zhang, Y. Hao, Z. Shao, F. Ciucci, Prog. Mater. Sci. 2021, 116, 100717.
- [226] D. He, H. Tang, Z. Kou, M. Pan, X. Sun, J. Zhang, S. Mu, Adv. Mater. 2017, 29, 1601741.
- [227] E. Roduner, Catal. Today 2018, 309, 263.
- [228] H. Wang, M. Jerigova, Jing Hou, N. Tarakina, S. Delacroix, N. L. Salas, V. Strauss, J. Mater. Chem. A 2022, 10, 24156.
- [229] G. Xu, L. Yuan, X. Chen, W. Jia, M. J. Wang, L. Yang, J. Zhu, H. Cheng, *Mater. Des.* 2021, 205, 109721.
- [230] H. Jiang, L. Zheng, Z. Liu, X. Wang, InfoMat 2020, 2, 1077.
- [231] Paolo Samorí, V. Palermo, X. Feng, P. Maisch, L. Lucera, C. Brabec, H.-J. Egelhaaf, in *Flexible Carbon-Based Electronics*, Wiley-VCH, Weinheim, Germany **2018**, pp. 51–69.
- [232] X.-H. Zhao, S.-N. Ma, H. Long, H. Yuan, C. Y. Tang, P. K. Cheng, Y. H. Tsang, ACS Appl. Mater. Interfaces 2018, 10, 3986.
- [233] S. Mulmi, V. Thangadurai, J. Electrochem. Soc. 2020, 167, 037567.
- [234] V. Nagal, T. Tuba, V. Kumar, S. Alam, A. Ahmad, M. B. Alshammari, A. K. Hafiz, R. Ahmad, New J. Chem. 2022, 46, 12333.
- [235] N. V Apollo, B. Murphy, K. Prezelski, al -, A. Bourrier, A. Szarpak-Jankowska, F. Veliev, M. Devi, M. Vomero, E. Fuhrer, E. Castagnola, C. Gueli, S. Nimbalkar, M. Hirabayashi, S. Kassegne, T. Stieglitz, S. Sharma, J. Neural Eng. 2021, 18, 041007.
- [236] P. A. Kumar, A. Pradeep, B. K. G. Nair, T. G. S. Babu, P. V. Suneesh, *Microchim. Acta* 2022, 189, 327.
- [237] J. Zhou, K. Pan, G. Qu, W. Ji, P. Ning, H. Tang, R. Xie, Chem. Eng. J. 2022, 449, 137853.
- [238] M. Vomero, E. Castagnola, F. Ciarpella, E. Maggiolini, N. Goshi, E. Zucchini, S. Carli, L. Fadiga, S. Kassegne, D. Ricci, *Sci. Rep.* 2017, 7, 40332.
- [239] D. W. Park, A. A. Schendel, S. Mikael, S. K. Brodnick, T. J. Richner, J. P. Ness, M. R. Hayat, F. Atry, S. T. Frye, R. Pashaie, S. Thongpang, Z. Ma, J. C. Williams, *Nat. Commun.* 2014, *5*, 5258.
- [240] K. Krukiewicz, D. Janas, C. Vallejo-Giraldo, M. J. P. Biggs, Electrochim. Acta 2019, 295, 253.
- [241] T. M. Swager, K. A. Mirica, Chem. Rev. 2019, 119, 1.
- [242] A. J. Bandodkar, J. Wang, Trends Biotechnol. 2014, 32, 363.

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- [243] W. Zhang, G. Li, H. Yin, K. Zhao, H. Zhao, T. An, *Environ. Sci.*: Nano 2022, 9, 81.
- [244] K. Kante, M. Florent, A. Temirgaliyeva, B. Lesbayev, T. J. Bandosz, *Carbon* **2019**, *146*, 568.
- [245] Y. Jiao, S. W. Cho, S. Lee, S. H. Kim, S.-Y. Jeon, K. Hur, S. M. Yoon, M.-W. Moon, A. Wang, Adv. Eng. Mater. 2018, 20, 1700608.
- [246] X. Zhang, B. Gao, A. E. Creamer, C. Cao, Y. Li, J. Hazard. Mater. 2017, 338, 102.
- [247] Y. Zhang, H. Zhu, P. Sun, C. K. Sun, H. Huang, S. Guan, H. Liu, H. Zhang, C. Zhang, K. R. Qin, *Electroanalysis* **2019**, *31*, 1334.
- [248] A. Di Bartolomeo, Phys. Rep. 2016, 606, 1.

- [249] D. Wu, Q. Peng, S. Wu, G. Wang, L. Deng, H. Tai, L. Wang, Y. Yang, L. Dong, Y. Zhao, J. Zhao, D. Sun, L. Lin, *Sensors* **2018**, *18*, 4405.
- [250] M. Dosi, I. Lau, Y. Zhuang, D. S. A. Simakov, M. W. Fowler, M. A. Pope, ACS Appl. Mater. Interfaces 2019, 11, 6166.
- [251] D. Li, Y. Shao, Q. Zhang, M. Qu, J. Ping, Y. Fu, J. Xie, Analyst 2021, 146, 5704.
- [252] S. Lee, A. Reuveny, J. Reeder, S. Lee, H. Jin, Q. Liu, T. Yokota, T. Sekitani, T. Isoyama, Y. Abe, Z. Suo, T. Someya, *Nat. Nanotechnol.* 2016, *11*, 472.
- [253] S. Zhao, R. Zhu, S. Zhao, R. Zhu, Adv. Mater. 2017, 29, 1606151.
- [254] R. Yang, W. Zhang, N. Tiwari, H. Yan, T. Li, H. Cheng, Adv. Sci. 2022, 9, 2202470.



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