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Editorial

Laser-Induced Graphene Film and Its Applications in Flexible Electronics

Huilong Liu * and Yun Chen *

State Key Laboratory of Precision Electronic Manufacturing Technology and Equipment, School of Electromechanical Engineering, Guangdong University of Technology, Guangzhou 510006, China
* Correspondence: huilong.liu@gdut.edu.cn (H.L.); chenyun@gdut.edu.cn (Y.C.)

Abstract: Laser-induced graphene (LIG) films and their derivatives have been regarded as one of the most outstanding functional flexible electrodes in the past decade, which will transform society and enable new devices and developments. The aim of this Special Issue is to provide a scientific platform for scholars in the LIG field to present their recent research towards a deeper understanding of forming mechanism, structure/ morphology, properties and behaviors of LIG films. This Special Issue gives readers the possibility to gain new insights into the applications of LIG films in flexible electronics, including mechanical/temperature/gas/electrochemical sensors, micro-supercapacitors, actuators, electrocatalysis, solid-state triboelectric nanogenerators, Joule heater, etc. We believe that the papers published in this Special Issue will provide a useful guidance for the manufacturing of nanostructured LIG electrodes in flexible electronics.

Keywords: laser-induced graphene; flexible electronics; laser processing; functional electrodes

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1. Introduction

Since it was first reported in 2014 [1], laser-induced graphene (LIG) film has gained extensive attention due to its unique characteristics of high throughput, direct patterning, and customizable fabrication. Through direct laser writing on aromatic polymers (e.g., polyimide, polyetherimide) or biomass (e.g., lignin, paper, textiles) in ambient air, a decimeter-sized LIG film with a 3D macro-porous structure can be achieved in one step, which makes it possible to fabricate flexible graphene electrodes with high efficiency, high yield, and low cost. Typically, multiple steps are required to convert the carbon precursors into porous LIG, including the dissociation of precursors, the release of generated gases, and the recombination of carbon atoms [2]. More specifically, a temperature as high as 3000 K can be generated once a matched laser beam irradiates the surface of carbon precursors. Such high temperature will destroy the carbon–oxygen bonds and carbon–nitrogen bonds of the precursor, so that the oxygen atoms are combined with a small amount of carbon and nitrogen atoms to escape in the form of gases, including carbon monoxide and methane, etc. The remaining carbon and nitrogen atoms recombine to form a small number of nitrogen-doped 3D graphene with atomic defects inside and a porous morphology outside. Thus, the sp3-carbon atoms are photothermally converted to sp2-carbon atoms. Moreover, due to the processing characteristics of rapid heating and rapid cooling of the laser, the resulting graphene lattice structure does not present the six-membered ring of intrinsic graphene, but instead becomes a mixed ring composed of five-, six-, and seven-membered rings [3]. To obtain high-quality LIG films, a reactive molecular dynamics model was developed by our group to study the light-material interactions in LIG fabrication processes [4]. The effect of rapid heating and cooling process on the formation of LIG was systematically investigated at the atomic level. Studies have shown that the initial rapid heating process requires a temperature high enough (e.g., 3000 K) for unbound atoms to be absorbed. In the subsequent heat holding process, the formation of carbon clusters needs to ensure a

long enough duration (>600 ps). In the eventual cooling to room temperature process, the defective bonds in the carbon cluster repair themselves to form a perfect graphene sheet.

To date, there are many kinds of laser sources employed for the fabrication of LIG films, such as ultraviolet ultrashort pulsed lasers, blue-violet/blue diode lasers, near-infrared pulsed lasers, and mid-infrared pulsed/continuous wave CO_2 lasers. However, not all lasers are suitable for forming LIG films, or even high-quality ones, which requires specific wavelengths, appropriate laser energy density, and sufficient holding duration [2]. Due to the maskless and programmable processing modes and in situ growth properties on flexible substrates, LIG films show several unique advantages over conventional graphene/binder composites, including high flexibility and foldability, good electric/thermal conductivity, and high surface area. Therefore, LIG films have successfully demonstrated their potential in the field of electronic devices, including mechanical/temperature/gas/electrochemical sensors, micro-supercapacitors, actuators, electrocatalysis, solid-state triboelectric nanogenerators, Joule heaters, etc.

2. Applications of Laser-Induced Graphene in Flexible Electronics

This Special Issue includes relevant works about the advanced manufacturing of LIG films and their applications in flexible electronics. As one of the most important components in the Internet of Things era, flexible wearable sensors are greatly needed in the near future. Based on its excellent physical and chemical properties, LIG film has been widely used in quite a variety of flexible sensors, such as sound sensors [5,6], gas sensors [7,8], humidity sensors [9], biosensors [10,11], electrochemical sensors [12], strain sensors [13], and pressure sensors [14,15]. For example, Tao et al. [5] developed an intelligent LIG artificial throat that can generate and detect sounds in a single device. Due to the porous structure, high thermal conductivity and low heat capacity of LIG films, the artificial throat has a completely different working mechanism compared with the conventional acoustic transducers. An intelligent artificial throat can detect simple throat vibrations and convert them into controllable sounds, thus showing great potential to assist people with disabilities affecting their speech. Tour et al. [8] fabricated LIG gas sensor arrays that can be incorporated on a variety of surfaces to detect a broad range of gases. The gas sensors exhibit fast response times owing to the large surface area (~350 $m^2\ g^{-1}$) and good thermal conductivity of LIG, wherein its thermal conductivity is similar to thermal conductivity detectors or katharometers. Ping et al. [9] employed porous LIG and graphene oxide as humidity-sensing materials and prepared a flexible capacitive-type interdigital humidity sensor with low hysteresis, high sensitivity, and long-term stability. In addition, LIG was also used in wearable biosensors with high accuracy and low detectable concentrations. However, the long-term chemical and electrochemical stability of LIG does not satisfy practical applications. In view of this, Zhang et al. [10] reported a strategy to engineer an LIG surface with Au clusters and chitosan to form C−Au−LIG electrodes with superhydrophilic and conductive 3D graphene surfaces, which show good performance and negligible attenuation in long-term storage and utility. Similarly, Li et al. [12] built a laser-enabled flexible LIG electrochemical sensing system on a finger to electrochemically identify chloramphenicol, clenbuterol and ractopamine in meat in situ and in a fast and real-time manner. In the aspect of strain and pressure sensors, LIG films also exhibit some unique advantages due to their good electrical conductivity. Yan et al. [15] developed a flexible high-resolution (8 dpi) triboelectric sensor array based on patterned high-quality LIG electrode (7 $\Omega\ sq^{-1}$) for self-powered, real-time tactile sensing. The sensor platform shows outstanding durability and synchronicity, enabling real-time visualization of multipoint touch, sliding, and tracking motion trajectory without power consumption. Based on the triboelectric sensor platform, a smart wirelessly controlled human–machine interaction system was also constructed to wirelessly control personal electronics.

In addition to flexible sensors, many of the publications collected in this Special Issue focus specifically on micro-supercapacitors and actuators. In terms of micro-supercapacitors, Tour et al. [1] first reported the processing technique of LIG films and their unique applica-

tions in flexible micro-supercapacitors. Due to their high surface area and high electrical conductivity (<15 Ω sq^{-1}), LIG films are very suitable for energy storage, especially for in-plane micro-supercapacitors [2]. The LIG-based micro- supercapacitors deliver an areal capacitance of >4 mF cm^{-2} and a power density of 9 mW cm^{-2}. To further improve the electrochemical performance of the micro-supercapacitors, many methods have been employed for enhancing the interactions between the LIG interdigital electrode and electrolyte from both the physical and chemical aspects, such as heteroatom (e.g., nitrogen, boron, phosphorus) doping [16,17], specific surface area enhancement [18,19], and surface functional group or microstructure modification [20], etc. For example, our group first developed an ultra-fast ultraviolet laser induction and activation technique for the fabrication of LIG films with the features of hierarchical porous structure, small amount of doped potassium (~0.50 wt%), high surface area (>1300 m^2 g^{-1}), and super-hydrophilicity (maximum droplet spreading velocity reaches 424.7 mm s^{-1}). The resulting in-plane micro-supercapacitors exhibit an ultrahigh areal capacitance of 128.4 mF cm^{-2}, which outperforms state-of-the-art laser-processed carbon- based micro-supercapacitors [18]. Moreover, a high-voltage micro-supercapacitors with voltage up to several hundred volts can also be realized through the in-plane or through-plane design of LIG electrode structure, including square electrode arrays [21], linear strip electrode arrays [22], and three-dimensional stacked arrays [23]. Furthermore, the addition of the paper-cut process also helps to improve the tensile properties of micro-supercapacitors [24]. On the other hand, patterned LIG films are also good candidates for light-driven actuators based on the Marangoni effect due to their good photothermal properties, reasonable mechanical strength, and broad-spectrum light absorption properties [25,26]. In 2020, Wang et al. [25] employed patterned LIG films as stick-on photothermal labels for developing 2D and 3D light-driven actuators. Under light irradiation, the patterned 2D and 3D light-driven actuators can be used for directional movement and translation and rotation motions under the guidance of photothermal Marangoni actuation. Similarly, electrothermally controlled actuators based on patterned LIG films were reported by Ling et al. [27], and its application in mechanically guided 3D assembly and human–soft actuators interaction was explored. The stress caused by the significant thermal expansion can deform strategically designed 2D precursors into programmed 3D architectures.

According to the advantages of LIG films over conventional graphene/binder composites, other applications were also developed in recent years through further improving the interface and/or electrically/thermally conductive networks of LIG films, including solid-solid/liquid triboelectric nanogenerators [28,29], electro-catalysis carriers [30], and Joule heaters [31,32]. For example, our group developed an in-situ growing LIG process that enables to one-step patterning of superhydrophobic fluorine-doped graphene on fluorinated ethylene propylene-coated polyimide films [29]. This method utilizes the various spectral responses of propylene and polyimide upon laser excitation to preferentially generate an environment for LIG formation, thus eliminating the need for multi-step processes and specific atmospheres (e.g., inert gas). The structured and water-repellant structures provided by the spectral-tuned interfacial LIG process are very suitable for the use as the electrode of a flexible droplet-based electricity generator, showing high power conversion efficiency with a peak power density of 47.5 W m^{-2} by releasing a 105 μL of water droplet from a height of 25 cm.

All these cases confirm the versatility and advancement of patterned LIG films as functionally integrated electrodes, developing flexible electronics with improved electrical/thermal/electrochemical/triboelectric behavior and new functionalities, which can be used in various wearable electronics for the coming Internet of Things in the near future. For this reason, LIG films and their derivatives have been regarded as one of the most outstanding functional flexible electrodes in the past decade, which will revolutionize society and provide it with new devices and developments.

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