The application of epoxy resin polymers by laser induction technologies

Abstract: The fabrication of robust and high-performance graphene-based electrodes on engineering plastics has garnered significant attention in recent years. In this study, we present a novel methodology to produce porous graphene structures derived from epoxy resin (EP) utilizing a straightforward laser direct-scribing process. Under the influence of a CO₂ laser in an ambient atmosphere, EP undergoes a transformation to yield laser-induced graphene (LIG-APP/EP). Furthermore, this LIG-APP/EP was employed to construct an electrode for lithium-ion batteries, which exhibited outstanding electrochemical performance. Notably, the initial charge and discharge capacities of the LIG-APP/EP electrode material were recorded at 976 and 1,452 mAh g⁻¹, respectively, with a coulombic efficiency of 67.2%. Such impressive performance can be ascribed to the hierarchical porous architecture of LIG-APP/EP and the concurrent doping with nitrogen (N) and phosphorus (P) atoms. Given these findings, LIG-APP/EP demonstrates significant potential for applications in advanced electrochemical systems. This innovative approach also offers profound implications for the sustainable recycling of discarded engineering plastics.

Keywords: porous graphene, CO₂ laser, hierarchical, electrode

1 Introduction

Epoxy resins (EP) are renowned for their superior mechanical attributes and exceptional corrosion resistance, finding extensive utilization in diverse applications ranging from composite materials to electronic packaging. However, the inherent flammability of EP curing compounds constrains their broader adoption [1,2]. Consequently, augmenting the flame retardancy of EP has emerged as an imperative strategy to amplify its applicability [3,4]. Utilizing ammonium polyphosphate (APP) as a flame retardant for EP represents a prevalent eco-friendly flame retardancy approach [5,6]. In the contemporary era, buoyed by technological advancements, the deployment of EP in electronic equipment has surged. Notably, plastic packaging dominates the electronic component encapsulation sphere, constituting over 90% of its landscape, with EP encapsulation coatings accounting for an astounding 90–97%. Moreover, certain manufacturing protocols yield peripheral residues rich in EP [7,8]. This amplifies the urgency to devise efficient strategies for EP waste management.

In a seminal discovery in 2014, Tour and colleagues unveiled a pioneering technique to metamorphose polyimide into graphene using a CO₂ laser, christening it Laser Induced Graphene (LIG) technology [9–12]. This modality empowers the transformation of engineering plastics possessing carbon-forming capabilities into graphene under transient elevated temperatures. Endowed with simplicity, expediency, and eco-friendliness, this innovation has captivated considerable academic intrigue.

To encapsulate, leveraging the carbonization propensity of APP/EP upon combustion in ambient conditions, this study introduces a groundbreaking method to recapture APP/EP waste. This reclaimed material then serves as a foundational substrate for the successful synthesis of N/P co-doped laser-induced graphene (LIG-APP/EP). When deployed as an anode material for lithium-ion batteries, LIG-APP/EP’s electrochemical energy storage characteristics were meticulously analyzed. Through this avenue, we have efficaciously addressed the APP/EP waste recycling conundrum and championed the waste-to-energy-material paradigm shift, ushering in an innovative avenue for plastic waste recycling.
2 Experimental

2.1 Materials

The materials and equipment used in the experiment are shown in Tables 1 and 2.

2.2 Preparation of LIG

2.2.1 Preparation of APP/EP

The fabrication procedure for APP/EP composite samples is delineated in Figure 1. Initially, bisphenol A type E44 EP was pre-conditioned in a vacuum oven at 80°C for 5 min to enhance its fluidity. Subsequent to achieving the desired viscosity, the EP was transferred to a beaker. Concurrently, an oil bath was maintained at 80°C, and upon stabilization, vigorous agitation was commenced at an approximate speed of 1,000 rpm. With the EP retaining optimal fluidity, incremental additions of APP were introduced, ensuring consistent high-speed mixing for a duration of 20 min. Thereafter, the curing agent, m-phenylenediamine (m-PDA), was incorporated in a predefined ratio (EP:m-PDA = 100:12). The resultant mixture underwent a brief mixing phase of 2 min to ensure uniformity. The composite was then degassed in a vacuum oven to eliminate entrapped air. Subsequently, a pre-warmed PTFE mold, conditioned at 80°C for 10 min within the vacuum oven, was loaded with the composite mixture. The curing protocol involved a two-stage thermal treatment: an initial phase at 80°C for 2 h, followed by an elevated temperature phase at 120°C for an additional 2 h. Post-curing, upon reaching ambient conditions, the fully cured APP/EP composite was extracted. A comprehensive visual representation of the process can be referred to in Figure 1.

Table 1: Materials, model, and manufacturers

<table>
<thead>
<tr>
<th>Materials</th>
<th>Model</th>
<th>Manufacturers</th>
</tr>
</thead>
<tbody>
<tr>
<td>Bisphenol A type E44 (EP)</td>
<td>Epoxy value 0.44</td>
<td>Sinopec Baling Petrochemical Branch</td>
</tr>
<tr>
<td>m-PDA (m-Phenylenediamine)</td>
<td>Analytical purity</td>
<td>Weiss Chemical Reagent Co.</td>
</tr>
<tr>
<td>APP</td>
<td>Polymerization degree &gt; 2,000</td>
<td>Qingyuan Pusefu Phosphorus Chemical Co.</td>
</tr>
<tr>
<td>Nickel foam</td>
<td></td>
<td>Kunshan Baiyida New Material</td>
</tr>
<tr>
<td>Mercury/methylene oxide electrode</td>
<td></td>
<td>Tianjin Aida Hensheng Technology Development Co.</td>
</tr>
<tr>
<td>Platinum sheet electrode</td>
<td>10 × 10 × 0.1 mm³</td>
<td>Tianjin Aida Hensheng Technology Development Co.</td>
</tr>
<tr>
<td>N-Methylpyrrolidone</td>
<td>Analytical purity (AR)</td>
<td>Tianjin Guangfu Fine Chemical Research Institute</td>
</tr>
<tr>
<td>Lithium-ion battery electrolyte</td>
<td>Battery grade</td>
<td>Zhangjiagang Guotai Huarong Chemical Co</td>
</tr>
<tr>
<td>Polyvinylidene fluoride</td>
<td>Battery grade</td>
<td>DuPont</td>
</tr>
<tr>
<td>Polypropylene film</td>
<td>20 μm</td>
<td>Henan Chaoli New Energy Co</td>
</tr>
<tr>
<td>Lithium flakes</td>
<td>Battery grade</td>
<td>Qinhuangdao Lithium Co., Ltd.</td>
</tr>
<tr>
<td>Anhydrous ethanol (C₂H₅OH)</td>
<td>Analytical purity</td>
<td>Beijing Chemical Factory</td>
</tr>
<tr>
<td>Deionized ultrapure water</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

Table 2: Instruments used in the experiments

<table>
<thead>
<tr>
<th>Experimental instruments</th>
<th>Model</th>
<th>Manufacturers</th>
</tr>
</thead>
<tbody>
<tr>
<td>CO₂ Laser engraving machine</td>
<td>Longitude-4060</td>
<td>Shandong Liaocheng Jingwei Technology Co.</td>
</tr>
<tr>
<td>Heated magnetic stirrer</td>
<td>DF-101s</td>
<td>Gongyi Yuhua Instrument Co.</td>
</tr>
<tr>
<td>Constant temperature water oil bath</td>
<td>RE-201D</td>
<td>Gongyi Yuhua Instrument Co.</td>
</tr>
<tr>
<td>Ultrasonic Cleaner</td>
<td>KQ5200B</td>
<td>Kunshan Ultrasonic Instruments Co.</td>
</tr>
<tr>
<td>Electric constant temperature blast drying oven</td>
<td>DZF-6213</td>
<td>Sartorius Group of Companies, Germany</td>
</tr>
<tr>
<td>Electronic scales</td>
<td>BSA2245-CW</td>
<td>Shanghai Chenhua Instruments Co.</td>
</tr>
<tr>
<td>Electrochemical workstation</td>
<td>CHI660E</td>
<td>Shanghai Michelena Glove Box Company</td>
</tr>
<tr>
<td>Glove box</td>
<td>Universal Series</td>
<td>Shenzhen Yongxing Precision Machinery Company</td>
</tr>
<tr>
<td>Manual hydraulic buckle type battery sealing machine</td>
<td>SF120 Shandong Liaocheng Jingwei Technology Co.</td>
<td></td>
</tr>
<tr>
<td>8-Point blue power battery test system</td>
<td>CT2001A</td>
<td>Wuhan Blue Electric Electronics Co.</td>
</tr>
</tbody>
</table>
2.2.2 Preparation of LIG-APP/EP

A 4060 non-metallic laser engraver, outfitted with a CO₂-pulsed laser head, was employed in this procedure. The laser head exhibits attributes such as a wavelength of 10.6 μm, a maximum power output of 50 W (adjustable within the range of 1–100%), a spot diameter of 100 μm, and a modifiable scanning rate. The synthesized APP/EP composite samples were systematically aligned on the engraver’s laser scanning platform. A comprehensive schematic of the preparation procedure is depicted in Figure 2.

As the CO₂ infrared laser scans over the APP/EP substrate in an ambient environment, selective regions of the APP/EP surface undergo a transformation into laser-induced graphene (LIG-APP/EP), while zones untouched by the laser retain their native morphology. Optimal LIG-APP/EP formation was observed under specific conditions: a laser power of 5 W, a scan rate of 10 mm s⁻¹, and a scan repetition of twice. Deviations from these parameters, either by escalating or reducing the laser power and scanning rate, resulted in either the ablation of the APP/EP substrate or failed LIG-APP/EP production.

3 Result and discussion

3.1 Morphological and structural characterization of LIG-APP/EP

The microstructure of LIG-APP/EP was elucidated using scanning electron microscopy (SEM). The surface displays a distinctive porous architecture (as presented in Figure 3a), interspersed with pores of varying dimensions and localized micro-cracks. These features can be attributed to the heterogeneous thermal radiation during laser exposure, inducing elevated temperatures in specific regions. Distinct morphological differences between the APP/EP substrate and LIG-APP/EP are demarcated with yellow lines in Figure 3b. While the LIG-APP/EP showcases a prototypical porous configuration, the regions untouched by the laser retain their original form. For a more granulated view of this porous architecture, a magnified image of a specific section is provided, with the portion highlighted in Figure 3c being expanded upon in Figure 3d. This magnified representation reveals a dense network of mesopores in proximity to larger pores,
interspersed with occasional microporous structures. Such intricate pore geometries arise from the thermal decomposition of certain APP/EP structures during laser irradiation, coupled with the expeditious release of gaseous byproducts. This three-dimensional hierarchical porous matrix augments electrolyte permeation, thereby enhancing the electrochemical performance of LIG-APP/EP.

To validate the hierarchical porous architecture of LIG-APP/EP, a suspension derived from the ultrasonicated LIG-APP/EP powder in deionized water was dispensed onto a grating copper grid to facilitate transmission electron microscopy (TEM) analysis. Figure 4 depicts representative TEM micrographs of LIG-APP/EP. As evident from Figure 4a–c, the LIG-APP/EP consists of a multi-layered graphene configuration, characterized by a distinctive ripple-like topographical arrangement. This surface undulation in LIG-APP/EP can be attributed to the abrupt high-temperature exposure from laser irradiation, which induces expansion and consequent deformation of the APP/EP substrate. High-resolution TEM images, presented in Figure 4d, further accentuate the sparse layering of the graphene in LIG-APP/EP, with the yellow arrows emphasizing regions comprising fewer than ten layers. The quantitative assessment revealed an average lattice spacing of approximately 0.34 nm, congruent with the interplanar distance of the (002) planes commonly observed in graphite. Corroborating these findings with previously discussed SEM analyses, it can be inferred that the synthesized LIG-APP/EP exhibits a three-dimensional stratified porous graphene structure.

The Brunauer–Emmett–Teller analysis was employed to assess the specific surface area and pore size distribution of LIG-APP/EP. Figure 5a presents the nitrogen (N2) adsorption–desorption isotherm for LIG-APP/EP, while Figure 5b delineates its corresponding pore size distribution. Owing to the hierarchical porous structure and the concurrent nitrogen/phosphorus (N/P) co-doping, LIG-APP/EP exhibited a specific surface area of 397 m2 g−1. The isotherm for LIG-APP/EP predominantly aligns with a type IV curve, complemented by H1-type hysteresis loops, which are characteristic of mesoporous materials with pore diameters ranging from 2 to 50 nm. The pore size distribution corroborates the presence of an intricate network of meso- and micropores.
interfaced with macropores. These findings are in congruence with the previously discussed SEM and TEM analyses.

Raman spectroscopy was utilized to ascertain the graphitization degree and the number of lamellae in LIG-APP/EP. As depicted in Figure 6, the Raman spectrum of LIG-APP/EP exhibits three pronounced peaks. The D peak at 1,356 cm$^{-1}$ is indicative of the disordered and defective nature of the material. The G peak, positioned at 1,588 cm$^{-1}$, and the 2D peak, located at 2,700 cm$^{-1}$, are manifestations of the interaction-driven electronic band structure alterations between graphene lamellae and the sp$^2$-hybridized carbon of graphene, respectively [13,14]. This spectral profile attests to the successful synthesis of few-layer graphene from an APP/EP substrate, a finding that is consonant with SEM and TEM characterizations.

![Figure 4: TEM image of LIG-APP/EP: (a) low magnification TEM image; (b) the magnification diagram of the part encircled in red in (a); (c and d) the high magnification TEM image of LIG-APP/EP.](image)

![Figure 5: (a) N$_2$ adsorption–desorption isotherm of LIG-APP/EP; (b) pore size distribution curve of LIG-APP/EP.](image)
The high graphitization degree of the produced LIG-APP/EP, denoted by the $I_G/I_D$ ratio (G-peak to D-peak intensity) in the Raman spectrum, suggests a limited number of lamellae, consistent with a value of ~1.27 for the $I_G/I_{2D}$ ratio. This is in alignment with lamellar observations derived from TEM studies.

In Figure 7, the X-ray diffraction (XRD) pattern of LIG-APP/EP is presented. Two distinct peaks emerge at 25.9° and 42.9°. The peak at 25.9° corresponds to the (002) crystal plane, with an interlayer spacing of 0.34 nm. The peak at 42.9° is associated with the (100) crystallographic plane of graphite. These findings underscore the elevated graphitization degree of the synthesized LIG-APP/EP. In tandem with high-resolution TEM imaging, the data indicate that LIG-APP/EP possesses commendable crystallinity. The affirmed 0.34-nm layer spacing is corroborative of a graphitized carbon architecture.

To discern the elemental composition of LIG-APP/EP, X-ray photoelectron spectroscopy (XPS) was employed. Figure 8 delineates the XPS spectra for LIG-APP/EP. For this analysis, the LIG-APP/EP was isolated from its APP/EP substrate. The spectra confirm that both LIG-APP/EP and its substrate comprise the same elemental quartet: C, N, O, and P. As elucidated in Figure 8, relative to the APP/EP precursor, there is a marked enhancement in the carbon content of LIG-APP/EP, elevating from 74.9 to 89.3%. Conversely, there’s a decline in the concentrations of O and N, with O dropping from 23.39 to 9.03% and N receding from 1.44 to 1.14%. This compositional shift can be attributed to the intense temperatures (exceeding 2,500°C) experienced during laser irradiation of the substrate surface [15], leading to the immediate partial decomposition of the APP/EP. This event catalyzes the disruption of C–O, C=O, and C–N/C=O bonds, resulting in the emission of gaseous compounds such as CO$_2$ and NO through the fusion of a minor proportion of C with a predominant fraction of O and N. The P content witnesses a decrement from 0.53 to 0.35%, a phenomenon linked to the thermal degradation of APP and consequent phosphate production. With
successive laser treatments, the residual carbon atoms undergo reorganization into sp² configurations, engendering porous graphite architectures [16,17], synonymous with laser-induced graphene.

### 3.2 Lithium performance study of LIG electrodes

To assess the lithium storage capabilities of LIG-APP/EP, a lithium-ion button half-cell was constructed with LIG-APP/EP serving as the anode. Comprehensive electrochemical analyses were performed within a voltage window of 0 to 3 V at a scan rate of 0.2 mV s⁻¹. Figure 9a and b elucidate the cyclic voltammetry (CV) and galvanostatic charge/discharge profiles, respectively. Notably, the inaugural cycle of Figure 9a unveils a prominent feature at 0.75 V, indicative of solid electrolyte interface (SEI) film formation on the anode, accounting for the non-reversible capacity in the initial cycle due to lithium-ion sequestration [18]. Subsequent cycles exhibit congruent profiles, underpinning the superlative reversibility of lithium insertion and extraction for the LIG-APP/EP.

The charge/discharge behavior for the initial three cycles, presented in Figure 9b, reveals a marked difference between the first discharge and charge capacities, congruent with the aforementioned CV data. The initial charge and discharge capacities for LIG-APP/EP are documented at 976 and 1,452 mAh g⁻¹, respectively, yielding a Coulombic efficiency of 67.2%. The inferior first-cycle Coulombic efficiency is attributed to SEI formation and ancillary electrolyte reactions [19,20]. Notably, ensuing cycles exhibit nearly indistinguishable profiles, attesting to the electrode’s robust electrochemical stability.

Rate capability assessments of LIG-APP/EP, showcased in Figure 9c, involve varied current densities spanning from 1 to 10 A g⁻¹ across ten cycles. Remarkably, the specific capacity recuperates to 805 mAh g⁻¹ upon reverting to a 1 A g⁻¹ regime, post-experiencing higher current densities, epitomizing the material’s resilience, and exceptional rate adaptability.

An examination of the long-term cyclability of LIG-APP/EP, portrayed in Figure 9d, accentuates consistent performance.
over 180 cycles at 1 A g$^{-1}$, maintaining an impressive 870 mAh g$^{-1}$ capacity with impeccable Coulombic efficiency. The three-dimensional porous morphology and deliberate N/P co-doping are conjectured to synergistically facilitate rapid ion/electron transport, conferring unparalleled cycle life to LIG-APP/EP.

Delving into the electrochemical kinetics of LIG-APP/EP, electrochemical impedance spectroscopy (EIS) was harnessed. The EIS spectra in Figure 10, post 100 cycles, demarcate characteristic high-frequency semicircles and Warburg tails in the low-frequency domain, reflective of charge transfer resistance ($R_{ct}$) and concentration-dependent diffusion phenomena, respectively. A minimal $R_{ct}$ value of 20 Ω is discerned, substantiating the electrode activation during electrochemical cycling.

4 Conclusion

Utilizing an ambient laser-induced strategy, three-dimensional porous graphene was synthesized employing EP as the precursor.


2. Electrochemically, LIG-APP/EP emerged as a formidable anode material, surpassing commercial graphite electrodes in terms of specific capacities and cycling robustness, evincing its promise for next-generation lithium-ion batteries.

Acknowledgements: Dr Yang and the co-author would like to thank all the reviewers who participated in the review of this manuscript. This work was financially supported by the Young Elite Scientists Sponsorship Program by CAST (2022QNRC001).

Funding information: This work was financially supported by the Young Elite Scientists Sponsorship Program by CAST (2022QNRC001).

Conflict of interest: There are no conflicts to declare.

Data availability statement: The datasets generated during and/or analysed during the current study are available from the corresponding author on reasonable request.

References


