Developing facile approaches to fit in large-scale fabrication of efficient and durable catalytic electrodes is highly desirable for oxygen electrocatalysis and metal–air batteries. Herein, a strategy based on phase separation and laser induction is proposed to prepare 3D binder-free integrated electrodes (IEs). The phase separation between a polybenzimidazole (PBI) solution and a coagulation bath containing metal precursors occurs to form a 3D interconnected porous catalyst precursor layer. After drying, IEs are obtained by laser induction, which simultaneously converts PBI into hierarchically porous laser-induced graphene (HPLIG) and reduces metal precursor to tiny nanoparticles. To demonstrate the versatility of this method, IEs with different HPLIG hybrid catalyst layers and substrates are fabricated. IE-NiFe/HPLIG and IE-Co/HPLIG using carbon paper as a substrate exhibit superior oxygen evolution reaction (OER) and oxygen reduction reaction (ORR) performance respectively. Flexible IE-NiCoFe/HPLIG with OER and ORR bifunctionality using carbon cloth as the substrate is applied as an air cathode in rechargeable aqueous Zinc–air batteries (ZABs) and provides a satisfactory power density of $163 \text{ mW cm}^{-2}$ and cycling stability of 1800 h at 10 mA cm$^{-2}$. The electrode also endows solid ZABs with good flexibility. This work offers an industrially viable solution to the challenge of rapid fabrication of IEs.

1. Introduction

The increasing demand of energy has attracted significant attention to the development of energy-conversion systems encompassing fuel cell and metal–air batteries. However, the performance of these devices is limited by the sluggish reaction kinetics of oxygen reduction reaction (ORR) and oxygen evolution reaction (OER).[1,2] Up to now, the most commercialized electrocatalysts are based on noble metals such as platinum/carbon (Pt/C) and ruthenium oxide (RuO$_2$).[3] The large-scale application of these precious metal-based electrocatalysts is severely hindered by their scarcity, high cost, and poor stability. Therefore, the development of high-performance, low-cost, and earth-abundant electrocatalysts is highly desired.

During the past few decades, enormous efforts have been devoted to investigating nonprecious metal-based electrocatalysts including carbons,[4,5] metals,[6] alloys,[7,8] oxides,[9,10] composites,[11] and so on. Although great progress has been made in materials design and synthesis, conventional electrode preparation by coating catalyst ink is ineffective. First, long-period sonication during ink preparation process inevitably damages macro- and meso-structures of catalysts, causing partial loss of active sites and pores. Second, the addition of polymer binder degrades the charge transfer efficiency of catalyst, further deteriorating the performance. On the contrary, these shortcomings can be easily mitigated through constructing integrated electrodes (IEs) which assemble catalysts with substrates directly without the use of binder.[12,13] Methods including electrospinning, hydrothermal synthesis and templating have been reported to fabricate IEs.[2,14,15] However, considerable time period and extra procedures are needed, leading to a cost-prohibitive process.[13] Therefore, it is necessary to develop highly convenient and efficient methods to fit in automatic, continuous, and scaled-up fabrication procedure for potential commercial applications. In addition, to maximize the performance of IEs, there are also...
some common issues to be solved. First, lack of 3D multiphase interphase leads to limited exposure of active sites and inhibits efficient mass diffusion.[16] Second, inevitable bury of active sites by matrix causes partial loss of active sites.[17] Third, self-agglomeration and peeling off of active sites under extreme working conditions have a negative impact on durability.[18]

To tackle the above-mentioned issues, we proposed a facile and versatile strategy based on phase separation and laser induction methods (PSLI) to prepare IEs. In which, phase separation between immiscible polymer solution and water solution was used as a self-templating method to construct catalyst precursor layer with 3D interconnected hierarchical pores. The interconnected pores are beneficial for fast removal of degraded gas under laser induction, thus preserving the nanoscale features mostly. The preserved 3D interconnected structure also benefits active sites exposure and mass transfer in oxygen electrocatalysis. According to the feature of phase separation, 3D interconnected channels are induced by metallic salt solution. Therefore, metal precursors are intended to be distributed on the surface of precursor channels, thus avoiding the resultant active species to be buried by matrix. In terms of thermal treatment of precursors, conventionally, a high-temperature furnace is used and issues including high thermal power, large consumption of expensive inert gas, and considerable time periods make the carbonization process energy-consuming, high-cost and inefficient. Laser has shown great promise in rapid materials processing and synthesis. Methods including pulsed laser ablation in liquids,[19–21] laser pyrolysis,[22,23] and so on have been widely investigated to prepare nanomaterials for catalysis applications. In addition, laser exhibits a great potential in inducing the conversion of membrane-based polymeric materials into graphene.[24,25] Some studies also demonstrated the direct synthesis of nanoparticles on graphene through laser induction of precursors containing metallic salts.[26–28] Therefore, it would be possible to combine phase separation and laser induction to overcome the drawbacks of the existing methods.

Taking the advantage of PSLI method, in this work, we demonstrated the rapid and sustainable construction of 3D binder-free IEs with breathable catalyst layers for the application of oxygen electrocatalysis. In the catalyst layer of IEs, the generated nanoparticles are spatially confined and uniformly distributed on the channel surface of 3D interconnected hierarchically porous laser-induced graphene (HPLIG). To demonstrate the versatility of the proposed method, IEs with different HPLIG hybrid catalyst layers including IE-NiFe/HPLIG and IE-Co/HPLIG were successfully prepared and exhibited superior OER and ORR performance respectively, which is comparable with commercial catalysts. To further expand the application of PSLI method, flexible air cathode IE-NiCoFe/HPLIG with OER and ORR bifunctional catalyst layer was developed and used in rechargeable Zinc-air batteries (ZABs), which presented longer cycling life, larger power density, and capacity than the battery assembled with benchmark catalyst of Pt/C and IrO₂.

2. Results and Discussion
2.1. Preparation and Characterization of IEs

The preparation process of IEs is illustrated in Scheme 1. Firstly, a homogeneous casting solution was prepared by mixing polybenzimidazole (PBI) and N,N-dimethylacetamide (DMAc). Then, a thin film was cast by a doctor blade on a conductive substrate, which was subsequently immersed in a coagulation bath (DI water or salt solution) at room-temperature. After 2 min, the substrate was taken out and dried under ambient conditions before laser induction. More details about IEs preparation can be found in Supporting Information. The resultant IEs are denoted by IE-M/HPLIG, the components of catalyst layer are represented by M/HPLIG, in which M stands for the metallic components of nanoparticles and HPLIG refers to hierarchically porous laser-induced graphene.

A DPD simulation was conducted to predict an occurrence of phase separation when two incompatible solutions are mixed together (Figure 1a and Video S1, Supporting Information). The results revealed a formation of a large number of channels and interfaces at the beginning and will end up with solution stratification. Similarly, PBI solution and coagulation bath are insoluble with each other as well. When they are mixed together, phase separation is
expected. And meanwhile, the DMAc is miscible with coagulation bath. Therefore, it can be assumed that a driving force caused by concentration difference could result in diffusion of the coagulation bath into the PBI solution as well as the diffusion of the DMAc into the coagulation bath. The gradually increasing concentration of coagulation bath in PBI solution could disturb the thermodynamics balance of PBI solution, causing the precipitation of PBI and formation of a bicontinuous microstructure. After drying under ambient conditions at 25 °C for 12 h, the water was believed to be completely evaporated as the weight loss measurement started to approach zero. In this case, hierarchically porous and multi-channel catalyst precursor layer can be obtained. As shown in Figure 1b, the top view of the prepared catalyst precursor layer exhibits macroscopic multichannel-like structures, which is in good agreement with the theoretical prediction (Figure 1a). In addition, abundant 3D interconnected macroporous and mesoporous structures can be observed with the pore size ranging from tens of nm to tens of µm (Figure 1b,c). However, the catalyst precursor layer made from direct solvent evaporation is dense with low porosity (Figure S1, Supporting Information), suggesting the efficacy of phase separation for preparing hierarchically porous catalyst precursor layer. The impact of PBI concentration on the microstructures of precursor catalyst layer was also investigated. As can be seen from Figure S2, Supporting Information, the higher the concentration of PBI, the denser the catalyst layer is. When the concentration is lower than 5 wt.%, the membrane formability is poor. Therefore, 5 wt.% is considered an appropriate concentration for the preparation of catalyst precursor layers in this work.

After dehydration, the samples were subject to laser irradiation. In order to understand the structural evolution of PBI during laser induction, MD simulations were carried out. The results show that graphene-like structure can be generated within extremely short time period due to high pressure and temperature created by instant and intensive energy input during laser induction process (Figure 1d, Figure S3, and Video S2, Supporting Information). In contrast, only disordered carbon structures can be synthesized under furnace pyrolysis within such short time period (Figure S4 and Video S3, Supporting Information). A major difference between the laser induction and furnace pyrolysis can be ascribed to their different reaction conditions. Although the penetration depth of laser is limited (from several hundred nm to tens of µm), it is suitable for IEs preparation in this work.

Figure 1. a) Representative snapshot of MD simulations of phase separation between two insoluble solutions. b,c) SEM images of top surface view of catalyst precursor layer. d) Snapshot of final products from MD NVT simulations of laser induction process. e,f) SEM images of HPLIG. g–i) TEM images of HPLIG.
In order to investigate the effect of phase separation on the microstructures of resultant catalyst layers of IEs, a comparative study was conducted between IE-HPLIG and IE-LIG. Their catalyst precursor layers were prepared using phase separation and direct evaporation respectively and no metallic precursors were added. As can be seen from Figure 1e,f, IE-HPLIG exhibits a hierarchically porous structure which is consistent with their precursor (Figure 1b,c). TEM images also confirm the existence of 3D interconnected hierarchical pores with a wide range of sizes, exhibiting good morphological heredity of catalyst precursor layers prepared with phase separation (Figure 1g,h). As can be seen from Figure 1i, dense mesopores with size of around 20 nm located on HPLIG can be observed, which is beneficial for exposing active sites. However, only macroporous structures can be seen from the catalyst layer of IE-LIG (Figure S5a, Supporting Information). The TEM image of LIG shows dense and flat surface (Figure S5b, Supporting Information). In order to quantitatively investigate the pore structure of HPLIG and LIG, N\textsubscript{2} adsorption-desorption test was also conducted. In Figure S6a, Supporting Information, type IV isotherms with H3 hysteresis loops can be observed, exhibiting profound characteristics of the mesopores and macropores of both HPLIG and LIG. However, a higher Brunauer–Emmett–Teller (BET) specific surface area of mesopores and macropores of both HPLIG and LIG. Nevertheless, LIG dominates with macropores centered at 14 nm. LIG also densely distributed on the surface of channels (Figure S8b, Supporting Information). It is worth mentioning that big specific surface area and hierarchical porous structures are expected to promote exposing more active species and facilitate gas or electrolyte transfer, thus enhancing the catalytic performance.

When salt solution is used as coagulation bath, phase separation is expected to occur due to incompatibility of PBI solution and the salt solution. Meanwhile, the salt precursors will be evenly distributed on the surface of channels after drying, thus obtaining catalyst precursor layer containing metallic salts directly. As reported in recent publications, NiFe-based electrocatalysts have demonstrated enhanced OER performance but poor ORR activity.\cite{30,31} While Co-based electrocatalysts have demonstrated enhanced OER performance but poor ORR activity.\cite{30,31} To demonstrate the versatility of PSLI method proposed in this work, two electrodes including IE-NiFe/HPLIG and IE-Co/HPLIG were prepared and applied as oxygen electrocatalysts for OER and ORR respectively. For IE-NiFe/HPLIG, the catalyst precursor layer containing mixed Ni and Fe elements was obtained by using coagulation bath containing NiCl\textsubscript{2}-6H\textsubscript{2}O and FeCl\textsubscript{3}-6H\textsubscript{2}O. The cross section of the catalyst precursor layer was observed by SEM in Figure S7a, Supporting Information. Structural features including 3D interconnected networks, hierarchical porosity, multi channels, and multi interfaces are evident, which is consistent with theoretical prediction described above. In addition, EDS mapping also reveals the elemental distribution of nanoparticles and N-doped graphene substrates and further confirms the successful synthesis of NiFe/HPLIG (Figure S7a–k). According to the EDS spectra in Figure S11, Supporting Information, the Ni/Fe molar ratio in resultant nanoparticles is 2.78 and close to the Ni/Fe molar ratio in the catalyst precursor layer and coagulation bath, exhibiting good controllability of nanoparticles’ elemental composition. XRD spectra also show the successful synthesis of NiFe alloy oxide (Figure S12, Supporting Information). In terms of the preparation of IEs, laser parameters especially laser fluence play an important role on the graphitization degree of HPLIG. In this case, IEs prepared under five different laser fluence settings were investigated. Raman spectroscopy with an excitation wavelength of 633 nm was used to characterize the chemical structures of catalyst layers of IEs. Figure S13a, Supporting Information, shows the typical Raman spectra of IE-NiFe/HPLIG catalyst layer obtained under different laser fluences. The D band located at ~1350 cm\textsuperscript{-1} corresponds to disordered structures, the G band at ~1580 cm\textsuperscript{-1} is induced by the ordered sp\textsuperscript{2} hybridized carbon.\cite{34,35} In addition, characteristic band at 561 cm\textsuperscript{-1} of NiFe nanoparticles can also be observed from Raman spectra demonstrating the coexistence of NiFe nanoparticles and HPLIG, which is in agreement with the TEM and XRD results after laser induction, the PBI precursor was transferred into HPLIG and salt precursors were reduced and converted into nanoparticles. MD simulation on structural evolution after organic–inorganic transfer was conducted and revealed that the generated HPLIG would spontaneously embrace the nanoparticles during the high-temperature laser induction process, thus preventing nanoparticles from aggregation (Figure 2e–f and Video S4, Supporting Information). This phenomenon offers benefits for achieving highly uniform distribution of tiny nanoparticles on HPLIG and enhancing the electronic transport from HPLIG to active sites. The physical constraint effect aroused by laser induction also prevents nanoparticles from aggregation and peeling off from graphene substrate under harsh working environment, thus enhancing the activity and durability of catalyst. This theoretical prediction was found consistent with the experimental observation. As can be seen in Figure 2a, the HRTEM images show that the generated nanoparticles are embraced by several layers of graphene. The lattice fringes with an interplanar distance of 0.205 and 0.34 nm correspond to (111) plane of NiFe alloy and HPLIG respectively (Figure 2b).\cite{13} In addition, most of the structural characteristics of catalyst precursor layers were maintained even after fierce laser irradiation (Figure S8a, Supporting Information). It is also evident that the catalyst layer was reinforced by carbon fiber from carbon paper substrate, avoiding peeling off of catalyst layer under harsh working conditions. Tiny nanoparticles are also densely distributed on the surface of channels (Figure S8b, Supporting Information). The high-angle annular dark field (HAADF)-STEM images further verify that the catalyst layer is highly porous with nanoparticles uniformly anchored on the surface of channels and interfaces (Figure 2c–d and Figure S9, Supporting Information). According to HAADF-STEM images from Figure 2f, the resultant nanoparticles exhibit a uniform size distribution and have an average size of 5.6 nm (Figure S10, Supporting Information). EDS mapping also reveals the elemental distribution of nanoparticles and N-doped graphene substrates and further confirms the successful synthesis of NiFe/HPLIG (Figure 2g–k). According to the EDS spectra in Figure S11, Supporting Information, the Ni/Fe molar ratio in resultant nanoparticles is 2.78 and close to the Ni/Fe molar ratio in the catalyst precursor layer and coagulation bath, exhibiting good controllability of nanoparticles’ elemental composition. XRD spectra also show the successful synthesis of NiFe alloy oxide (Figure S12, Supporting Information). In terms of the preparation of IEs, laser parameters especially laser fluence play an important role on the graphitization degree of HPLIG. In this case, IEs prepared under five different laser fluence settings were investigated. Raman spectroscopy with an excitation wavelength of 633 nm was used to characterize the chemical structures of catalyst layers of IEs. Figure S13a, Supporting Information, shows the typical Raman spectra of IE-NiFe/HPLIG catalyst layer obtained under different laser fluences. The D band located at ~1350 cm\textsuperscript{-1} corresponds to disordered structures, the G band at ~1580 cm\textsuperscript{-1} is induced by the ordered sp\textsuperscript{2} hybridized carbon.\cite{34,35} In addition, characteristic band at 561 cm\textsuperscript{-1} of NiFe nanoparticles can also be observed from Raman spectra demonstrating the coexistence of NiFe nanoparticles and HPLIG, which is in agreement with the TEM and XRD results.
described earlier. It is obvious that proper increment of laser fluence results in decreased ID/IG value and increased intensity of 2D peak, indicating the improvement of graphitization degree of HPLIG, which is beneficial for electronic conduction. When the laser fluence reaches 25.2 mJ cm$^{-2}$, the lowest ID/IG value is obtained. However, the ID/IG value is still slightly high. This is because the intrinsic porosity and defects contribute to the intensity of D band. With further increment of the laser fluence, D band and G band gradually merge and the intensity of 2D band sharply decreases, showing more defects are introduced. This might be caused by severe oxidization of HPLIG at high temperature under ambient atmosphere. The impact of laser fluence on OER performance is revealed by electrochemical test as well. Linear scanning voltammetry (LSV) curves in Figure S13b show that the overpotentials of IEs prepared under different laser fluences to achieve the current density of 10 mA cm$^{-2}$ are similar and the difference in overpotential is gradually enlarged at higher current density, indicating IE-NiFe/HPLIGs with higher-graphitization-degree catalyst layers need smaller overpotential to achieve specific current density. This can be further explained by electrochemical impedance spectroscopy (EIS). EIS plots in Figure S13c, Supporting Information, exhibit that the catalysts with higher graphitization degree have smaller charge-transfer resistance, further demonstrating the enhanced reaction kinetics. Therefore, 25.2 mJ cm$^{-2}$ was chosen to be the best laser fluence parameter for IEs preparation in this work.

To demonstrate the novelty of laser induction process, a control experiment using high-temperature furnace to treat IE with the same catalyst precursor layer was conducted. As can be seen from Figure S14a, Supporting Information, only large alloy clusters are observed, which is different from NiFe/HPLIG obtained by laser induction. In addition, the resultant carbon-based substrate is flat and dense with very limited nanoparticles loading (Figure S14b,c, Supporting Information). Such structural difference is caused by the different reaction characteristics between laser induction and furnace treatment. The laser induction with a pulse width of picosecond results in instantaneous high temperature and high pressure. This leads to spontaneous conversion of PBI to graphene and reduction of metal salt precursors, and the initial 3D interconnected hierarchically porous microstructure is preserved within such a short period of time on picosecond scale. On the other hand, furnace treatment at high temperature takes a few hours, which allows PBI polymer chains to move and fuse, readily causing densification and collapse of the initial structure. As a result, a dense carbonized microstructure was observed after furnace treatment. Therefore, it may conclude that furnace treatment cannot transfer PBI into graphene-like structure, and reduced nanoparticles tend to merge and aggregate into large clusters under high-temperature without confinement effect of graphene occurred in laser induction. In this case, the alloy clusters do not adhere to the substrate firmly and peeling off from the substrate can easily occur, leading to a negative impact on electronic conductivity and stability. What is more, furnace treatment inevitably causes thermal damage to substrates, thus hindering the application of IEs. In comparison, laser induction can avoid this issue and shows a great potential in mass production of IEs by roll-to-roll manufacturing.

To further investigate the versatility of PSLI method, IE-Co/HPLIG was prepared through the same procedure by using Co containing coagulation bath. The EDS
mapping of cross section of the catalyst precursor layer shows Co element is dispersed evenly (Figure S15). After laser induction, IE-Co/HPLIG catalyst layer with the same configuration as that of IE-NiFe/HPLIG catalyst layer can be observed (Figure S16, Supporting Information). HAADF-STEM images and EDS mapping results also confirm the resultant tiny Co oxide nanoparticles are uniformly distributed on N doped 3D interconnected HPLIG (Figure S17, Supporting Information). As can be seen from Figure S18, Supporting Information, Raman characteristic bands at \(\approx 194\), \(\approx 479\), and \(\approx 686\) \(\text{cm}^{-1}\) of Co oxide nanoparticles\cite{37} and \(\approx 1350\), \(\approx 1580\), and \(\approx 2700\) \(\text{cm}^{-1}\) of graphene can be observed.\cite{34,35} confirming the coexistence of Co oxide nanoparticles and HPLIG. XRD was conducted and verified the successful synthesis of Co/HPLIGIE as well (Figure S19, Supporting Information).

X-ray photonic spectroscopy (XPS) measurements were performed to further investigate the elemental composition and chemical states of each element in the catalysts. In Figure 3a, the XPS survey spectrum exhibits the existence of elemental Ni, Fe, C, N, and O in NiFe/HPLIG. The high-resolution XPS spectrum of Ni 2p exhibits two spin-orbit peaks at 855.8 eV (Ni 2p\(_{3/2}\)) and 873.4 eV (Ni 2p\(_{1/2}\)) along with two satellite peaks (identified as "Sat."), which can be attributed to NiII.\cite{38} For Fe element, the 2p\(_{3/2}\) and 2p\(_{1/2}\) peaks are located at 710.8 and 724.1 eV respectively, along with two sat. peaks, which is consistent with the characteristic binding energy of FeIII oxidation state.\cite{39} In Figure 3d, the C 1s spectrum displays a characteristic peak at 284.5 eV that can be ascribed to the sp\(^2\) carbon from HPLIG.\cite{25} For O 1s spectrum shown in Figure 3e, two distinct peaks located at 529.7 and 531.5 eV are corresponding to metal–O and metal–OH respectively.\cite{40} In addition, a small peak at 533.0 eV can be seen, which originates from the oxygen-containing functional groups such as C=O and C=O in HPLIG. The low oxidation degree shows good carbon quality which is in good agreement with C 1s and Raman results. As shown in Figure 3f, N 1s spectrum can be deconvoluted into three peaks including pyridinic N (398.8 eV), pyrrolic N (400.6 eV), and graphitic N (401.7 eV).\cite{41} The contents of pyridinic and pyrrolic N are much higher than that of graphitic N. This is because the mesoporous structure plays a key role in tuning the relative concentrations of pyridinic and pyrrolic N during laser induction process. The higher the mesopores density, the higher the relative contents of pyridinic and pyrrolic N are.\cite{41} This further confirms that HPLIG has high mesopores density. The strong affinity of pyridinic and pyrrolic N to transition metal will create strong bonding between active sites and N-doped HPLIG substrate as well, thus enhancing the interfacial electron transfer of HPLIG hybrid catalysts.

As can be seen from Figure S20, Supporting Information, the survey spectrum of Co/HPLIG confirms the existence of Co, C, N, and O elements. The existence of Co\(_{\text{N}}\) species manifests the interactions between the Co nanoparticles and N-doped HPLIG, which may activate Co nanoparticles and improve electrocatalytic activity for oxygen electrocatalysis.\cite{42}

2.2. Electrochemical Analysis and Zinc–Air Battery Application

To demonstrate the electrocatalytic applications of the as-prepared IE-NiFe/HPLIG and IE-Co/HPLIG, their performances were evaluated by cyclic voltammetry (CV) and LSV respectively. Since NiFe alloy has shown great promise to be

![Figure 3. a) XPS survey and high-resolution XPS spectra of b) Ni 2p, c) Fe 2p, d) C 1s, e) O 1s, and f) N 1s for NiFe/HPLIG.](image-url)
a good candidate for OER. In this work, the catalytic performance of IE-NiFe/HPLIG with respect to OER was investigated. The OER polarization voltammogram was obtained at a scanning rate of 10 mV s\(^{-1}\) in oxygen saturated 1.0 M KOH electrolyte. The OER polarization curves (Figure 4a) reveal that IE-NiFe/HPLIG displays an OER performance with a small overpotential of 260 mV at 10 mA cm\(^{-2}\). As a benchmark, the OER performance of the electrode with the same substrate and similar loading of commercial IrO\(_2\) was tested under the same condition. To achieve the current density of 10 mA cm\(^{-2}\), IrO\(_2\) requires a slightly higher overpotential of 280 mV. In addition, a comparison between IE-NiFe/HPLIG and traditional ink-coating electrode was also conducted. The results show that the catalytic performance of NiFe/HPLIG ink-coating electrode is inferior to IE-NiFe/HPLIG and a higher overpotential of 310 mV is needed at 10 mA cm\(^{-2}\). This can be explained by the destruction of 3D interconnected structure and addition of polymer binder for the ink-coated electrode. As can be seen from Figure S21a, Supporting Information, the catalyst powder is evenly distributed on the electrode surface. However, the 3D-interconnected and hierarchically porous structures of the catalyst are severely destroyed due to fierce ultrasonication during ink preparation. In addition, the catalyst surface is densely covered with polymer binder (Figure S21b, Supporting Information), which further deteriorates the mass transfer and electronic conduction. ECSA is strongly related with catalytic activity of electrocatalysts. To better understand the reasons for the superior OER performance of IE-NiFe/HPLIG, ECSA of electrodes was evaluated based on double-layer capacitance (C\(_{dl}\)) due to their linear relationship. In this case, a higher value of C\(_{dl}\) indicates a bigger ECSA and more active sites. As shown in Figure S22, Supporting Information, IE-NiFe/HPLIG has a bigger C\(_{dl}\) value of 9.75 than 3.62 mF cm\(^{-2}\) of NiFe/HPLIG ink-coating electrode, suggesting that IE-NiFe/HPLIG has larger ECSA and exposes more active sites to reactants. In addition, IE-NiFe/HPLIG exhibits a smaller Tafel slope (55.28 mV dec\(^{-1}\)) than that of commercial IrO\(_2\) (62.5 mV dec\(^{-1}\)) and NiFe/HPLIG ink-coating electrode (60.38 mV dec\(^{-1}\)), indicating excellent OER kinetic activity (Figure 4b). These results are in good consistency with EIS, in which IE-NiFe/HPLIG shows the lowest charge transfer resistance, indicating the faster charge transfer kinetics (Figure S23, Supporting Information). In addition, inductively coupled plasma-optical emission spectrometry (ICP-OES) reveals that the mass loadings of Ni and Fe in NiFe/HPLIG are 19.39 and 6.02 wt.% respectively. Therefore, IE-NiFe/HPLIG exhibits a higher mass activity (0.78 A mg\(^{-1}\)) and TOF (0.112 s\(^{-1}\)) at overpotential of 300 mV, compared with CM IrO\(_2\) which has a mass activity of 0.064 A mg\(^{-1}\) and TOF of 0.037 s\(^{-1}\) at the same overpotential, suggesting that IE-NiFe/HPLIG has superior OER performance to CM IrO\(_2\). As can be seen from Figure 4c, the Chronoamperometry testing at 10 mA cm\(^{-2}\) was also conducted to assess the durability of electrodes. The overpotential of IE-NiFe/HPLIG only positively moved 16 mV after 200 h testing, while the electrode with commercial catalysts degraded severely.
in a few hours due to intrinsic instability of precious-metal-based catalysts. In addition, the electrode with NiFe/HPLIG ink coating degraded gradually due to weak attachment to the substrate by polymer binder. As shown in Figure S24, Supporting Information, hierarchically porous structures of IE-NiFe/HPLIG were mostly maintained even after 200 h OER test. Densely tiny nanoparticles were uniformly distributed on the channel surface without peeling off due to the confinement effect of HPLIG caused by laser induction. The overpotential of IE-NiFe/HPLIG at 10 mA cm$^{-2}$ and Tafel slope are outperforming the majority of the literature values (Table S1, Supporting Information). The low overpotential and small Tafel slope along with the good durability of IE-NiFe/HPLIG present its great potential for OER.

For IE-Co/HPLIG, the catalytic performances corresponding to ORR have been measured and compared with a traditional Co/HPLIG ink-coating electrode and commercial Pt/C benchmark electrode. First, the electrodes are directly used as working electrodes for ORR in O$_2$ saturated 0.1 M KOH electrolyte without rotating. As can be seen from Figure 4d, the LSV response of IE-Co/HPLIG has a positive onset potential of 0.92 V versus reversible hydrogen electrode (RHE), which is slightly higher than 0.91 V versus RHE of Co/HPLIG ink-coating electrode and close to 0.96 V versus RHE of benchmark Pt/C electrode. However, the current density of IE-Co/HPLIG is obviously higher than the other two electrodes under high overpotential. This can be ascribed to the enhanced electronic and mass transferring ability of the IE with 3D interconnected porous structures. To further evaluate the reaction kinetics of Co/HPLIG catalysts, rotating disk electrode tests were conducted by dropping the ink of Co/HPLIG catalyst onto glassy carbon electrode. The LSV response of Co/HPLIG as a function of rotation speed in an O$_2$ saturated 0.1 M KOH electrolyte is shown in Figure 4e. The inset Koutechy–Levich relation of LSVs shows a good linearity with an average electron transfer number of 3.87, suggesting a four-electron reduction to OH$^-$ is largely operative (Inset of Figure 4e). As shown in Figure S25a, Supporting Information, Co/HPLIG exhibits a half-wave potential of 0.85 V versus RHE, which is close to that of the CM Pt/C (0.88 V versus RHE), indicating comparable activities. Tafel plots suggest a slightly enhanced Tafel value of 66.7 mV dec$^{-1}$ for Co/HPLIG compared with that of Pt/C (1379 mV dec$^{-1}$) (Figure S25b, Supporting Information). ICP-OES shows that the mass loading of Co in Co/HPLIG is 16.78 wt.%. Hence, Co/HPLIG exhibits a mass activity of 0.024 A mg$^{-1}$ and TOF of 0.0036 s$^{-1}$ at 0.85 V versus RHE. Furthermore, CM Pt/C has a mass activity of 0.028 A mg$^{-1}$ and TOF of 0.014 s$^{-1}$ at the same potential. Therefore, the ORR performance of Co/HPLIG is comparable with CM Pt/C. Such excellent ORR activity should be attributed to the highly dispersed active sites and synergistic effect of nanoparticles and pyridinic N-doped HPLIG substrate. Furthermore, the Chronoamperometric tests of Co/HPLIG and Pt/C catalysts were conducted under 1600 rpm to evaluate the stability. Co/HPLIG shows excellent stability with a current retention of 98% after 10 h, superior to that of Pt/C (84%) (Figure 4f). No obvious decay of $E_{1/2}$ (with only 5 mV negative shift) is observed after stability test (Figure S26, Supporting Information), which further confirms the excellent stability. The halfwave potential and Tafel slope of Co/HPLIG are outperforming the majority of the literature values (Table S2, Supporting Information).

Recently, rechargeable zinc–air batteries (ZABs) have attracted increasing attention due to their high energy density, high safety, low cost, and environmental friendliness. Air cathode with bifunctionality of OER and ORR is the most important component for rechargeable ZABs. Although NiFe alloy and Co metal catalysts exhibited good OER and ORR performances respectively, they suffered from unsatisfactory bifunctionality. Nevertheless, homogeneous ternary NiCoFe alloy has been proven to be efficient bifunctional electrocatalysts recently. To synthesize ternary alloy nanoparticles with uniform elemental distribution, high-temperature and high-pressure conditions are required. Since the laser induction process results in an instantaneous high temperature and high pressure, it is highly possible to prepare ternary NiCoFe nanoparticles based on PSLI. To further expand the application of (PSLI) method, NiCoFe/HPLIG air cathode with bifunctionality of OER and ORR was proposed and developed with the same procedure by using coagulation solution containing NiCl$_2$·6H$_2$O, CoCl$_2$·6H$_2$O and FeCl$_2$·6H$_2$O. Furthermore, triggered by the rapid development of wearable electronics, flexible energy storage system attracts ever-increasing attention. Flexible zinc–air battery has shown great promise. Meanwhile, PSLI method is also versatile for various substrates. In this case, flexible carbon cloth was chosen as substrate to prepare air cathodes.

As can be seen from Figure S27, Supporting Information, HAADF-STEM EDS images exhibit the uniform distribution of Ni, Co, and Fe in the nanoparticles, indicating the successful preparation of ternary IE-NiCoFe/HPLIG by PSLI. XRD results also confirm the successful synthesis of NiCoFe alloy oxide. (Figure S28, Supporting Information). On the other hand, the same IE treated by furnace generates alloy clusters with larger size and uneven elemental distribution, indicating the efficacy of laser induction in multimetallic alloy nanoparticles preparation (Figure S29, Supporting Information). The OER and ORR performance of IE-NiCoFe/HPLIG were evaluated as well. The overpotential of IE-NiCoFe/HPLIG to achieve a current density of 10 mA cm$^{-2}$ for OER is 283 mV and the half-wave potential of OER for NiCoFe/HPLIG is 0.85 V (Figure S30, Supporting Information). The above results indicate IE-NiCoFe/HPLIG has good bifunctionality for oxygen electrocatalysis.

Considering the bifunctionality for OER and ORR, IE-NiCoFe/HPLIG was directly applied as air cathode and assembled into rechargeable aqueous ZABs. As a benchmark, the mixture of commercial Pt/C and IrO$_2$ was used as electrocatalysts for air cathodes of aqueous ZABs as well. It is noted that the battery with IE-NiCoFe/HPLIG displays a higher open circuit voltage (OCV) of 1.568 V than 1.484 V of Pt/C-IrO$_2$ based aqueous ZAB (Figure 5a). As demonstrated, aqueous ZAB with IE-NiCoFe/HPLIG can easily power a light-emitting diode panel (Figure S31, Supporting Information). Figure 5b further compares their charging and discharging polarization curves, ZAB with IE-NiCoFe/HPLIG shows a narrower voltage gap under various current densities than the benchmark-based ZAB, indicating the battery with IE-NiCoFe/HPLIG outputting a higher voltage when discharging or requiring a lower voltage when charging at the same current density. The excellent rechargeable ability can be attributed to the bifunctional activity of IE-NiCoFe/HPLIG. Their discharging polarizations and corresponding power densities are
shown in Figure 5c, the aqueous ZAB with IE-NiCoFe/HPLIG exhibits an obvious hysteresis of voltage decrease, which can be ascribed to unique 3D interconnected porous structure of catalyst layers decreasing the ohmic and diffusion polarization. A maximum power density of 163 mW cm$^{-2}$ was achieved by aqueous ZAB with IE-NiCoFe/HPLIG at 278 mA cm$^{-2}$, which is significantly higher than that of the benchmark-based ZAB (98 mW cm$^{-2}$ at 136 mA cm$^{-2}$), exhibiting superior discharging performance. Figure 5d shows ZAB with IE-NiCoFe/HPLIG has a higher specific capacity of 806 mAh g$_{zn}^{-1}$ at 10 mA cm$^{-2}$ than that of the benchmark-based (750 mAh g$_{zn}^{-1}$). In addition, charging/discharging cycling stability is a crucial evaluation for rechargeable zinc–air batteries. Figure 5e shows the cycling curves recorded at the constant current density of 10 mA cm$^{-2}$. The Voltage gap of aqueous ZAB with IE-NiCoFe/HPLIG changed slightly even after 1800 h charging–discharging cycling stability test and increased from 0.8 to 0.84 V. However, the benchmark-based ZAB shows an increasing voltage gap and degrades significantly after 150 h stability test. The excellent stability of the aqueous ZAB with IE-NiCoFe/HPLIG is comparable or superior to many recently published studies (Table S3, Supporting information). These results suggest better stability and activity of IE-NiCoFe/HPLIG than Pt/C + IrO$_2$ benchmark. Herein, PSLI method further exhibits its versatility for the preparation of high-performance air cathode in ZABs.

Due to the flexibility of IE-NiCoFe/HPLIG, it can also be directly assembled into flexible solid-state ZABs by using Zn plate as anode, IE-NiCoFe/HPLIG as cathode and gel polymer as electrolyte. As can be seen from Figure 6a, flexible ZAB with IE-NiCoFe/HPLIG has a stable OCV of 1.460 V, which is much higher than 1.373 V of Pt/C + IrO$_2$ benchmark flexible ZAB. In addition, flexible ZAB with IE-NiCoFe/HPLIG exhibits superior charging and discharging profiles to those of benchmark-based flexible ZAB (Figure 6b). A higher power density of 88 mW cm$^{-2}$ was achieved by flexible ZAB with IE-NiCoFe/HPLIG at 223 mA cm$^{-2}$ than benchmark-based flexible ZAB (37 mW at 72 mA cm$^{-2}$) (Figure 6c). The voltage platform for flexible ZAB with IE-NiCoFe/HPLIG changes slightly at different current densities (Figure 6d). The excellent rate performance should be attributed to the 3D interconnected structure of IE, which exposes abundant active sites. In addition, flexible ZAB with IE-NiCoFe/HPLIG also shows an excellent cycling stability of 47 h. After replacing the electrolyte layer with a fresh one, the battery can easily recover its performance and run another 37 h (Figure 6e). Hence, the development of highly efficient solid electrolyte is also key for long-lifespan flexible ZAB. However, the benchmark-based flexible ZAB can only operate for 16 h under the same measurement conditions and the battery is difficult to fully recover its performance after changing a new electrolyte layer (Figure S32, Supporting Information). The instability of commercial catalysts is consistent with half-reaction measurements of oxygen electrocatalysis. Furthermore, the assembled flexible ZAB with IE-NiCoFe/HPLIG shows high mechanical flexibility and can be easily charged and discharged at 0°, 90°, and 150° (Figure 6f). As shown in Video S5, Supporting Information, a mini fan was powered by the flexible ZAB with IE-NiCoFe/HPLIG and even ran smoothly under bending conditions, further demonstrating the excellent flexibility. This shows a good promise to be used in wearable electronics. To further demonstrate potentials of the flexible ZABs with IE-NiCoFe/HPLIG for practical application, three batteries were connected in series. The tandem-junction ZABs exhibit an OCV of 4.35 V and can easily light up a LED strip and charge a commercial mobile phone (Figure 6g).

3. Conclusions

In summary, we have developed a versatile strategy based on phase separation and laser induction to prepare IEs including...
IE-NiFe/HPLIG, IE-Co/HPLIG, and IE-NiCoFe/HPLIG, exhibiting superior performance on oxygen electrocatalysis and zinc-air batteries. Three key features have been recognized. The first one is the phase separation. The phase separation was used as a self-templating method offering a unique opportunity to construct catalyst precursor layer with 3D interconnected hierarchical pores, and facilitate the uniform distribution of metal precursors on channel surfaces, thus avoiding the resultant active species being buried by matrix; the second one is the morphological heredity, that is, the structure formed by the phase separation can be preserved after laser treatment using 355 nm ps laser, so that the catalyst layer is highly porous with nanoparticles uniformly anchored on the surface of channels and interfaces, maximizing the exposure of active sites of the alloy nanoparticles; the third one is that the incident laser irradiation enabled a reduction of metal precursors to form tiny alloy nanoparticles and conversion of PBI to graphene at the same time, and the generated graphene layers spontaneously embrace the alloy nanoparticles, preventing nanoparticles from aggregation and enhancing the stability. The present work shows that such structures are unlikely to be generated by furnace treatment, due to the high-pressure and high-temperature conditions created by intensive laser energy input within the short period of laser irradiation of picosecond. This process is rapid and operated in ambient condition without the need of inert gas protection. The obtained IEs exhibited superior electrocatalytic activity and durability. It is worth pointing out that the resultant spatial confinement effects of outer graphene layers for nanoparticles and macro-scale 3D interconnected structures played an important role of enhancing the stability. This would be beneficial for mitigating erosion under harsh electrocatalytic environment. This work demonstrated the versatility of the technique which was used successfully to generate binary (NiFe) and ternary alloy (NiCoFe) nanoparticles by single-step laser induction. This technique offers an economically feasible, and industrially viable solution to the challenge of rapid fabrication of IEs of alloy nanoparticles on graphene-based supporting materials for electrocatalysis. It also opens a new route to manufacture IEs in the future.

Supporting Information
Supporting Information is available from the Wiley Online Library or from the author.

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Conflict of Interest
The authors declare no conflict of interest.

Data Availability Statement
Research data are not shared.

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