Nitrogen and Sulfur Codoped Graphite Foam as a Self-Supported Metal-Free Electrocatalytic Electrode for Water Oxidation

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The oxidation of water to produce oxygen gas is related to a variety of energy storage systems. Thus, the development of efficient, cheap, durable, and scalable electrocatalysts for oxygen evolution reaction (OER) is of great importance. Here, a high-performance OER catalyst, nitrogen and sulfur codoped graphite foam (NSGF) is reported. This NSGF is prepared from commercial graphite foil and directly applied as an electrocatalytic electrode without using a current collector and a polymeric binder. It exhibits an extremely low overpotential of 0.380 V to reach a current density of 10 mA cm⁻² and shows fast kinetics with a small Tafel slope of 96 mV dec⁻¹ in 0.1 M KOH. This electrocatalytic performance is superior or comparable to those of previously reported metal-free OER catalysts.

1. Introduction

Electrochemical splitting of water to generate hydrogen fuel and oxygen gas is an important process for solar energy storage and fuel cells. Oxygen evolution reaction (OER) at anode is the most sluggish step in overall water splitting because of its high overpotential and slow kinetics. Iridium (Ir) and ruthenium (Ru) oxides have been tested as strong catalysts for OER. However, the scarcity, high cost, and poor long-term stability of these noble metal oxides limit their practical applications. Nonprecious first-row transition metals (such as Fe, Co, Ni, Mn) and perovskite-based catalysts have been extensively explored, and their catalytic performances were tested to be comparable to or even surpass those of IrO₂ and RuO₂ catalysts. However, most of these non-noble metal-based catalysts are intrinsically insulating and easy to be chemically corroded. To address these issues, carbon nanotubes (CNTs) and graphene materials have been introduced to these catalysts because of their large specific surface areas and high electrical conductivity. Very recently, nitrogen-doped and oxygen-containing carbon materials have been reported to be metal-free OER catalysts with activities stronger than those of traditional catalysts. In these catalysts, the carbon atoms adjacent to electron-negative nitrogen (C=–N) or oxygen (C=O) atoms are positively charged. They can adsorb OH⁻ ions with charge transfer to decrease the activation energy of OER, and support the recombination of OER intermediates (e.g., O₂⁻ and O₂²⁻) to form oxygen gas during OER process. Furthermore, the nitrogen species (e.g., pyridinic N atoms) can also participate in the electrocatalytic reaction. Consequently, the carbon materials doped with N atoms or containing oxygenated groups can remarkably accelerate OER process, and they are expected to be effective substitutions of metal catalysts.

Conversely, the reported OER electrocatalysts usually were powders; thus they have to be anchored onto glassy carbon electrodes or other conductive planar electrodes (e.g., carbon cloth) with polymeric binders for practical applications. Unfortunately, in these cases, the surfaces of electrocatalysts were partly inaccessible to reactants, and the 2D substrates are not suitable for desorption of O₂ bubbles, weakening the activity and restricting the recovery of active sites of OER catalysts. To overcome these problems, 3D structured electrodes with nickel foams or porous carbon hydrogel films have been developed to immobilize catalysts. The high macroporosity of nickel foam can greatly increase the accessible specific surface areas of loaded catalysts, and facilitate the removal of gases. The intrinsic instability of nickel decreased the long-term durability of these catalysts. Furthermore, the weak contacts between catalysts and nickel substrate frequently led to the releasing of catalysts during oxygen generation reaction. The OER electrocatalysts with carbon hydrogel films were mainly explored by Qiao’s group. These 3D self-supported frameworks avoid using current collectors and polymeric binders (e.g., nafion or polytetrafluoroethylene), and the catalysts exhibited excellent activities. However, the hydrogel films were prepared from chemical converted graphene (CCG) sheets by filtration. The preparation of CCG sheets usually involves a multistep complicated process, and using large amounts of acids, oxidants, and reducing agents. Moreover, the as-obtained CCG films (without adding conductive additives or annealing treatment) have relatively low conductivities and brittle mechanical properties, possibly resulting in high overpotential and poor long-term stability.

Commercial graphite foils (GFLs) are usually made of exfoliated graphite flakes. They are cheap, available in large areas, flexible, highly conductive, and thermally stable. Furthermore, they compose of nearly only carbon atoms without any...
additives, having excellent chemical compatibility and stability in various electrolytes.\textsuperscript{[27,28]} Here, we fabricated a nitrogen and sulfur codoped graphite foam (NSGF) from GFL, and directly used it as an electrocatalytic electrode for OER. This electrode exhibited a low overpotential of 0.380 V at a current density of 10 mA cm\textsuperscript{−2} with a Tafel slope of 96 mV dec\textsuperscript{−1} in 0.1 M KOH, exceeding the performances of most other metal-free OER catalysts.

2. Results and Discussion

2.1. Morphological and Structural Studies

The fabrication of NSGF is schematically illustrated in Scheme 1. A pristine commercial GFL was used as the starting material. It has a smooth surface and a thickness of about 130 µm (Figure 1A), composed of interlaced graphite layers that are parallel to the surface of the foil (Figure S1, Supporting Information). First, a GFL sheet was oxidized using a mixed acid of HNO\textsubscript{3} (65%) and H\textsubscript{2}SO\textsubscript{4} (98%) with a volume ratio of 1:3. The as-prepared oxidized graphite foam (OGF) has a rough surface and its thickness was expanded for 3.2 times to around 550 µm compared with that of original GFL (Figure 1A). The graphite layers in OGF are loosely piled up and they have a wrinkled morphology (Figures S2,S3, Supporting Information).

Successively, the OGF was treated by hydrothermal reaction at 180 °C for 12 h in an aqueous solution of thiourea. During this process, thiourea molecules were decomposed to NO\textsubscript{2}, SO\textsubscript{2}, and H\textsubscript{2}O gases to react with OGF, forming nitrogen and sulfur codoped graphite foam (NSGF). The surface morphology and thickness of NSGF are similar to those of OGF (Figure 1A); the interlaced graphite layers in NSGF are also crumpled and loosely stacked in thickness direction (Figure 1B). There are many microvoids between wrinkled graphite layers, possibly formed by releasing various gases during hydrothermal process (Figure 1B,C; Figure S4, Supporting Information). These voids partly prevented the aggregation of exfoliated graphite sheets, and they will provide effective pathways for releasing O\textsubscript{2} bubbles in OER. The transmission electron micrograph (TEM) of an NSGF sheet has a poor contrast with its substrate (Figure 1D), implying this sheet consists of a few layers of graphene sheets. The sharp diffraction spots in the selected-area electron diffraction (SAED) pattern of an NSGF sheet reflect the perfect crystalline structure of NSGF with few structural defects (inset in Figure 1D).\textsuperscript{[29]} The SAED pattern of an NSGF sheet is nearly identical to those of its GFL and OGF precursors (Figure S5, Supporting Information), implying the graphitic structure of GFL has been inherited to the final NSGF because of the mild preparation process shown in Scheme 1. Energy dispersive spectra (EDS) mappings of NSGF indicate the uniform distributions of C, N, O, and S elements on its surface (Figure 1E–H) and in its internal microstructure (Figure S6, Supporting Information). The EDS line-scan profiles along the cross-section of NSGF further confirmed that N and S elements uniformly doped the inner layers of graphite foam (Figure S7, Supporting Information).

The Raman spectrum of GFL, OGF, or NSGF shows a strong G-band at around 1580 cm\textsuperscript{−1} and a G’-band at around 2700 cm\textsuperscript{−1}; they are typical graphitic characteristics for sp\textsuperscript{2} carbon networks (Figure 2A).\textsuperscript{[30]} The asymmetric shape of G’-bands reveals these carbonaceous materials compose of a few layers of graphene sheets,\textsuperscript{[30]} in agreement with the results of TEM and SAED examinations (Figure 1D; Figure S5, Supporting Information). The D-band located at 1350 cm\textsuperscript{−1} is related to the structural defects or partially disordered graphitic domains.\textsuperscript{[31]} The nearly absence of D-band in GFL indicates its perfect graphitic structure with a high crystallinity. The relatively strong D-band in the spectrum of OGF is related to the oxygen-containing groups in its graphitic domains. The D-band in the Raman spectrum of NSGF is much weaker than that in the spectrum of OGF, suggesting the hydrothermal treatment partly restored the conjugated graphitic structure.

The microstructures of GFL, OGF, and NSGF were characterized by X-ray diffraction (XRD, Figure 2B). The XRD patterns of GFL, OGF, and NSGF exhibit intensive (002) reflection.
peaks around 26° of native graphite with a slight difference in their full widths at half maximum (FWHM). The peak of OGF has the widest FWHM (0.590°), indicating its most disordered microstructure. The FWHM of the peak in the pattern of NSGF (0.496°) is slightly smaller than that of OGF while it is still much larger than that of GFL (0.268°), revealing that the structural integrity of NSGF was partly recovered by hydrothermal treatment.

Thermogravimetric analysis (TGA) indicates that GFL is thermally stable even at a high temperature of 800 °C because of its nearly pure graphite composition (Figure 2C). The small weight loss of 0.5% before 150 °C in the TGA curve of NSGF is...
attributed to the evaporation of the physically adsorbed water.\cite{31} This value is much smaller than that of OGF (2.5%), because the former has relatively higher hydrophobicity (Figure S8, Supporting Information). The sharp weight loss of NSGF (about 30%) in the temperature range of 150 to 500 °C is resulted from the decomposition of its nitrogen and sulfur containing groups, and followed by decarboxylation and elimination of hydroxyl functionalities.\cite{34} In comparison, in the same temperature range, the oxygen-containing groups in OGF are slowly decomposed to give a mass loss of 11.5%. Thermal degradation at temperature higher than 500 °C is related to the thermal oxidation of the residual disordered carbon.\cite{35} This phenomenon can be observed only from the TGA curve of OGF, which is originated from its oxygenated defects formed by the oxidation with mixed acid. In contrast, the TGA curve of NSGF has a plateau between 500 to 800 °C, reflecting the absence of disordered carbon in its graphitic matrix.

X-ray photoelectron spectral (XPS) examinations indicated that the C/O ratio of GFL was as high as 46.48, and those of OGF and NSGF were decreased to 14.34 and 19.40, respectively (Figure S9 and Table S1, Supporting Information). The C 1s XPS spectrum of NSGF has a strong band of C−C/C−C species (284.6 eV) with a weak shoulder of C−SO$_2$SO$_3$S (164.9 eV), C−SO$_3$O groups (163.8 eV), C−O species (168.6 eV), and C−S species (164.9 eV).\cite{37,39} In contrast, the S 2p spectra of GFL and OGF only show the bands related to C−SO$_2$−C and C−SO$_3$−C species (Figure S14, Supporting Information). These results confirm that N and S atoms in GFL and OGF were decreased to 14.34 and 19.40, respectively (Figure S9 and Table S1, Supporting Information). The C 1s XPS spectrum of NSGF reveals the existence of four types of C species (Figure S14, Supporting Information). These observations revealed that N and S elements were uniformly doped throughout NSGF, and this conclusion has also been strongly supported by the EDS mapping and line-scanning results described above (Figure 1E–H; Figure S6 and S7, Supporting Information).

NSGF is a pure carbonaceous material without any metal residuals. The high-resolution Ni 2p and Fe 2p XPS spectra do not show any signals in the corresponding regions of binding energy (Figure S16, Supporting Information). Inductively coupled plasma mass spectrometry (ICP-MS) showed the Fe content of NSGF was only 46 ppb (Table S2, Supporting Information) and the contents of other metals reported to be active for OER (e.g., Co, Ni, Mn) were below the detection limits of ICP-MS.

2.2. Electrochemical Studies

2.2.1. Electrochemical Activities of the Electrodes

Potassium ferricyanide has frequently been used as a molecular probe to evaluate the electrochemical behavior of carbon based electrodes.\cite{40} Chronocoulometric curves of GFL, OGF, and NSGF electrodes were recorded in an aqueous solution containing 1 M K$_3$Fe(CN)$_6$ and 2 M KCl (Figure S17, Supporting Information). According to the slope of the plot of Q versus t$^{1/2}$ (Q is the integrated charge and t is time, Figure 3A),\cite{41,42} the electrochemical active surface area (EASA) of a GFL electrode was calculated to be 8.4 cm$^2$, much larger than its geometric surface area (0.25 cm$^2$), reflecting that it has abundant active edging sites in exfoliated graphite sheets. The EASA of OGF was measured to be 75.7 cm$^2$, about nine times that of GFL. This is mainly attributed to its expanded foam-like microstructure and the hydrophilic oxygen-containing groups intercalated into the graphite layers. In comparison, the EASA of NSGF was reduced to 23.1 cm$^2$, mainly due to the partial removal of oxygenated functional groups and its relatively hydrophobic property (Figure S8, Supporting Information).

The electrochemical properties of these three electrodes were also compared in an aqueous solution containing 5 × 10$^{-3}$ M K$_3$Fe(CN)$_6$ and 1 M KCl by cyclic voltammetry (CV) (Figure 3B). The CV of GFL electrode shows the largest capacitance and the widest peak-to-peak potential separation (ΔE$_p$) of 118 mV, reflecting the charge transfer kinetics of the redox reaction of K$_3$Fe(CN)$_6$, at OGF is worse than those at GFL and NSGF electrodes. In contrast, the CV of NSGF electrode exhibits a pair of well-defined redox waves with the smallest ΔE$_p$ of 68 mV, lower than that of GFL (78 mV). Differential pulse voltammetry (DPV) technique can exhibit electrochemical current densities excluding capacitive effects. The DPV of an NSGF electrode demonstrates a current density of 7.3 mA cm$^{-2}$, much higher than that of OGF (5.8 mA cm$^{-2}$) and GFL (1.2 mA cm$^{-2}$) (Figure 3C). The electrochemical comparisons described above reflect that the NSGF electrode has the fastest charge transfer kinetics, and the highest density of active sites among these three electrodes, while its EASA is medium.
2.2.2. The Electrocatalytic Performances for OER

The transverse electrical conductivity of NSGF was measured to be $562 \text{ S cm}^{-1}$ by using a conventional four-probe technique. This value is much higher than those of CCG papers [43–45] and exfoliated graphite papers [46,47], mainly due to the perfect crystalline graphitic structure of NSGF. The electrical conductivity of NSGF is a little lower than that of the reported annealed graphene paper [48], CVD graphene [49] and the GFL precursor (1065 S cm$^{-1}$) (Table S3, Supporting Information). In addition, the NSGF is flexible; it can be bent to a large angle (Figure S18A, Supporting Information). Its tensile strength and Young's modulus were tested to be 2.3 and 102 MPa (Figure S18B, Supporting Information). Thus, the unique 3D architecture, high electrical conductivity, and strength of NSGF allow it to be directly applied as a working electrode for OER without using a current collector and a polymeric binder.

The OER performances of different electrodes were studied in a standard three-electrode electrochemical cell containing an electrolyte of 0.1 M KOH aqueous solution (Figure S19, Supporting Information). The linear sweep voltammetry (LSV) curve of GFL electrode exhibits a large overpotential of 0.820 V at a current density of 10 mA cm$^{-2}$, reflecting its weak electrocatalytic activity. The OGF electrode showed remarkably enhanced OER activity and faster reaction kinetics comparing with those of GFL electrode; it needs only an overpotential of 0.410 V to reach a current density of 10 mA cm$^{-2}$ (Figure 3D), and has a lower Tafel slope of 137 mV dec$^{-1}$ than that of GFL electrode (195 mV dec$^{-1}$) (Figure 3E). The improved OER performance of OGF electrode is mainly attributed to its higher content of C=O groups (Figure S11C, Supporting Information). The C atoms of C=O groups in carbon materials bring more positive charges than those of the C atoms in other oxygen-containing groups (e.g., C=O and O=C=O groups), thus they can adsorb OH$^-$ ions more strongly via electrostatic interaction to accelerate the OER [17,22]. The charge transfer resistance of OGF electrode (7.1 $\Omega$) was measured to be much smaller than that of GFL electrode (87 $\Omega$, Figure S20, Supporting Information), thus the OER kinetics was distinctly increased at the former electrode. The OER performance of OGF electrode can be further improved by N and S doping. The overpotential of NSGF electrode for OER was measured to be 0.380 V at the current density of 10 mA cm$^{-2}$. This value is lower than that of OGF electrode (0.410 V), and also much lower than those of carbon films reported previously, such as N, O-dual doped graphene–CNT hydrogel film (NG/CNT, $\approx 0.484$ V) [21], oxidized carbon cloth (OCC-8, 0.477 V) [22], 3D hybrid film of porous N-doped graphene–NiCo$_2$O$_4$ (PNG-NiCo,0.432 V) [24] and 3D N-doped carbon film assembled by graphene and graphitic carbon nitride (G-C$_3$N$_4$, 0.415 V) [25] (Figure 3F and Table S4, Supporting Information). The electrocatalytic activity of NSGF electrode is also superior to those of previously reported metal-free catalysts, including mildly oxidized multiwalled CNTs that activated by hydrothermal and electrochemical treatments (e.g., MWCNTs, 0.450 V) [23], N-doped graphene/single-walled CNT hybrid (NGSH, 0.400 V) [50], graphitic carbon nitride/graphene composites (g-C$_3$N$_4$/graphene, 0.539 V) [31], thermally reduced graphene oxide/N-doped CNTs (TRGO/NCNT, 0.505 V) [32], 3D Ni foam/porous carbon/anodized Ni electrode (3D-NF/PC/AN, 0.520 V) [23], N-doped coaxial carbon nanocables (CNT@NCNT, 0.527 V) [33], and even comparable to those of N-doped carbon material (N/C, 0.380 V) [20] and g-C$_3$N$_4$ nanosheets-CNTs composite (g-C$_3$N$_4$ NS-CNT, 0.370 V) [54] (Table S4, Supporting Information). It is worth mentioning that our NSGF electrode...
is a pure carbonaceous catalyst containing only C, N, O, and S nonmetallic elements, without blending other catalysts such as widely used g-C$_3$N$_4$, or metal species.

N and S codoped carbon materials have been explored as the electrocatalysts for oxygen reduction reaction (ORR) and hydrogen evolution reaction (HER). However, they have rarely been used for catalyzing OER. We found that the N and S codoped NSGF electrode had much higher activity than that of N-doped graphite foam (NGF, Figure S21, Supporting Information) for OER. Previous theoretical and experimental studies revealed that the N, S codoping of carbon materials including graphene caused the redistribution of spin and charge densities to create more active carbon atoms for catalysis. The electronegativity of N (3.04) is higher than that of C (2.55). Therefore, a doping N atom increased the densities of positive charges on its adjacent C atoms, thus remarkably increasing their catalytic activity. The electronegativity of S (2.58) is close to that of C, making the charge distribution around a S atom to be slightly changed. On the other hand, in our NSGF electrode, the S species are mainly doped at edges or defective sites of graphite foam in the forms of C=S=C and C=S, or on the surface of graphite foam in the form of C=SO$_x$=C. These S containing species contributed a large spin density for enhancing the catalytic activity of NSGF. Moreover, the combination of N and S dopants at the defects of carbon materials created more active C atoms as the electrocatalytic sites, and provided fast charge transfer paths for OER. Actually, the electrode prepared by hydrothermal treatment of OGF without using thiourea molecules (nominated as RGF electrode) showed much worse OER performance than those of NGF and NSGF electrodes (Figure S21, Supporting Information), indicating that the N and S atoms doped in graphitic frameworks play an important role in OER catalysis. Thiourea molecule is a good choice as the sources of N and S elements in hydrothermal reaction because it can decompose to N and S oxides at high temperature. GFL is chemically stable and lacks of oxygen-containing groups; thus it is nearly inert to thiourea under hydrothermal reaction. As expected, the thiourea treated GFL (nominated as GFL-TU) shows a poor OER performance, comparable to that of GFL precursor (Figure S22, Supporting Information). This fact revealed that the oxygen functional groups in OGF provided reactive sites for thiourea. On the other hand, the Tafel slope of NSGF electrode (96 mV dec$^{-1}$) was measured to be much lower than those of OGF (137 mV dec$^{-1}$) and GFL (195 mV dec$^{-1}$) electrodes (Figure 3E). This phenomenon is mainly due to that the proper hydrophilicity of NSGF electrode facilitated the desorption of the generated O$_2$ bubbles. Furthermore, the reduced charge transfer resistance of NSGF electrode (5.4 vs 7.1 $\Omega$ for OGF) further accelerated the kinetics of OER (Figure S20, Supporting Information). The OER kinetics at NSGF electrode is also superior to those reported NG-CNT (141 mV dec$^{-1}$), PNG-NiCo (156 mV dec$^{-1}$), and G-C$_x$N$_y$ (128 mV dec$^{-1}$) based carbon films (Figure 3F; Table S4, Supporting Information).

We also tested the OER performance of NSGF electrode in the electrolyte with a higher KOH concentration (1.0 M). In this media, the overpotential of NSGF electrode was measured to be only 0.346 V at 10 mA cm$^{-2}$ and the Tafel slope was calculated to be 78 mV dec$^{-1}$ (Figure 4A,B). The remarkable activity...
of NSGF electrode is even superior to that of surface-oxidized multiwalled CNTs (overpotential = 0.360 V at 10 mA cm$^{-2}$) tested under the same condition.\cite{17} As expected, the electrocatalytic performance of NSGF electrode in 1.0 m KOH is much better than that tested in 0.1 m KOH, because the high OH$^-$ concentration (in 1.0 m KOH) significantly reduced the resistance of electrolyte, and the interfacial resistance between NSGF electrode and electrolyte (0.7 $\Omega$, Figure 4C).

The stability of NSGF electrode for OER was tested in 0.1 m KOH by operating at a constant potential of 1.640 V (vs. RHE) for a long time of 60 h (Figure 4D). The current density of NSGF electrode retained about 77% of its initial value after the long-term test. In addition, this NSGF electrode can be reused, and the current density in LSV curve at 1.670 V (vs. RHE) decreased by only 16% (inset in Figure 4D). Meanwhile, the morphology of NSGF electrode did not show any observable changes (Figure 1B–D; Figure S23, Supporting Information). These results reflect the excellent stability and durability of NSGF electrode in alkaline media because of its stable 3D graphitic structure and easy desorption of generated bubbles. The slight decrease in the performance of NSGF electrode after long-term test is mainly due to that part of its C–O and C=S–C=S groups were oxidized at high operating potentials (Figure S24, Supporting Information). In order to further confirm the generated bubbles are O$_2$ gases rather than the gases released through the corrosion of carbon materials, we measured the Faradaic efficiency (FE) of OER by gas chromatography (Figure S25, Supporting Information). The FE was tested to be about 98%, implying that the huge current increment in LSV curve and the generated bubbles on the surface of NSGF electrode are directly related to O$_2$ evolution.

3. Conclusions

We developed a facile two-step method to fabricate NSGF from commercial GFL. NSGF has a high electrical conductivity, good flexibility, and mechanical strength. It can be directly used as an electrocatalytic electrode for OER, exhibiting a low overpotential of 0.380 V at 10 mA cm$^{-2}$ and a small Tafel slope of 96 mV dec$^{-1}$ in 0.1 m KOH. Its electrocatalytic performance for OER is superior to those of reported nonmetal catalysts including carbonaceous films. To the best of our knowledge, this work is the first example of using N and S codoped carbon materials as the electrocatalytic electrode for OER.

4. Experimental Section

**Preparation of OGF:** First, a commercial GFL (Alfa Aesar, thickness of 0.13 mm) was cut into small pieces with a size of 0.5 cm $\times$ 1.5 cm. Then, these sheets were immersed in an mixed acid solution (3 mL 65% HNO$_3$ + 9 mL 98% H$_2$SO$_4$) and kept at 30 °C for 12 h (the oxidation condition has been optimized by changing the temperature from 25 to 35 °C and oxidation time from 6 to 24 h). The resulting OGF sheets were purified by dialysis with copious of water till the solution is neutral.

**Preparation of NSGF:** OGF sheets were put into a 50 mL Teflon-lined autoclave containing 30 mL de-ionized water (18 M2 cm$^{-2}$) and 0.05 mol thiourea (Sinopharm Chemical Reagents Co. Ltd., Analytical grade, 99%); the amount of thiourea in the reaction system was optimized by varying from 0.025 to 0.200 mol), then the system was sealed and maintained at 180 °C for 12 h. Finally, the prepared NSGF sheets were dialyzed with a large amount of water and they were kept in water before use.

**Preparation of NGF:** OGF sheets were put into a 50 mL Teflon-lined autoclave containing 30 mL de-ionized water and 0.05 mol urea (Analytical grade, 99%), then the system was sealed and maintained at 180 °C for 12 h. The as-prepared NGF sheets were finally dialyzed by copious of water.

**Preparation of RGF:** OGF sheets were put into a 50 mL Teflon-lined autoclave only containing 30 mL deionized water, then the system was sealed and maintained at 180 °C for 12 h. Finally, the as-obtained RGF sheets were dialyzed with a large amount of water.

**Preparation of GFL-TU:** Pristine GFL sheets were directly put into a 50 mL Teflon-lined autoclave containing 30 mL deionized water and 0.05 mol thiourea, then the system was sealed and maintained at 180 °C for 12 h. Finally, the prepared GFL-TU sheets were washed with copious of water.

**Materials Characterization:** SEM images were obtained from a field-emission Sirion-200 SEM (JEOL, Japan) at 10 kV. TEM, STEM, SAED, and EDS were recorded on a Tecnai F20 TEM. The contact angle images were taken on an OCA20 machine (Data-Physics, Germany) at room temperature. Raman spectra were recorded on a LabRAM HR instrument (Horiba Jobin Yvon) with a 514-nm wavelength laser. XRD patterns were carried out on a D8 Advanced X-ray diffractometer with Cu $K\alpha$ radiation ($\lambda = 0.15418$ nm, Bruker, Germany). TGA was conducted on a PerkinElmer TGA Q50 thermal degradation analyzer ($N_2$, flow 60 mL min$^{-1}$, heating rate 10°C min$^{-1}$). XPS analyzes were performed on an ESCALAB 250 photoelectron spectrometer (Thermo Fisher) with Al $K\alpha$ as the X-ray source and the pass energy of 30 eV for a high resolution scan, and the XPS peaks were divided using by a XPS-PEAK software. The transverse electrical conductivity ($\sigma = I/l$) of GFL or NSGF was measured by using a four-probe conductivity test meter (KDY-1) at room temperature, and calculated by the equation of $\rho = 4.3 W I l/W I$ where $W$, $l$ and $I$ are the voltage and current directly read from the conductivity test meter, $W$ is the thickness of the film, and 4.3 is a correction factor. This equation is limited to study the conductivity of the films thinner than 4 mm. The electrical conductivity for each sample is an average value of five measurements.

Samples for SEM measurements were prepared by freeze drying the GFL and NSGF overnight using a lyophilizer. Samples for TEM studies were prepared by dispersing the GFL, OGF, and NSGF samples in ethanol and finally drop drying the diluted solution on copper grids. Samples for contact angle, Raman, XRD, XPS, and TGA tests were all prepared for drying the resulting OGF and NSGF at room temperature.

**Electrochemical Measurements:** Electrochemical tests were all performed in a standard three-electrode system by using a CHI 760 D Electrochemical workstation (CH Instrument Inc.) at room temperature. The obtained GFL, OGF, or NSGF was directly used as the working electrode, and a platinum (Pt) mesh and a saturated calomel electrode (SCE) were used as the counter and reference electrodes, respectively. The EASAs of electrodes were measured by chronocoulometry in the potential range of 0.65 to –0.05 V (vs SCE) with a pulse with of 0.25 s, using an aqueous solution of $1 \times 10^{-2} M$ K$_2$Fe(CN)$_6$ and 2 m KCl as the electrolyte. CVs and DPPs were all performed in a solution of $5 \times 10^{-3} M$ K$_2$Fe(CN)$_6$ and 1 m KCl in the potential range of 0–0.5 V (vs SCE) and the recorded curves were not subject to IR-drop compensation. CV studies were carried out at a scan rate of 50 mV s$^{-1}$. DPV studies were conducted at a pulse width of 0.2 s and pulse period of 0.5 s. The above mentioned electrolytes were all purged with $N_2$ for at least 15 min before tests.

OER studies were performed in an O$_2$-saturated solution of 0.1 m KOH (pH = 13) or 1.0 m KOH (pH = 14). A Luggin capillary was used in this system to reduce the solution resistance, and the IR-drop for each curve was directly compensated by electrochemical workstation. The compensation level in test was 100% and the compensated resistance was about 2.0 $\Omega$. LSVs and Tafel plots were recorded at a scan rate of 10 and 1 mV s$^{-1}$, respectively. EIS tests were conducted in the frequency range of 1.0 to 100 kHz with a 5 mV ac amplitude; and the initial potential was open circuit potential. The EIS spectra were fitting by the Zsimpwin software, and the results reported were all the...
fitted parameters. The stability tests of NSGF electrodes were recorded by time dependent-current density curves in a certain potential. The Faradaic efficiency was measured by Gas chromatography (GC-2014C) in a sealed electrochemical cell. The potentials related to the OER tests were all calibrated to the reversible hydrogen electrode potential ($E_{\text{RHE}}$) using equation: $E_{\text{RHE}} = E_{\text{SCE}} + 0.24 + 0.059 \times \text{pH}$, where $E_{\text{VS SCE}}$ is the potential measured against the SCE reference electrode. The current densities for OER were normalized by the geometric surface area of 0.25 cm$^2$ and the overpotential ($\eta$) was calculated by using the equation of $\eta = E_{\text{VS RHE}} - 1.23$.

Supporting Information

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

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