

# Facile in Situ Preparation of Graphitic-C<sub>3</sub>N<sub>4</sub>@carbon Paper As an Efficient Metal-Free Cathode for Nonaqueous Li–O<sub>2</sub> Battery

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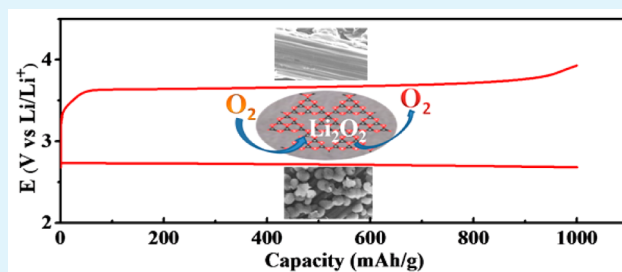
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## S Supporting Information

**ABSTRACT:** The rechargeable Li–O<sub>2</sub> batteries with high theoretical specific energy are considered to be a promising energy storage system for electric vehicle application. Because of the prohibitive cost, limited supply, and weak durability of precious metals, the developments of novel metal-free catalysts become significant. Herein, the graphitic-carbon nitride@carbon papers have been produced by a facile in situ method and explored as cathodes for Li–O<sub>2</sub> batteries, which manifest considerable electrocatalytic activity toward oxygen reduction reaction and oxygen evolution reaction in nonaqueous electrolytes because of their improved electronic conductivity and high nitrogen content. The assembled Li–O<sub>2</sub> batteries using graphitic-carbon nitride@carbon papers as cathodes deliver good rate capability and cycling stability with a capacity retention of more than 100 cycles.

**KEYWORDS:** graphitic-carbon nitride, metal-free, oxygen reduction/evolution reaction, cathode, lithium oxygen battery



## 1. INTRODUCTION

Because of the high theoretical specific energy, the Li–O<sub>2</sub> battery has attracted tremendous attention as a promising energy storage system for electric vehicle application. However, because of the sluggish kinetics of the cathodic oxygen reduction reaction (ORR) and oxygen evolution reaction (OER), its attractive implementation is overshadowed by unsatisfactory electrochemical characteristics of poor rate capability and short span life, which are mainly derived from the large overpotential between discharge and charge.<sup>1,2</sup> Many efforts have been made to develop efficient catalysts for Li–O<sub>2</sub> batteries.<sup>3,4</sup> Until now, numerous catalysts, including metal oxides, nonprecious and precious metals, etc., have been examined as the cathodic catalysts for ORR and OER.<sup>5,6</sup> Although precious metals have been adopted as an effective ORR electrocatalysts, large-scale commercial application has been restricted by their prohibitive cost, limited supply and weak durability. Hence, the development of novel metal-free catalysts with comparable performance become significant.<sup>7</sup> Because of their facilitation on the formation of a localized electron-donor state near the Fermi level and enhancement of the electron-donor property for carbon matrixes, recently, the state-of-the-art, metal-free, nitrogen-doped carbon (N-carbon) materials have been generally accepted as a potential substitute for precious metals to reduce the cost and enhance the stability of ORR electrocatalysts.<sup>8,9</sup> However, the relatively low nitrogen content (2–5%) and a leaching of nitrogen active sites lead to low and unstable catalytic activity of N-carbon materials. To

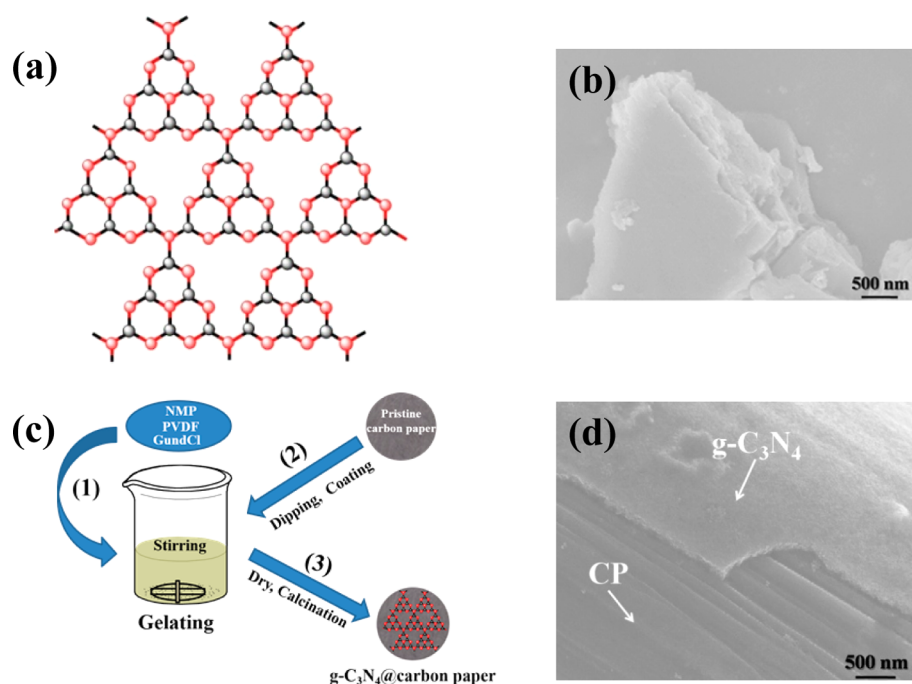
this end, the development of a completely metal-free electrocatalyst with high nitrogen content and stable structure is highly desirable.<sup>10</sup>

Graphitic-carbon nitride, hereafter referred to as g-C<sub>3</sub>N<sub>4</sub>, can be prepared from a simple precursor via a series of polycondensation reactions without any metal involvement.<sup>11,12</sup> Recently, g-C<sub>3</sub>N<sub>4</sub> has become increasingly significant because of the theoretical prediction of their unusual properties and promising applications ranging from photocatalysis and heterogeneous catalysis, to fuel cells.<sup>13–15</sup> Unfortunately, few investigations have been carried out on the application of g-C<sub>3</sub>N<sub>4</sub> as cathodic catalyst for nonaqueous Li–O<sub>2</sub> battery.<sup>16</sup> Moreover, as semiconductor with limited electronic conductivity, the active sites facilitating catalytic activity on g-C<sub>3</sub>N<sub>4</sub> are restricted. To overcome this problem, one effective way to increase the number of electrons accumulated on the g-C<sub>3</sub>N<sub>4</sub> surface, and then to extend the concentration of active sites, is to add an electron-conductive material as a support for the g-C<sub>3</sub>N<sub>4</sub> catalyst.<sup>17</sup> Because of its excellent electronic conductivity, carbon paper (CP) has been widely used as the current collector for nonaqueous Li–O<sub>2</sub> battery.<sup>18</sup> Therefore, the combination of carbon paper and g-C<sub>3</sub>N<sub>4</sub> can develop an efficient cathode for nonaqueous Li–O<sub>2</sub> battery. In this study, we explored graphitic-carbon nitride@carbon paper (GCN@

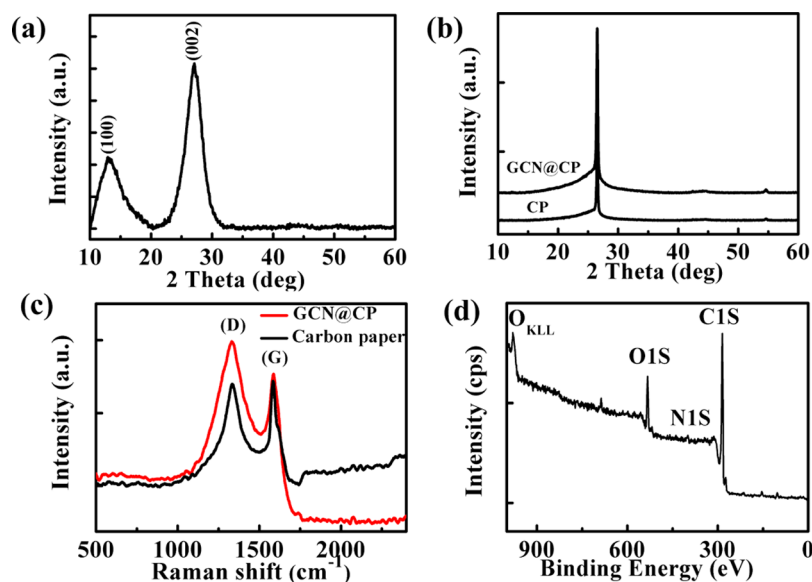
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**Figure 1.** (a) Scheme of tri-s-triazine-based connection in g-C<sub>3</sub>N<sub>4</sub>. Red and gray spheres represent nitrogen and carbon atoms, respectively. (b) SEM image of bulk g-C<sub>3</sub>N<sub>4</sub>. (c) Schematic illustration of the routes for the facile in situ preparation of GCN@CP. (d) SEM image of GCN@CP.



**Figure 2.** (a) XRD patterns of bulk g-C<sub>3</sub>N<sub>4</sub> and (b) GCN@CP and CP. (c) Raman spectra of GCN@CP and carbon paper. (d) XPS spectra of GCN@CP.

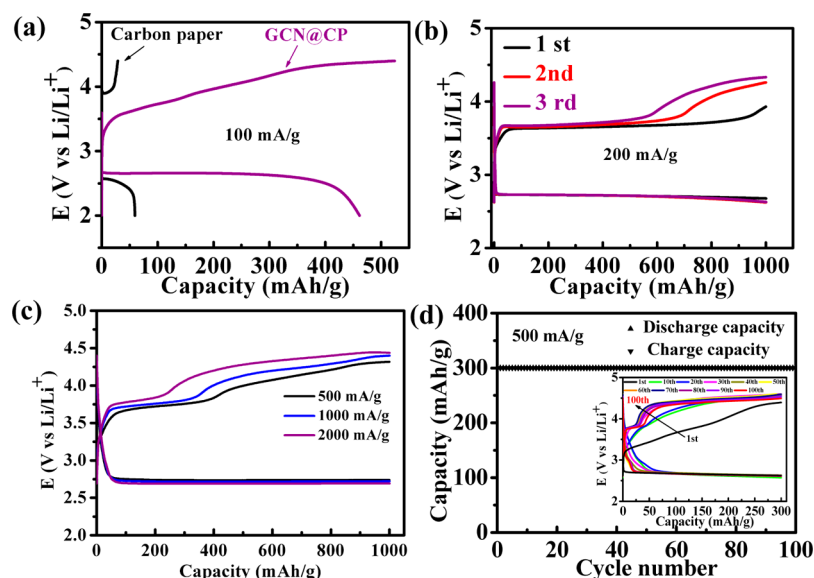
CP) as a new efficient bifunctional cathode for nonaqueous Li–O<sub>2</sub> battery. Through elaborate design, as expected, GCN@CP has been prepared through a facile in situ method and shows efficient catalytic reactivity for nonaqueous Li–O<sub>2</sub> battery.

## 2. EXPERIMENTAL SECTION

**2.1. Preparation of Cathode.** The graphitic-C<sub>3</sub>N<sub>4</sub>@carbon paper (GCN@CP) was prepared as follows: a gelating solution was prepared by mixing 2.85 g of *N*-methylpyrrolidone (NMP) with 0.15 g of polyvinylidene fluoride (PVDF) and 0.2 g of guanidine hydrochloride (GundCl) followed with stirring until the formation of transparent gelating solution. Carbon papers were dipped in the above solution and dried at 100 °C for 2 h to remove the solvent. Finally, the GCN@CPs were obtained after calcination at 550 °C for 3 h under Ar flow.

For comparison, the bulk graphitic-C<sub>3</sub>N<sub>4</sub> was obtained through the solid-state method under the same calcination conditions only using GundCl as precursor.

**2.2. Structural Characterization.** X-ray powder diffraction (XRD) patterns were recorded on a Bruker D8 X-ray diffractometer using Cu K $\alpha$  ( $\lambda = 1.54$  Å) radiation. The images of all the samples and electrodes were examined using scanning electronic microscope (SEM) on a JSM-6700F instrument. The discharged and charged SEM cathodes were both washed with dimethoxyethane and followed by removing the dimethoxyethane in vacuum. Galvanostatic discharge/charge was conducted on the Hokuto discharge/charge system at 25 °C. Raman spectrum was conducted on a Micro Raman spectrophotometer (Ventuno21, JASCO). X-ray photoelectron spectroscopy (XPS) was carried out on a PerkinElmer PHI 5300



**Figure 3.** (a) Discharge/charge curves at the current density of 100 mA/g for carbon paper and GCN@CP based on the mass of the whole electrode within a voltage window from 2.0 to 4.4 V. The electrochemical performance of GCN@CP based on the mass of  $g\text{-C}_3\text{N}_4$  on the cathodes: (b) the initial discharge/charge curves of GCN@CP at a current density of 200 mA/g and fixed capacity of 1000 mAh/g, (c) rate capability at different current densities when discharged to 1000 mAh/g, and (d) cycling performance and the corresponding discharge/charge profiles (inset) at a current density of 500 mA/g with a capacity limit of 300 mAh/g.

spectrometer with a monochromatized Al K $\alpha$  X-ray source (14 kV, 250 W).

**2.3. Electrochemical Investigation.** After calcination, the GCN@CPs were directly used as cathodes. While, the bulk  $g\text{-C}_3\text{N}_4$  was mixed with 10 wt % PVDF in a NMP solution, and the resulting slurry was coated on a carbon paper (GDL 35BA, SIGRACET Gas Diddusion Media). The total mass loading of  $g\text{-C}_3\text{N}_4$  is about 0.5 mg/cm<sup>2</sup>. Li–O<sub>2</sub> batteries were assembled in coin cells with 7 holes exposed to O<sub>2</sub> (purity, 99.9%) and comprising a Li metal anode ( $\Phi$  10 mm), an electrolyte (DMSO-0.5 M LiClO<sub>4</sub>, stored in the presence of a shining Li foil) impregnated into a glass fiber filter separator (Whatman), and a cathode. The Li–O<sub>2</sub> batteries were held in a glass chamber with a capacity of 650 mL.

### 3. RESULTS AND DISCUSSION

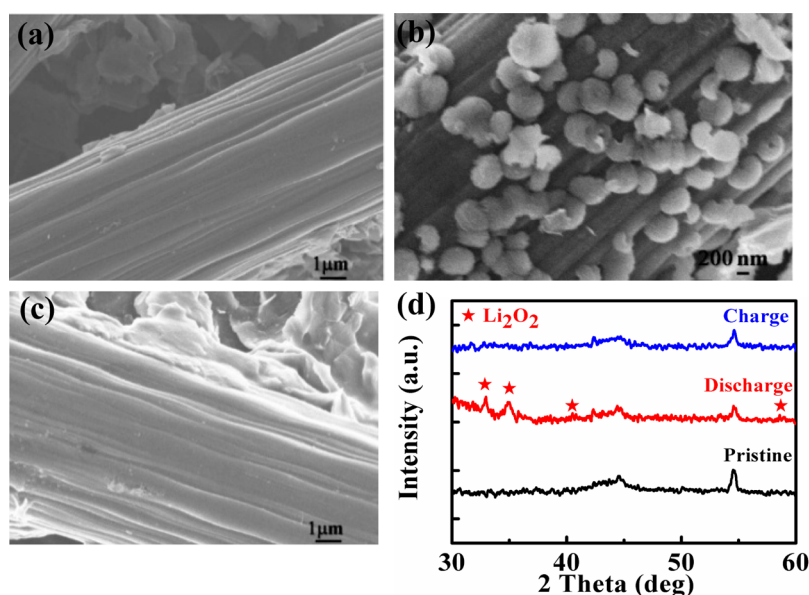
As the most stable allotrope of N-carbon structures under ambient conditions, the  $g\text{-C}_3\text{N}_4$  has a stricter structure of 2D sheets of tri-s-triazine connected via tertiary amines, as presented in Figure 1a, and confirmed from the SEM image shown in Figure 1b. Nevertheless, the limited electron transfer ability of  $g\text{-C}_3\text{N}_4$  is one of the main obstacles for its application in catalytic reactions.<sup>19</sup> To solve the above problem, we have prepared the GCN@CP through a facile in situ preparation method, as displayed in Figure 1c. From the SEM image shown in Figure 1d, it can be clearly seen that the  $g\text{-C}_3\text{N}_4$  film has been successfully coated on the carbon paper. Therefore, the in situ supported  $g\text{-C}_3\text{N}_4$  structure allows for improved electrochemical performance due to the obviously enhanced electronic conductivity. For comparison, the bulk  $g\text{-C}_3\text{N}_4$  was prepared by a solid-state method only using guanidine hydrochloride as precursor.

The two peaks at around 13 and 27.4° shown in Figure 2a, indexed as (100) and (002) peaks, respectively, correspond to in-plane structural packing motif of tris-triazine and interlayer graphitic packing motif of aromatic segments for bulk  $g\text{-C}_3\text{N}_4$  and consistent with the reported results.<sup>20</sup> Meanwhile, because of the overlap of diffraction peaks of  $g\text{-C}_3\text{N}_4$  and carbon paper, it is difficult to detect the existence of  $g\text{-C}_3\text{N}_4$  on the GCN@

CP, as demonstrated in Figure 2b. To obtain further insight concerning the structure of  $g\text{-C}_3\text{N}_4$  supported on carbon paper, we adapted the Raman spectra to analyze the influence of  $g\text{-C}_3\text{N}_4$  on the structure of electrode after coating. The bands at 1348 and 1554 cm<sup>-1</sup> are indexed as disordered (D) and graphitic (G) modes of carbon, respectively, as exhibited in Figure 2c. The relative  $I_D/I_G$  values for carbon paper and GCN@CP are 0.99 and 1.02, respectively, which is evidence that the high C (sp<sup>2</sup>)-hybridized  $g\text{-C}_3\text{N}_4$  has been successfully coated on carbon paper.<sup>21</sup> Moreover, C, N, and a small amount of O derived from adsorbed water are detected in the XPS survey spectrum of GCN@CP, as given in Figure 2d.

As previously reported, the carbon paper has some catalytic activity for O<sub>2</sub> reduction, and thus contributes some capacity on discharge.<sup>17</sup> To investigate the contribution of carbon paper, we conducted a comparison between the carbon paper and GCN@CP under the same current density based on the mass of the whole electrodes. It can be found that a discharge capacity of about 60 and 460 mAh/g is achieved for CP and GCN@CP, which means that about 13% discharge capacity of GCN@CP is derived from the CP and consistent with the recent reports.<sup>22</sup> Figure S1a in the Supporting Information gives the discharge/charge voltage profile of the Li–O<sub>2</sub> battery using bulk  $g\text{-C}_3\text{N}_4$  as the catalyst material at a current density from 100 to 1000 mA/g based on the mass of  $g\text{-C}_3\text{N}_4$  in the cathodes. It can be detected that the battery displays a discharge capacity of 500 mAh/g with an average voltage of 2.7 V at the current density of 100 mA/g. Unfortunately, a large voltage gap, poor rate capability, and cyclic stability are observed (Figure S1a, b in the Supporting Information), which are arised predominantly from the undesirable electronic conductivity.

After being in situ prepared on carbon paper, the electrochemical performance of GCN@CP has been obviously improved, as shown in Figure 3b. When discharged to 1000 mAh/g at the current density of 200 mA/g, a decreased voltage gap of 0.95 V is obtained (compared with 1.68 V for bulk  $g\text{-C}_3\text{N}_4$  at 200 mA/g, displayed in Figure S1a in the Supporting



**Figure 4.** Morphologies of GCN@CP at various states: (a) pristine state, (b) after discharge, (c) after recharge, and (d) the corresponding XRD patterns.

Information). What is more, even at the high current density of 2000 mA/g, the voltage gap of 1.58 V (shown in Figure S2 in the Supporting Information) is achieved as presented in Figure 3c. Furthermore, the GCN@CP also shows good cyclic performance with negligible decay during 100 cycles, as illustrated in Figure 3d. We found, however, that the side reactions between the discharge product  $\text{Li}_2\text{O}_2$  and carbon may occur and form the  $\text{Li}_2\text{CO}_3$ -like species or other reaction intermediates, such as  $\text{HCO}_2\text{Li}$ , which lead to high overpotential upon charging, as shown in the inset of Figure 3(d) and similar to the previous reported results.<sup>23,24</sup> Therefore, further improvement of cycling stability can be achieved by the selection of a carbon-free current collector in the further work to avoid the side reactions between  $\text{Li}_2\text{O}_2$  and carbon.

The discharged and charged cathodes were analyzed by SEM to examine the reversibility of the electrochemical reactions. Compared with the pristine GCN@CP electrode shown in Figure 4a, the discharge products of  $\text{Li}_2\text{O}_2$  (Figure 4b) have a toroidal morphology with diameter of  $\sim 300$  nm, and then they are removed during the charging process (Figure 4c).<sup>25</sup> The reversible formation and decomposition of  $\text{Li}_2\text{O}_2$  product is further supported by the XRD observations (Figure 4d). The diffraction peaks of  $\text{Li}_2\text{O}_2$  can be clearly observed after discharge, which suggests that  $\text{Li}_2\text{O}_2$  is the dominant crystalline product in the discharging process of the Li–O<sub>2</sub> battery with a GCN@CP cathode. Furthermore, the above diffraction peaks of  $\text{Li}_2\text{O}_2$  are disappeared after recharge, which means the reversible discharge and charge capacities mainly result from the desirable formation and decomposition of  $\text{Li}_2\text{O}_2$ .<sup>26</sup>

Above results show the potential of g- $\text{C}_3\text{N}_4$  as an efficient cathodic catalyst for nonaqueous Li–O<sub>2</sub> battery. However, big challenges are faced in terms of application. The low electronic conductivity of g- $\text{C}_3\text{N}_4$  may cause a large voltage gap between discharge and charge. Thus, combination with electronic conductive material is useful for this material in future use. Moreover, previous study has proved that chemical doping (phosphorus-doped,<sup>27</sup> iodine modified<sup>28</sup>) is an effective strategy to modify the electronic structures of g- $\text{C}_3\text{N}_4$  as well as their surface properties, thus improving their performances.

## 4. CONCLUSIONS

In summary, graphitic- $\text{C}_3\text{N}_4$  @ carbon paper (GCN@CP) has been successfully prepared through a facile in situ method using guanidine hydrochloride as precursor. The GCN@CP exhibits an efficient synergistic catalysis for nonaqueous Li–O<sub>2</sub> battery, showing low voltage gap, good rate capability, and cyclic stability. The results presented here illustrate the benefits of combination between carbon paper and g- $\text{C}_3\text{N}_4$ , and give much space to further improve the catalytic reactivity of graphitic- $\text{C}_3\text{N}_4$  for Li–O<sub>2</sub> batteries. Its encouraging performance offers hope to design more advanced g- $\text{C}_3\text{N}_4$  cathode architectures for Li–O<sub>2</sub> batteries, although the electronic conductivity is still a challenge for the practical application of Li–O<sub>2</sub> batteries with g- $\text{C}_3\text{N}_4$  cathode. We believe that this simple and straightforward method provides an opportunity to investigate the catalytic reactivity of g- $\text{C}_3\text{N}_4$  as cathodic catalyst for Li–O<sub>2</sub> batteries.

## ■ ASSOCIATED CONTENT

### 📄 Supporting Information

The electrochemical performance of bulk g- $\text{C}_3\text{N}_4$  and the discharge/charge curves of GCN@CP are provided. The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acsami.5b01727.

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### Notes

The authors declare no competing financial interest.

## ■ ACKNOWLEDGMENTS

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