Graphitic Carbon Nitrides Supported by Nitrogen-Doped Graphene as Efficient Metal-Free Electrocatalysts for Oxygen Reduction

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Abstract:

Owing to its low cost and rich nitrogen content, graphitic carbon nitride (g-C₃N₄) is promising metal-free catalyst for oxygen reduction reaction (ORR). However, the electrocatalytic performance of carbon nitride is limited by its low conductivity. In order to circumvent this limitation, we incorporated g-C₃N₄ with nitrogen-doped graphene (N-G) by ball-milling g-C₃N₄ and N-G to produce g-C₃N₄@N-G of an ORR catalytic activity comparable to the commercial Pt/C catalyst, along with a better long-term stability and more tolerance to the methanol crossover effect.

Keywords: carbon nitride, graphene, metal-free catalyst, oxygen reduction, ball milling

1. Introduction

Instead of burning fossil fuels, fuel cells can convert chemical energy directly into electricity by reducing oxygen gas at cathode and oxidizing hydrogen gas at anode with water as the only by-product and free from pollution. Due to the slow kinetics of the oxygen reduction reaction (ORR), catalysts are required for ORR. Platinum (Pt) has been known to be the best electrocatalyst for the cathodic oxygen reduction. However, commercial Pt/C catalysts are still

suffered from multiple drawbacks, including their high cost, limited reserve, sluggish kinetics, and susceptible to the methanol crossover/CO poisoning effect. Therefore, it is highly desirable to develop new low-cost, high-performance ORR catalysts to reduce/replace the commercial Pt/C catalysts for practical applications [1].

We have previously demonstrated that heteroatom-doped carbon materials could act as metal-free catalysts with superb ORR activities. Examples include N-doped carbon nanotubes [2, 3], N-doped graphene (N-G) [4], BCN graphene [5], and N, P co-doped VACNTs [6]. Among them, nitrogen-doping has been demonstrated to be most effective to improve the ORR electrocatalytic activities of carbon nanomaterials. In this regard, carbon nitrides with a high nitrogen content is very promising metal-free electrocatalysts. Carbon nitrides have different crystal structures, including tetrahedral carbon nitride (b-C₃N₄) and graphitic carbon nitride (g-C₃N₄). b-C₃N₄ is predicted to possess a high hardness and low compressibility similar as diamond while g-C₃N₄ is regarded as the most stable allotrope at ambient conditions [7]. For g-C₃N₄, two structural isomers have been identified: one comprises condensed melamine units containing a periodic array of single carbon vacancies; the other is made up of condensed melem (2,5,8-triamino-tri-s-triazine) subunits containing larger periodic vacancies in the lattice [8]. Recently, carbon nitrides have been proved to be effective catalysts for water splitting under visible light [9], splitting of CO₂ [10], and cyclotrimerization of various nitriles [11]. However, the electrocatalytic performance of carbon nitride for ORR was found to be very poor due to its low conductivity [8]. In order to improve the electrocatalytic activity of g-C₃N₄, various carbon materials have been used as the support to enhance charge-transfer, and hence the catalytic performance of g-C₃N₄. Examples include the combined g-C₃N₄ and carbon black [8,12], g-C₃N₄ immobilized graphene sheets [13-15], g-C₃N₄ incorporated mesoporous carbon (CMK-3) [16,

17], and 3D ordered macroporous g-C₃N₄/C [19]. Of particular interest, N-G is a promising candidate for supporting carbon nitride to enhance the electron transfer, though yet reported.

In collaboration, we have previously used ball milling technique for low-cost, scalable production of various edge-functionalized graphene materials, including nitrogen-edge-doped graphene, as metal-free electrocatalysts for oxygen reduction [20-23]. Herein, we report new metal-free ORR electrocatalysts based on N-G and g-C₃N₄ hybrid materials (g-C₃N₄@N-G) produced by ball milling g-C₃N₄ prepared from pyrolysis of cyanamide under a flow of argon gas and N-doped graphene from modified Hummer's method.

2. Experimental section

2.1. Synthesis of graphitic carbon nitride from cyanamide

The graphitic carbon nitride was prepared by pyrolysis of cyanamide under a flow of argon gas. In a typical experiment, the cyanamide precursor was placed into a quartz boat, which was then inset into a quartz tube in a muffle furnace. Thereafter, the quartz tube was gradually heated up to 550°C within 2 hours and kept at 550°C for additional 4 hours under the flow of argon gas (200 sccm), followed by air cooling down to room temperature whilst kept the argon flowing through inside of the quartz tube. [18, 19]

2.2. Preparation of graphene oxide

Graphene oxide was prepared using the modified Hummers' method [24]. Typically, graphite powder (3.0 g) was added into a mixture solution of concentrated H₂SO₄ (70 mL) and NaNO₃ (1.5 g) in an ice bath. To the resulting mixture, KMnO₄ (9.0 g) was added slowly, followed by stirring at 35°C for 2 hours. Then the newly-produced mixture was added into deionized water (150 mL) slowly, which was poured into 500 mL deionized water containing 15 mL 30% H₂O₂.

After filtration, the solid component was recovered from the mixture and washed by HCl (10 wt.%) and deionized water. The resultant solid was then added into water and sonicated for 1 hour for exfoliation of graphene oxide. The graphene oxide dispersion thus produced was then centrifuged at 4000 rpm for 20 min, and the graphene oxide was recovered by filtration (0.45 μ m Millipore PVDF membrane) of the supernatant and vacuum drying (10 mTorr, 25°C for 72 h). Alternatively, the graphene oxide solution was freeze-dried according to published procedures (typically, freeze-drying at 10 mTorr for 3 days) [25].

2.3. Preparation of nitrogen-doped graphene

Following our previous work [26], we prepared nitrogen-doped graphene by annealing the freeze-dried graphene oxide in a quartz tube furnace under ammonia/argon gas mixture ($\text{NH}_3\text{:Ar} = 1\text{:}1$ v/v, 200 sccm) at 800°C for 1 hour.

2.4. Preparation of g-C₃N₄@N-G and g-C₃N₄&N-G mixture

g-C₃N₄@N-G was prepared by ball milling g-C₃N₄ and N-G (1:3 wt/wt). Briefly, g-C₃N₄ (10 mg) was first dispersed in 20 mL DI-water and sonicated for 20 min, which was placed together with N-G (30 mg) into a stainless steel container with 100 g stainless steel balls of 5-mm in diameter. The container was then fixed in a planetary ball-mill machine and agitated with 500 rpm for 24 h. The resultant product was washed with HCl (10 wt.%) to remove metal impurities, if any, and then collected by filtration and vacuum drying. g-C₃N₄&N-G mixture was prepared simply by mixing 10 mg g-C₃N₄ and 30 mg N-G in 20 mL DI-water under stirring for 24 h, followed by filtration and vacuum drying.

2.5. Structure characterization

Transmission electron microscopic (TEM) images were taken using a JEOL2100 high resolution transmission electron microscope operating at an acceleration voltage of 200 kV. X-ray diffraction (XRD) was carried out on a Miniflex Desktop X-ray Diffractometer while X-ray photoelectron spectroscopy (XPS) was conducted on VG Microtech ESCA 2000 using a monochromic Al X-ray source (97.9 W, 1486.6 eV). Raman spectra were collected on a Raman spectrometer (Renishaw) using 514 nm laser. Thermogravimetric analysis (TGA) was performed on a TA instrument (Q50) with a heating rate of 10 °C/min in air.

2.6. Electrochemical characterization

Electrochemical measurements were performed on an electrochemical workstation (CHI760C, CH Instrument) in a three-electrode electrochemical cell at room temperature. A platinum wire was used as the counter electrode, and a saturated calomel electrode (SCE) was used as the reference electrode. The catalyst with a loading amount of 200 $\mu\text{g}/\text{cm}^2$ was drop-cast onto the glass carbon electrode (CH Instrument, $d = 0.5\text{cm}$), followed by casting with 10 μL Nafion solution (0.05 wt % in ethanol) as the binder. Catalytic activities of the electrocatalysts were evaluated by cyclic voltammetry (CV) and linear sweep voltammetry (LSV) techniques on rotating disk electrodes (RDEs) in an oxygen saturated aqueous solution of 0.1 M KOH at room temperature.

3. Results and discussion

Fig. 1(a) shows a typical TEM image of the g- C_3N_4 while Fig. 1(b) reproduces a TEM image for the wrinkled N-G sheets. The TEM image for the ball-milled g- C_3N_4 @N-G is given in Fig. 1(c), which shows that the g- C_3N_4 nanosheets were uniformly distributed on the N-G sheets with an intimate contact between them – an advantage for conductivity enhancement of the g- C_3N_4

nanosheets, and hence their electrocatalytic activities. A comparison of Fig. 1(a) with Fig. 1(c) shows that the g-C₃N₄ sheets were mechanically cracked into smaller nanosheets and then deposited onto the N-G sheets during the ball milling process.

Fig. 2(a) shows the X-ray diffraction (XRD) patterns for g-C₃N₄, N-G and g-C₃N₄@N-G. As expected, g-C₃N₄ shows a strong peak at 27.4°, corresponding to the in-plane ordering of tri-s-triazine units [27]. The interlayer-stacking peak around 13.0° [27] is largely absent, indicating the lack of a through-thickness order. The N-G shows a relatively broad peak at around 26.2° characteristic of graphitic carbons while g-C₃N₄@N-G shows a similar peak at around 26.4° with a slight up-shift. This, together with the appearance of a broad band, albeit very weak, centered around 13°, indicates the successful deposition of g-C₃N₄ onto the graphene sheets to restore the through-thickness order to a certain degree. The structural order of g-C₃N₄@N-G was further investigated using Raman spectroscopy with respect to N-G. As can be seen in Fig. 2(b), a D-band at around 1356 cm⁻¹ and G-band at around 1588 cm⁻¹ were observed for both N-G and g-C₃N₄@N-G. The peak intensity ratio of the D-band to G-band (I_D/I_G) was estimated to be about 0.94 and 0.99 for N-G and g-C₃N₄@N-G, respectively. The observed increase in the I_D/I_G ratio indicates that more defects were introduced on the graphene basal plane due to the deposition of g-C₃N₄ nanosheets – an additional advantage for electrocatalysis. Thermogravimetric analysis (TGA) was employed to investigate the thermo stability of g-C₃N₄@N-G and its constituent components (*i.e.*, g-C₃N₄, N-G). As seen in Fig. 2(c), g-C₃N₄ exhibited a decomposition temperature at around 650 °C whereas the N-G and g-C₃N₄@N-G decomposed at a lower temperature (*ca.* 600 °C). Furthermore, the g-C₃N₄@N-G showed a lower thermo stability over 300~600 °C due, most probably, to the increased defects associated with the deposition of g-C₃N₄ onto the N-G sheets, in a good agreement with the Raman results.

To evaluate the chemical structure, we further performed X-ray photoelectron spectroscopic (XPS) analyses. Fig. 2(d) shows an XPS survey spectrum for g-C₃N₄@N-G. The corresponding XPS spectra for g-C₃N₄ and N-G were given in Fig. S1. All of the XPS spectra show a pronounced C 1s peak, along with a N 1s and O 1s peak. As we shall see later, the O 1s peak arises mainly from physically adsorbed oxygen since graphitic carbon is known to be susceptible to oxygen adsorption even at pressures as low as 10⁻⁸ to 10⁻¹⁰ Torr [28], typical for the XPS measurements. The strong oxygen adsorption capacity offers an additional advantage for ORR [electrocatalysis](#). As can be seen in Fig. S1(b), the C1s spectrum of g-C₃N₄ shows two main carbon component peaks at the binding energies of 284.6 and 288.0 eV, corresponding to C–N–C and C–(N)₃, respectively [27]. On the other hand, N1s spectrum of g-C₃N₄ given in Fig. S1(c) shows two peaks at around 398.8 and 401.0 eV corresponding to pyridinic-N and graphitic-N, respectively, in consistent with the molecular structure of g-C₃N₄ [29]. The high resolution N1s spectrum of N-G given in Fig. S1(f) was deconvoluted into three peaks at 398.6, 400.5 and 405.7 eV corresponding to the pyridinic-N, pyrrolic-N and N-oxides, respectively [26,30] while the corresponding C1s spectrum in Fig. S1(e) could be fitted into C=C, C-C and C-N with no O-containing peak component, indicating no oxygen-bonded carbon (*vide supra*). The C1s spectrum of g-C₃N₄@N-G given in Fig. 2(e) could also be deconvoluted into a dominated peak for sp²-C at 284.6 eV, along with the other two weaker peaks associated with sp³-C at 285.6 eV, C-N at 286.0 eV, respectively, with no O-containing peak component, indicating once again that physical adsorption is responsible for the O 1s peak seen in Fig. 2(d). The N1s spectrum of g-C₃N₄@N-G shown in Fig. 2(f) was fitted to pyridinic-N at ~398.6 eV, pyrrolic-N at ~400.6 eV, graphitic-N at ~401.0 eV and N-oxides at ~405.7 eV, respectively [31]. Overall, the XPS spectra of g-C₃N₄@N-G exhibited the characteristic peaks of both g-C₃N₄ and N-G, indicating an

intimate combination of the N-G with g-C₃N₄ by ball milling, as also revealed by the TEM examination (*cf.* Fig. 1(c)).

The incorporation of N-G into g-C₃N₄ or vice versa could increase the electrical conductivity and nitrogen content (Fig. 2(d), 8.9% of g-C₃N₄@N-G *vs.* 4.0% for N-G. Fig. S1(d)) of the catalyst, leading to improved ORR electrocatalysis. The ORR electrocatalytic activity of g-C₃N₄@N-G was tested by conventional three-electrode cyclic voltammetry (CV) in O₂ and N₂ saturated 0.1M KOH aqueous solutions, respectively. Fig. S2(a) shows that a characteristic ORR peak starting at about -0.10 V was observed for oxygen reduction on the g-C₃N₄@N-G electrode in the O₂ saturated 0.1M KOH, but not in the N₂ saturated 0.1M KOH. For comparison, the CV curves of g-C₃N₄ and N-G were shown in Figs. 3(a) and S2(b), along with the corresponding curve for g-C₃N₄@N-G. As can be seen, the peak intensity of g-C₃N₄@N-G, with a more positive onset potential, is much stronger than those of N-G and g-C₃N₄, indicating a more effective ORR process on the g-C₃N₄@N-G electrode. A series of linear sweep voltammograms (LSVs) for g-C₃N₄, N-G and g-C₃N₄@N-G were measured on a rotating disk electrode (RDE) from 400 to 1600 rpm, showing an typically increased current with increasing rotation speeds (Fig. 3(b)). Fig. 3(b) shows an increased ORR onset potential and enhanced limited current density in the order of g-C₃N₄ < N-G < g-C₃N₄@N-G in good agreement with the CV results, indicating a synergistic effect for g-C₃N₄@N-G as the ORR catalyst. Due to the low quality of the N-G produced from the GO precursor with respected to those produced by chemical vapor deposition (CVD) [4, 33, 34], relatively poor electrocatalytic performance was observed for the N-G in Figure 3b.

To better investigate the kinetics of ORR, we used rotation ring-disk electrode (RRDE) to evaluate ORR performance of the g-C₃N₄@N-G. From Fig. 3(c), the electron transfer number was calculated to be about 4.0 [2, 4, 32], indicating a four-electron ORR process. In addition, the

transferred electron numbers per O_2 were also determined by the Koutecky-Levich equation [32], as shown in the supporting information. From the K-L plots shown in Figs. 3(d) and S2(d & e), the electron transfer number (n) of g- C_3N_4 , N-G and g- C_3N_4 @N-G at different potential were presented in Fig. 3(e). As can be seen, g- C_3N_4 @N-G showed $n = 4.0$, which is in good agreement with the corresponding value estimated from RRDE, whereas the N-G and g- C_3N_4 exhibited $n = 3.1$ and 2.0 , respectively. Clearly, the combination of g- C_3N_4 and N-G has greatly enhanced the oxygen reduction process on the g- C_3N_4 @N-G electrode.

As shown in Fig. S2(c), the ORR onset potentials of g- C_3N_4 , N-G, and g- C_3N_4 @N-G are about $-0.31V$, $-0.15V$ and $-0.02V$ (E vs. SCE), respectively. Similarly, the ORR half-wave potential ($E_{1/2}$) of g- C_3N_4 @N-G is about $-0.22V$ (E vs. SCE), which is much better than that of g- C_3N_4 ($E_{1/2} \approx -0.44V$) and N-G ($E_{1/2} \approx -0.40V$). Fig. S2(c) shows an ORR catalytic activity comparable to the commercial Pt/C catalyst for g- C_3N_4 @N-G. In a control experiment, the g- C_3N_4 and N-G mixture was also prepared by simply stirring mixing for 24h without ball milling, which was demonstrated to show an inferior ORR performance than g- C_3N_4 @N-G (Fig. S2(c)), indicating that ball milling played an important role in improving the catalytic activity.

The g- C_3N_4 @N-G electrode was further subjected to stability assessment and tested for possible methanol crossover effect. As shown in Fig. 4(a), the original cathodic ORR current of g- C_3N_4 @N-G at $-0.3 V$ did not show a significant change after the sequential addition of methanol into the electrolyte solution (a total methanol concentration of $3M$), suggesting that g- C_3N_4 @N-G is free from the methanol crossover effect. In contrast, the commercial Pt/C showed an immediate change upon the addition of methanol, indicating a conversion of the dominated oxygen reduction to the methanol oxidation reaction, which can be considered as a poisoning of the catalyst. The durability of g- C_3N_4 @N-G was evaluated by the chronoamperometric response at $-0.3 V$. As shown in Fig. 4(b), the metal-free g- C_3N_4 @N-G catalyst exhibited high stability

with a very slow attenuation and a high current retention (96.3%) even after 30000 s, showing a much better durability than that of the commercial Pt/C catalyst. To the best of our knowledge, g-C₃N₄@N-G showed the best performance among the carbon nitride based electrocatalysts for oxygen reduction, as seen in Table S1.

4. Conclusions

By ball-milling g-C₃N₄ generated by pyrolysis of cyanamide under a flow of argon gas and N-doped graphene from the modified Hummer's method, we have produced a new class of low-cost, metal-free ORR catalysts with g-C₃N₄ intimately supported by N-G sheets. The resultant g-C₃N₄@N-G exhibited excellent catalytic activity towards oxygen reduction, comparable to commercial Pt/C catalyst, with an onset potential at about -0.02V (E vs. SCE) and half-wave potential at about -0.22V (E vs. SCE). The superb ORR performance observed for the g-C₃N₄@N-G could be attributed to the synergetic effect arising from the ball-milling-induced intimate combination of nitrogen-rich g-C₃N₄ and N-G with a good conductivity. This work represents an important step forward in the scalable production of advanced high-performance, low-cost, metal-free catalysts by ball milling techniques.

Conflict of interest

There is no conflict of interest among the authors.

Acknowledgments

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Fig. 1. TEM images of (a) C_3N_4 (scale bar: 100 nm), (b) N-G (scale bar: 500 nm), and (c) $C_3N_4@N-G$ (scale bar: 100nm).

Fig. 2. (a). XRD patterns of g-C₃N₄, N-G and g-C₃N₄@N-G, (b) Raman spectra of N-G and g-C₃N₄@N-G, (c) TGA curves of g-C₃N₄, N-G and g-C₃N₄@N-G under air atmosphere, (d) XPS survey spectrum of g-C₃N₄@N-G, (e) Curve-fitted high resolution XPS C 1s spectrum of g-C₃N₄@N-G, and (f) Curve-fitted high resolution XPS N 1s spectrum of C₃N₄@N-G.

Fig. 3. Catalytic activity towards electrochemical reduction of oxygen in 0.1 M O₂-saturated KOH aqueous solution at room temperature. (a) Cyclic voltammetry (CVs) of g-C₃N₄, N-G and g-C₃N₄@N-G obtained at a sweep rate of 50 mV s⁻¹, (b) Comparison of linear sweep voltammograms (LSVs) of g-C₃N₄, N-G and g-C₃N₄@N-G at different rotating speed (400 rpm, 600 rpm, 900 rpm, 1200 rpm and 1600 rpm) at a sweep rate of 5 mV s⁻¹, (c) LSVs of g-C₃N₄@N-G on the RRDE at 1600 rpm. Insert shows the electron transfer number of g-C₃N₄@N-G estimated from the ring and disk currents, (d) Koutecky-Levich plot for g-C₃N₄@N-G obtained from LSVs in (b), and (e) Electron transfer number of g-C₃N₄, N-G and g-C₃N₄@N-G calculated from Koutecky-Levich equation.

Fig. 4. (a) The current-time (i-t) chronoamperometric responses for ORR at the g-C₃N₄@N-G and Pt/C electrode in 0.1M O₂-saturated KOH aqueous solution at -0.3 V versus SCE, and 3.0 M methanol was added at around 200 s, (b) Durability curves (i-t) of g-C₃N₄@N-G and Pt/C obtained in at -0.3V versus SCE at a rotation rate of 1000 rpm.