

## Supporting Information

for *Adv. Sci.*, DOI: 10.1002/advs.201400015

Paper-Based N-Doped Carbon Films for Enhanced Oxygen  
Evolution Electrocatalysis

*Sheng Chen, Jingjing Duan, Jinrun Ran, and Shi-Zhang Qiao\**

Supporting Information

**Paper-based N-doped carbon films for enhanced oxygen evolution electrocatalysis**

*Sheng Chen, Jingjing Duan, Jinrun Ran, and Shi-Zhang Qiao\**

[\*] Prof. Shi-Zhang Qiao, Sheng Chen, Jingjing Duan, Jinrun Ran  
School of Chemical Engineering, the University of Adelaide,  
Adelaide, SA 5005, Australia  
E-mail: [s.qiao@adelaide.edu.au](mailto:s.qiao@adelaide.edu.au)

## I. Experimental Section

### 1. Chemicals

Graphite flakes, cyanamide (CN-NH<sub>2</sub>, 99%), potassium permanganate (KMnO<sub>4</sub>, 99%), potassium persulfate (K<sub>2</sub>S<sub>2</sub>O<sub>8</sub>, 99%), iridium(IV) oxide (IrO<sub>2</sub>, 99%), potassium hydroxide (KOH, 99%), sulfuric acid (H<sub>2</sub>SO<sub>4</sub>, 95-98%), phosphorus pentoxide (P<sub>2</sub>O<sub>5</sub>, 98%), hydrochloric acid (HCl, 38 wt%), hydrazine hydrate (N<sub>2</sub>H<sub>4</sub>·H<sub>2</sub>O, 80 wt%), , hydrogen peroxide (H<sub>2</sub>O<sub>2</sub>, 35 wt%), ethanol (EtOH, absolute), isopropanol ((CH<sub>3</sub>)<sub>2</sub>CH-OH, absolute), were purchased from Sigma-Aldrich and directly used without further treatment or purification.

### 2. Synthesis

Cyanamide (2 g) was calcined under an argon atmosphere at 550 °C for 6 h at a heating rate of 5 °C min<sup>-1</sup> to form bulk graphitic carbon nitrate (g-C<sub>3</sub>N<sub>4</sub>). Then the bright yellow powder (3 mg) was mixed with isopropanol (1 mL), and subjected to bath ultrasonication for 12 h. The resultant dispersion was centrifuged at 1000 rpm for 30 min. It reveals that both single- and few-layer C<sub>3</sub>N<sub>4</sub> nanosheets are produced in the top of resultant solution.<sup>[1]</sup> On the other hand, graphene oxide (GO) was prepared by chemical oxidation of natural graphite *via* the Hummer's method.<sup>[2]</sup> In a typical synthetic process of G-C<sub>3</sub>N<sub>4</sub>, GO dispersion (2 mg mL<sup>-1</sup>, 1 mL) was mixed with C<sub>3</sub>N<sub>4</sub> (1 mL), and casted onto a piece of cellulosic paper. The hybrid film was dried at 50 °C for 6 h in the oven. Next, the GO and C<sub>3</sub>N<sub>4</sub>-coated paper was placed in an autoclave, and 500 μL hydrazine monohydrate (80 %) was added to the autoclave. After that, the autoclave was heated at 80 °C for 6 h. For the purpose of comparison, individual graphene film was prepared similarly without C<sub>3</sub>N<sub>4</sub>; C<sub>3</sub>N<sub>4</sub> film was prepared by casting C<sub>3</sub>N<sub>4</sub> solution on CF papers in a similar condition.

### 3. Characterization

X-ray diffractometer (XRD) measurements were performed on a Philips 1130 X-ray

diffractometer (40 kV, 25 mA, Cu K $\alpha$  radiation,  $\lambda=1.5418$  Å); Fourier transform infrared spectra (FTIR) were recorded on a Nicolet 6700 spectrometer; ultraviolet-visible (UV-vis) spectra were recorded on a SHIMADZU UV-2600 spectrophotometer; Raman spectra were obtained on an WiTEC alpha300R Raman microscope with a 532 nm solid laser as an excitation source; Thermogravimetric analyses (TGA) were recorded on a TGA/SETARAM thermogravimetric analyzer from 100 to 500 °C with a heating rate of 10 °C·min<sup>-1</sup> in O<sub>2</sub> flow; the contact angle was measured on a Theta/Attension Optical Tensiometer; X-ray photoelectron spectra (XPS) were performed on an Axis Ultra (Kratos Analytical, UK) XPS spectrometer equipped with an Al K $\alpha$  source (1486.6 eV); morphologies of the samples were observed on transmission electron microscopy (TEM, Tecnai G2 Spirit) and scanning electron microscopy (SEM, QUANTA 450); Energy Dispersive Spectrometer (EDS) and elemental mapping patterns were acquired on the SEM (QUANTA 4500). Moreover, methylene blue (MB) adsorption experiments were used to probe the accessible surface area of the samples.<sup>[3, 4]</sup> Specifically, the samples were added into a MB-containing ethanol solution (0.1 mg ml<sup>-1</sup>) and were left at 25 °C for 48 h to allow the accessible surface of the samples to be covered by MB molecules. The amount of the adsorbed MB was calculated by using the change in the MB concentration measured by using UV-Vis spectroscopy. The surface area was estimated under the assumption that each milligram of adsorbed MB occupies 1.35 m<sup>2</sup> of the surface.<sup>[3, 4]</sup>

#### 4. Electrochemical testing

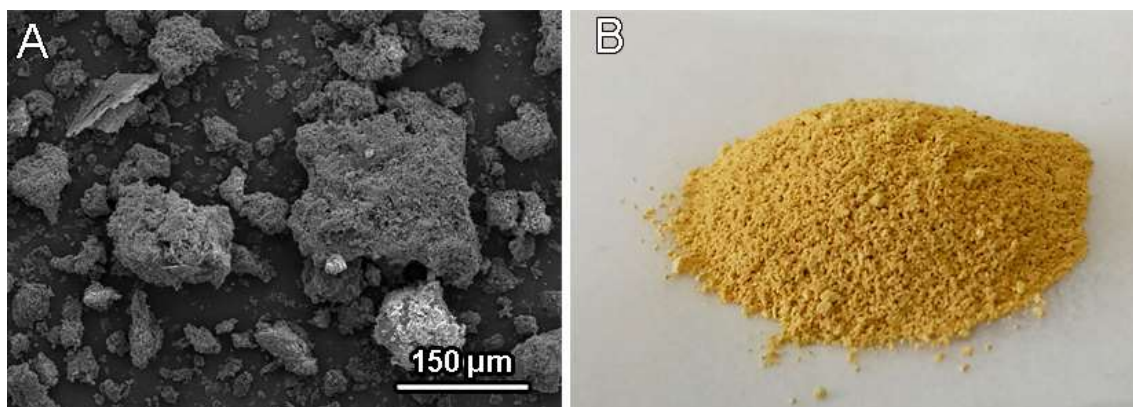
Electrochemical measurements were conducted in a standard three-electrode glass cell on a 760 workstation (Pine Research Instruments, US) using hybrid films as working electrodes, platinum wire as a counter electrode and Ag/AgCl/KCl (3 M) as a reference electrode (please see the testing devices in supplementary results). The mass density of G-C<sub>3</sub>N<sub>4</sub> was ~0.1 mg cm<sup>-2</sup>. The electrolyte was prepared using Milli-Q water (18 M  $\Omega$  cm<sup>-1</sup>) and KOH. OER data were collected under N<sub>2</sub> (ultra-high-grade purity, Airgas) LSV and CV were

recorded with the scan rates in the range of 5~100 mV s<sup>-1</sup>; the current density was normalized to the geometrical area; the measured potentials *vs.* Ag/AgCl were converted to a reversible hydrogen electrode (RHE) scale according to the Nernst equation ( $E_{\text{RHE}} = E_{\text{Ag/AgCl}} + 0.059 \text{ pH} + 0.197$ ).<sup>[5, 6]</sup> The overpotential was obtained according to the equation:  $\eta = E_{\text{RHE}} - 1.23 \text{ V}$ . Tafel slope was calculated according to the Tafel equation:  $\eta = b \log j + a$ , where  $\eta$  is overpotential (V),  $j$  is current density (mA cm<sup>-2</sup>), and  $b$  is Tafel slope (mV dec<sup>-1</sup>). Exchange current density ( $j_0$ , mA cm<sup>-2</sup>) was calculated by applying extrapolation method to the Tafel plots, *i.e.*,  $\log(|j_0(\text{mA cm}^{-2})|)$  at  $\eta=0 \text{ V}$ .

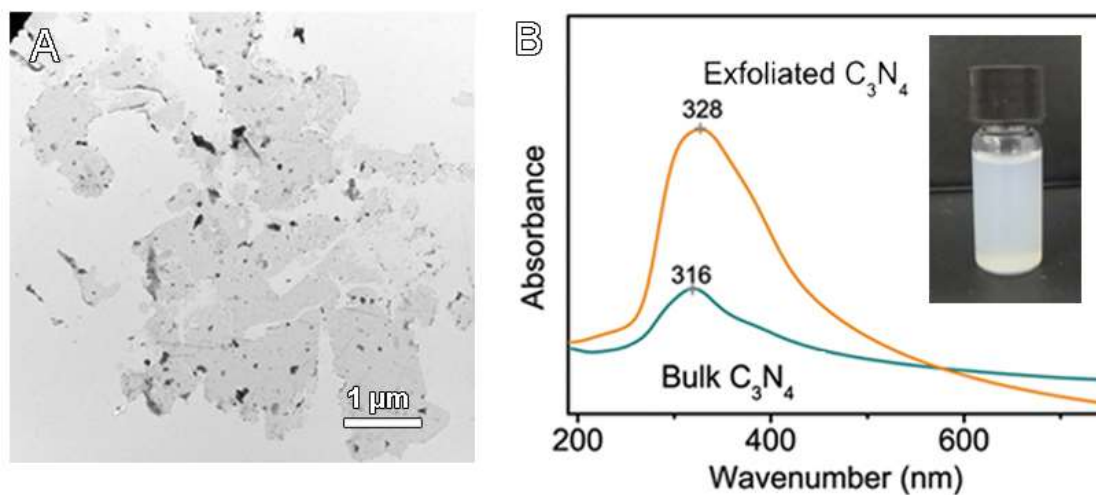
Moreover, analysis of ORR has been conducted in a similar three-electrode system in 0.1 M KOH electrolyte. A 30 mL min<sup>-1</sup> of O<sub>2</sub> flows into the electrolyte during the collection of electrochemical data in order to ensure the O<sub>2</sub>/H<sub>2</sub>O equilibrium at 1.23V *vs.* RHE. LSV plot was collected at 5 mV s<sup>-1</sup> from 0.1 V to -0.8 V (*vs.* Ag/AgCl).

For the purpose of comparison, the catalytic performance of IrO<sub>2</sub> powder was tested on a glassy carbon working electrode under similar conditions. The working electrode was prepared by the drop casting method. Specifically, IrO<sub>2</sub> (2 mg) was ultrasonically dispersed in Milli-Q water (1 mL) with Nafion (30  $\mu\text{L}$  of 0.1%), and then the catalyst dispersion was transferred onto the glassy carbon electrode and dried (catalyst loading  $\sim 0.1 \text{ mg cm}^{-2}$  for IrO<sub>2</sub>).

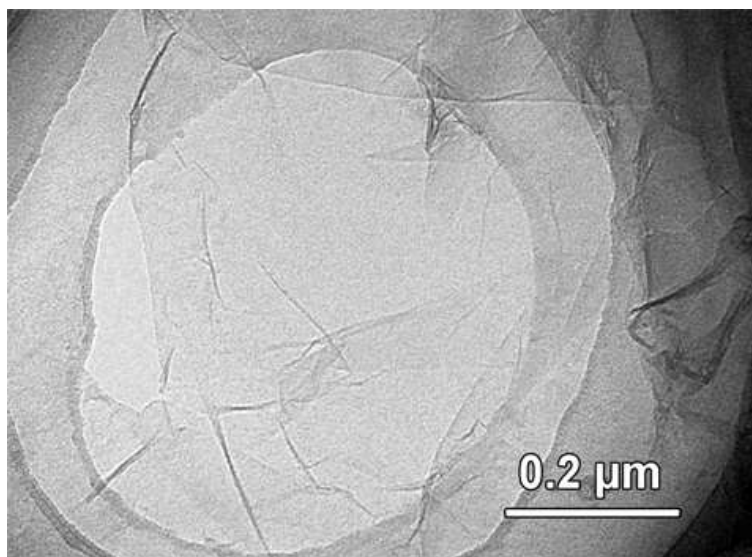
## II. Supplementary Results



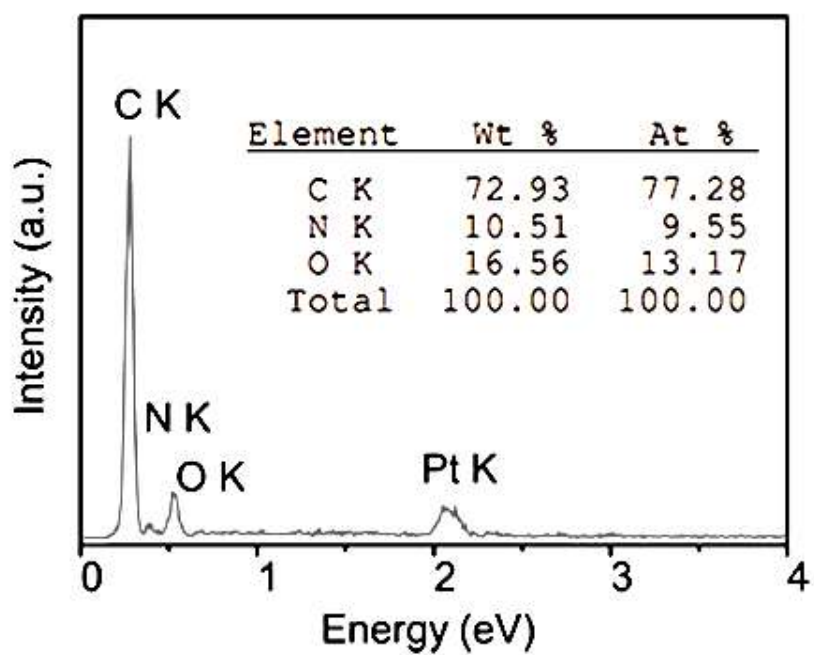
**Figure S1.** Structural characterizations of bulk  $C_3N_4$ : (A) SEM image; (B) Optical image.



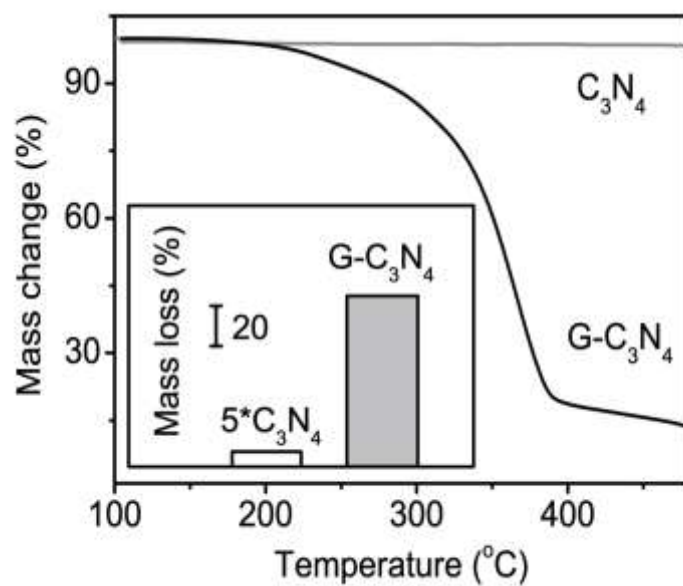
**Figure S2.** (A) SEM image of exfoliated  $C_3N_4$  nanosheets; (B) UV-vis spectra of exfoliated  $C_3N_4$  nanosheets in comparison to their bulk counterpart; (C) Optical image of exfoliated  $C_3N_4$  nanosheets.



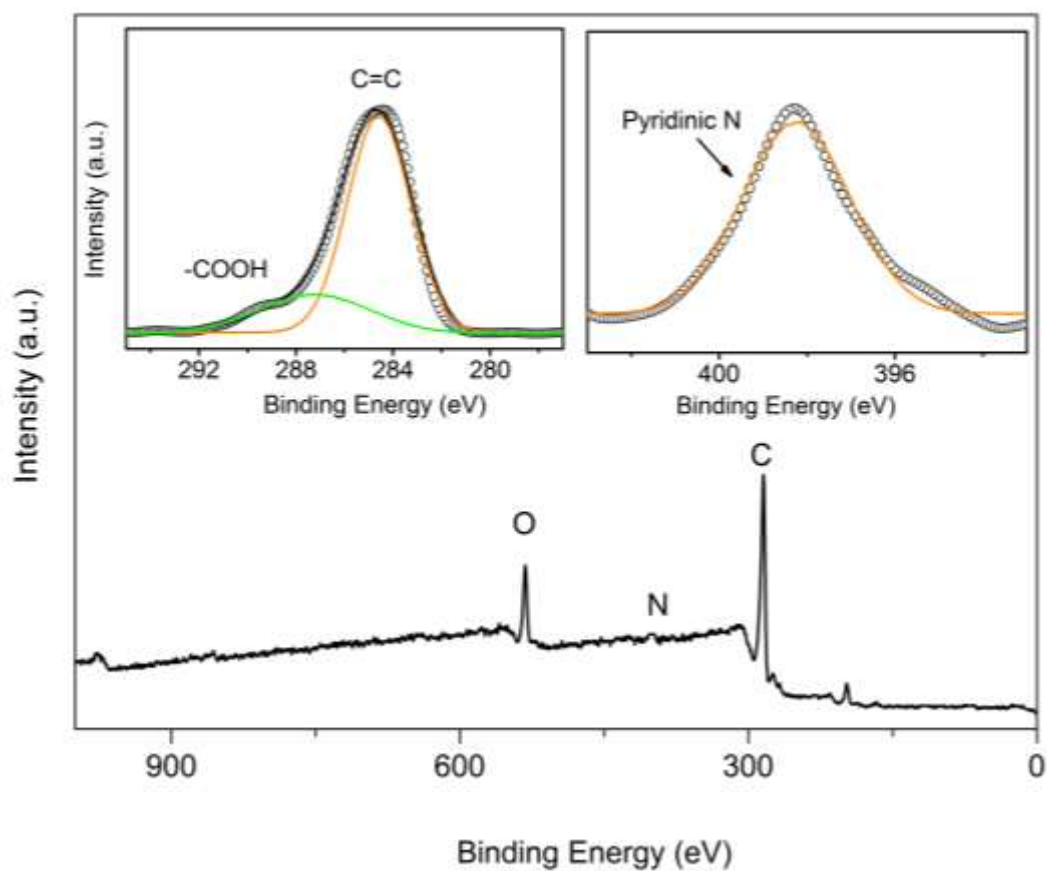
**Figure S3.** TEM image of graphene film.



**Figure S4.** EDS analysis of G-C<sub>3</sub>N<sub>4</sub> film.

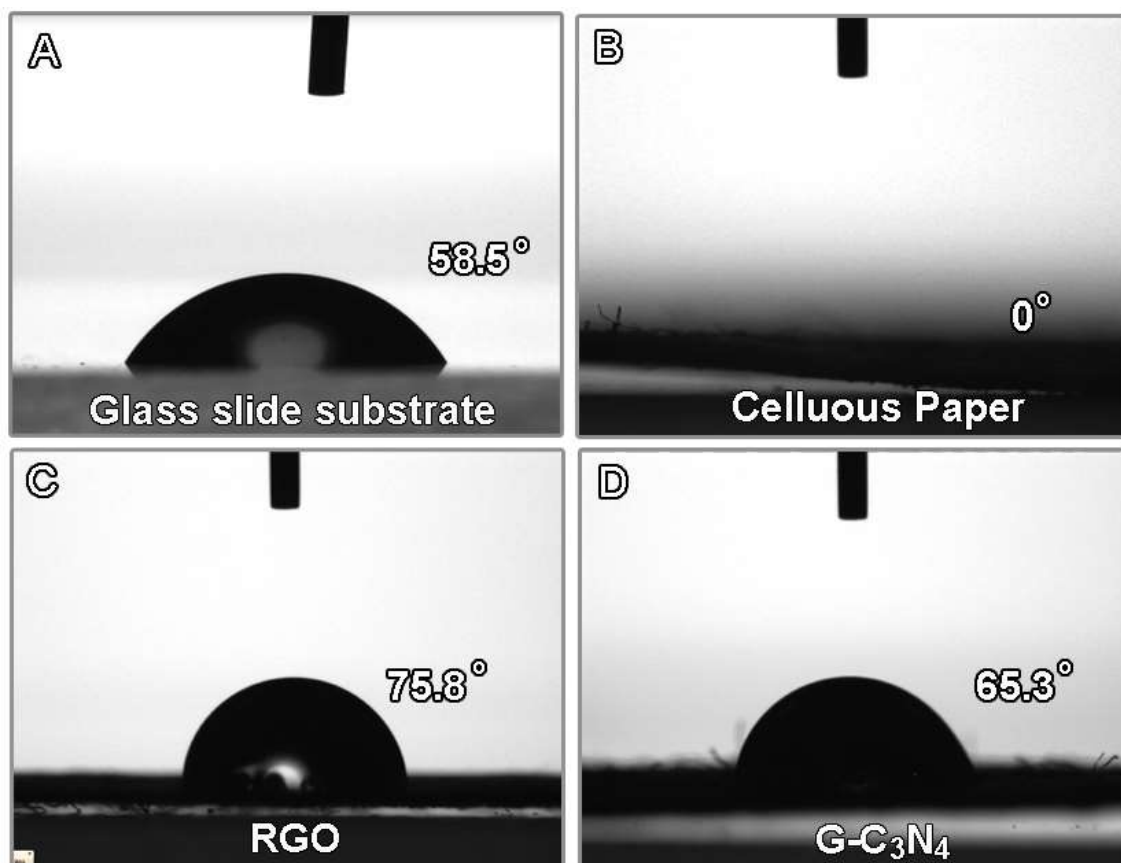


**Figure S5.** TGA analysis of  $G-C_3N_4$  in comparison to  $C_3N_4$

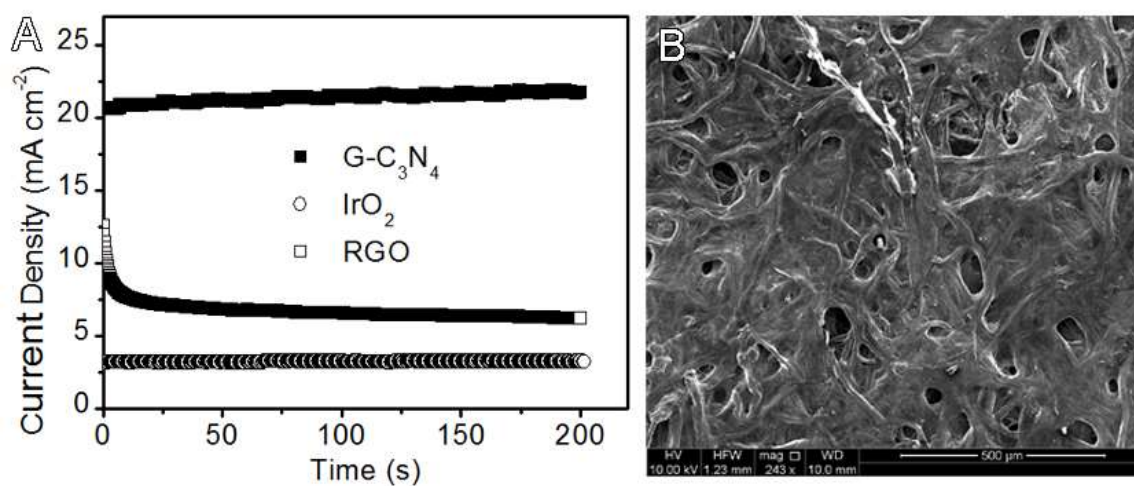


**Figure S6.** XPS analyses of graphene film.

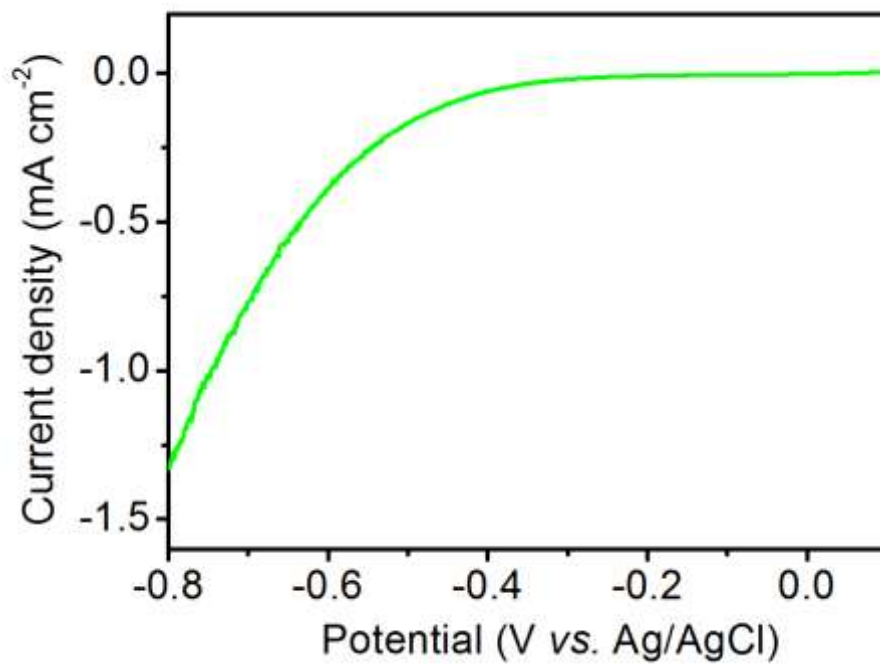




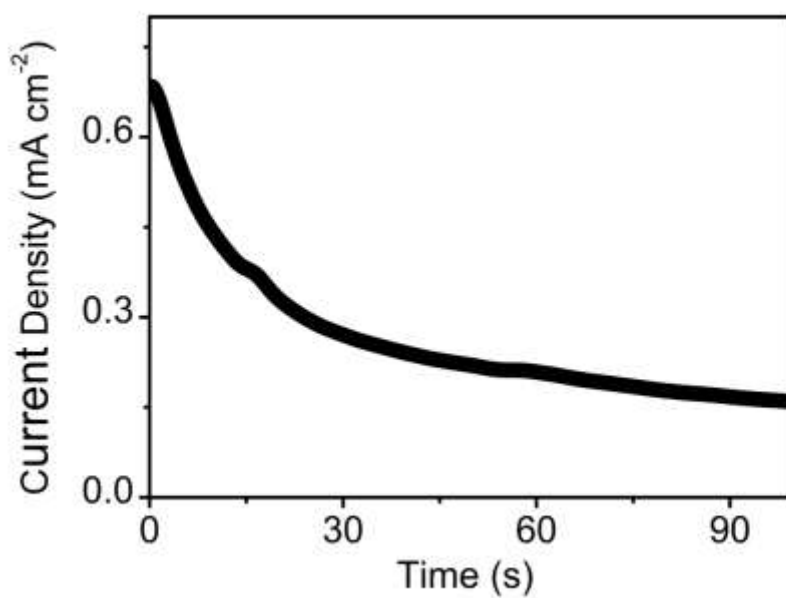
**Figure S7.** Contact angles of different samples: (A) Glass slider substrate; (B) Cellulose Paper; (C) graphene (RGO); (D) G-C<sub>3</sub>N<sub>4</sub>.



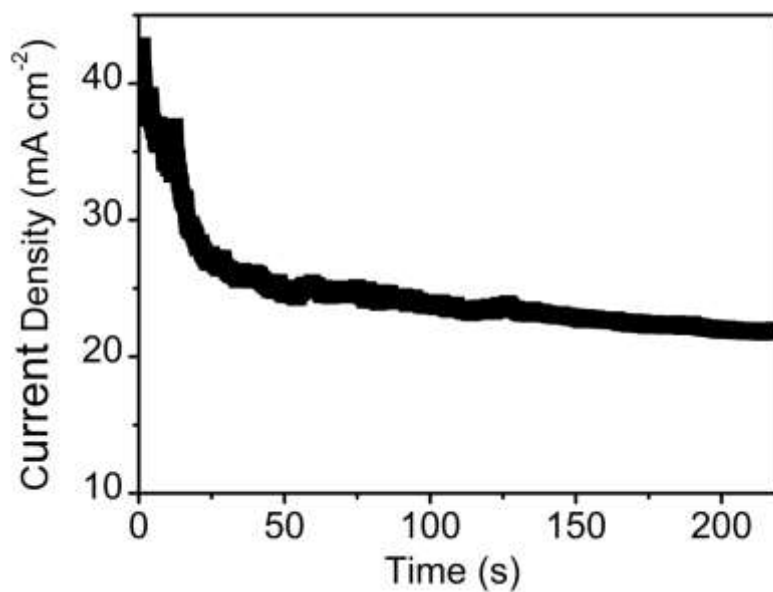
**Figure S8.** (A) Chronometric response of G-C<sub>3</sub>N<sub>4</sub> in comparison to RGO and IrO<sub>2</sub>; (B) SEM image of G-C<sub>3</sub>N<sub>4</sub> after cycling operation for 40 h.



**Figure S9.** Electrochemical study of G-C<sub>3</sub>N<sub>4</sub> in 0.1 M KOH for electrocatalytic oxygen reduction reaction (ORR).



**Figure S10.** Chronometric response of G-C<sub>3</sub>N<sub>4</sub> on glassy carbon electrode.



**Figure S11.** Chronometric response of G-C<sub>3</sub>N<sub>4</sub> on nickel foam substrate.

## References

- [1] S. Yang, Y. Gong, J. Zhang, L. Zhan, L. Ma, Z. Fang, R. Vajtai, X. Wang, P. M. Ajayan, *Adv. Mater.* **2013**, *25*, 2452.
- [2] W. S. Hummers, R. E. Offeman, *J. Am. Chem. Soc.* **1958**, *80*, 1339.
- [3] M. F. El-Kady, V. Strong, S. Dubin, R. B. Kaner, *Science* **2012**, *335*, 1326.
- [4] P. T. Hang, G. Brindley, *Clays Clay Miner.* **1970**, *18*, 203.
- [5] T. Y. Ma, S. Dai, M. Jaroniec, S. Z. Qiao, *Angew. Chem. Int. Ed.* **2014**, *53*, 7281.
- [6] Y. Zhao, R. Nakamura, K. Kamiya, S. Nakanishi, K. Hashimoto, *Nat. Commun.* **2013**, *4*, 2390.