Direct nitrogen fixation at the edges of graphene nanoplatelets as efficient electrocatalysts for energy conversion

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Nitrogen fixation is essential for the synthesis of many important chemicals (e.g., fertilizers, explosives) and basic building blocks for all forms of life (e.g., nucleotides for DNA and RNA, amino acids for proteins). However, direct nitrogen fixation is challenging as nitrogen (N₂) does not easily react with other chemicals. By dry ball-milling graphite with N₂, we have discovered a simple, but versatile, scalable and eco-friendly, approach to direct fixation of N₂ at the edges of graphene nanoplatelets (GnPs). The mechanochemical cracking of graphitic C₂C bonds generated active carbon species that react directly with N₂ to form five- and six-membered aromatic rings at the broken edges, leading to solution-processable edge-nitrogenated graphene nanoplatelets (NGnPs) with superb catalytic performance in both dye-sensitized solar cells and fuel cells to replace conventional Pt-based catalysts for energy conversion.
established\textsuperscript{20}. The large quantity of the edge-nitrogenated graphene nanoplatelets (NGnPs) produced through such a simple, low-cost, and eco-friendly ball-milling process were further demonstrated to be effective metal-free catalysts for the replacement of precious Pt-based catalysts in DSSCs and PEMFCs for energy conversion. Therefore, the approach developed in this study can be regarded as a versatile technique toward multifunctional carbon nanomaterials of practical significance.

**Results**

As schematically shown in Fig. 1a, the ball-milling-induced direct nitrogen fixation at the broken edges of graphitic frameworks involves the breakage of large grain size of graphite (Fig. 1b) into small ones (Fig. 1c). The cleavage of graphitic C—C bonds by ball-milling created active carbon species to react with nitrogen, as shown in Fig. S1 (Electronic Supplementary Information, ESI). Thermodynamically, the most preferred edge formation of NGnPs is to maintain the aromaticity. The calculated binding energies (\(\Delta E\)) of nitrogen onto the zigzag-shaped and armchair-shaped broken edges were \(-2.50\) eV/N\(_2\) (\(-57.65\) kcal/N\(_2\) mol) (Fig. 1d) and \(-1.96\) eV/N\(_2\) (\(-45.20\) kcal/N\(_2\) mol) (Fig. 1e), respectively, indicating an exothermic (spontaneous) reaction to form nitrogenated aromatic rings at the broken edges. Both aromatic 5-membered pyrazole and 6-membered pyridazine rings could form at the edges of NGnPs via the zigzag and armchair cracking, respectively (Fig. S1). The unreacted residual active carbon species could be terminated by air moisture upon opening the lid as judged by violent sparking (Supplementary Video), leading to the formation of some oxygenated groups at the edges (Figs. 1a and S1). The available number of active carbon atoms at the broken edges was calculated to exponentially increase as an average grain size reduces (Fig. S2, ESI for detailed calculation). This leads to high nitrogen content at the edges, though not all active carbon atoms could react with nitrogen.

The corresponding TEM images given in Figs. S3a–S3c clearly show relatively small and uniform NGnPs with a round shape compared with starting large graphite flake (Fig. 1b). Fig. S3b reveals the edge-stripes associated with a few graphitic layers of a high crystallinity. These results, together with a dramatic increase (39 times) in the Brunauer-Emmett-Teller (BET) surface area of NGnPs (Table S1), indicate an effective and spontaneous delamination of the starting graphite into small GnPs even in the solid state by dry ball-milling. Dark field TEM image also shows similar morphology (Fig. S3c) with carbon- (Fig. S3d), nitrogen- (Fig. S3e) and oxygen-mappings (Fig. S3f) clearly showing the effective incorporation of nitrogen into the resultant NGnPs.

Elemental analyses (EA) indicate that the starting graphite has a carbon content of 99.64 wt% and oxygen content of 0.13 wt% from physisorption (Table S2)\textsuperscript{21}. The resultant NGnPs have a decreased carbon content of 70.67 wt% and a high nitrogen content of 14.84 wt% (equivalent to a carbon/nitrogen atomic ratio of 5.6, see Table S2), assuring that significant amount of nitrogen has been fixed at the edges of NGnPs via the mechnochemical reaction of graphite with the inert nitrogen (Figs. 1a and S1). In addition, hydrogen and oxygen contents as much as 0.79 and 7.43 wt%, respectively,

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**Figure 1** | (a) A schematic representation of physical cracking of graphite flake in a ball-mill crusher (500 mL) containing stainless steel balls (500.0 g, diameter 5 mm) agitated at 500 rpm for 48 h in the presence of nitrogen and subsequent exposure to air moisture to produce NGnPs. SEM images: (b) starting graphite flake; (c) NGnPs after ball-milling. Scale bars are 1 \(\mu\)m. The ring formation mechanisms depending upon the cracking patterns of unzipped edges: (d) the formation of 5-membered pyrazole ring after the reaction between the active zigzag-edge carbon atoms and nitrogen; (e) the formation 6-membered pyridazine ring after the reaction between the active armchair-edge carbon atoms and nitrogen.
were also observed arising from the remnant active carbon species, which reacted with air moisture to introduce oxygenated groups.

Fourier transform infrared spectrum of NGnP shows strong aromatic C−N stretching peak at 1400 cm⁻¹ and C=O stretching peak at 1624 cm⁻¹ (Fig. S4a), implying the presence of nitrogen-containing aromatic rings and carboxylic acid groups, respectively. In addition, the strong peak at 3400 cm⁻¹ is attributable to the hygroscopic nature of NGnP and crystal water associated with KBr used for the specimen preparation. NGnP also display sp² C−H peaks at around 2927 cm⁻¹ associated with defects created during ball-milling. However, the corresponding spectrum for the starting graphite shows only a weak band at 1632 cm⁻¹ characteristic of the vibration mode of adsorbed water molecules²⁻².

The NGnP powder was further characterized by Raman spectroscopy. As expected, the starting graphite showed the G and 2D bands at 1585 and 2722 cm⁻¹, respectively (Fig. S4b), with undetectable edge distortion and structural defects, and hence the ratio of the D- to G-band intensity equals zero (I_D/I_G = 0.0). In contrast, NGnP exhibited a broad and strong D band over 1364 cm⁻¹ with the I_D/I_G ratio of 1.0 (Fig. S4b), indicating the grain size reduction by mechanochemical cracking (see Fig. 1c) and significant edge distortion by edge-nitrogenation (see Figs. 1a and S1).

TGA thermogram of the pristine graphite displays negligible weight loss up to 900 °C in nitrogen (Fig. S4c and Table S3). However, the NGnP showed gradual weight loss up to 600 °C, followed by a dramatic weight loss at around 723 °C. Due to the hygroscopic and polar nature of pyrazole and pyridazine rings at the NGnP edges, the initial weight loss could be originated from bound moisture (H₂O), hydrochloric acid (HCl, see Experimental Section) and oxygenated groups²⁻². The weight loss at 723 °C could be attributed to the loss of relatively much stable edge-heterocyclic rings (see Figs. 1a and S1). The observed gradual weight loss for NGnP, unlike the stepwise weight loss for GO⁴⁻⁴, suggests the presence of strong inter-sheet interactions (e.g., polar interaction and H-bonding) between some of the edge-oxygenated groups to alter their decomposition temperature depending on their specific location along the edges of NGnP. The much higher stepwise decomposition temperature (~723 °C) for NGnP than that (~165 °C) for GO indicates a significantly improved overall thermal stability for the NGnP due, most probably, to the edge-selective functionalization in NGnP without basal plane distortion.

XRD diffraction pattern for the starting graphite shows a strong [002] peak at 26.5° corresponding to a layer-to-layer d-spacing of 0.34 nm (Fig. S4d). Compared with the starting graphite, the NGnP showed only a very weak [002] peak (less than 0.1% intensity) centered at 25.6° (Fig. S4d, inset), indicating the occurrence of delamination of the highly edge-functionalized graphite into a few layer graphene nanoplatelets (GNPs) even in the solid state during the ball-milling and workup processes.

Further evidence for the presence of nitrogen at the edges of NGnP comes from the XPS spectroscopic measurements. As expected, the starting graphite showed only a pronounced C 1s peak at 284.3 eV (Fig. 2a) with a very weak, but noticeable, O 1s band at ~532 eV attributable to the presence of a trace amount of physically adsorbed oxygen²². In addition to the C 1s and O 1s peaks, NGnP showed the characteristic N 1s peak at 399 eV. High-resolution XPS spectra with curve fittings for the C 1s (Fig. 2b) and O 1s (Fig. 2c) peaks showed that the aromatic C−N in pyrazole (pyrrolic−N) and pyridazine (pyridinic−N) rings are the dominant N components in the NGnP. It is noteworthy that the ratio of pyrazole (5N)/pyridazine (6N) nitrogen is 2.9 (Fig. 2d and Table S3), implying that zigzag unzipping is major process (cf. Fig. S1). Furthermore, XPS measurements were performed on the NGnP having thermally annealed at 400 (below 723 °C) and 1000 °C (above 723 °C) for 30 min under.

![Figure 2](https://www.nature.com/scientificreports)

**Figure 2**  (a) XPS survey spectra of the pristine graphite and the as-prepared NGnP. High-resolution XPS spectra of NGnP: (b) C 1s; (c) O 1s; (d) N 1s.
NGnPs into a stable dispersion with similar Zeta-potential values of the solvents tested, DMAc was found to be the best for dispersing sufficient to ensure good dispersion stability Zeta-potential value either more negative or positive than (DMF) and N,N and isopropyl alcohol, but also polar aprotic solvents, including acet-water, basic water (containing ammonium hydroxide), methanol readily dispersible not only in polar protic solvents, such as neutral impon and oxygenation) for an enthalpic enhancement could greatly improve solubility of the NGnPs. Indeed, NGnPs were found to be dispersible not only in polar protic solvents, such as neutral water, basic water (containing ammonium hydroxide), methanol and isopropyl alcohol, but also polar aprotic solvents, including acetone, N,N-dimethylacetamide (DMAc), N,N-dimethylformamide (DMF) and N-methyl-2-pyrrolidone (NMP) (Fig. S7). Among all the solvents tested, DMAc was found to be the best for dispersing NGnPs into a stable dispersion with similar Zeta-potential values of −42.4 and −31.9 mV at the concentrations of 0.02 and 0.10 mg/mL (Figs. S7c, S7d and Table S4), respectively. It is well known that a Zeta-potential value either more negative or positive than ±30 mV is sufficient to ensure good dispersion stability via charge repulsion.

**Discussion**

Having assured the structure and solubility of NGnPs, we further investigated their applications as electrode materials for energy conversion in dye-sensitized solar cells (DSSCs) and fuel cells (FCs). To start with, we performed density functional calculations, using the Vienna *Ab initio* Simulation Package (VASP)²⁷,²⁸, to analyze the stability and electronic structure of the nitrogenated edges. The plane-wave basis set with an energy cut-off of 400 eV, and the PBE-type gradient-corrected exchange-correlation potential were employed²⁹. The passivation of the active carboradicals with the uncleaved N₂ resulted in 5-membered pyrazole (Fig. 3a) and 6-membered pyridazine (Fig. 3c) rings at the zigzag- and armchair-shaped broken edges, respectively. As shown in Figs. 3b and 3d, the lone-pair states of nitrogen in-plane orbitals constituted the distinctive edge-localized bands just below the Fermi level. More remarkably, however, the π states of graphene are well preserved including the nitrogen pₓ-orbitals in the conjugated networks. These unique edge-localized band structures, in conjunction with the undamaged basal plane of NGnPs, can lead to advantageous catalysts that surpass the performance of Pt for DSSC and FC applications described below.

For construction of DSSCs, a uniform NGnP film on fluorine (F)-doped tin oxide (SnO₂, FTO)/glass was deposited by an electrostatic spray (e-spray) deposition technique from an NGnP dispersion in 2-propanol (Fig. S8a). SEM images of the bare FTO (Fig. S8b) and NGnP deposited FTO (NGnP-FTO) (Fig. S8c) exhibit different surface morphologies. DSSC with O-alkylated-JK-225-sensitizer³⁰ and HC-A as a coadsorbent was fabricated using the resultant NGnP-FTO as a counter electrode (CE). For comparison purpose, DSSC with Pt-FTO CE was also fabricated. As judged by the peak-to-peak separations (Eₓₓ) and current densities, the cyclic voltammograms (CV) of NGnP-FTO electrode for the Co(bpy)₃³⁺/²⁺ redox couple showed very similar curve shape with apparently much higher

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**Figure 3** | The NGnP with edge 5-membered pyrazole rings. (a) the model structure; (b) the PDOS for N atoms. The NGnP with edge 6-membered pyridazine rings: (c) the model structure; (d) the PDOS for N atoms. The isosurfaces of the squared Kohn-Sham orbitals of edge-localized states are shown in the insets.

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electrocatalytic activity than that of the Pt-FTO electrode (Fig. S9a). In addition, the oxidation peak of NGnP-FTO CE located at less positive potential than that of the Pt-FTO CE electrode, implying better electrocatalytic performance for the former. The higher current density observed for the NGnP-FTO CE with respect to the Pt-FTO CE could be attributed to an efficient charge transfer resulted from the sufficient nitrogen doping (~15% by EA, see Table S2).

On the basis of promising CV results (Fig. S9a), the electrocatalytic activities of the sample electrodes were further examined by electrochemical impedance spectroscopy (EIS) using symmetrical dummy cells (Fig. S9b)[2]. The EIS results could be fitted by using a Randles-type circuit (Fig. 4a), where $R_s$ is the Ohmic serial resistance, $R_{CT}$ is the charge transfer resistance at the interface between the electrode surface and the electrolyte, $Z_W$ is the Nernst diffusion impedance in the bulk electrolyte solution between the two identical electrodes, and CPE is a constant phase element describing the deviation from the ideal capacitance due to the surface roughness of the electrodes[2]. As seen in Fig. 4b, both impedance spectra of NGnP and Pt exhibited two distinct semicircles, while semicircles in between them at low frequency regions are no significant difference, e.g., diffusion coefficients of Co(bpy)$_3^{3+}$ in the NGnP- and Pt-FTO dummy cells were almost similar values, which were found to be $4.5 \times 10^{-8}$ and $3.2 \times 10^{-9}$ cm$^2$/s, respectively, and other EIS parameters were summarized in Table S5. The result implies that ionic diffusion in the bulk electrolyte solution is independent of the electrodes (i.e., this parameter is invariant with the electrocatalytic activities of the electrodes). However, the $R_{CT}$ of the NGnP-FTO is lower than that of the Pt-FTO. The result provides strong evidence that the intrinsic catalytic activity of the NGnP-FTO is much higher than that of the Pt-FTO.

On the basis of the in-depth evaluation of the NGnP CE described in Fig. S9 and corresponding explanation, we further investigated the photocatalytic activities of the NGnP electrodes as the CE in actual devices in Co(bpy)$_3^-$-mediated solar cells. The NGnP-based DSSC outperformed its Pt counterpart (Fig. 4c and Table S6). The Pt-based DSSC exhibited a short circuit current ($J_{sc}$) of 14.113 mA/cm$^2$, open circuit voltage ($V_{oc}$) of 886 mV, fill factor (FF) of 70.8%, and an overall power conversion efficiency (PCE) of 8.85%. The DSSC with the NGnP-based DSSC showed an even higher $V_{oc}$ of 890 mV, FF of 74.1% and PCE of 9.34%, but a similar $J_{sc}$ of 14.162 mA/cm$^2$. On the basis of the EIS measurements (Fig. S10a) and curve fittings with an equivalent circuit (Fig. S10b), the $R_{CT}$ value of the DSSC with the NGnP-FTO CE is much lower than that of Pt-FTO CE (Table S7), and it might allow for an increase in FF of DSSC. Clearly, therefore, the NGnP CE with a higher electrocatalytic activity, less $R_{CT}$ and better stability outperformed the Pt CE in DSSCs.

To investigate the electrocatalytic activity of NGnP for oxygen reduction in fuel cells (FCs), we further measured the reduction capability of the NGnPs on glassy carbon (GC) in N$_2$- and O$_2$-saturated alkaline electrolytes (0.1 M aq. KOH solution). The pristine graphite and commercially available Pt/C (Vulcan XC-72R) with the same mass loadings on GC were also measured as references. While the NGnP/GC electrode showed featureless CV in the N$_2$-saturated 0.1 M aq. KOH solution (Fig. 4d), it exhibited an obvious oxygen reduction peak in the corresponding O$_2$-saturated electrolyte (Fig. 4e). The pristine graphite showed a single cathodic reduction peak at $-0.43$ V with a current density of $-0.19$ mA cm$^{-2}$ in the O$_2$-saturated 0.1 M aq. KOH solution. The corresponding cathodic reduction peak for the NGnP was positively shifted to $-0.28$ V with a current density of $-0.54$ mA cm$^{-2}$. The Pt/C exhibited a single peak at $-0.43$ V with a current density of $-0.19$ mA cm$^{-2}$.

**Figure 4** | (a) Equivalent circuit diagram for fitting the EIS data. (b) Nyquist plots of EIS spectra measured at 0 V from 10$^6$ Hz to 0.1 Hz on dummy cells of Pt and NGnP, and solid lines are fitted curves. (c) Current-voltage characteristics of DSSCs with the Pt-FTO and NGnP-FTO CEs under simulated AM 1.5 light. The TiO$_2$ film thickness and active area are 9(6 + 3) μm and 0.16 cm$^2$ with a black metal mask, respectively. Cyclic voltammograms (CV) of samples on glassy carbon (GC) electrodes with a scan rate of 0.01 V/s: (d) in N$_2$-saturated 0.1 M aq. KOH solution; (e) in O$_2$-saturated 0.1 M aq. KOH solution. Sky blue arrows indicate the contributions of hydrogen evolution at around $-0.7$ V and out of Pt limiting potential ($-0.8$ V).
cathodic reduction peak at $-0.10 \text{ V}$ with a current density of $-0.52 \text{ mA cm}^{-2}$. The current density from NGnP is over 2.8 times that of the pristine graphite and comparable to that of Pt/C. Furthermore, the NGnP electrode has high capacitances of 126.6 and 161.3 $\text{F g}^{-1}$ with superb cycle stabilities in both $N_2$- and $O_2$-saturated electrolytes, respectively (Figs. S11-S14 and Table S8), which can be attributed to the relatively high BET surface area (Table S1) and structural stability of NGnPs (see Fig. S5c).

To gain further study the kinetics of the NGnP-catalyzed ORR process, the rotating disk electrode (RDE) measurements were performed in an $O_2$-saturated, 0.1 M aq. KOH solution at various rotating speeds and a constant scan rate of 0.1 $\text{V s}^{-1}$. As shown in Figs. S14a-14c, the diffusion current densities increased with increasing the rotating rates, while the onset potentials remained almost constant. The number of electron transfers ($n$) per $O_2$ molecule involved in the ORR process can be calculated from the slope of the Koutecky-Levich equation (see Experimental section in ESI) (Figs. S14d-14f). As summarized in Fig. S15 and Table S9, while the number of transferred electrons for the pristine graphite is close to the classical two-electron process ($n \approx 2$), the ORR processes at the NGnP and Pt electrodes are an ideal four-electron process ($n \approx 4.0$). Therefore, the edge-nitrogenation played an important role to significantly improve the ORR performance of NGnPs (Table S10).

In summary, we have developed a simple and eco-friendly ball-milling process to efficiently exfoliate the pristine graphite directly into edge-nitrogenated graphene nanoplatelets (NGnPs). A plausible reaction mechanism for the direct nitrogen fixation (C-N bond formation) by ball-milling process in the presence of nitrogen was proposed and confirmed by various microscopic and spectroscopic measurements. The resultant NGnPs were demonstrated to be highly dispersible in various polar solvents suitable for solar fuel processes. The solution-cast NGnP electrodes exhibited superior catalytic properties towards DSSCs and FCs with respect to the precious Pt counterparts. Hence, direct nitrogen fixation developed in this study using ball-milling technique could be regarded as a general approach toward low-cost, mass production of NGnPs for multifunctional materials and devices applications.

**Methods**

**Preparation of NGnPs.** NGnPs were prepared by ball-milling the pristine graphite flake in a planetary ball-mill machine (Pulverisette 6, Fritsch) in the presence of nitrogen ($N_2$). The pristine graphite (3.0 g, Alfa Aesar, natural graphite, 100 mesh ($< 150 \mu \text{m}$), 99.9995% metals basis, Lot#J4735) was placed into a stainless steel ball-mill capsule (500 mL) containing stainless steel balls (500 g, diameter 5 mm). The capsule was sealed and charged with $N_2$ (8 bar of cylinder pressure) after five charging-discharging cycles and then it was fixed in the planetary ball-mill machine and agitated at 500 rpm for 48 h. The resultant product was Soxhlet extracted with methanol and 1 M aq. HCl solution to get rid of metallic impurities, if any. Further repeated treatments with ethylenediaminetetraacetic acid (EDTA), concentrated ammonium hydroxide (NH$_4$OH) and 1 M aq. HCl solution were carried until there is no metallic residue detected by XPS. Final product was freeze-dried at $-120 \text{ C}$ under a reduced pressure (0.05 mmHg) for 48 h to yield 5.67 g (at least 0.87 g $N_2$ uptake) of dark black powder, implying the occurrence of nitrogen-fixation to the ball milled graphite.

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