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Selective Nitrogen Doping Graphene Oxide by Laser Irradiation for Enhanced Hydrogen Evolution Activity

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Selective nitrogen-doping graphene oxide with high pyridinic N ratio (51%; L-GO) was achieved by laser irradiation of graphene oxide with ammonia. The resulting L-GO exhibited the enhanced electrocatalytic properties, specifically, the overpotential of hydrogen evolution reaction (HER) was improved over 400 mV at 10 mA/cm^2 compared to the pristine graphene oxide.

Graphene or graphene oxide has attracted a lot of interest due to the unique physical and chemical properties, such as large surface area, excellent electrical conductivity, and ease of functionalization.[1, 2] Doping of graphene (oxide) with heteroatoms, such as nitrogen (N), boron (B), phosphorus (P), fluorine (F), or sulphur (S), influences the charge distribution of carbon atoms, which is an effective approach to tailor its electronic structure and electrochemical properties.[3-5] For example, in N-doped graphene, the spin density and charge distribution of carbon atoms are influenced by the neighbouring nitrogen dopants, which introduce “activation regions” on the graphene surface.[6] Many interesting properties arising from these “activation regions” have been found in N-doped graphene. It has been recognized that N-doped graphene is a potential candidate for various applications, such as electrocatalysts[3, 7], biosensors[8], field effect transistors[9], Li-batteries[10, 11] and ultracapacitors[12]. Nitrogen doped graphene has also been used as substrate materials for electrocatalysts[13, 14]. It was considered that N-doped graphene as the substrates contribute to the improved hydrogen evolution reaction (HER) performance due to the interactions between the metal catalysts and the active sites on the substrate[13, 14].

Nitrogen atoms can be incorporated into the graphene carbon lattice in three predominant bonding types, namely, graphitic N, pyridinic N, and pyrrolic N (Fig. 1a).[6, 15] It has been reported that both graphitic N and pyridinic N facilitate the oxygen reduction reaction (ORR) activities.[15, 16] Theoretical calculations demonstrated that pyridinic N in N-doped graphene can increase the absorption of H*, thus improving the catalytic HER performance.[17] However, achieving selective pyridinic N is still challenging and most processes require multistep, high temperature or prolonged reaction time.

Here, we report a one-step facile synthesis of N-doped graphene oxide with abundant pyridinic N dopants. Laser irradiation is an effective approach to introduce foreign atoms and functional groups into the materials[18, 19]. Previously, we employed laser irradiation to create dangling bonds in graphene oxide and introduced C-N bonds subsequently by solvothermal reaction.[20] In this work, we prepared N-doped graphene oxides by laser irradiation of a solution containing ammonia and graphene oxide, and achieved high pyridinic N ratio (51%). We show that such N-doped graphene oxide with a high pyridinic N ratio, for use as an electrode material for HER, displays an improved HER performance. The overpotential at 10 mA/cm^2 was reduced by over 400 mV compared with the pristine graphene oxide (GO). Our studies support that pyridinic N are the potential active sites for the catalytic HER properties. The findings contribute to the fundamental understanding of N-doped graphene oxide as the catalytic material or as the substrate material for HER or other electrochemical activities.

As illustrated in Fig. 1b, a pulsed Q-switch Nd: YAG nanosecond laser (energy per pulse = 225 mJ, wavelength = 1064 nm, pulse duration = 7 ns) was used to irradiate ammonia solution that contained graphene oxide with the concentration of graphene oxide 0.2 mg·mL^{-1} and ammonia ~15.9 mol·L^{-1}. The solution in a quartz tube was immersed in ice water mixture with vigorously stirring. The graphene oxide (Fig. 1c) reacted with ammonia (between Fig. 1c and Fig. 1d), producing the

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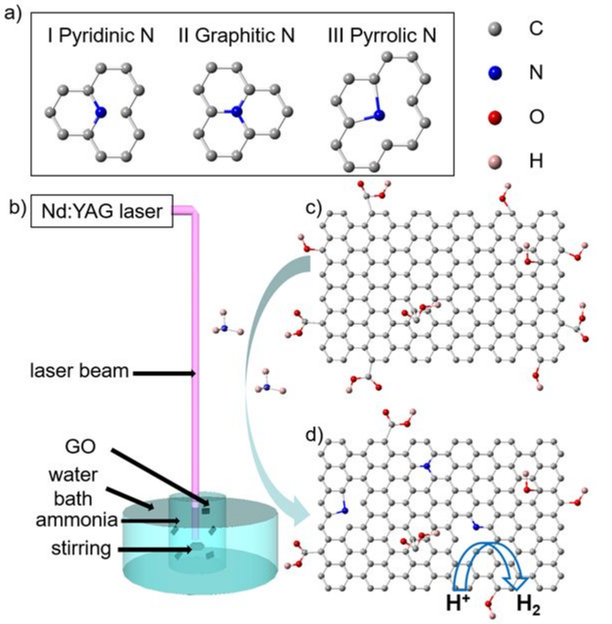

Fig. 1. An illustration of the preparation of nitrogen doping graphene oxide by laser irradiating a solution containing graphene oxide with ammonia. (a) Three types of bonding configurations for N in graphene (oxide). (b) A schematic view of the experimental set up. (c) The structure model of graphene oxide (GO). (d) The structure model of nitrogen doped GO after laser irradiation (L-GO).

nitrogen doped material (Fig. 1d). The laser parameters were varied to optimize the N-doping and catalytic properties (see details in SI).

A scanning transmission electron microscope (STEM) image of laser treated graphene oxide (L-GO) and the corresponding electron energy dispersive spectroscopy (EDS) mappings show the uniform distribution of carbon, oxide and nitrogen within the 2D nanosheets (Fig. 2). The EDS quantification gives the atomic percentage of 60.7%, 36.02% and 3.28% corresponding to carbon, oxygen and nitrogen, respectively. The electron energy loss spectroscopy (EELS) provides more detailed information on the doped nitrogen (Fig. 2f). The pre-peak near 401 eV is associated to π* bonding and the feature over 410eV corresponds to σ* bonding of N.[21, 22] From these measurements, we conclude that nitrogen has been introduced into graphene oxide through laser irradiation of the solution of graphene oxide with ammonia.

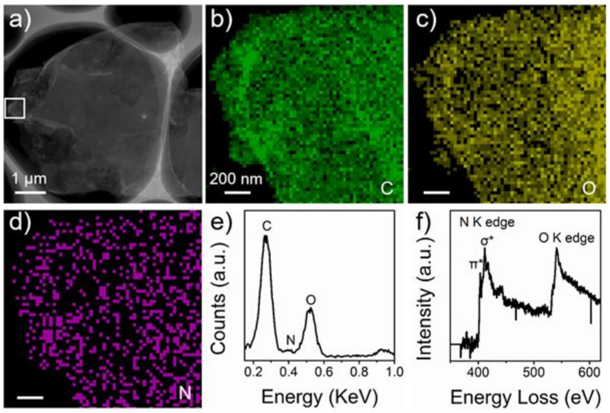

Fig. 2. TEM characterizations of the N-doped graphene oxide by laser irradiation (L-GO). (a) STEM image, and the corresponding EDS maps of (b) C, (c) O and (d) N for the selected area in (a), (e) EDS spectrum, (f) EELS spectrum.

The X-ray photoelectron spectroscopy (XPS) and X-ray absorption spectroscopy (XAS) measurements were further performed to elucidate the bonding states of carbon and nitrogen in L-GO. The XPS survey clearly shows the existence of doped-N in L-GO. The total N doping level in L-GO is about 3.57 at.% (table S1), which is consistent with the estimated value from EDS. High resolution XPS spectra of N 1s and C 1s are further obtained to gain more insights into the atomic sites and bonding types of N in L-GO (Fig. 3b and 3c). Based on the characteristics of the N peak, the doped-N sites in L-GO marked as N1, N2, N3 are composed of pyridinic, pyrrolic-nitrilic and graphitic with the peaks locating at 398.5 eV, 399.7 eV and 401.2 eV, respectively.[23] The calculated ratio of each of these nitrogen ratios is 51% for pyridinic N, 30% for pyrrolic-nitrilic commixture N and 19 % for graphitic N (see Table 1). The pyridinic N ratio (51%) in L-GO is considerably high. The C 1s XPS spectra of L-GO and pristine GO ranging from 280 to 290 eV are measured, as shown in Fig. 3c. The peaks marked with C1, C2 and C3 are related to C-C, C-OH and COOH, respectively. After nitrogen doping, the C2 (C-OH) peak was dramatically weakened, whereas two new peaks at 285.7 and 287.0 eV appeared, which correspond respectively to the N-sp^2 C and N-C=O.[16]

Figure 3d shows XAS spectra measured in total electron yield (TEY) mode at nitrogen K edge for GO and L-GO. The N K edge XAS spectrum of L-GO shows sharp peaks around 400 eV, which are marked as N1, N2 and π* corresponding to the pyridinic N, pyrrolic-nitrilic N and graphitic N. They are in good

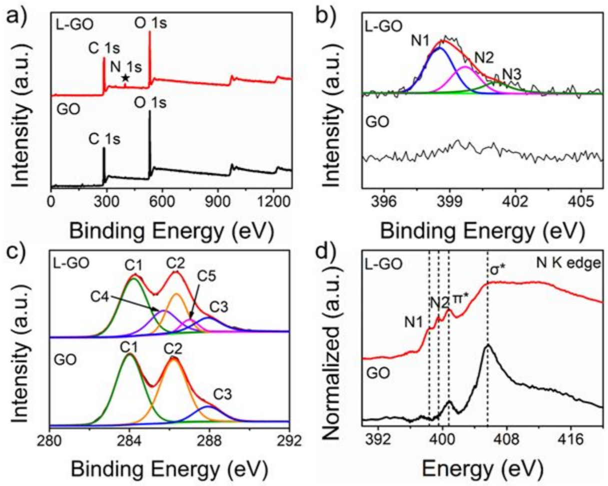

Fig. 3. XPS and XAS measurements of pristine GO and N-doped graphene oxide by laser irradiation (L-GO). (a) XPS survey spectra. (b) XPS spectra showing N 1s features. (c) XPS spectra showing C 1s features. (d) XAS spectra showing N K peaks.

Table 1. The ratios (%) of different types of doped nitrogen in L-GO and H-GO from the XPS measurements

Sample	Pyridinic N	Pyrrolic-Nitrilic N	Graphitic N
L-GO	51	30	19
H-GO	28	51	21

agreement with the results obtained from XPS. In the XAS spectrum of pristine GO, there is no distinct N 1s peaks as expected. The peaks in C K edge XAS of the pristine GO and L-GO (Fig. S2) are similar, which is consistent with the low concentration of the nitrogen doping in graphene oxide.[24] There is an increase of the intensity of π^* peak and a decrease of σ peak for L-GO compared with the pristine GO, indicating the π network is dominant.[25]

In order to identify the role of pyridinic N in the electrocatalytic hydrogen evolution reaction (HER) performance, we compare the HER properties of L-GO with N-doped graphene oxide by using hydrothermal reaction method (H-GO). The solution of graphene oxide with ammonia was heated under 150 ℃ using a stainless-steel autoclave. It is noted that it takes 12 hours to achieve the N-doped graphene oxide in contrast to 20 mins using the laser irradiation method. The total N-doping level in H-GO is about 5.31 at.% (Fig. S4 and Table S1), however, the ratio of pyridinic N is much lower (28 %) compared to L-GO (Table 1 and Fig. S5). The electrochemical measurements were performed using a three-electrode system. The working electrode is glassy carbon (GC), and the geometric area of the (GC) is about 7.065 mm^2. 0.015 mg catalyst was fully covered on the GC. The details are included in SI. The electrochemical HER performance of N-doped L-GO, N-doped H-GO and the pristine GO is shown in Fig. 4. Remarkably, there is a significant improvement of the electrochemical property for L-GO prepared under the laser energy of 225 mJ per pulse, the overpotential at the current density of 10 $mA \cdot cm^{-2}$ is more than 400 mV and 80 mV lower than those of the pristine GO and H-GO, respectively. We also find that H-GO has a slightly lower Tafel slope than the L-GO (100.56 mV/dec vs 133.81 mV/dec), which may result from the lower oxygen content and higher electron transfer in H-GO.

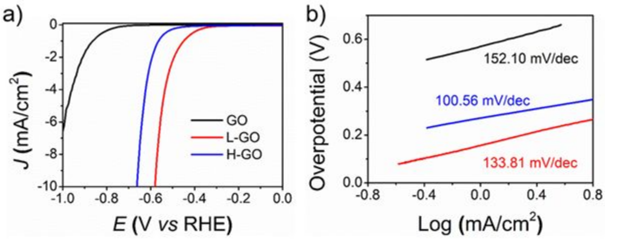

Fig. 4. HER measurements. (a) The linear sweep voltammetry (LSV) of the pristine GO, N-doped graphene oxide by laser irradiation (L-GO) and N-doped graphene oxide by hydrothermal method (H-GO) measured in N_2-saturated 0.5 M H_2SO_4. (b) Tafel slope of the pristine GO, L-GO and H-GO with the plot colour corresponding to those in (a).

It is interesting that H-GO has a higher nitrogen doping level than L-GO, but L-GO has better electrochemical HER performance in terms of the overpotential. We consider that the improved HER properties of L-GO arise from the higher pyridinic N ratio. Other factors, such as defects may also play a role, on which further quantification is needed to draw any conclusion.

Lastly, we have also done systematic study with different laser energy and with different kinds of nitrogen sources (Fig. S1 and S6). The electrochemical performance of these samples obtained from different experimental conditions suggests good controllability and reproducibility of the laser N doping methods.

In summary, nitrogen has been successfully doped into graphene oxide by laser irradiation of the solution of graphene oxide with ammonia under the optimized laser conditions. The N-doped graphene oxide obtained by the laser irradiation method shows a higher pyridinic N ratio than that prepared by the hydrothermal method. Compared to the hydrothermal method, the laser irradiation is a simple and fast approach to prepare N-doped graphene oxide. The N-doped graphene oxide shows the improved electrochemical HER performance, which can be attributed to the high pyridinic N ratio.

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Conflicts of interest

The authors declare no conflict interests.

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