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# Supporting Information

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

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## Methods

## Nitrogen doping graphene oxide by laser irradiation (L-GO)

All chemicals, including graphene oxide and ammonia, were used as received. 3 mg graphene oxide and 15 mL ammonia were mixed and sonicated for 1 h. Then the solution was transferred to a quartz tube for laser irradiation. Laser energies per pulse of 150 mJ, 225 mJ, and 300 mJ were used. After 20 min irradiation, the solution was washed by deionized (DI) water and centrifuged. Then, the solution was dried by a freeze-drying machine.

## Nitrogen doping graphene oxide by hydrothermal method (H-GO)

20 mg graphene oxide was mixed with 30 ml deionized water, 1 ml ammonia and 0.4 ml hydrazine hydrate. The solution was heated at 95 ℃ for 3 h. Then the product solution was cleaned with DI water by centrifugation 3 times. Subsequently, for N doping, the product was mixed with 30 ml of ammonia in a 50 mL Teflon-lined autoclave under 150 ℃ for 12 h. The final products were centrifuged for several times and then dried by a freeze-drying machine.

## Characterizations

X-ray photoelectron spectroscopy (XPS) analysis was performed using a PHI Quantum 2000 scanning ESCA Microprobe spectrometer. The sepctra were analyzed using XPSPEAK 4.1 software. X-ray absorption spectroscopy was conducted using the light source at Stanford SLAC National Accelerator Laboratory. FEI ThemIS TEM was used at 300 kV for the BF TEM images and for the EDS mapping. FEI Tecnai at 200 kV was used for the EELS data.

## Electrochemical measurements

Electrochemical measurements were carried out on a Versastat 3 potentiostat electrochemical workstation with a three-electrode system. The glassy-carbon (GC) (diameter 3 mm) was used as working electrode. A graphite rod and the Ag/AgCl with saturated KCL solution were the counter and reference electrodes, respectively.

The sample solution was made by mixing the 2 mg of the graphene oxide powder products with 300 μL deionized water, 100 μL isopropyl alcohol and 8 μL nafion. Then 3 μL of sample solution was drop cast on the glassy carbon electrode for electrochemical measurements. The electrolyte of 0.5 M $H_2SO_4$ was used. A flow of $N_2$ was maintained over the electrolyte during the experiment to eliminate the dissolved oxygen.

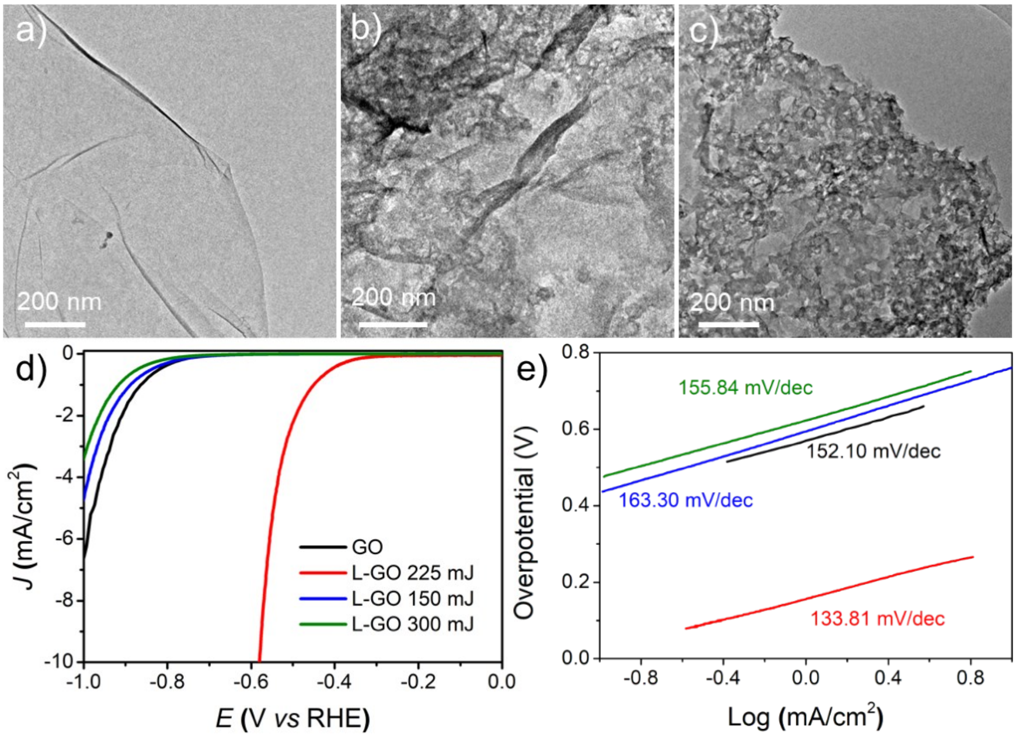

Fig. S1. TEM images, the LSV and Tafel slope of the pristine GO and L-GO prepared under different laser energy per pulse: 150 mJ, 225 mJ and 300 mJ. (a-c) TEM images of L-GO prepared using the laser energy of (a)150 mJ, (b) 225 mJ and (c) 300mJ. (d) LSV plots. (e) Tafel slope. The TEM images show that graphene oxides (GO) treated using different laser energy show structure variations. The L-GO 150 mJ sample is similar as the pristine GO, suggesting N-doping is not effective. For the L-GO 300 mJ sample, the GO has been damaged with too many holes, which could lead to low conductivity. Therefore, the L-GO 225 mJ sample has the optimum structure, which account for the excellent electrochemical performance.

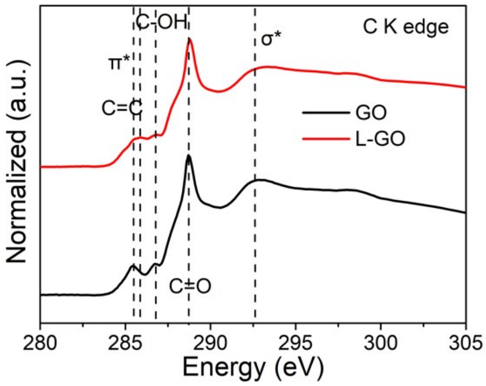

Fig. S2. XAS C K edge of GO and L-GO. The peaks at ~285 eV and ~293 eV correspond to π* and σ* of C=C bond resonances.[1-3] The peak at 286.7 eV can be assigned to π* (C-OH), and the peak at 288.8 eV shows the π*(C=O).[4]

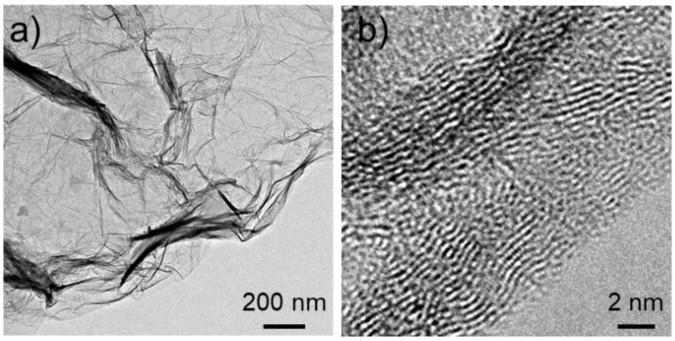

Fig. S3. TEM images of the nitrogen-doped graphene synthesized by the hydrothermal method (H-GO). (a) low magnification TEM image. (b) HRTEM image.

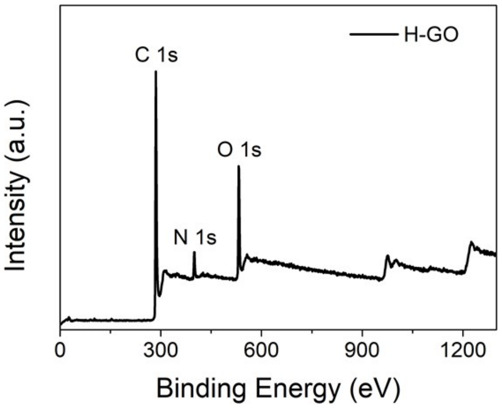

Fig. S4. The XPS survey of nitrogen-doped graphene oxide prepared by hydrothermal method (H-GO).

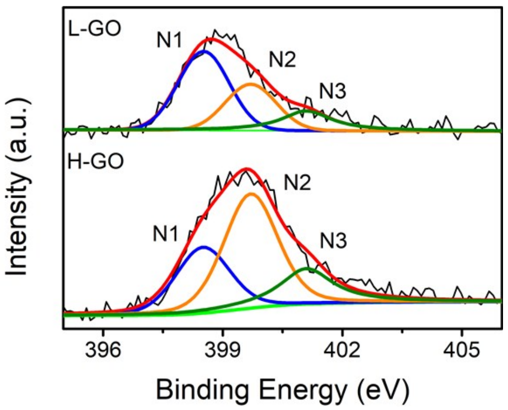

Fig. S5. XPS spectra showing N 1s features of L-GO and H-GO. The peaks marked with N1, N2 and N3 are related to pyridinic, pyrrolic-nitrilic and graphitic N, respectively.

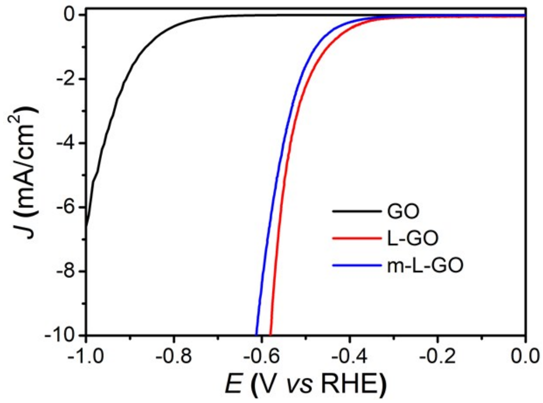

Fig. S6. The linear sweep voltammetry (LSV) of pristine GO, N-doped graphene oxide by laser irradiation under 225 mJ per pulse with different nitrogen source: ammonia (L-GO) and melamine (m-L-GO). The overpotential of m-L-GO is similar with that of the L-GO.

The HER performance was measured in $N_2$-saturated 0.5 M $H_2SO_4$ solution. 3 mg graphene oxide, 15 mL ammonia, and saturated melamine were mixed and sonicated for 1 h (m-L-GO). Then the solution was transferred to a quartz tube for laser irradiation. Laser energy of 225 mJ per pulse was used. After 20 min irradiation, the solution was washed by deionized (DI) water and centrifuged. Then, the solution was dried by a freeze-drying machine.

Table S1. The percentage (at.%) of carbon, nitrogen and oxygen in pristine GO, L-GO and H-GO from XPS measurements.

| Sample | C | N | O |
|---|---|---|---|
| GO | 68.1 | - | 30.62 |
| L-GO | 67.78 | 3.57 | 27.65 |
| H-GO | 77.86 | 5.31 | 16.3 |

Table S2. The nitrogen contents and pyridinic ratio of nitrogen doping graphene in literature.

| Sample | Pyridinic N (%) | N contents (at.%) | Pyridinic N (at.%) | Synthesis | Citation |
|---|---|---|---|---|---|
| NG-650 | 38.58 | 7.67 | 2.96 | sonication | [5] |
| NG-750 | 35.05 | 4.33 | 1.52 |  | [5] |
| HOPG-4 |  | 0.60 | 0.57 |  | [6] |
| HOPG-5 |  | 4.9 | 2.2 |  | [6] |
| HOPG-6 |  | 5.5 | 3.1 |  | [6] |
| HOPG-7 |  | 13 | 3.9 |  | [6] |
| HOPG-8 |  | 11 | 6.5 |  | [6] |
| N-GNS-1 |  | 1.7 | 0.72 |  | [6] |
| N-GNS-2 |  | 2.4 | 1.9 |  | [6] |
| N-GNS-3 |  | 8.1 | 6.3 |  | [6] |
| This paper | 51 | 3.57 | 1.82 | Laser irradiation |  |

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