

Supplementary information:

N-doped Graphene as an Electron Donor of Iron Catalyst for CO Hydrogenation to Light Olefins

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Experimental Section

Catalyst preparation:

N-doped graphene (NG) synthesis. NG was synthesized by a solvothermal method as our previous report.¹ Briefly, 1 g lithium nitride (Alfa Aesar, 99.4%, metals basis) and 20 mL tetrachloromethane reacted at 250 °C for 10 h in a 40 mL stainless steel autoclave in nitrogen, followed by washing with 18 wt.% HCl, water and ethanol, and drying at 120 °C. The obtained product was denoted as NG-4.5. To increase the nitrogen content, 0.3 g or 0.5 g cyanuric chloride was mixed with 2 g lithium nitride and 5 mL tetrachloromethane, and reacted at 350 °C for 6 h, followed by a same post-treatment process with NG-4.5. The obtained products were denoted as NG-8.4 and NG-16.4, respectively.

Fe/NG catalysts were synthesized by an ultrasound-assisted impregnation method

with a load of 8 wt.% Fe. Briefly, 300 mg N-doped graphene was dispersed into a 30 mL solution of ethanol and water with a volume ratio of 1:1 by stirring, then 2.4 ml of ferric nitrate solution (iron concentration: 10 mg/ml) was added dropwise, followed with an ultrasound for 2 h and then stirring until the sample became dry. The final Fe/NG catalyst was obtained after treating the sample at 140 °C for 2 h.

Carbon black Vulcan XC-72 was purchased from Cabot Corporation. XC-N was prepared via heat-treating XC-72 at 800 °C under ammonia for 6 h. The Fe/XC and Fe/XC-N catalysts was prepared by a same process with Fe/NG catalysts.

Characterization:

Inductively coupled plasma optical emission spectrometry (ICP-OES) was conducted on a Perkin-Elmer Optima 7300DV to determine the iron loading (relative standard deviation is around 1% on the final results). Raman spectroscopy of the powder samples was performed on a LabRAM HR 800 Raman spectrometer with a 633 nm excitation laser at a power of around 0.5 mW. Transmission electron microscopy (TEM) was carried out on a FEI Tecnai F30 microscope and a G2 microscope operated at an accelerating voltage of 300 and 120 kV, respectively. X-ray diffraction (XRD) was measured on a Rigaku D/Max 2500 diffractometer with a Cu K α ($\lambda=1.541 \text{ \AA}$) monochromatic radiation source. X-ray photoelectron spectroscopy (XPS) analysis was conducted with an Omicron UHV multiprobe surface analysis system and a VG ESCALAB MK2 spectroscope with Al K α x-rays as the excitation source at 12.5 kV and power of 250 W. The binding energies were calibrated by the contaminant carbon (C1s 284.6 eV). Fe L-edge X-ray absorption spectra (XAS) was carried out at SGM

beamline of Canadian Light Source using a total electron yields (TEY) mode. Fe K-edge X-ray absorption fine structure spectra (XAFS) was carried out at BL14W1 beamline at Shanghai Synchrotron Radiation Facility with a transmission mode.

Catalytic reaction:

The CO hydrogenation reaction was carried in a quartz inner lining fixed-bed reactors at a gas hourly space velocity (GHSV) of 5000 h⁻¹, 0.5 MPa, and the temperature of 320 °C, 340 °C or 360 °C. The feed flow was a mixture of H₂/CO/Ar (47.5/47.5/5, vol. %) and Ar was used as an internal standard. All products of CO hydrogenation were analyzed by an online gas chromatography (Agilent 7890A), which was equipped with a thermal conductivity detector (TCD) and a flame ionization detector (FID). Three chromatography columns were installed, i.e. Porapak Q and 5 Å molecular sieves packed columns, and modified Al₂O₃ capillary columns. The selectivity of hydrocarbons was calculated on a carbon atom basis excluding CO₂, i.e. (moles of product X) × (carbon atoms in product X) / (total carbon atoms in hydrocarbons produced). The total carbon balance is over 95% by using this method.

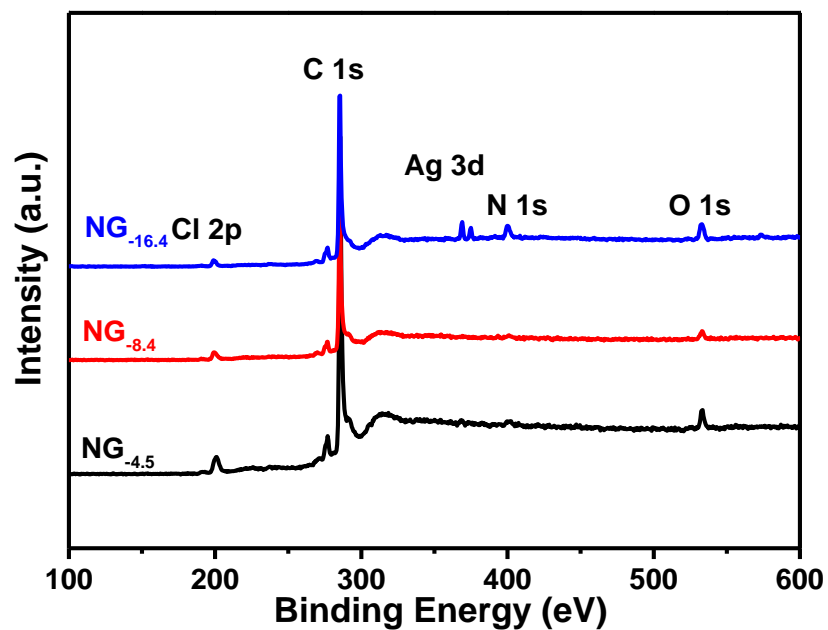


Figure S1. XPS wide spectra of NG_{-4.5}, NG_{-8.4} and NG_{-16.4}. The Ag 3d signals come from the Ag substrate. The XPS spectra of NG_{-4.5} and NG_{-16.4} are cited from the reference 1 in the supplementary information.

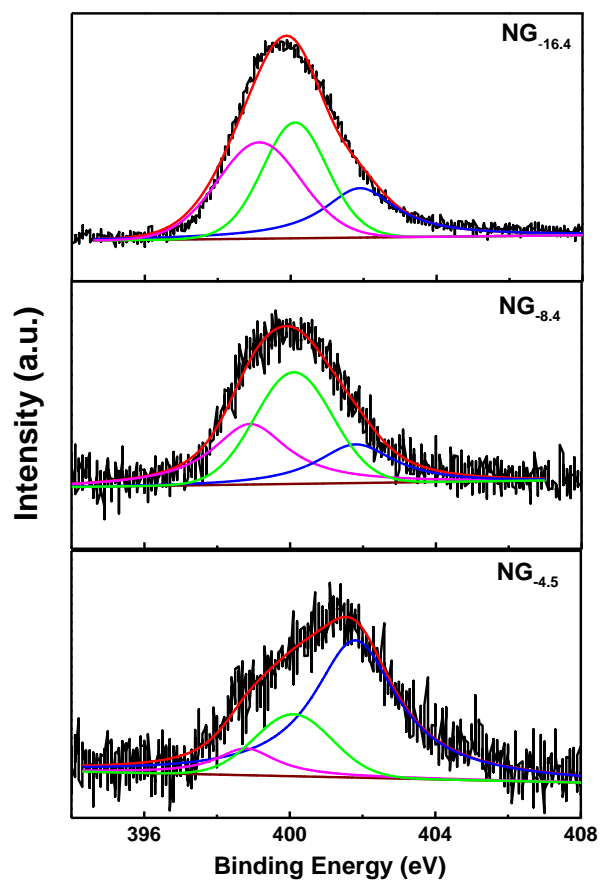


Figure S2. N1s XPS spectra of NG_{-4.5}, NG_{-8.4} and NG_{-16.4}. Fitting these peaks indicating the presence of three types of nitrogen species: pyridinic N (398.9 eV), pyrrolic N (400.1 eV) and graphitic N (401.8 eV). The XPS spectra of NG_{-4.5} and NG_{-16.4} are cited from the reference 1 in the supplementary information.

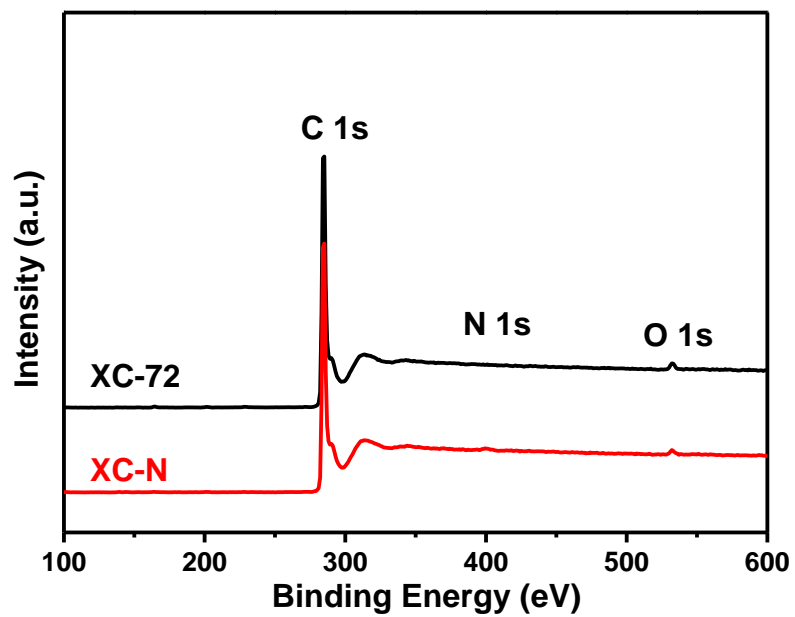


Figure S3. XPS wide spectra of XC-72 and XC-N.

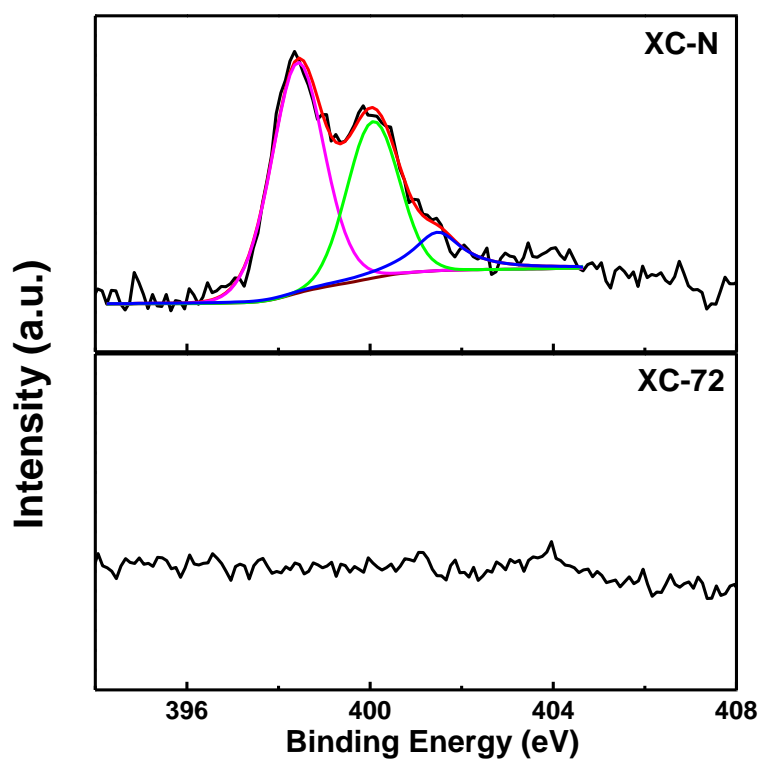


Figure S4. XPS spectra of N1s of XC-72 and XC-N. Fitting the peak of the XC-N sample indicating the presence of three types of nitrogen species: pyridinic N (398.5 eV), pyrrolic N (400.1 eV) and graphitic N (401.5 eV).

Table S1. Composition of NG samples, XC-72 and XC-N estimated by XPS.

Sample ^a	C (at. %)	N (at. %) (Graphitic\Pyridinic\ Pyrrolic N)	O (at. %)	Cl (at. %)	N/C (%)
NG- _{4.5}	89.6	4.0(2.8\0.4\0.8)	3.7	2.7	4.5
NG- _{8.4}	86.1	7.2(1.4\3.3\2.5)	4.0	2.7	8.4
NG- _{16.4}	79.2	13.0(3.3\5.0\4.7)	6.0	1.8	16.4
XC-72	98.7	-	1.2	0.1	-
XC-N	98.2	0.7(0.1\0.2\0.4)	1.0	0.1	0.8

^a The XPS composition of NG-_{4.5} and NG-_{16.4} are cited from the reference 1 in the supplementary information.

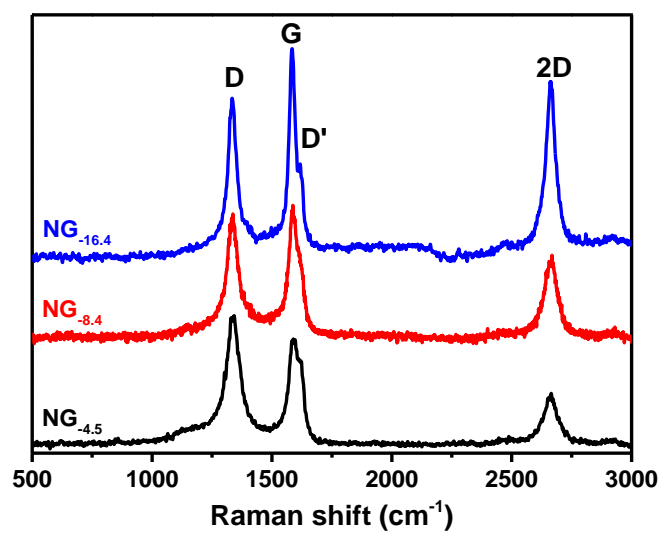


Figure S5. Raman spectra of NG-4.5, NG-8.4 and NG-16.4.

Table S2. The iron loading of different samples tested by ICP-OES.

Sample	Fe/NG-4.5	Fe/NG-8.4	Fe/NG-16.4	Fe/XC	Fe/XC-N
Iron loading (wt.%)	7.97	8.04	7.65	8.53	7.81

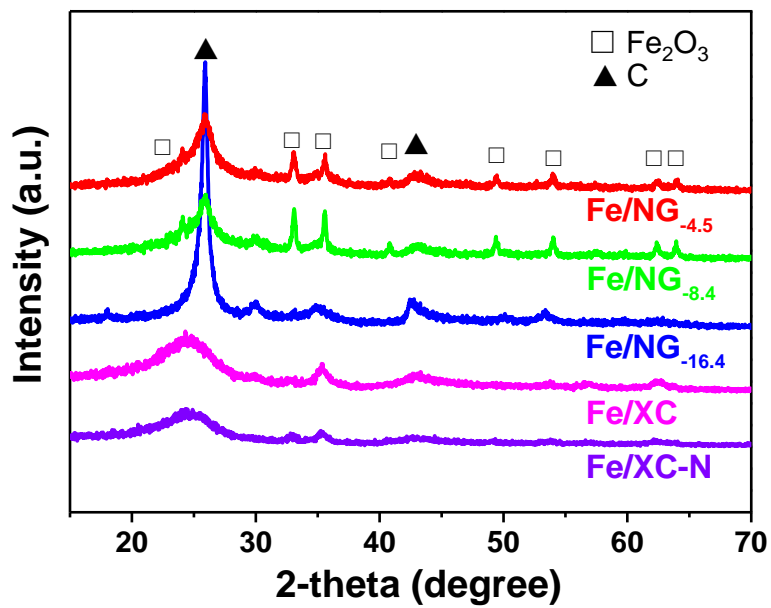


Figure S6. XRD patterns of Fe/NG, Fe/XC and Fe/XC-N samples. The samples were treated at 350 °C in Ar for 1 h before the measurements.

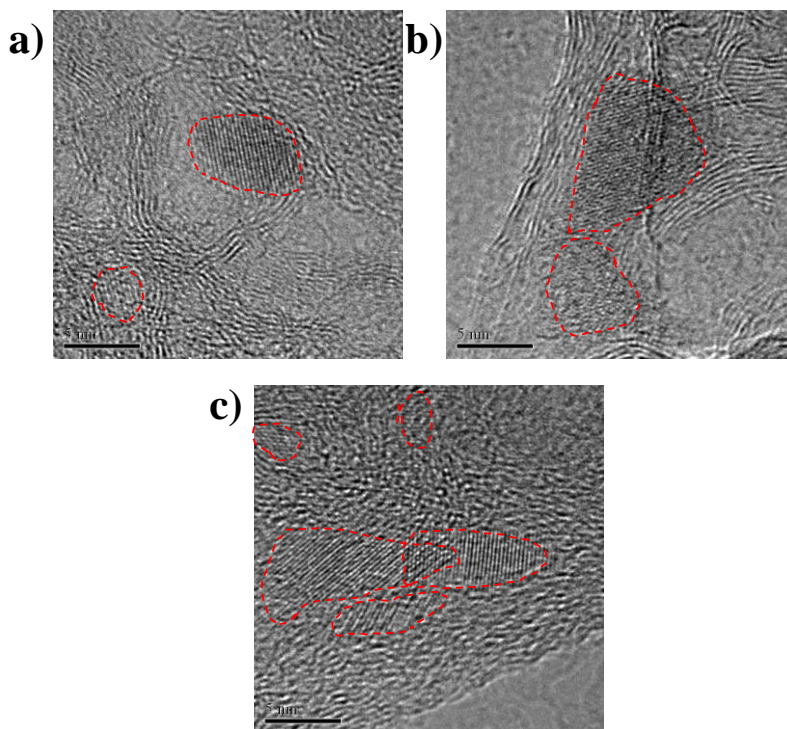


Figure S7. HRTEM images of Fe/NG_{4.5} before reaction. Red dashed cycles show the dispersed Fe₂O₃ nanoparticles. The Fe/NG_{4.5} sample was first treated at 350 °C in Ar for 1 h before TEM measurements.

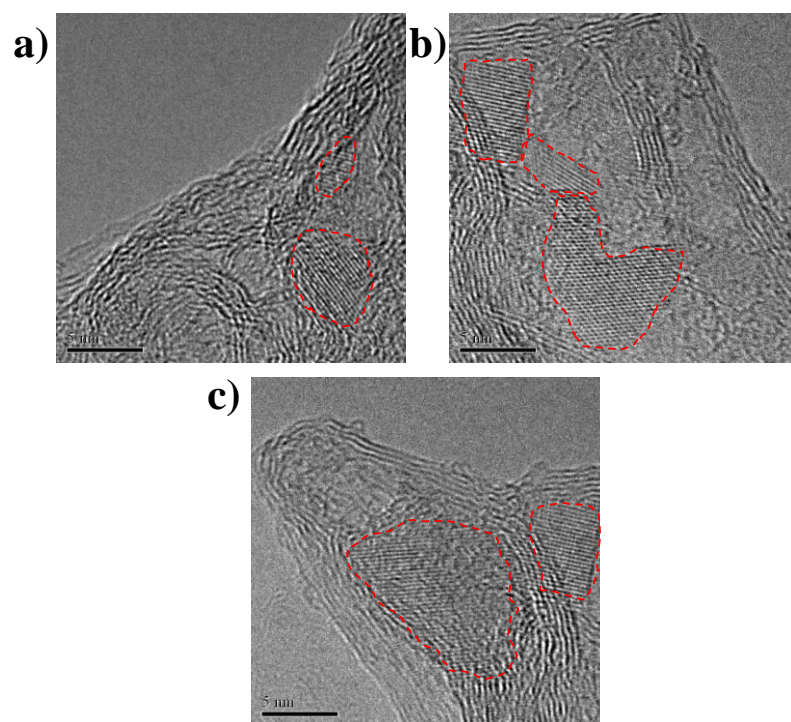


Figure S8. HRTEM images of Fe/NG-_{8.4} before reaction. Red dashed cycles show the dispersed Fe₂O₃ nanoparticles. The Fe/NG-_{8.4} sample was first treated at 350 °C in Ar for 1 h before TEM measurements.

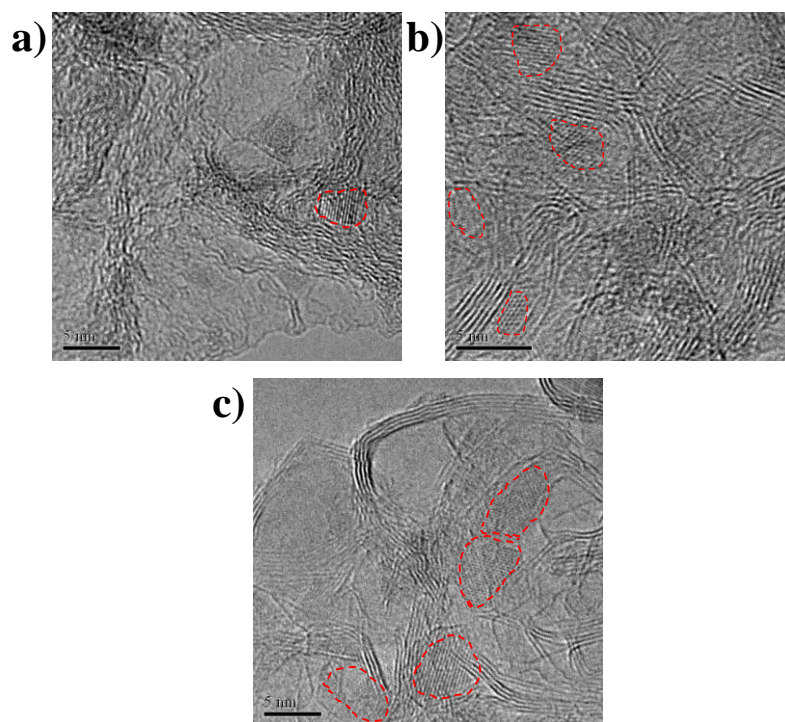


Figure S9. HRTEM images of Fe/NG-_{16.4} before reaction. Red dashed cycles show the dispersed Fe₂O₃ nanoparticles. The Fe/NG-_{16.4} sample was first treated at 350 °C in Ar for 1 h before TEM measurements.

Table S3. The catalytic performance of Fe/NG samples for CO hydrogenation.

Catalysts	Fe/NG-4.5 ^a	Fe/NG-4.5 ^b	Fe/NG-8.4 ^a	Fe/NG-8.4 ^b	Fe/NG-16.4 ^a	Fe/NG-16.4 ^b
CO conversion	0.38	1.3	0.24	2.7	1.1	5.0
CO ₂ selectivity	23.3	27.6	11.9	26.9	13.0	26.8
CH distribution						
CH ₄	13.8	14.2	34.5	23.2	34.0	29.2
C ₂ ⁼ -C ₄ ⁼	47.1	43.4	50.0	41.8	49.8	45.8
(C ₂ ⁼ -C ₄ ⁼)/(C ₂ ⁰ -C ₄ ⁰)	16.5	14.5	7.5	10.0	7.7	4.8
C ₅ ⁺	36.3	39.4	8.9	30.8	9.7	15.5

Reaction condition: 100 mg catalyst, Fe loading = 8 wt.%, GHSV = 5000 h⁻¹, H₂ :

CO = 1:1, 340 °C, ^a P = 0.5 MPa, ^b P = 1.0 MPa.

Table S4. The catalytic performance of Fe/XC and Fe/XC-N for CO hydrogenation.

Catalysts	Fe/XC ^a	Fe/XC ^b	Fe/XC-N ^a	Fe/XC-N ^b
CO conversion	3.2	24.1	2.9	10.3
CO ₂ selectivity	26.0	46.5	36.7	28.8
CH distribution				
CH ₄	31.6	29.2	36.9	30.1
C ₂ ⁼ -C ₄ ⁼	29.0	17.5	35.6	35.9
(C ₂ ⁼ -C ₄ ⁼)/(C ₂ ⁰ -C ₄ ⁰)	0.90	0.39	1.8	2.0
C ₅ ⁺	7.1	8.9	8.0	15.8

Reaction condition: 100 mg catalyst, Fe loading = 8 wt.%, GHSV = 5000 h⁻¹, H₂ :

CO = 1:1. 340 °C, ^a P = 0.5 MPa, ^b P = 1.0 MPa.

Reference:

1. D. Deng, X. Pan, L. Yu, Y. Cui, Y. Jiang, J. Qi, W.-X. Li, Q. Fu, X. Ma, Q. Xue, G. Sun and X. Bao, *Chem. Mater.*, 2011, **23**, 1188-1193.