Supporting Information

N-doped holey graphene assembled on fibrous aluminium silicate for efficient carbocatalysis in fixed-bed system

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KEYWORDS: nitrogen doped holey graphene, assembly, carbocatalysis, fixed-bed system, nitroarene reduction

1. General information

1.1. Materials.

Nano graphite powder(40 nm), sulfuric acid (98%), sodium nitrate, potassium permanganate, hydrochloric acid, ammonium hydroxide (NH_4OH), hydrogen peroxide (H_2O_2), nitrobenzene, 4-chloronitrobenzene, 3-chloronitrobenzene, 3-bromonitrobenzene, 4-bromonitrobenzene, 4-nitroaniline, 4-nitroanisole, 4-nitrophenol (99%), and sodium borohydride (96%) were purchased from Sinopharm Chemical Reagent Co., Ltd. (Shanghai, China). Aluminium silicate fibers (ASFs) were purchased from Xinshenshi Chemicals Co. Ltd. (Wuhan, China). Deionized water (resistivity > 18 $\Omega \cdot cm^{-1}$) was used for all synthesis and experiments.

1.2. Instrumentation

The morphology of the synthesized NHG catalyst was characterized using a TESCAN VEGA3 scanning electron microscope (SEM, Czech). Transmission electron microscopy (TEM) and high-resolution transmission electron microscopy (HRTEM) images were obtained using a TECNAI G2 20 U-Twin instrument (Netherlands) operated at an acceleration voltage of 200 kV. The samples for SEM characterization were prepared by drop-casting the sample suspensions (dispersed in ethanol, 1mg/mL) on pre-cleaned silicon wafers. For TEM, 5 μL of the sample suspensions (dispersed in ethanol, 0.5 mg/mL) were drop-casted on a carbon-coated copper grid. X-ray photoelectron spectroscopy (XPS) was performed with an ESCALAB MKII spectrometer (VG Co., UK), using Mg Kα radiation (1253.6 eV) at a pressure of 2.0×10^{-10} mbar. The peak positions were internally referenced to the C 1s peak at 284.6 eV. Raman spectrum was measured by a confocal laser micro-Raman spectrometer (DXR, USA) equipped with a He–Ne laser of excitation of 532 nm at a laser power of 0.6 mW. Nitrogen adsorption/desorption isotherms were obtained at 77 K on an accelerated surface area and porosimetry system (ASAP 2020, Micromeritics, USA) to measure the surface area of the material using the Brunauer-Emmett-Teller (BET) method. The UV-vis measurements of the synthesized NHG carbocatalyst along with the time-dependent kinetic spectra during catalysis were performed on a UV-2550 spectrophotometer (Shimadzu, Japan). High-performance liquid chromatography (HPLC) analysis was performed on an Agilent-1100 system with a Zorbax Eclipse XDB-C18 4.6×150 mm column (Agilent, USA). The intermediates involved in nitroarenes reduction were analyzed by Gas Chromatography-Mass Spectrometer (GC-MS) (Agilent Technologies 7890A (GC) / Agilent Technologies 5975C (inert XL MSD with Triple-Axis Detector, USA)

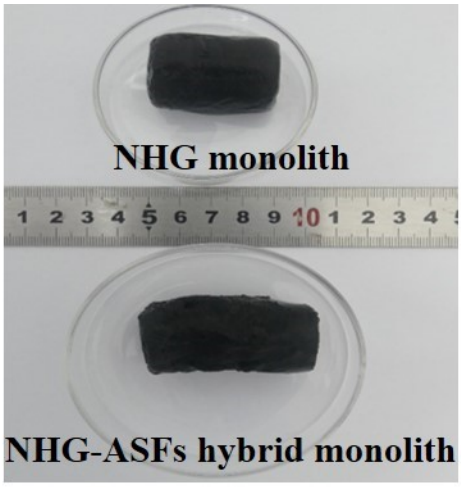


Fig. S1. Photograph of NHG monolith hydrogel and hybrid NHG-ASFs monolith hydrogel.

Fig. S2. Photograph of fixed-bed system based on NHG monolith hydrogel.

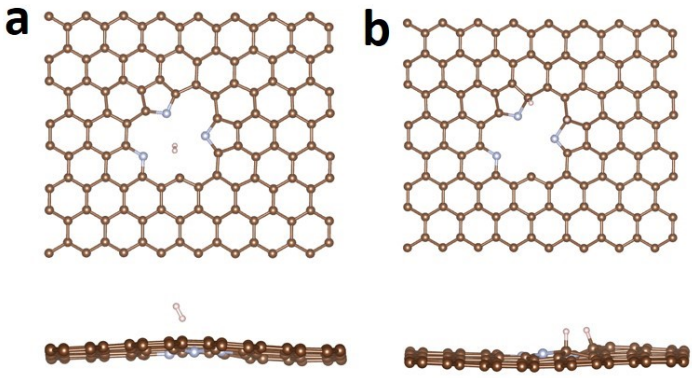


Fig. S3 DFT models of the hydrogen capture and activation on NHG catalyst

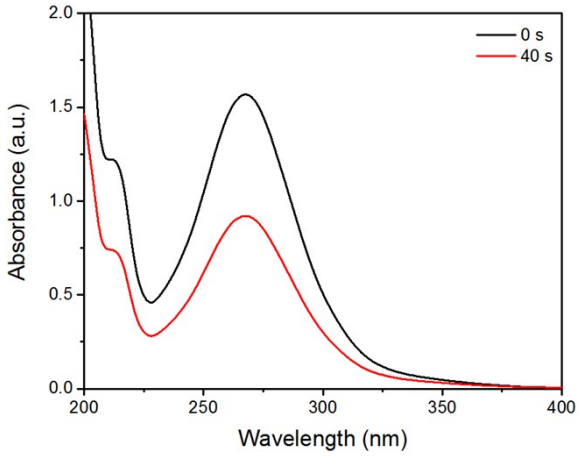


Fig. S4 (a) UV/Vis spectra of the nitrobenzene control solution (black), and nitrobenzene solution after flow through fixed-bed system (red). Both the nitrobenzene control solution and exiting nitrobenzene solution were diluted from 3 mM to 0.2 mM for UV/Vis analysis.

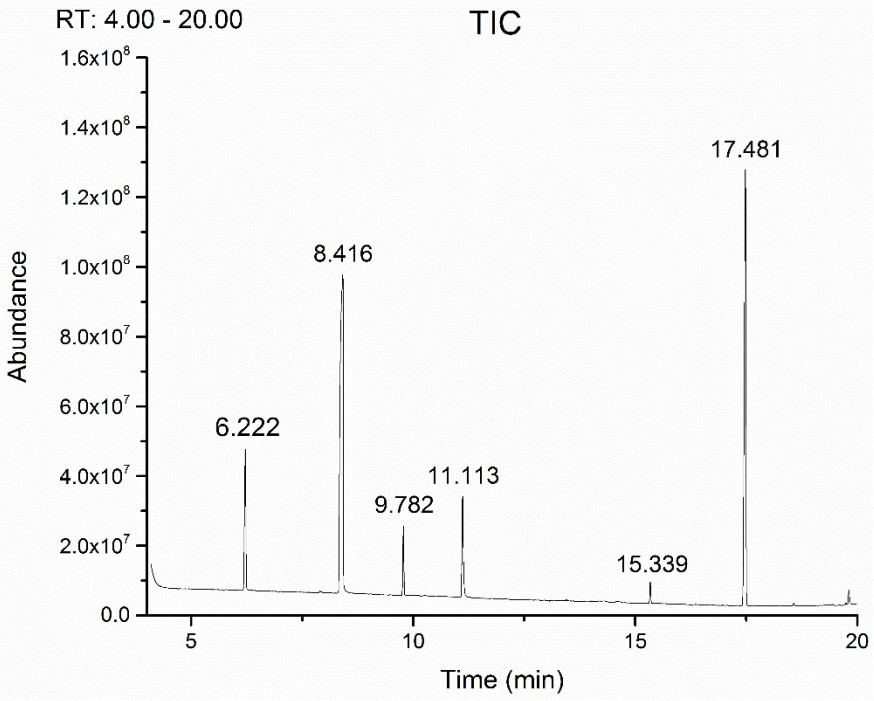


Fig. S5. GC-MS analysis. Total ion chromatograph (TIC) for the reaction mixture of 4-chloronitrobenzene reduction.

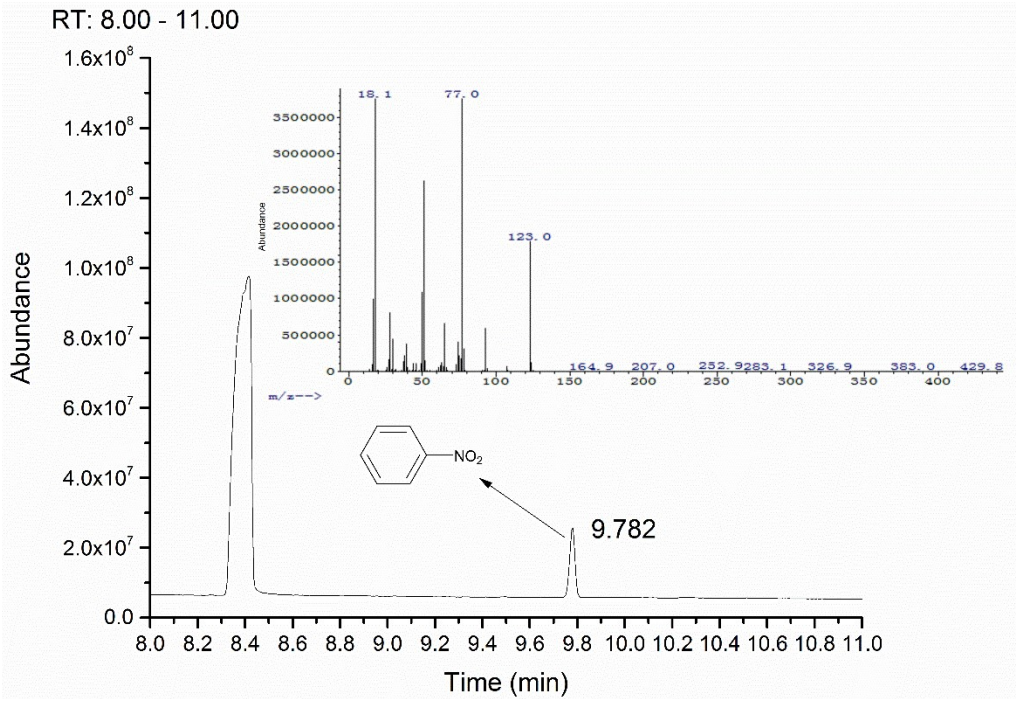


Fig. S6. GC-MS spectrum of the substrate (nitrobenzene).

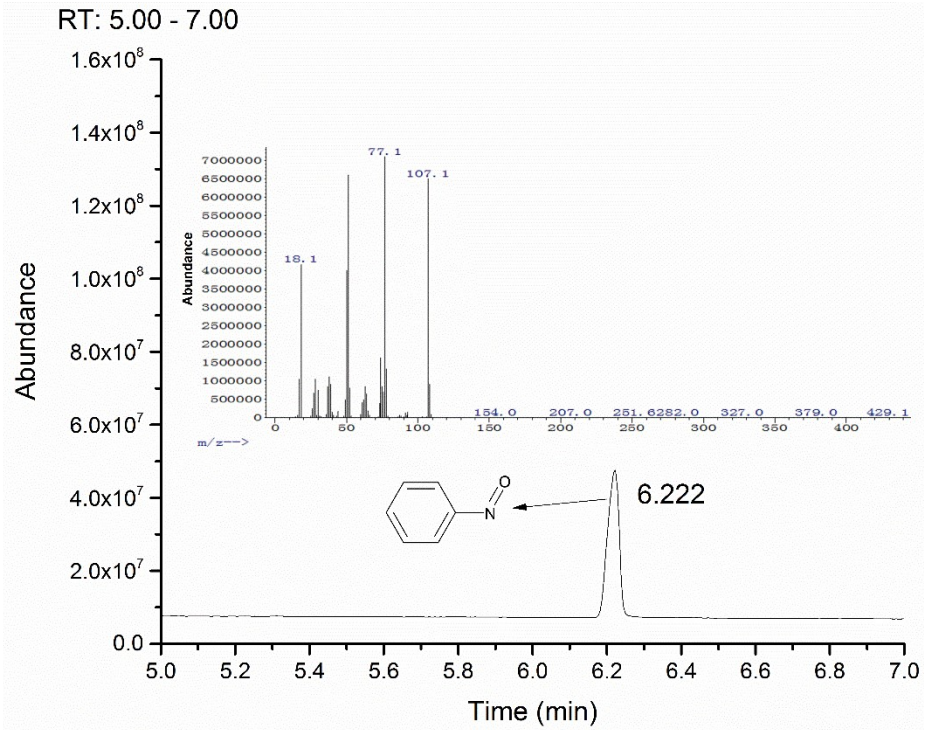


Fig. S7. GC-MS spectrum of the intermediate (nitrosobenzene) of nitrobenzene reduction reaction.

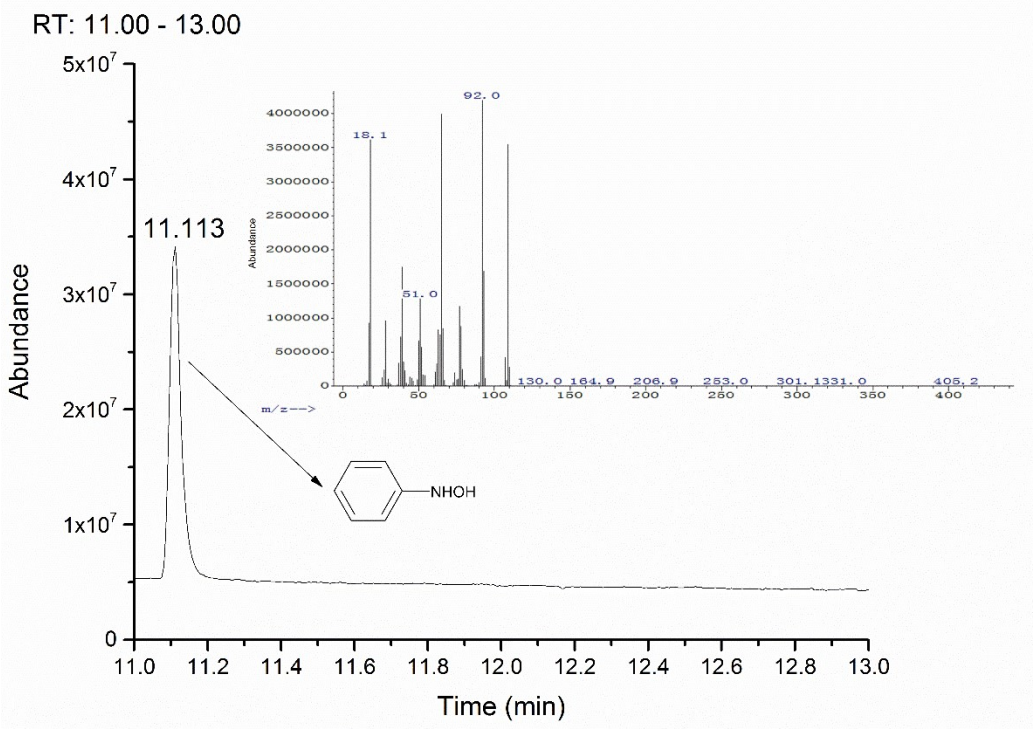


Fig. S8. GC-MS spectrum of the intermediate (hydroxyaniline) of nitrobenzene reduction reaction.

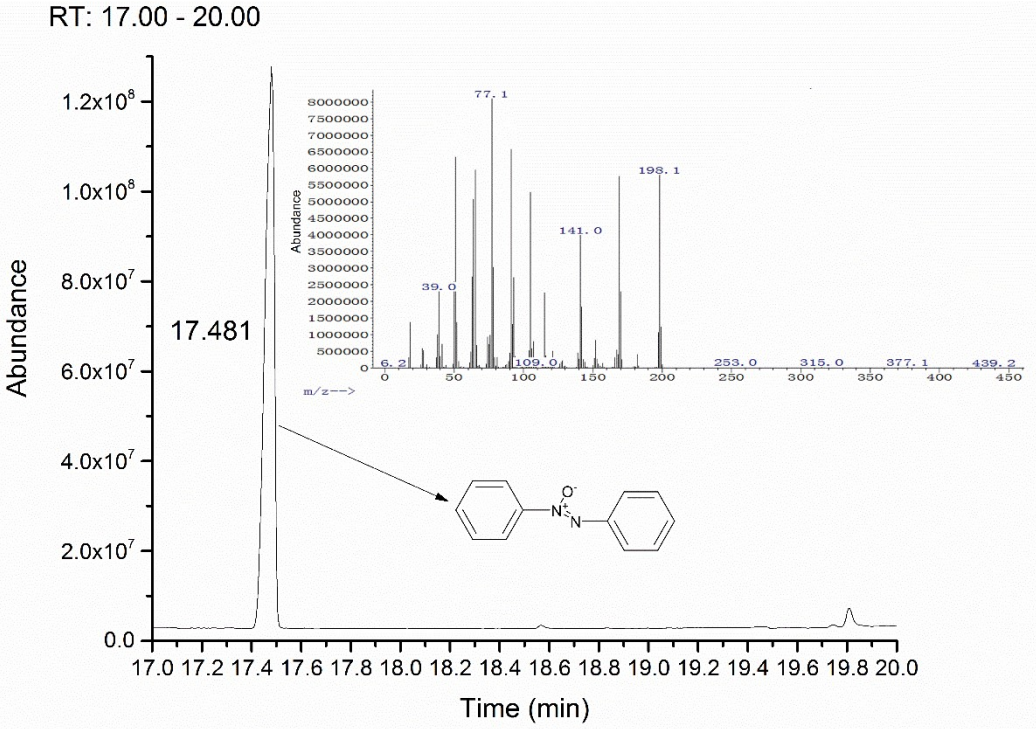


Fig. S9. GC-MS spectrum of the intermediate (azoxybenzene) of nitrobenzene reduction reaction.

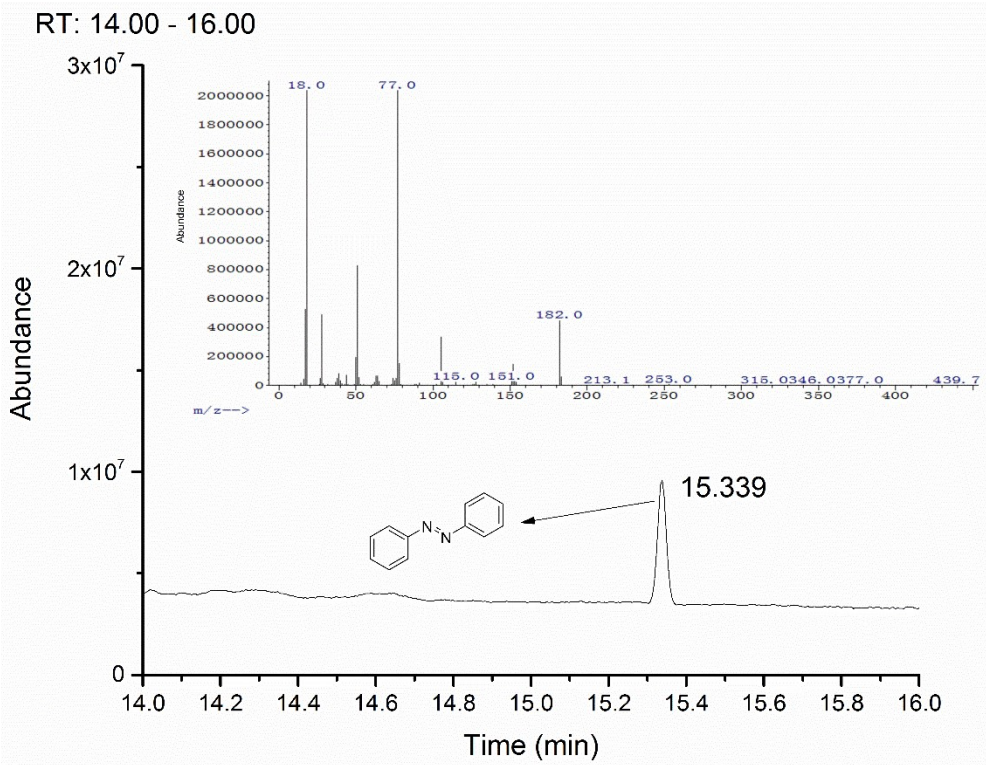


Fig. S10. GC-MS spectrum of the intermediate (azobenzene) of nitrobenzene reduction reaction.

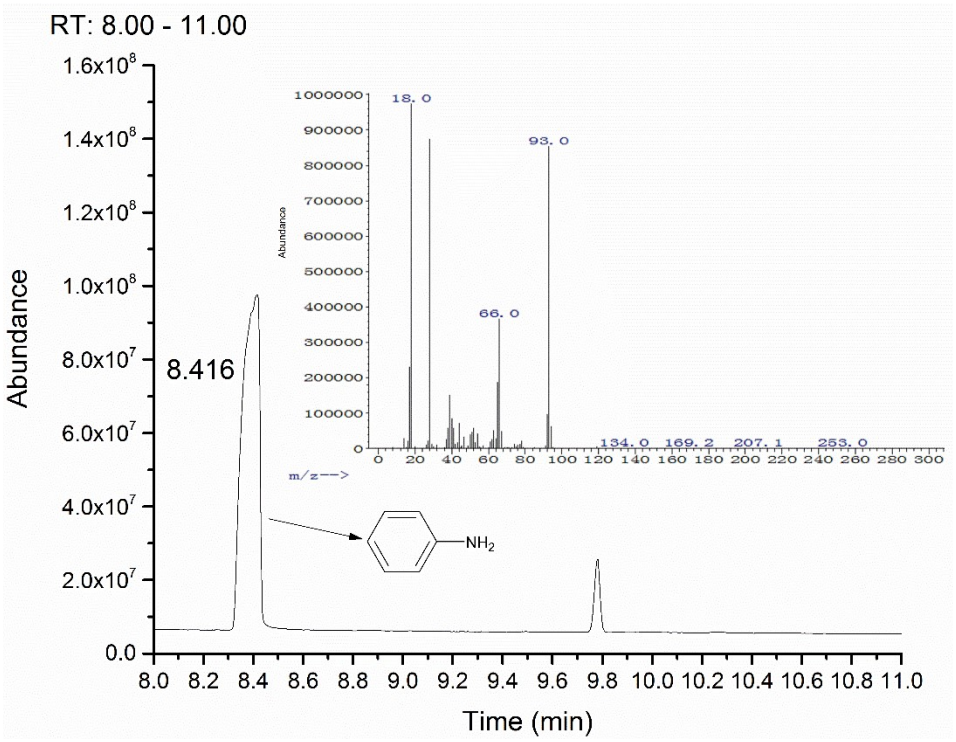


Fig. S11. GC-MS spectrum of the product (aniline).

Table S1 DFT calculated total energy of H species involved in the hydrogen activation on NHG.

Species	E_{DFT} (hatree)
H_2	-1.16201673934951
H	-0.46400208856406
H_2@NHG	-720.1961670727
2H@NHG	-720.1926675408

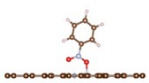
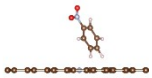
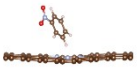
Direct dissociation energy of H_2 molecule:

E_{dis}=(-0.46400208856406*2+1.16201673934951)*27.2≈6.37 eV

Dissociation energy of H_2 molecule on NHG:

E_{dis}=(-720.1926675408+720.1961670727)*27.2≈0.095 eV

Table S2 Different configurations of nitrobenzene on NHG and the corresponding adsorption energies derivated via DFT calculation.

	Config. 1	Config. 2	Config. 3	NHG	Nitrobenzene
Initial				------	-------
Final					
E_{DFT} (hatree)	-798.07006	-798.06875	-798.07194	-719.03611	-79.01227
E_{ads} (eV)	-0.59	-0.55	-0.64	------	------