

Supporting Information

One-pot synthesis of Gamma-graphyne supported Pd nanoparticles with high catalytic activity

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Section S1. Materials and Methods

Hexabromobenzene, Acetylenedicarboxylic acid, cuprous iodide, triethylamine, Dichlorobis(triphenylphosphine)Palladium(II) and N,N-Dimethylformamide were purchased from Shanghai Titan Scientific Co., Ltd..

¹³C Solid-state NMR spectra were obtained using a Bruker AVANCE III Fourier 400 M spectrometer equipped with a 7.5 mm T3HX probe at 100.54 MHz and a spinning rate of 9 kHz. Fourier transform infrared (FT-IR) spectra was acquired using a Thermofisher Scientific Nicolet IS5 Fourier transform infrared spectroscopy. Renishaw inVia was used to obtain Raman data. X-ray Powder Diffractometer (XRD) was measured on a Bruker D8 Advance. Field-emission Scanning (FE-SEM) was carried with an accelerating voltage ranging from 1.0 to 15 kV on a HITACHI S4800. Energy Dispersive Spectrometer (EDS) was recorded on a Bruker Quantax 400. The sample was prepared by dispersing the material onto conductive adhesive tapes attached to a flat aluminum sample holder and then coated with Aurum. Transmission Electron Microscope (TEM) was recorded on a FEI Tecnai G2 F20. Energy Dispersive X-ray Spectrometer (EDX) was obtained on a Oxford 60T. Atomic Force Microscope (AFM)

was measured on a Veeco Multimode through Tapping Mode in air at room temperature. Impedance measurement was collected on a BAS Epsilon Electrochemical Workstation. X-ray photoelectron spectra (XPS) was acquired on Thermofisher Scientific Escalab 250Xi. Ultraviolet photoelectron spectra (UPS) was performed on a Thermofisher Scientific Escalab 250Xi. UV-Vis Diffuse Reflection Spectroscopy (UV-Vis DRS) was measured on a SHIMADZU UV- 3600Plus. Thermogravimetric analysis (TGA) from 20-800 °C was obtained on a NETZSCH STA 449 F3 in nitrogen atmosphere using a 10 °C/min ramp without equilibration delay. The nitrogen isotherms were recorded at 77 K with a Micromeritics ASAP 2020 surface area size analyzer. Before measurement, the samples were degassed in vacuum at 100 °C for 12 h.

Section S2 Synthesis and Methods

Synthesis of γ -Graphyne (γ -GY) through decarboxylative coupling ^[S1, S2]. The reactants hexabromobenzene (551.5 mg, 1.0 mmol) and Acetylenedicarboxylic acid (1368.7 mg, 12 mmol), catalyst Dichlorobis(triphenylphosphine)Palladium(II) (210.6 mg, 0.3 mmol) and cuprous iodide (114.3 mg, 0.6 mmol) were loaded into a Schlenk Flask, and dissolved in DMF (10 ml) mixed with triethylamine(2.125 ml). The solution was stirred at 60 °C for 24 h under argon gas atmosphere. At the end of the reaction, a black solid was produced. After filtration and rinsing with DMF, the product was then sonicated in benzene for 5 min to remove the unreacted reactants. After that, the product was rinsed with DMF, ethanol and water repeatedly, and the crude product of γ -GY was obtained by filtration; the crude product was refluxed by 4 M NaOH, 6 M HCl and 4 M NaOH for 2 h successively, and the solution was kept slightly boiling during reflux. Finally, the product of γ -GY was obtained by centrifugation at 9000 rpm for 10 min and freeze-drying for 12 hours.

Synthesis of Pd/GO, Pd/TRGO and Pd/MWNT. GO, HGO and CNT were sonicated in water for several minutes to form homogeneous aqueous dispersions (0.5 mg/mL), after which the metal salts K_2PdCl_4 (0.2 mL, 10 mmol) were mixed with the

homogeneous aqueous dispersions (2 mL, 0.5 mg/mL) separately in an ice bath and stirred vigorously for 30 minutes each. The resulting products, i.e, Pd/GO, Pd/HGO and Pd/CNT, were collected by centrifugation and washing several times with pure water.

Catalytic Reduction of 4-Nitrophenol (4-NP) ^[S3]. The reduction of 4-NP was tested in a quartz cuvette and monitored by UV-Vis spectroscopy at room temperature. The aqueous solution of NaBH₄ (1.72 mL, 0.2 M) and 4-nitrophenol (0.28 mL, 1 mM) were mixed into water (4 mL). The mixture was stirred at room temperature for 5 min, 3 mL of which was removed and then different types of dispersions of Pd/ γ -graphyne, Pd/GO, Pd/HGO, Pd/CNT and commercial Pd/C (10 μ L, 0.5 mg/mL) were added, respectively. Each mixture was immediately monitored by UV-Vis measurements, with spectra recorded every 2 s.

Control experiment: The Control experiment was carried out in a quartz cuvette and monitored by using UV-vis spectroscopy at room temperature. The aqueous solution of NaBH₄ (1.72 mL, 0.2 M) and 4-nitrophenol (0.28 mL, 1 mM) was mixed into water (4 mL), 3 mL of which was removed, and the mixture was immediately monitored by UV-Vis measurements, with spectra recorded every 2 s.

Determination of the rate constant of Catalytic Reduction of 4-NP. The determination of the reaction rate was measured in quartz cuvettes and monitored by UV-Vis spectroscopy at room temperature. The aqueous solutions of 4-NP (0.28 ml, 20 μ M, 30 μ M, 40 μ M, 50 μ M and 60 μ M) and NaBH₄ (1.72 mL, 0.2 M) were mixed into water (4 ml). Then a dispersion of Pd/ γ -graphyne (10 μ L, 0.5 mg/mL) was added. The mixture was immediately monitored by UV-Vis measurements, with spectra recorded every 2 s. A linear relationship was observed between the rate constant and the concentration of 4-NP, indicating that the reaction is first order.

Section S3 Characterization of γ -graphyne

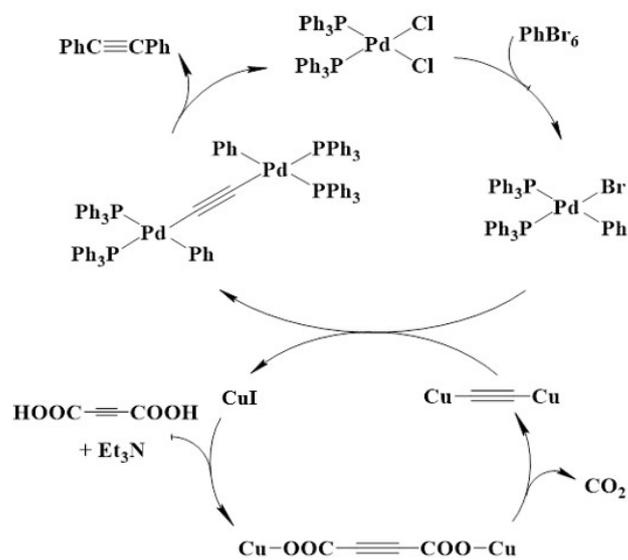


Figure S1. Schematic Diagram of Reaction Mechanism

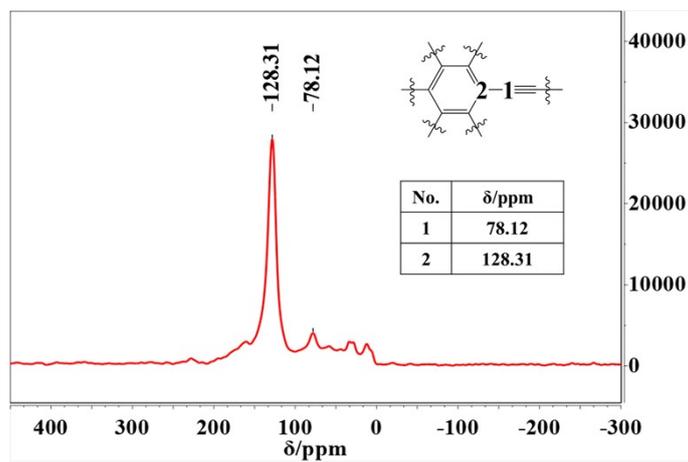


Figure S2. Solid state ^{13}C -ssNMR of γ -graphyne (9 kHz)

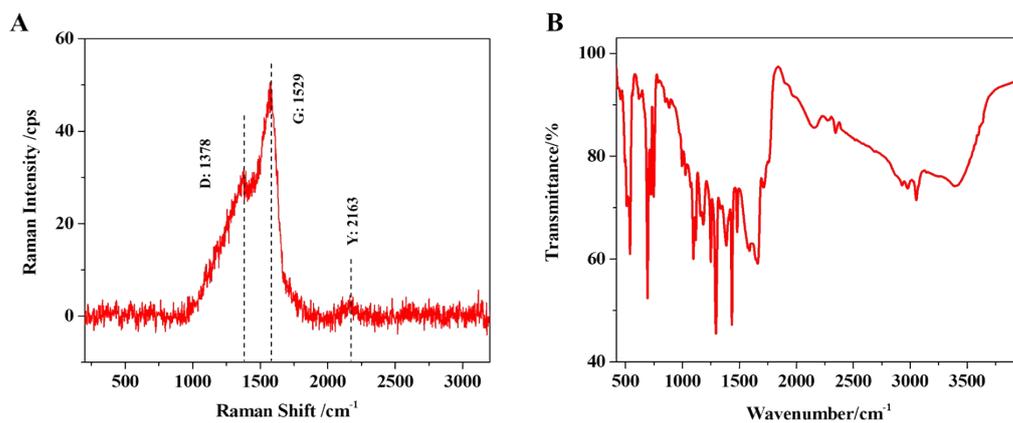


Figure S3. (A) Raman and (B) FT-IR spectra of γ -graphyne

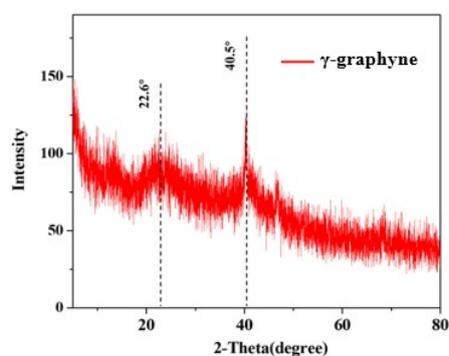


Figure S4. XRD of γ -graphyne

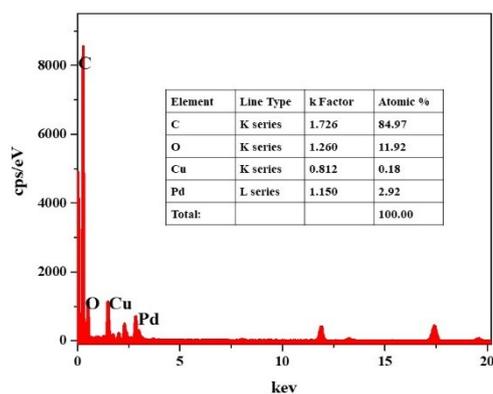


Figure S5. EDX of γ -graphyne (detail information)

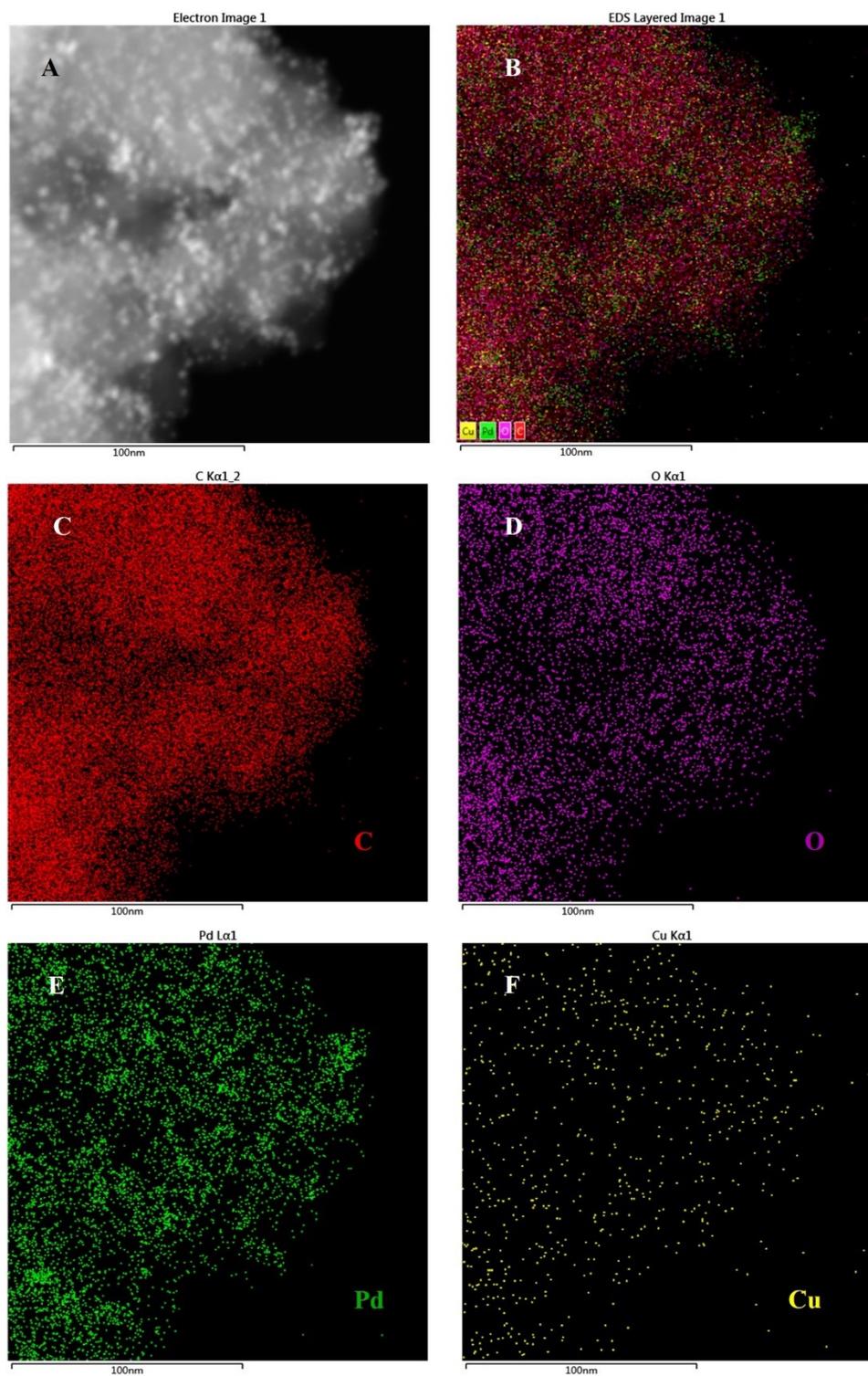


Figure S6. (A) HAADF-STEM image, (B) EDS layered image and (C, D, E, F) the elemental mapping of C (red), O (purple), Pd (green) and Cu (yellow) of γ -graphyne

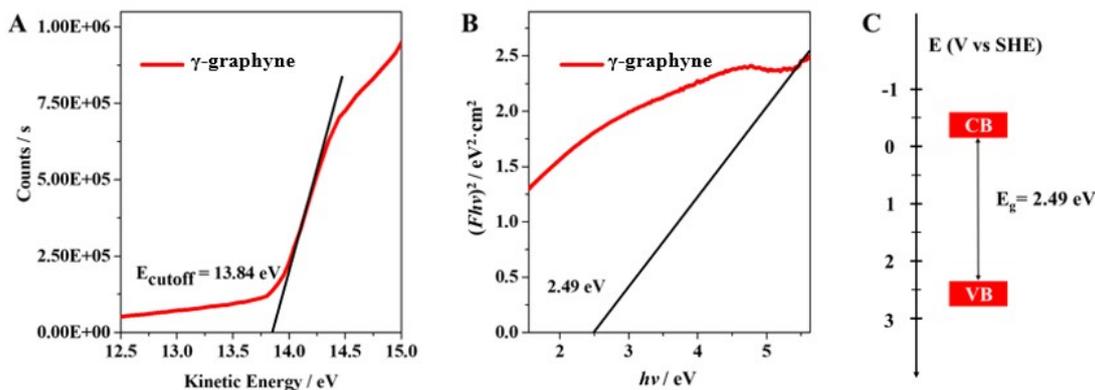


Figure S7. Bandgaps and band-edge positions. (A) Ultraviolet photoelectron spectra of γ -graphyne; (B) $(Fhv)^2$ as a function of photon energy ($h\nu$), where F is the Kubelka–Munk function of the diffuse reflectance R from Ultraviolet–visible diffuse reflectance spectra (UV–Vis DRS). The intercepts of extrapolated straight lines give the corresponding direct bandgap of γ -graphyne powders; (C) Band diagrams of graphyne according to the bandgap and flat-band potential obtained from (A) and (B). CB denotes conduction band. VB denotes valence band.

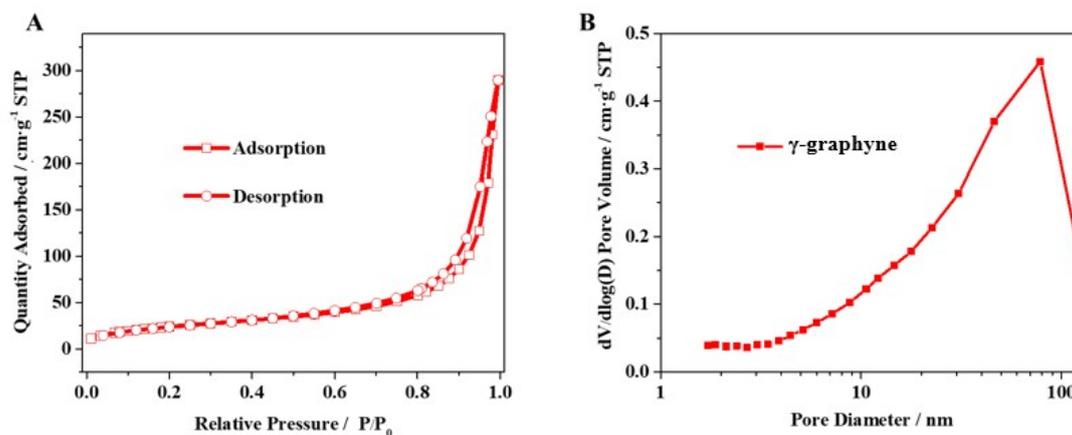


Figure S8. Gas sorption measurements for γ -graphyne. (A) N_2 adsorption and desorption isotherms at 77 K; (B) Pore size distribution

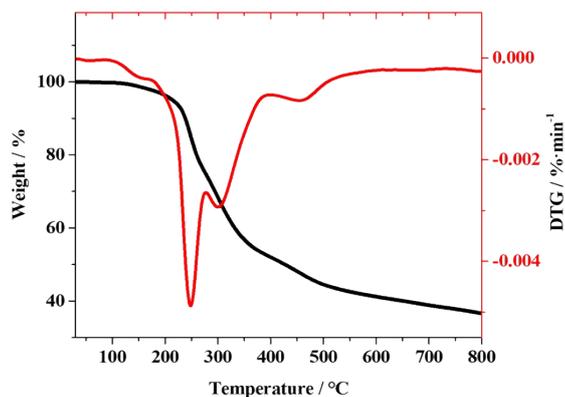


Figure S9. TG-DTG of γ -graphyne

Section S4 Characterization of Reduction of Nitroarenes intermediate and product

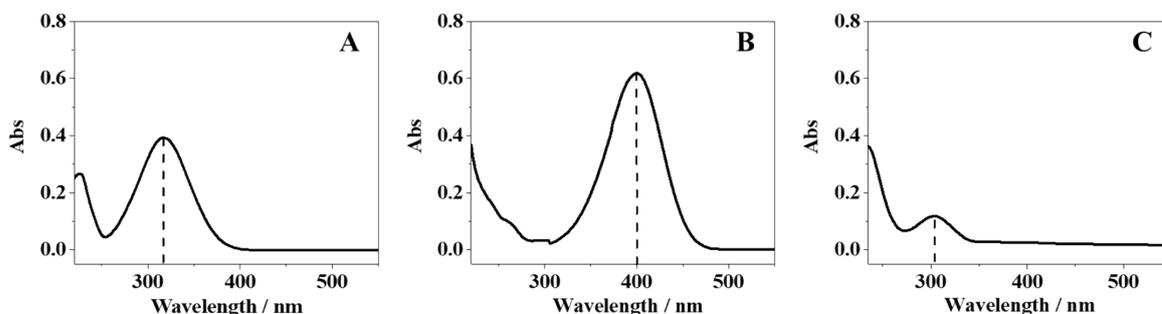


Figure S10. UV-vis spectra of 4-NP(A) before and (B) after adding NaBH₄ solution; (C) the solution of 4-NP with the addition of NaBH₄ and Pd/ γ -graphyne.

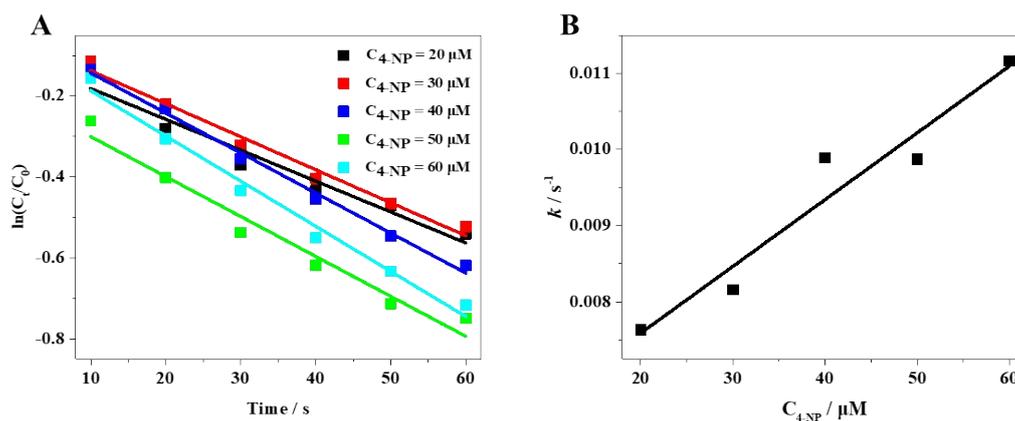


Figure S11. The reduction of 4-nitrophenol (4-NP) by NaBH₄ catalyzed by Pd/ γ -graphyne. (A) $\ln[C_t/C_0]$ as a function of absorbance (400 nm) vs time (sec), (B) The observed rate constants for the reduction of 4-NP as a function of the concentration with excess NaBH₄ used.

REFERENCES

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