

Supplementary Material

Enhanced catalytic performance and sulfur resistance of reduced graphene oxide-promoted MnO₂ nanorods-supported Pt nanoparticles for benzene oxidation

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Catalyst characterization procedures:

The actual Pt contents in the $x\text{Pt-yrGO}/\alpha\text{-MnO}_2$ samples were determined using the ICP–AES technique on a Thermo Electron IRIS Intrepid ER/S spectrometer (Thermo Elemental, America). The samples were dissolved in a mixture of concentrated HCl (37 wt%) and HNO_3 (75 wt%) aqueous solutions with a volumetric ratio of 3.0 : 1.0 prior to Pt content analyses. X-ray diffraction (XRD) patterns of the samples were determined on a Bruker D8-Advance diffractometer (Bruker/AXS, Germany) in the 2θ range of 10° – 80° with Cu $K\alpha$ radiation ($\lambda = 0.15406$ nm), in which the operating voltage and current were 50 kV and 30 mA, respectively. Fourier transform infrared (FTIR) spectra of the samples in the range of 400 – 4000 cm^{-1} were recorded on a Thermo Scientific Nicolet 6700 FTIR spectrometer (Thermo Fisher Scientific, USA) with a resolution of 4 cm^{-1} . Brunauer–Emmett–Teller (BET, BK 200C, Beijing JWGB Corporation, China) surface areas and pore-size distributions of the samples were obtained via the nitrogen adsorption at the liquid N_2 temperature using the BET equation and the Barrett–Joyner–Halenda (BJH) method, respectively. Morphologies of the samples were directly observed on a Hitachi S-4300 scanning electron microscope (SEM, Hitachi Corporation, Japan). High angle annular dark field (HAADF) images and element mapping were acquired on the equipment FEI G2 80-200/Chemi-STEM Cs-corrected transmission electron microscopy (TEM) (JEOL-2010, JEOL Corporation, Japan) with probe corrector. Thermogravimetric (TG, STA 449 F5, NETZSCH Scientific Instruments Trading, Germany) tests were carried out on a microcomputer-differential thermal balance of Beijing Hengjiu Scientific Instrument Factory. Each sample was dried at 120 $^\circ\text{C}$ for 2 h and kept at 25 $^\circ\text{C}$ for 50 min in a N_2 flow of 60 mL/min, the heating rate was 10 $^\circ\text{C}/\text{min}$, and the test

temperature range was 25–300 °C. X-ray photoelectron spectroscopy (XPS, ESCALAB 250 Xi spectrometer, Thermo Fisher Scientific, USA) was used to determine the binding energies (BEs) of Mn 2p, Pt 4f, O 1s, and C 1s of surface species using monochromatic Al K α X-ray source ($h\nu = 1486.6$ eV). The C 1s signal at 284.6 eV was taken as a reference for BE calibration.

H₂ temperature-programmed reduction (H₂-TPR) of the samples was performed on a Builder PCA-1200 analyzer (JW-BK132, Beijing JWGB Corporation, China). Prior to the H₂-TPR experiment, 100 mg of the sample was pretreated in a 5 vol% O₂/N₂ (balance) flow of 30 mL/min at 400 °C for 1 h, then cooled to room temperature, and finally reduced in a 5 vol% H₂/N₂ (balance) flow of 30 mL/min at a ramp of 10 °C/min from room temperature to 900 °C. The reduction peaks were calibrated against the data of a standard powdered CuO reduction. Oxygen temperature-programmed desorption (O₂-TPD) of the samples was conducted on a Builder PCA-1200 analyzer (JW-BK132, Beijing JWGB Corporation, China). A total of 100 mg of the sample was pretreated at 400 °C and saturated with O₂ (10 vol% O₂/He (balance), 30 mL/min) at 50 °C. After being purged in pure He of 30 mL/min at 50 °C for 1 h, O₂ desorption took place in He flow of 30 mL/min at a ramp of 8 °C min⁻¹ from 30 to 900 °C.

The in situ diffuse reflectance infrared Fourier transform spectroscopic (DRIFTS) experiments were conducted on a Bruker TENSOR II spectrometer (Bruker Optics, Germany) characterized by a reaction chamber that could withstand high temperatures (Harrick Praying Mantis). The catalyst sample was packed into the sample cup of the reaction chamber and heated to 400 °C at a total N₂ flow of 50 mL/min for 1 h to eliminate the influence of surface

impurities (H_2O , CO_2 , and etc.), then the catalyst exposed to 1000 ppm benzene + N_2 (balance) + 20 vol% O_2 at different temperatures for 60 min, each spectrum had a resolution of 4 cm^{-1} with 32 accumulated scans.

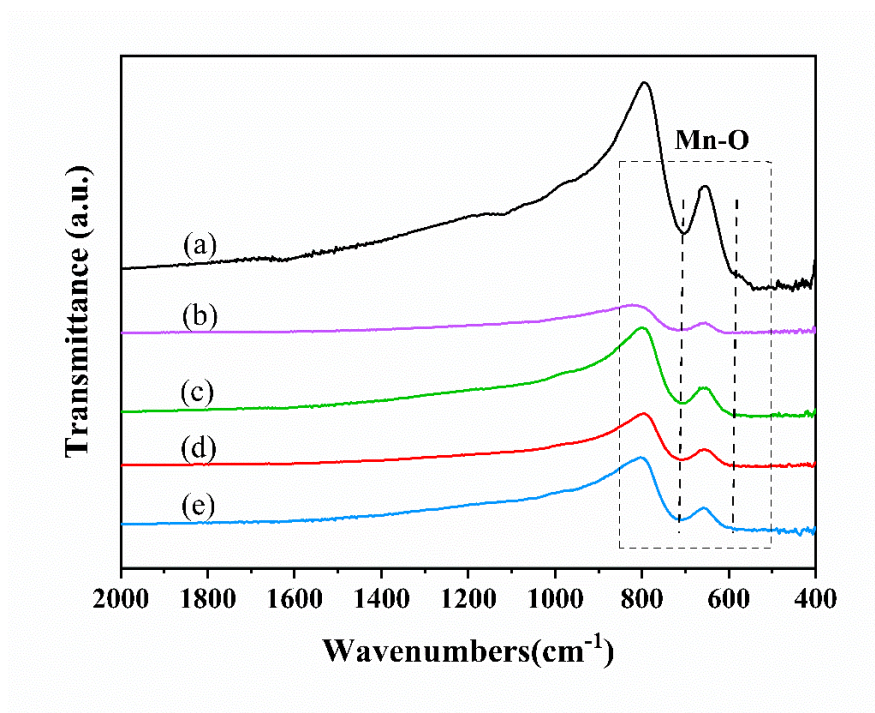


Figure S1. FTIR spectra of (a) $\alpha\text{-MnO}_2$, (b) $0.93\text{Pt}/\alpha\text{-MnO}_2$, (c) $0.91\text{Pt}-0.5\text{rGO}/\alpha\text{-MnO}_2$, (d) $0.94\text{Pt}-1.0\text{rGO}/\alpha\text{-MnO}_2$, and (e) $0.92\text{Pt}-2.0\text{rGO}/\alpha\text{-MnO}_2$.

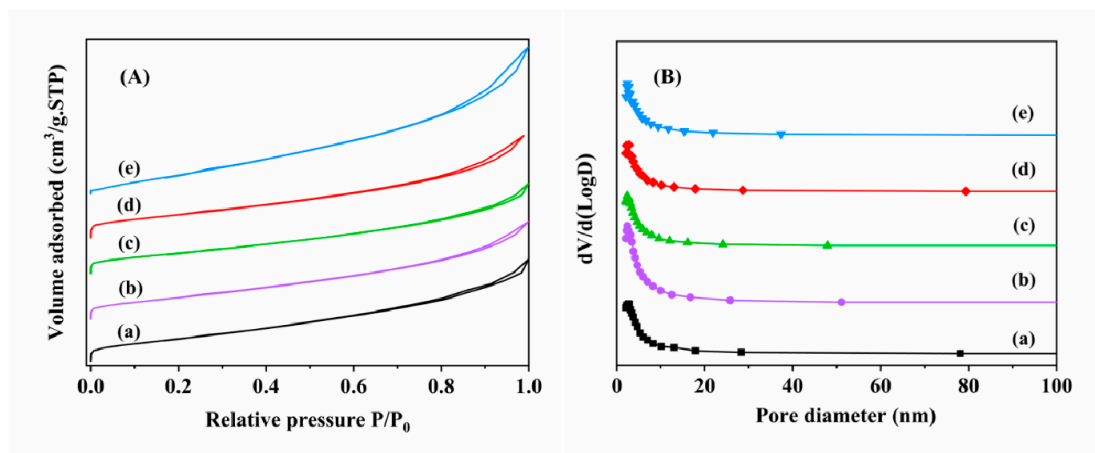


Figure S2. (A) Nitrogen adsorption–desorption isotherms and (B) pore-size distributions of (a) α -MnO₂, (b) 0.93Pt/ α -MnO₂, (c) 0.91Pt-0.5rGO/ α -MnO₂, (d) 0.94Pt-1.0rGO/ α -MnO₂, and (e) 0.92Pt-2.0rGO/ α -MnO₂.

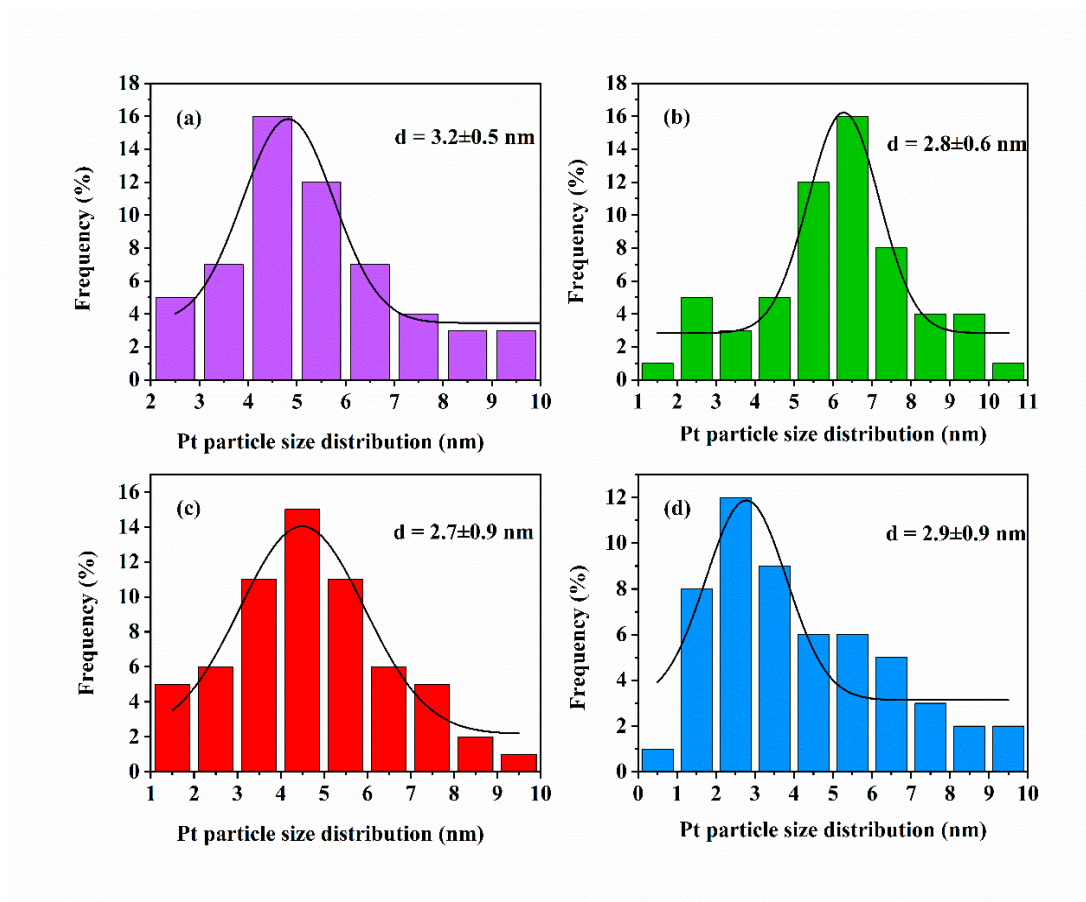


Figure S3. Noble particle-size distributions of (a) 0.93Pt/ α -MnO₂, (b) 0.91Pt-0.5rGO/ α -MnO₂, (c) 0.94Pt-1.0rGO/ α -MnO₂, and (d) 0.92Pt-2.0rGO/ α -MnO₂.

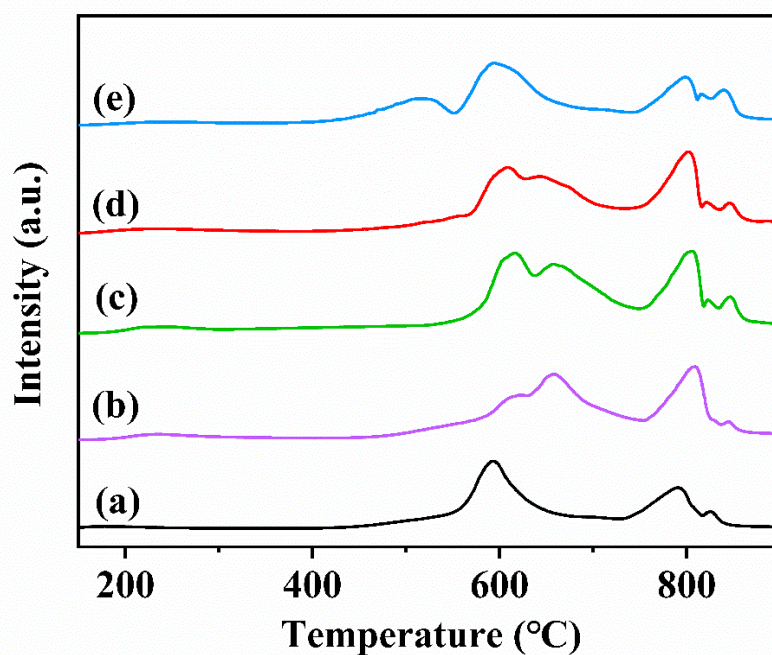


Figure S4. O₂-TPD profiles of (a) α -MnO₂, (b) 0.93Pt/ α -MnO₂, (c) 0.91Pt-0.5rGO/ α -MnO₂, (d) 0.94Pt-1.0rGO/ α -MnO₂, and (e) 0.92Pt-2.0rGO/ α -MnO₂.

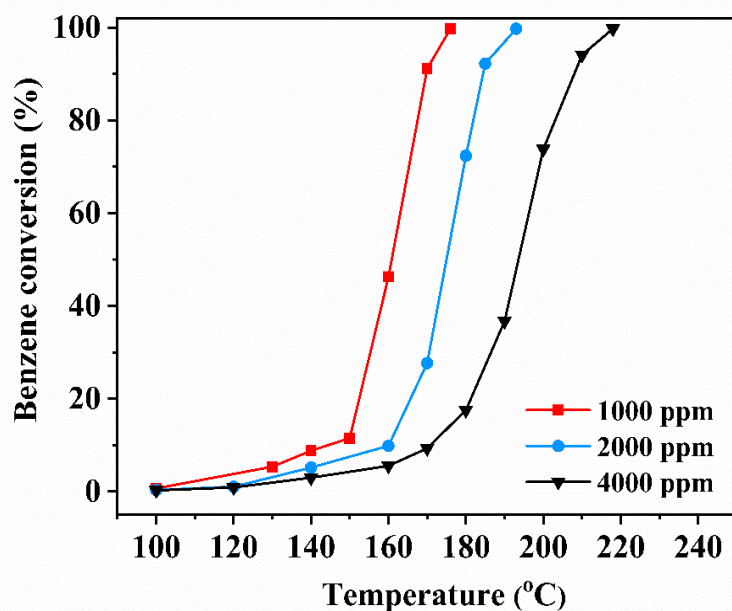


Figure S5. Effect of benzene concentration on catalytic activity of 0.94Pt-1.0rGO/ α -MnO₂ at GHSV = 60,000 mL/(g h).

Table S1. Comparison on specific reaction rates (r_{cat}) for benzene oxidation at 160 °C over the catalysts studied in the present work and reported in the literature.

Catalyst	Reactant concentration	GHSV (mL/(g h))	r_{cat} (mol/(g _{Pt} s))	Ref.
0.94Pt-1.0rGO/ α -MnO ₂	1000 ppm benzene	60,000	3.14×10^{-4}	This study
Pt/TMS	400 ppm benzene	60,000	8.18×10^{-5}	[13]
Pt/TS-1	120 ppm benzene	60,000	7.77×10^{-5}	[14]
Pt/eggshell	1000 ppm benzene	80,000	1.55×10^{-5}	[15]
Pt/OMS-2	1000 ppm benzene	20,000	9.27×10^{-5}	[16]
Pt ₁ /meso-Fe ₂ O ₃	1000 ppm benzene	20,000	2.32×10^{-5}	[17]

Table S2. Average Pt particle sizes and actual Pt loadings of the as-obtained samples determined by the ICP–AES technique.

Sample	Average particle size of Pt (nm)	Actual Pt content (wt%)
α -MnO ₂	–	–
0.93Pt/ α -MnO ₂	3.2 ± 0.5	0.93
0.91Pt-0.5rGO/ α -MnO ₂	2.8 ± 0.6	0.91
0.94Pt-1.0rGO/ α -MnO ₂	2.7 ± 0.9	0.94
0.92Pt-2.0rGO/ α -MnO ₂	2.9 ± 0.9	0.92