Supplementary Information

Hydrophobic Carbon Dots as Spatial Confiners for Isolating Pd Nanoparticles for Efficient Nitrobenzene Hydrogenation

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Experimental details

Materials

Fluid catalytic cracking slurry (FCC slurry) was purchased from Sinopec Corp. (22.0 wt.% saturates, 49.0 wt.% aromatics, 22.8 wt.% resins, and 6.2 wt.% asphaltenes). Toluene, HCl (36-38 wt.%), and K_2PdCl_4 (99 wt.%, AR) were purchased from Sinopharm Chemical Reagent Co., Ltd. NaCl (99 wt.%, AR), KCl (99 wt.%, AR), melamine (99 wt.%, AR), glucose (99 wt.%, AR), acetaldehyde (99 wt.%, AR), NaOH (99 wt.%, AR), ethylene glycol (99 wt.%, AR), anhydrous ethanol (99 wt.%, AR), nitrobenzene (99 wt.%, AR) and other nitroarene substrates were purchased from Aladdin Industrial Corporation. All the reagents were directly used without further purification.

Synthesis of nitrogen-doped carbon nanosheets (NCNS)

To prepare NCNS, 0.75 g of FCC oil slurry was dissolved in a beaker containing 50 mL of toluene using an ultrasonic cleaner for 10 minutes until the slurry was completely dissolved. NaCl (11.81 g), KCl (3.19 g), and melamine (1.00 g) were thoroughly mixed and ground together. The mixture was added to a beaker and heated in an oil bath at 85 °C under stirring until complete solvent evaporation yielded a dark brown powder. The powder was ground, transferred to a corundum boat, and placed in a tube furnace. Air was purged with inert gas, followed by heating to 800 °C under nitrogen atmosphere at 5 °C/min and holding for 3 h. After cooling to room temperature, the product was stirred with 1 M HCl at 80 °C for 24 h. The sample was then filtered, washed with deionized water to neutrality, and dried in an oven at 60 °C, yielding nitrogen-doped carbon nanosheets, denoted as NCNS.

Synthesis of hydrophobic carbon dots (hy-CDs)

The preparation process of hy-CDs is illustrated in Fig. S1. To prepare the sample, 1.0 g of glucose was dissolved in 40 mL of aqueous acetaldehyde solution (40 wt.%) through ultrasonic dispersion for 5 min. The resulting mixture was stirred at a 60 °C, and slowly added with 8.0 g of NaOH. Upon complete addition of the alkali solution, the reaction mixture was stirred for an additional 1 h, resulting in the formation of a brownish-black solid. The formation mechanism of this solid can be explained as follows: under high-temperature and alkaline conditions, carbon chains generated via aldol condensation using acetaldehyde as the carbon source aggregate, twist to form nuclei, and subsequently undergo further linking and growth. The mixture was then allowed to stand at room temperature for 24 h, during which it stratified into an upper layer of brownish-black solid and a lower layer of brownish-yellow liquid. The solid was then dispersed by stirring it with deionized water, titrated with dilute HCl to neutrality, and allowed to stand for 8 h before delamination occurred. After removing the supernatant, the lower orange-yellow precipitate was dispersed again with deionized water, left to stand, layered, separated, and repeated three to four times. Finally, the mixture was centrifuged, washed more than three times at 8,000 r/min, and freeze-dried for 24 h, weighed, and stored in a sealed container.

Synthesis of hydrophilic carbon dots (hp-CDs)

The synthesis route for hp-CDs is presented in Fig. S2. Firstly, low-temperature petroleum coke and petroleum asphalt were dissolved with appropriate amount of dichloromethane, and the dichloromethane was evaporated after sufficient mixing, and the mixed solids were hot-pressed into tablets, and placed in an inert atmosphere at a high-temperature calcination at 800 °C for 2 h to obtain the spare electrode tablets. The electrode sheet was fixed on the electrode clamp and inserted into the electrolytic cell containing 100 mL of ammonia solution, and the electrolysis voltage was set at 40 V. During the electrolysis process, the anode electrode sheet was peeled off, and the electrolyte turned into black color, and the electrolysis ended when the current was zero. The electrolyte was pump-filtered to remove NH_3 and freeze-dried to obtain hydrophilic carbon dots (hp-CDs).

Synthesis of Pd/hy-CDs@NCNS, Pd/hp-CDs@NCNS and Pd@NCNS catalysts

The Pd/hy-CDs@NCNS catalyst was prepared using a liquid-phase reduction method (Fig. 1). First, 5.0 mg of CDs was dispersed in 2 mL of anhydrous ethanol by ultrasonication and then further dispersed in 40 mL of deionized water. Next, 60.0 mg of NCNS was added to the solution and ultrasonically dispersed for 10 min before being stirred sufficiently for 1 h at room temperature to allow full combination of CDs with NCNS. Then, 3.0 mg of K_2PdCl_4 was dissolved in 10 mL of deionized water, added dropwise to the mixture at a rate of 1.5 mL/min^{-1}, and stirred for 1 h at room temperature. Afterwards, 50 mL of ethylene glycol was added dropwise at the same rate and stirred for 4 h under a water bath at 50 °C to reduce Pd^{2+} to Pd particles and adsorb them onto the surface of supports. The resulting mixture was filtered, washed, and dried overnight at 60 °C to obtain the Pd/hy-CDs@NCNS catalyst. The same strategy was used to prepare undoped Pd@NCNS catalysts with carbon dots and Pd/hp-CDs@NCNS catalysts doped with hydrophilic carbon dots (hp-CDs).

Catalytic performance evaluation

The hydrogenation reactions were conducted in a 50 mL high-pressure reactor using nitrobenzene as substrate, hydrogen gas as the reductant, and ethanol as the solvent. In a typical procedure, the reactor was charged with 10 mL of ethanol, 0.5 mmol of nitrobenzene, and 10 mg of catalyst. After sealing, the air inside the reactor was displaced by sequential purging with nitrogen and hydrogen (three times). The reaction was then initiated under a hydrogen pressure of 0.1 MPa and stirred at 40 °C for 4 h. For substrate scope investigation, the standard conditions were applied, replacing nitrobenzene with various substituted nitroarenes. In catalyst recyclability tests, the catalyst was separated from the reaction mixture by filtration after the reaction, thoroughly washed with ethanol, and dried at 60 °C for 12 h prior to reuse in subsequent cycles.

Upon completion of the hydrogenation reaction, the obtained filtrate was subjected to quantitative analysis by gas chromatography. Qualitative identification of the components was performed by comparing retention times with those of authentic standards or by GC-MS spectral matching. Quantitative determination of reactant and product concentrations was achieved using the internal standard method with dodecane as the reference. For reaction systems involving high-boiling nitroarene substrates, it is explicitly noted whether derivatization or the application of make-up gas was employed to ensure analytical accuracy. To guarantee data reliability, each filtrate sample was analyzed in triplicate, with relative errors maintained within 2%. Furthermore, regular instrument calibration and method validation were performed using standard samples to ensure that the precision and accuracy of the analytical protocol met the required specifications.

Catalyst Characterization

This paper employed multiple instruments for data acquisition and analysis. X-ray diffraction patterns were collected on a polycrystalline powder X-ray diffractometer, model X'Pert Pro MPD from the Netherlands, utilizing Cu Kα radiation ($\lambda = 1.5406$ Å) operated at 40 kV and 40 mA over a 2θ range of 5-90°, with data analysis conducted using MDI-JADE software. Material micro-morphology was examined using a high-resolution field emission transmission electron microscope, model Tecnai F20 from FEI, USA, operating at an accelerating voltage of 200 kV. Raman spectroscopy was performed on a Renishaw 200 Raman analyzer with a 532 nm excitation laser over a spectral range of 100-3200 cm^{-1}. X-ray photoelectron spectroscopy was conducted on a Thermo Scientific K-Alpha spectrometer employing monochromatic Al Kα radiation ($h\nu = 1486.6$ eV) with a pass energy of 50 eV. Infrared absorption spectra were obtained using a Nicolet 6700 diffuse reflectance infrared Fourier transform spectrometer, covering a range of 4000-400 cm^{-1} at a resolution of 4 cm^{-1}. Finally, the composition and content of the reaction products were determined using a BF-6050 gas chromatograph manufactured by Beijing Beifen Ruili Analytical Instruments Co., Ltd., China.

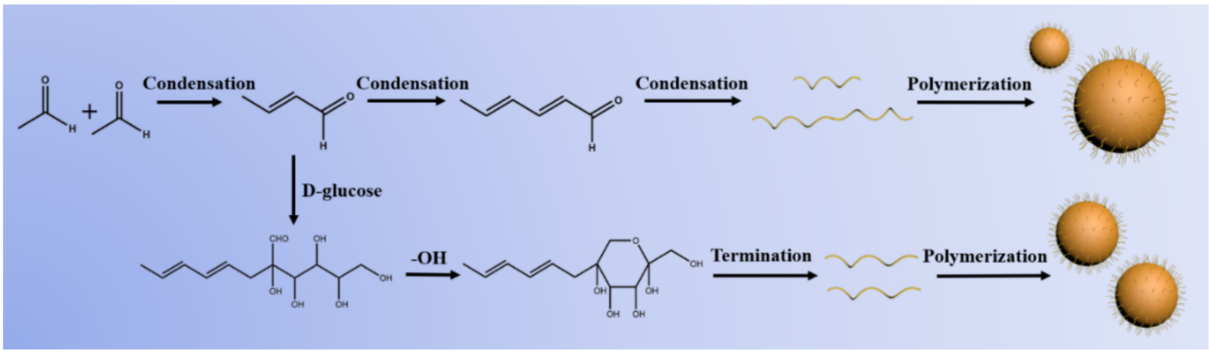


Fig.S1. Schematic illustration for the preparation procedure of hydrophobic carbon dots.

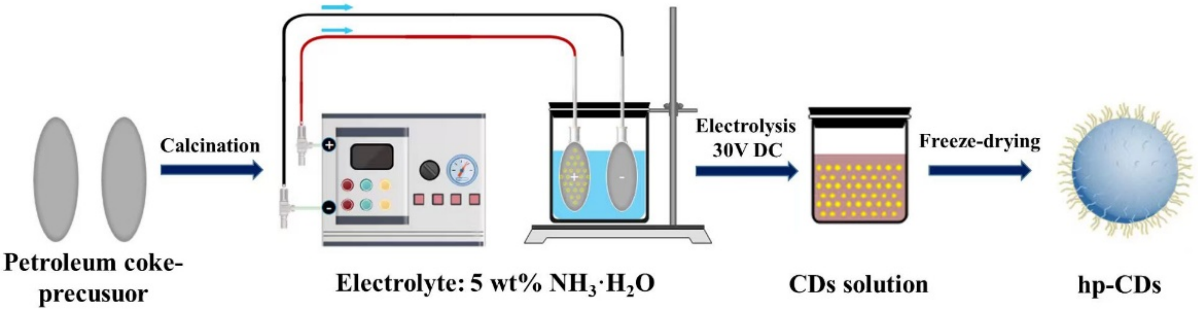


Fig. S2. Schematic illustration for the preparation procedure of hydrophilic carbon dots.

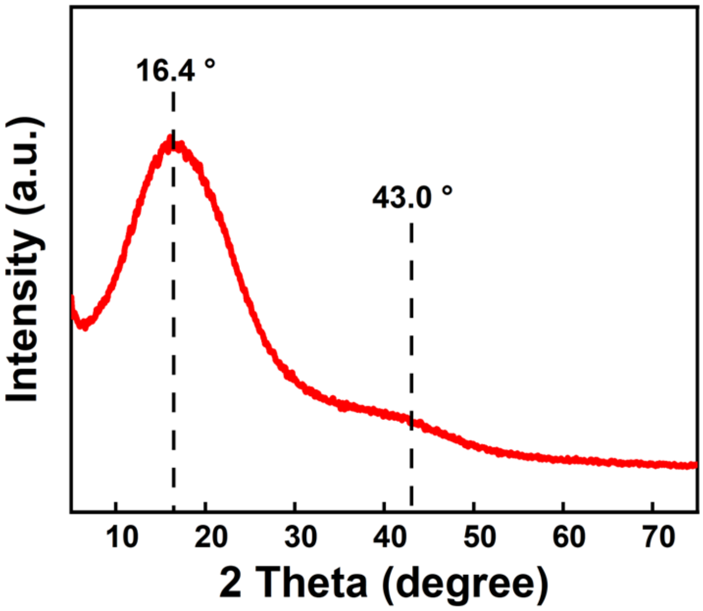


Fig. S3. XRD pattern of hy-CDs.

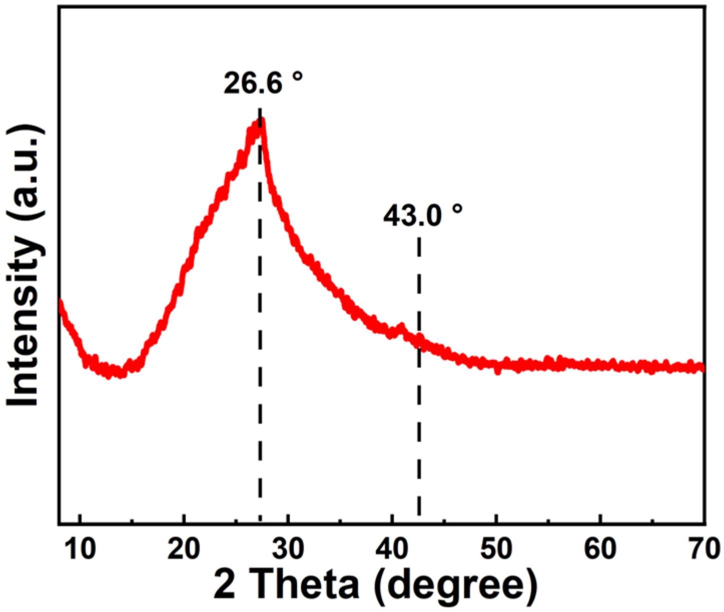


Fig. S4. XRD pattern of hp-CDs.

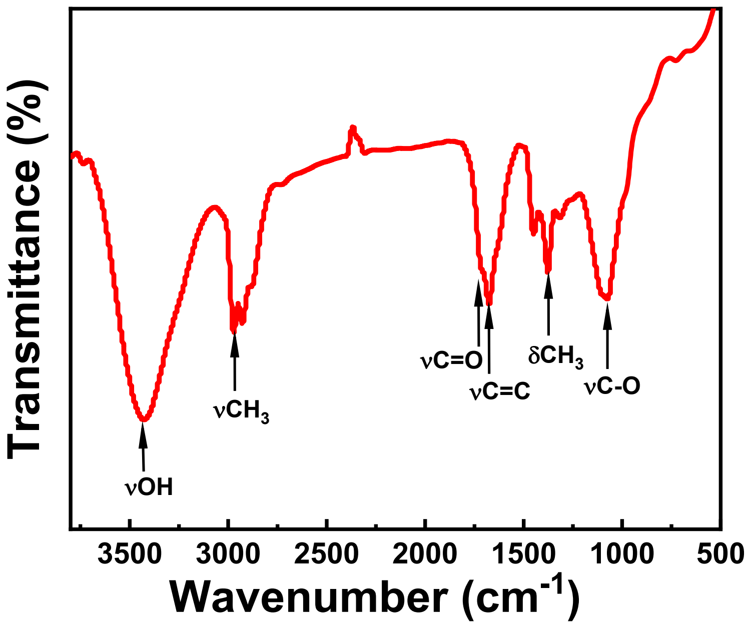


Fig. S5. FT-IR spectrum of hy-CDs.

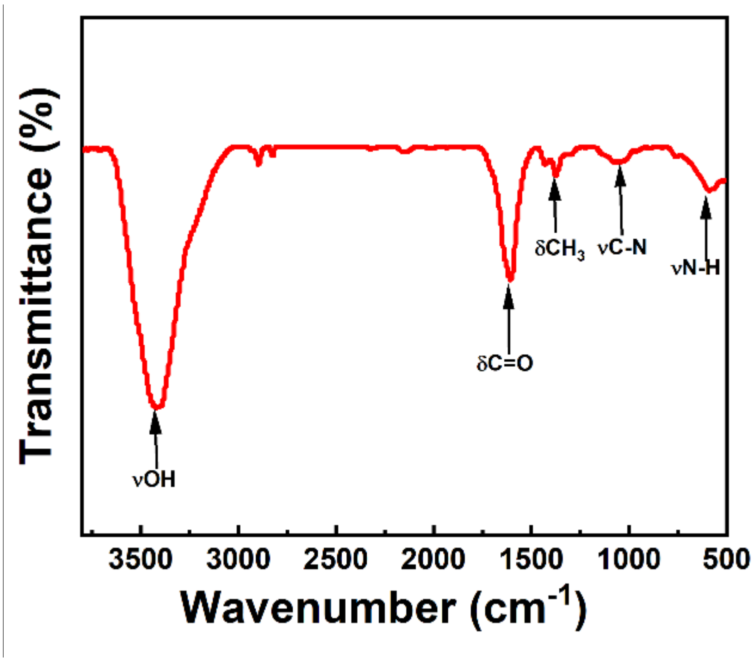


Fig. S6. FT-IR spectrum of hp-CDs.

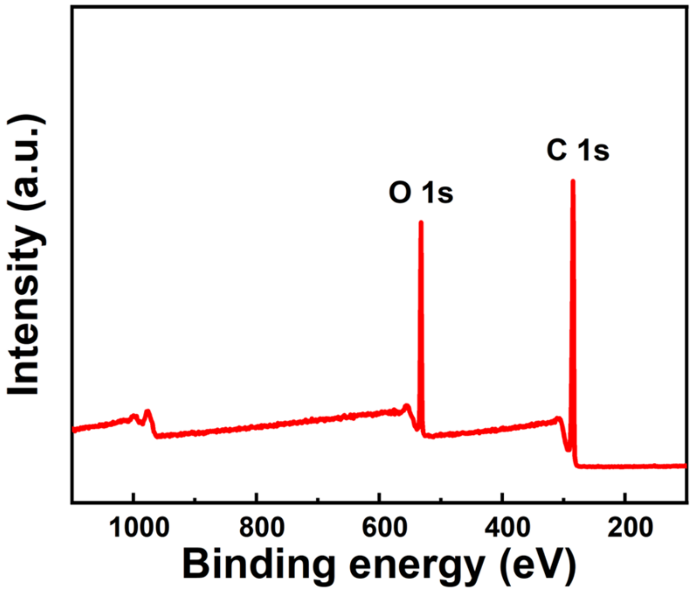


Fig. S7. XPS survey spectrum of hy-CDs.

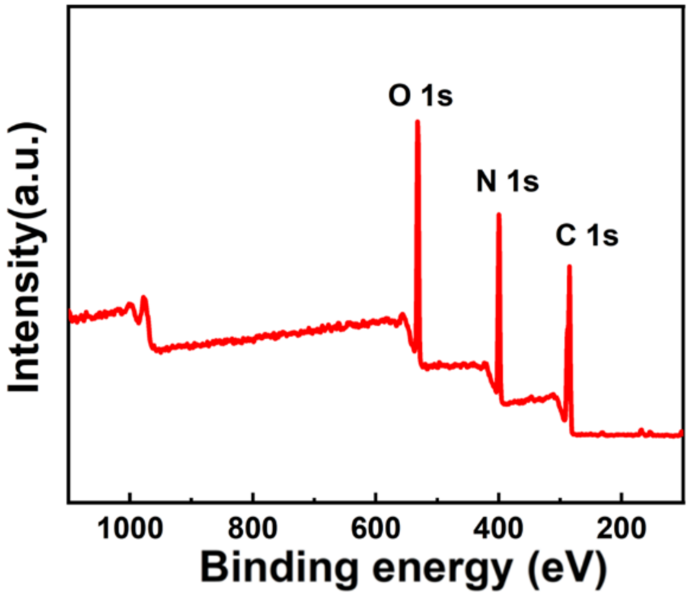


Fig. S8. XPS survey spectrum of hp-CDs.

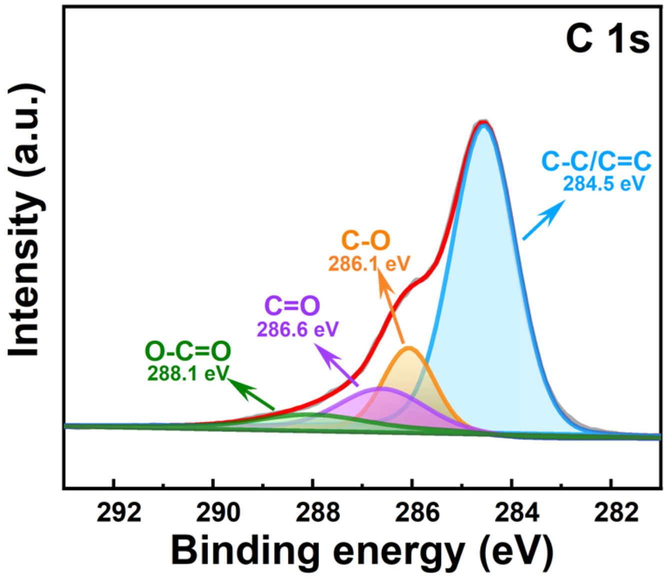


Fig. S9. High-resolution C 1s spectrum of hy-CDs.

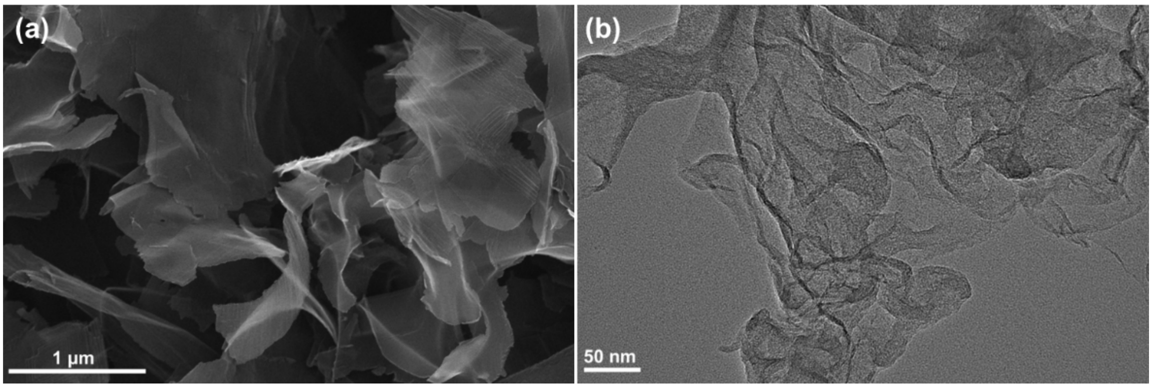


Fig. S10. (a) SEM image and (b) HR-TEM image of N-CNS.

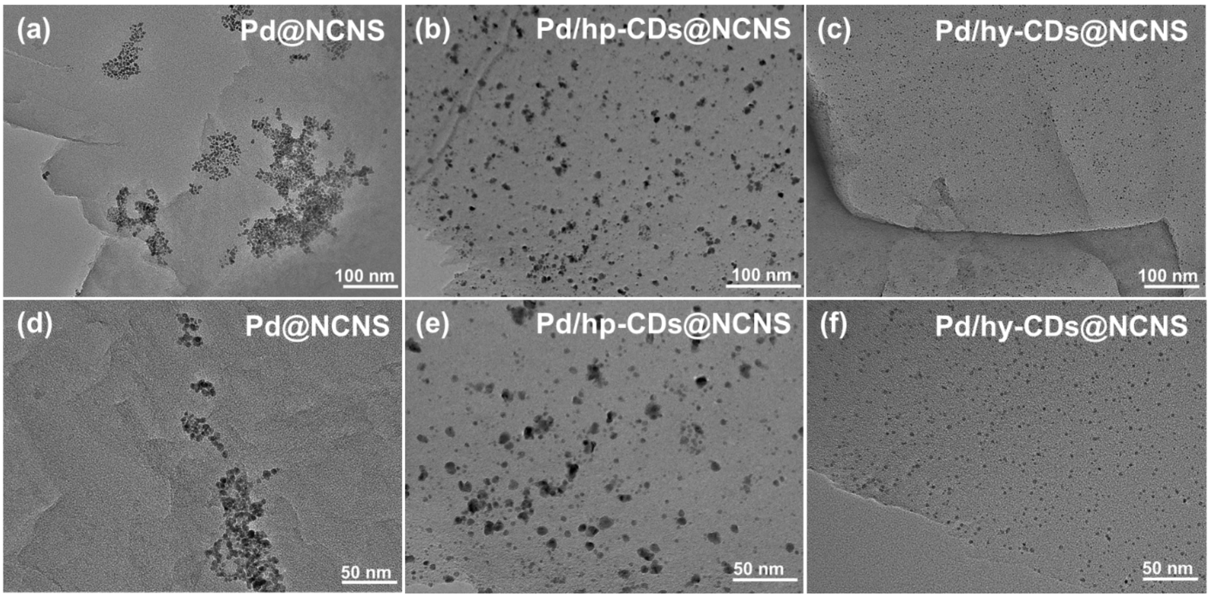


Fig. S11. (a, d) TEM images of Pd@NCNS. (b, e) TEM image of Pd/hp-CDs@NCNS. (c, f) TEM image of Pd/hy-CDs@NCNS.

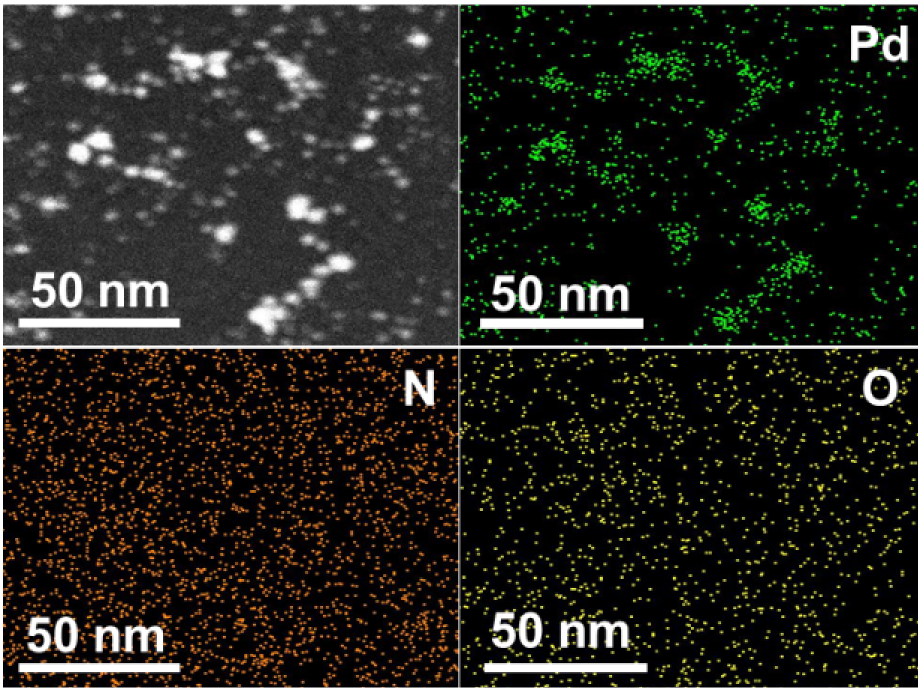


Fig. S12. Mapping diagram of Pd/hy-CDs@NCNS and its Pd, N, and O elements.

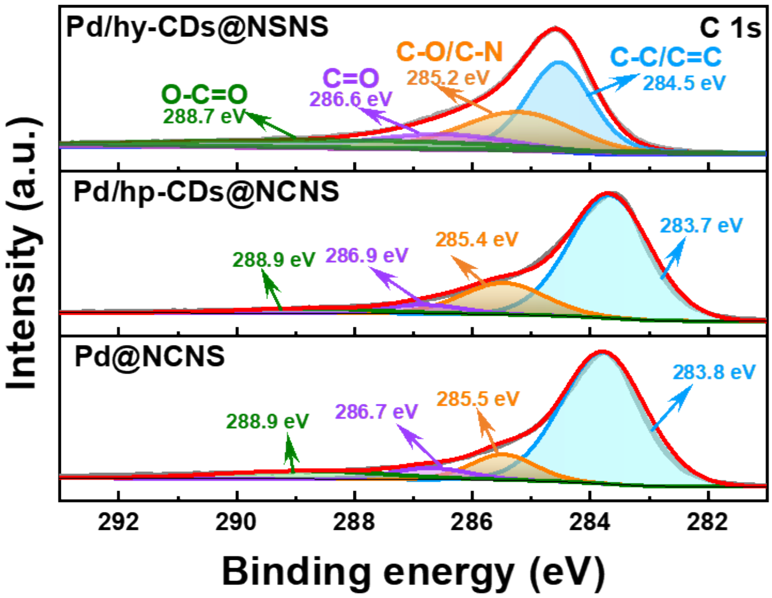


Fig. S13. C 1s spectra of Pd/hy-CDs@NCNS, Pd/hp-CDs@NCNS and Pd/@NCNS.

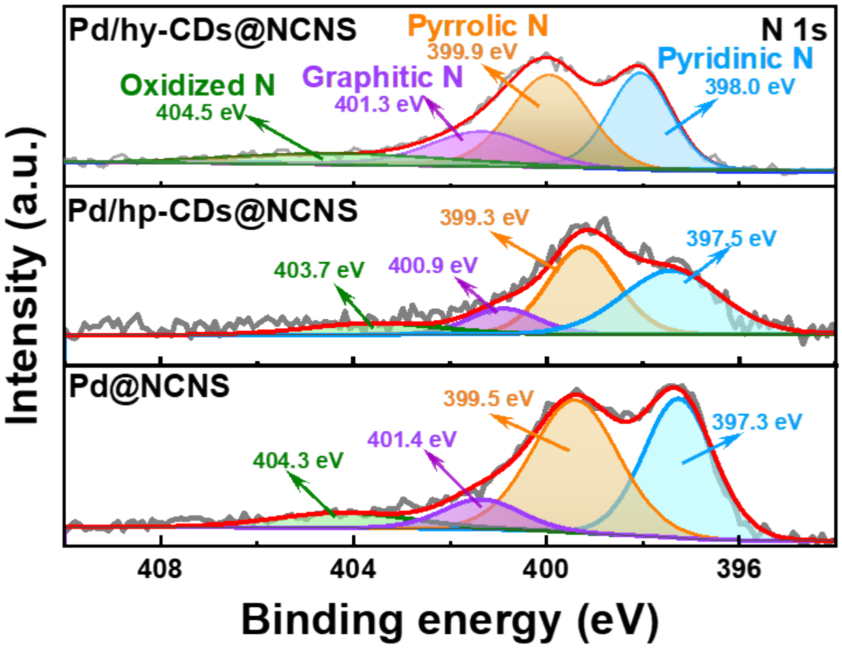


Fig. S14. N 1s spectra of Pd/hy-CDs@NCNS, Pd/hp-CDs@NCNS and Pd@NCNS.

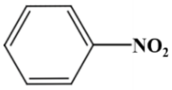
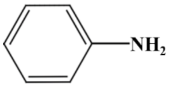
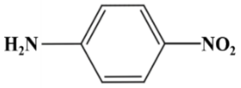
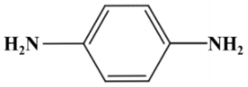
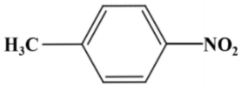
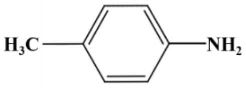
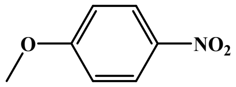
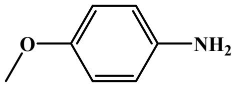
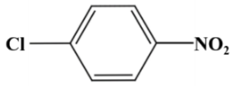
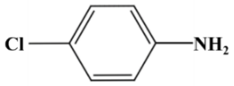
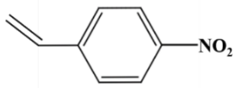
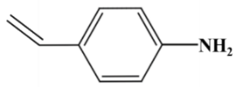
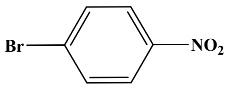
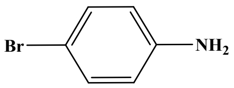
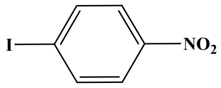
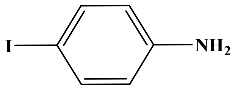
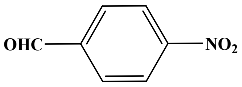
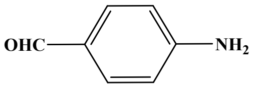
Table S1. Quality content of Pd element in Pd/hy-CDs@NCNS, Pd/hp-CDs@NCNS and Pd@NCNS.

Sample	Pd/hy-CDs@NCNS	Pd/hp-CDs@NCNS	Pd@NCNS
Pd (wt%)	8.23	7.50	6.70

Table S2. Element-specific peak fitting and corresponding binding energies for different catalysts.

	Peak fitting	Pd/hy-CDs@NCNS (eV)	Pd/hp-CDs@NCNS (eV)	Pd@NCNS (eV)
C	C-C/C=C	284.5	283.7	283.8
	C-O/C-N	285.2	285.4	285.5
	C=O	286.6	286.9	286.7
	O-C=O	288.7	288.9	288.9
N	Pyridinic N	398.0	397.5	397.3
	Pyrrolic N	399.9	399.3	399.5
	Graphitic N	401.3	400.9	401.4
	Oxidized N	404.5	403.7	404.3
Pd	Pd^0	335.87	-	335.79
	Pd^{2+}	337.77	337.80	337.89
	Pd^0	341.07	-	-
	Pd^{2+}	342.97	343.11	342.85

Table S3. Catalytic performance of Pd/hy-CDs@NCNS for various nitroaromatic hydrocarbons.

Entry	Substrate	Product	Conversion (%)	Selectivity (%)
1			>99	>99
2			>99	>99
3			>99	>99
4			>99	>99
5			>99	>99
6			>99	91
7			>99	86
8			>99	>99
9			>99	>99
10			>99	>99

Reaction conditions: 10 mg catalyst, 0.5 MPa H_2, 0.5mmol nitroaromatic substrates, 10 mL ethanol, 2h and 40 ^{o}C.

Table S4. The comparison of the activity of Pd/hy-CDs@NCNS in the hydrogenation of nitrobenzene with other catalysts.

Catalysts	Temperature (°C)	H_2 pressure (MPa)	Reaction time	Yield (%)	Ref.
Pd/hy-CDs@NCNS	40	0.1	4 h	99	This work
Pd/hy-CDs@NCNS	60	0.1	0.5 h	99	This work
Pd/MoS_2	80	4.0	1.5 h	99	[S1]
Pd/CF	30	2.0	1 h	99	[S2]
Pd/Co catalyst	R.T.	0.4	2 h	99	[S3]
Pd/Fe@N/C	40	0.8	4 h	99	[S4]
$Pd_{0.33}Ni_{0.67}$/BCNT	50	2.0	4 h	97.8	[S5]
Pd–B	45	4	70 min	99	[S6]

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