SUPPORTING INFORMATION

Semi-Encapsulated PdRh Alloy Heterojunction for the Selectively Catalytic Hydrogenation of Nitrophenylacetylene to Nitrostyrene

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Contents:

1. Synthesis of TCPP:

   4-carboxybenzaldehyde (3.0 g) was dispersed into 50 mL propionic acid in a 100 mL round bottom flask. After the solid was fully dissolved, 1.4 mL of pyrrole was added drop by drop to the mixed solution. Then the mixture was put into an oil bath and heated at 140 °C for 12 h. The product was cooled to room temperature and filtered. It was washed three times with deionized water and three times with a small amount of acetone. Finally, vacuum dried at 60 °C for 24 h to obtain black powder.

2. Catalyst characterization

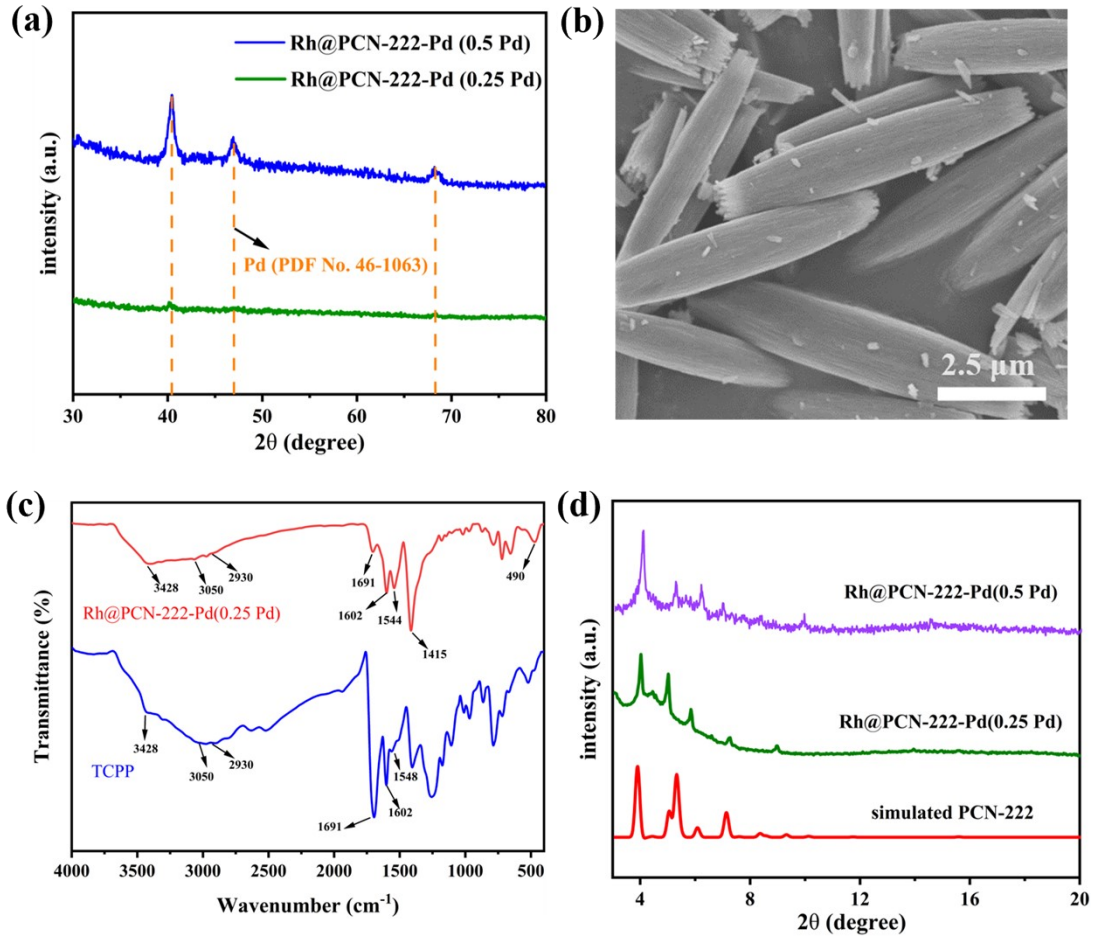


Fig. S1 (a and d) Powder X-ray diffraction pattern analysis (PXRD) of Rh@PCN-222-Pd (0.25 Pd) and Rh@PCN-222-Pd (0.5 Pd); (b) SEM of Rh@PCN-222-Pd (0.25 Pd); (c) FT-IR spectra of Rh@PCN-222-Pd (0.25 Pd) and TCPP.

It could be found that the peaks at 3428 cm $^{-1}$ corresponds to the stretching vibration of active H containing groups, N-H and O-H[1]. The two characteristic peaks at 3050 and 2930 cm $^{-1}$ arise from the C-H stretching of the aromatic ring[2]. The results show that the peak located at 1691 cm^{-1} is assigned to the imine group (C=N bond), which is included in the porphyrin ring structure, and the peak appearing at 1602 cm $^{-1}$ is caused by the skeleton characteristic absorption peak of the benzene ring. The peaks at 1544 cm $^{-1}$ and 1415 cm $^{-1}$ correspond to the asymmetric and symmetric

stretching vibrations of multielectron conjugate -COO^-, respectively[3]. Meanwhile, the peak at 490 cm^{-1} could be attributed to the Zr-O bonds of PCN-222 (Fig. S1 c)[4].

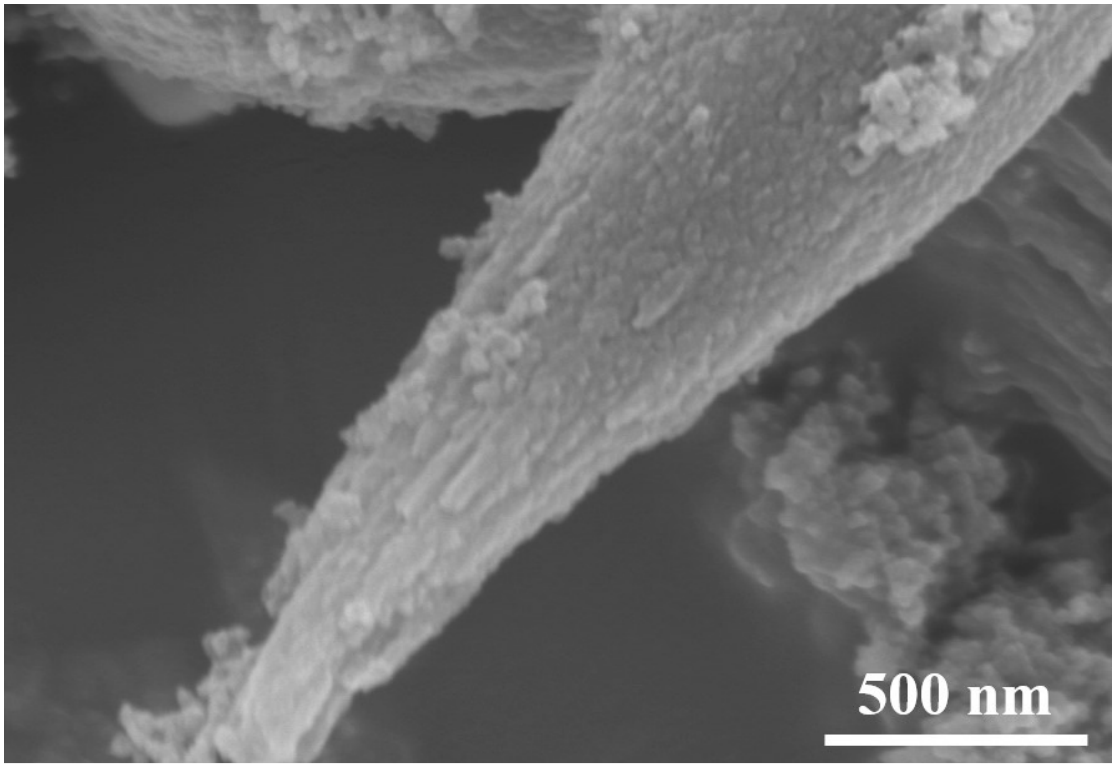


Fig. S2 The SEM of Pd-Rh@PC (0.25 Pd).

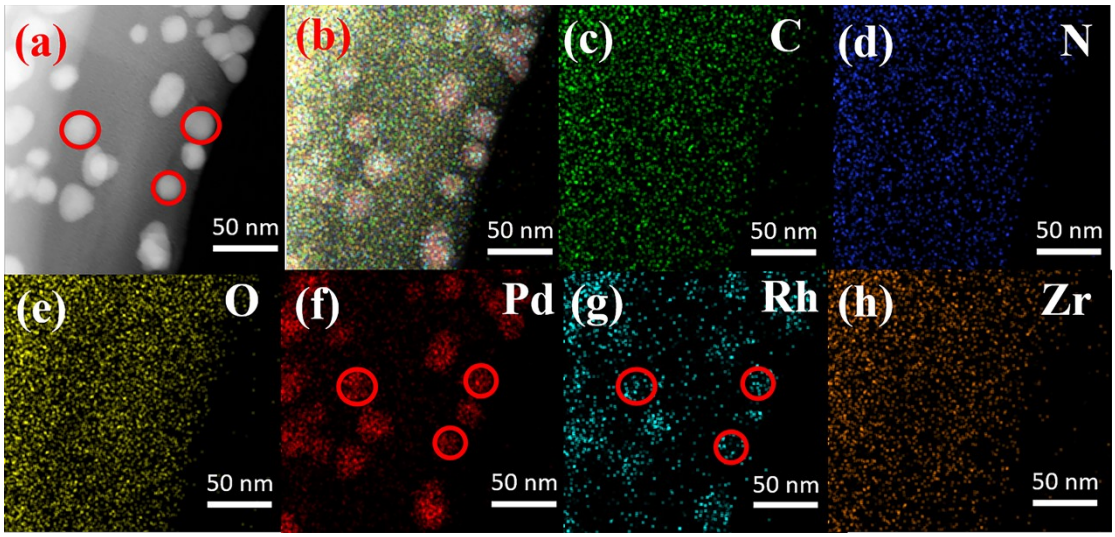


Fig. S3 Elemental mapping of Pd-Rh@PC (0.25 Pd).

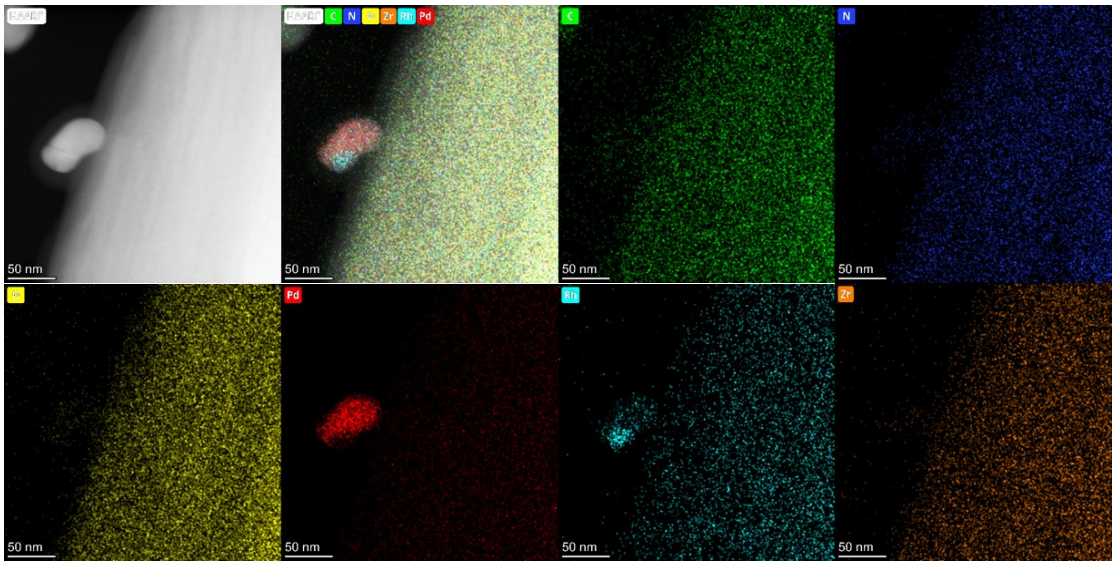


Fig. S4 Elemental mapping of Pd-Rh@PC (0.25 Pd).

Fig. S4 shows that the other elements are evenly distributed.

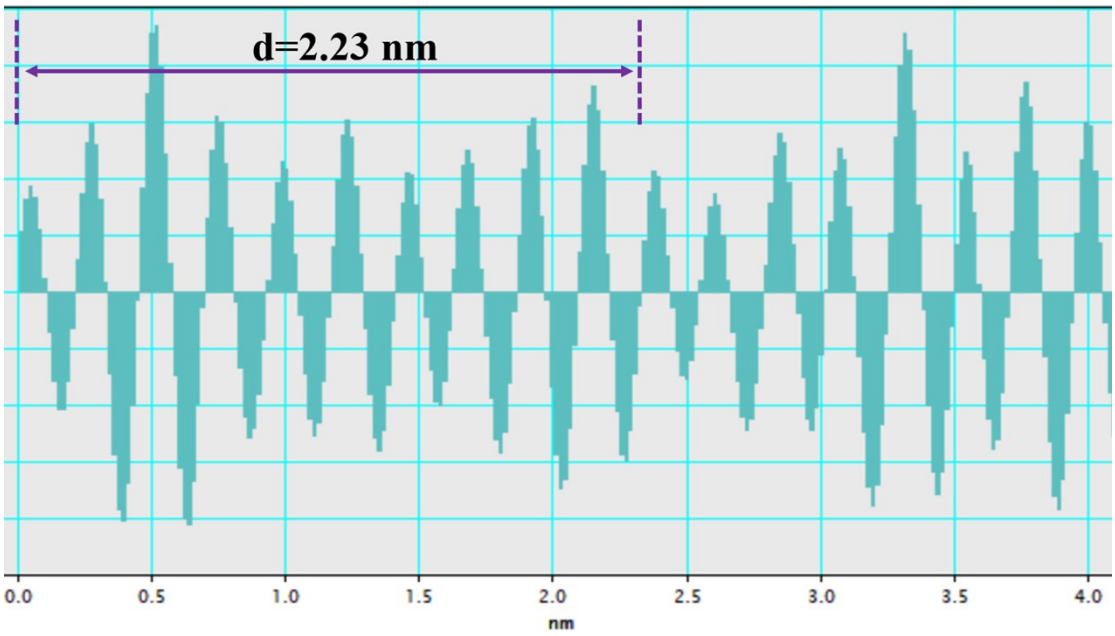


Fig. S5 Lattice spacing of Pd-Rh@PC (0.25 Pd) (taken from the Fig. 2c).

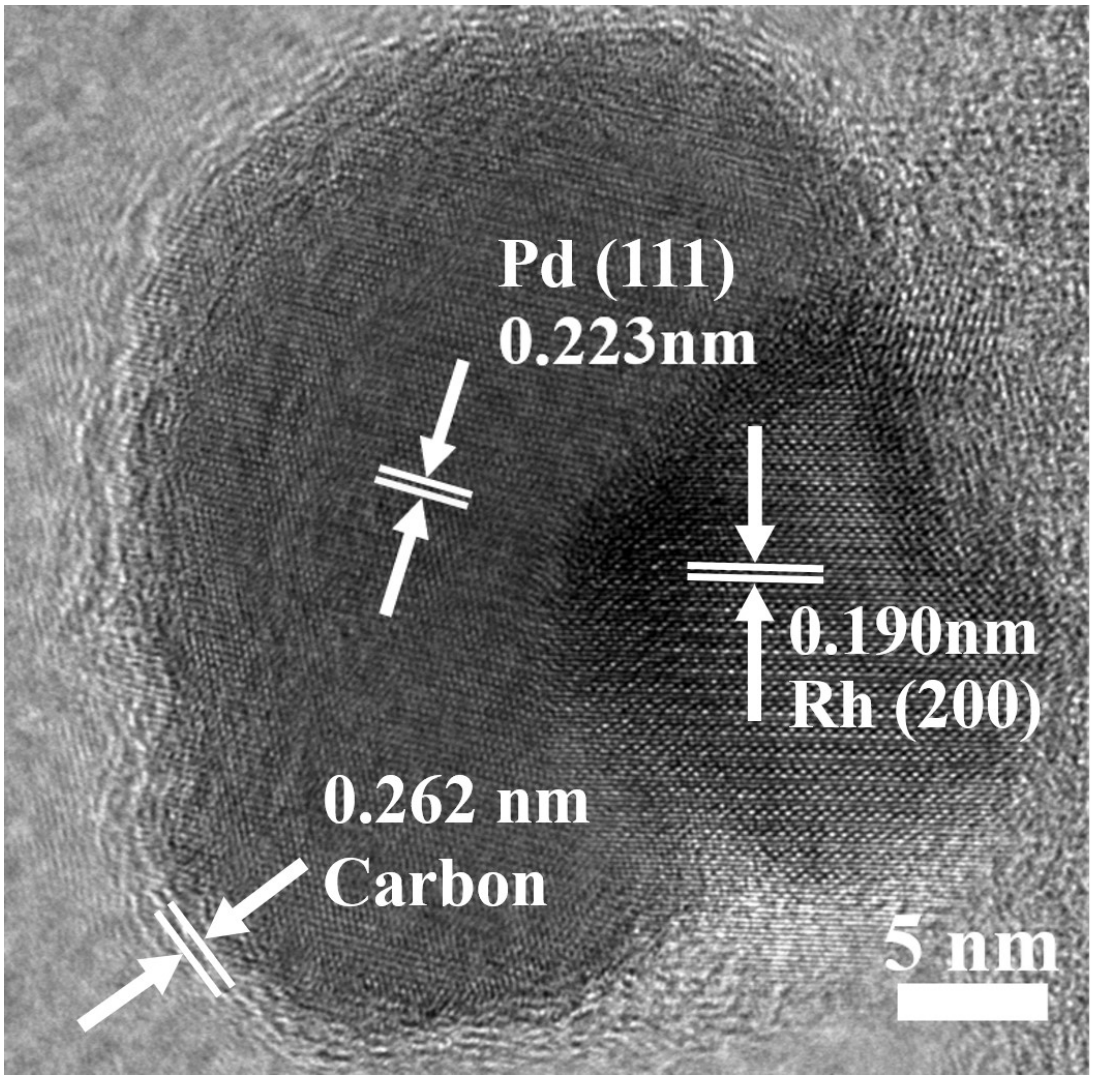


Fig. S6 The HRTEM image of Pd-Rh@PC (0.25 Pd).

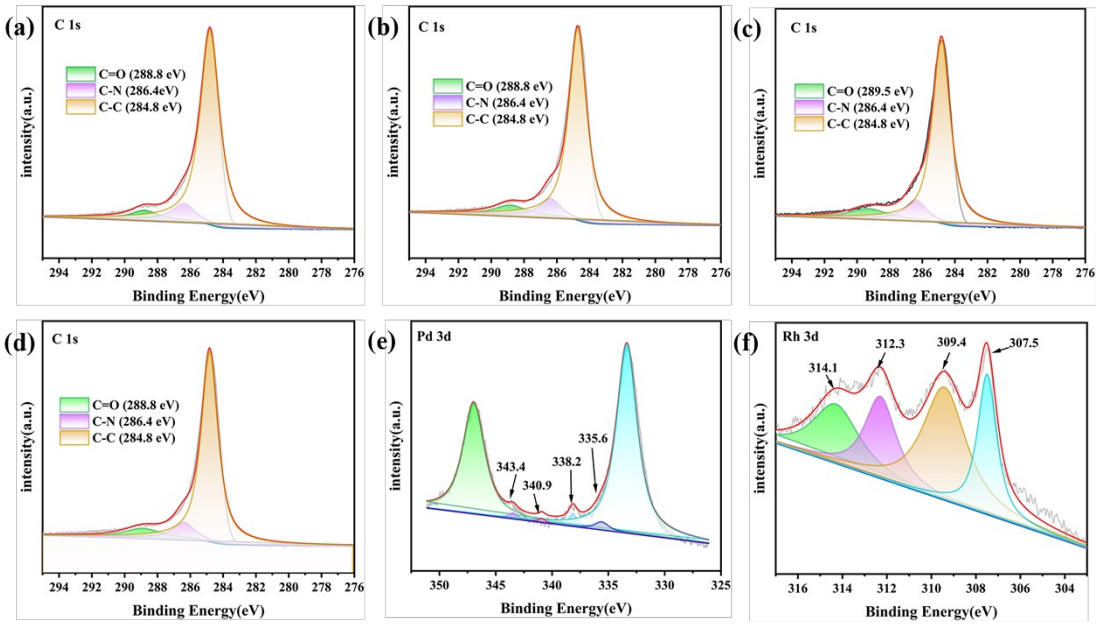


Fig. S7 XPS spectra of C 1s of (a) Pd-Rh@PC (0.5 Pd), (b) Pd-Rh@PC (0.25 Pd), (c) Rh@PC and (d) Pd@PC (0.25 Pd), respectively; XPS spectra of Pd 3d of (e) Pd@PC (0.25 Pd) and Rh 3d of (f) Rh@PC.

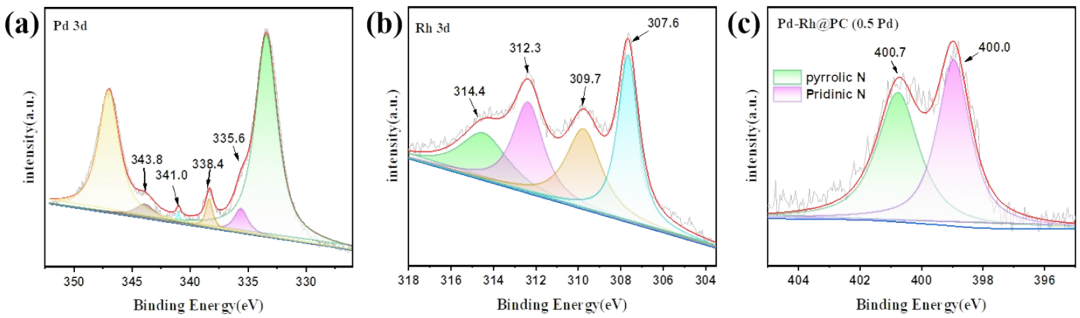


Fig. S8 XPS spectra of (a)Pd 3d, (b) Rh 3d and (c) N 1s of Pd-Rh@PC (0.5 Pd).

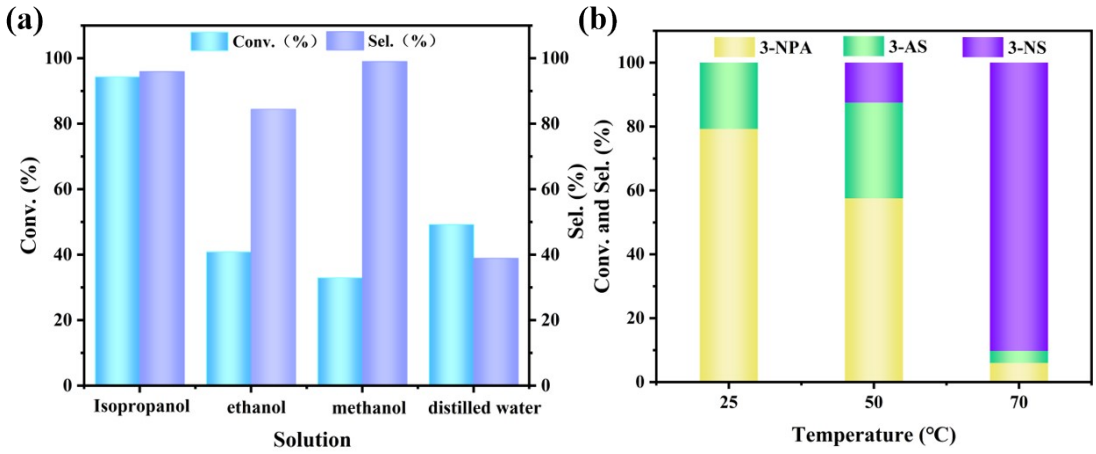


Fig. S9 (a) Different solvents for catalytic reactions; (b) Catalytic reactions at different temperatures.

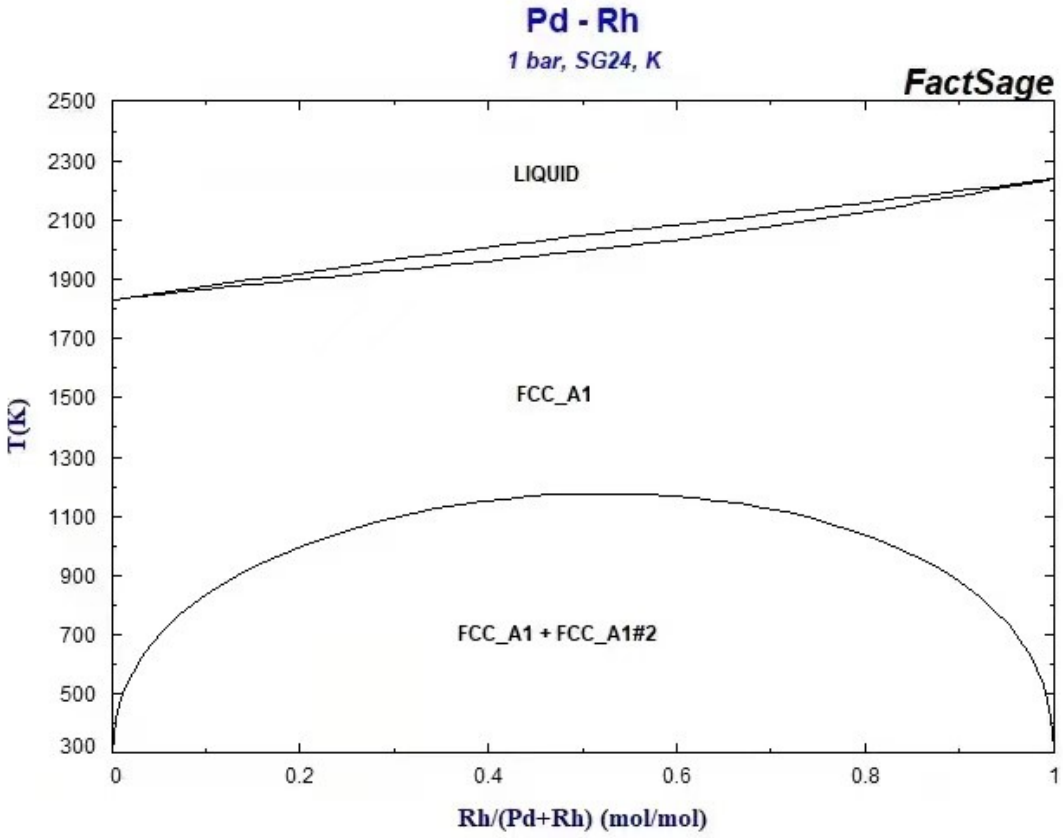
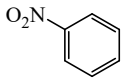
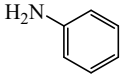
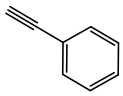
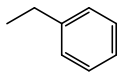


Fig. S10 Solubility Phase Diagram of Pd-Rh.

Table S1

The reduction of nitrobenzene and phenylacetylene over the Pd-Rh@PC (0.25 Pd) catalyst. [a]

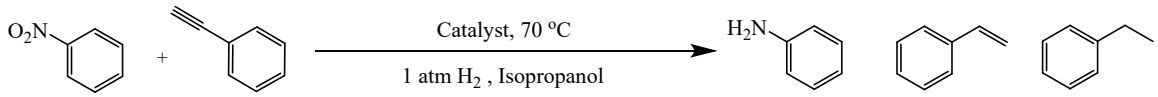
Entry	Substrate	Catalyst	Time	Conv. (%) [b]	Sel. (%) [b]	Product
1		Pd-Rh@PC (0.25 Pd)	10 h	99	99	
2			10 h	96	99	

[a] Reaction condition: substrate (1 mmol), catalyst (20 mg), isopropanol (5 mL).

[b] Conversion and selectivity were analyzed by GC.

Table S2

The reduction of nitrobenzene and phenylacetylene over the Pd-Rh@PC (0.25 Pd) catalyst. [a]



Substrate 1 Substrate 2 Product 1 Product 2 Product 3

Entry	Catalyst	Time (h)	Conv. (%) [b]	
			1	2
1	Pd-Rh@PC (0.25 Pd)	10	-	98

[a] Reaction condition: nitrobenzene (0.5 mmol), phenylacetylene (0.5 mmol), catalyst (20 mg), isopropanol (5 mL).

[b] Conversion was analyzed by GC.

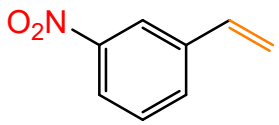
Table S3

Comparison of catalyst performance based on selectivity and activity of 3-NPA semi-hydrogenation to 3-NS.

Entry	Catalyst	T (°C)	Hydrogen Source	Time	Conv (%)	Sel. (%)	Ref.
1	Co clusters/N-C	60	1 atm H_2	30 min	93	87	Ref[5]
2	$[Ir(cod)Cl]_2$	70	Ethanol	20 h	99	93	Ref[6]
3	Pd_1/Ni@G	30	5 atm H_2	8 h	99	92	Ref[7]
4	Au_3Pd_1 NDs	15	1 atm H_2	8 min	77	98	Ref[8]
5	Pd-Rh@PC (0.25 Pd)	70	1 atm H_2	10 h	94	96	This work

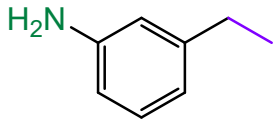
Characterization of compounds:

3-Nitrostyrene:



A yellow oil (96%). GC-MS: m/z (%) 149 (96), 103 (87), 77 (100), 51 (37).

3-Ethylaniline:



A colorless oil (99%). GC-MS: m/z (%) 121 (85), 106 (100), 77 (22).

References

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