Supporting Information

Graphdiyne-Based Pd Single-Atom Catalyst for Semihydrogenation of Alkynes to Alkenes with High Selectivity and Conversion under Mild Conditions

Xue-Peng Yin, Shang-Feng Tang, Chao Zhang, Hong-Juan Wang,* Rui Si,* Xiu-Li Lu,* and Tong-Bu Lu*

X. Yin, S. Tang, C. Zhang, H. Wang, X. Lu, Prof. T. Lu
MOE International Joint Research Laboratory of Materials Microstructure, Institute for New Energy Materials & Low Carbon Technologies, School of Materials Science and Engineering, Tianjin University of Technology, Tianjin, 300384 (China)
Prof. R. Si
Shanghai Synchrotron Radiation Facility, Shanghai Institute of Applied Physics, Chinese Academy of Sciences Shanghai 201204 (China)
E-mail: hongjuanwang@tjut.edu.cn, sirui@sinap.ac.cn, luxiuli@email.tjut.edu.cn, lutongbu@tjut.edu.cn

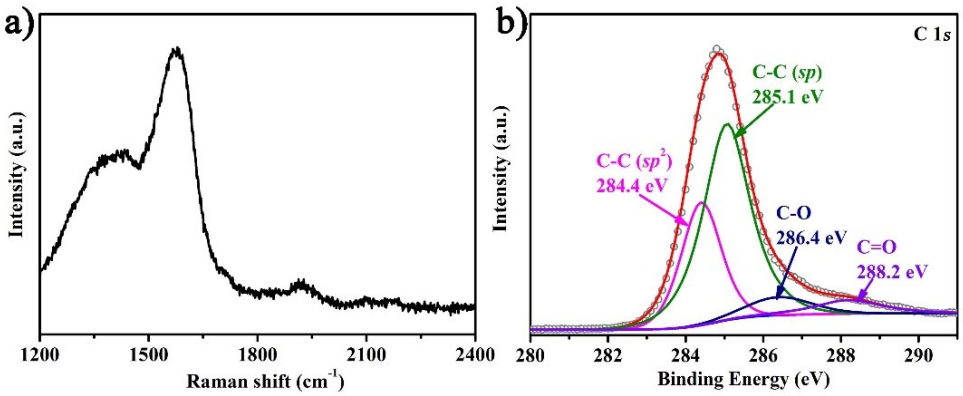


Figure S1. Raman and XPS spectra of pure GDY.

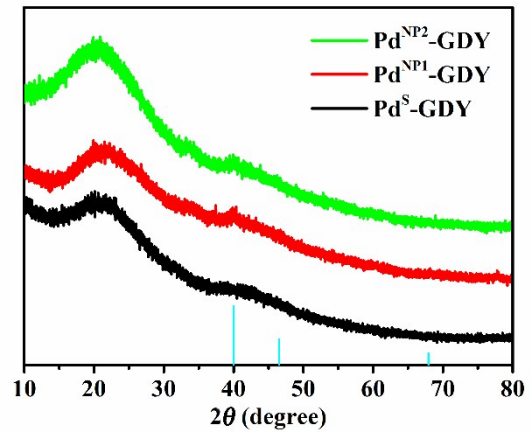


Figure S2. XRD spectra of Pd^{s}-GDY, Pd^{NP1}-GDY, and Pd^{NP2}-GDY.

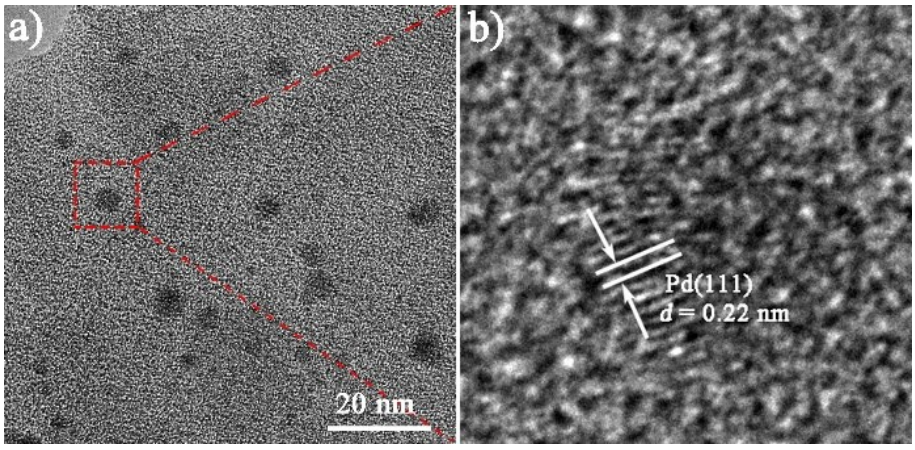


Figure S3. HRTEM images of Pd^{NP1}-GDY.

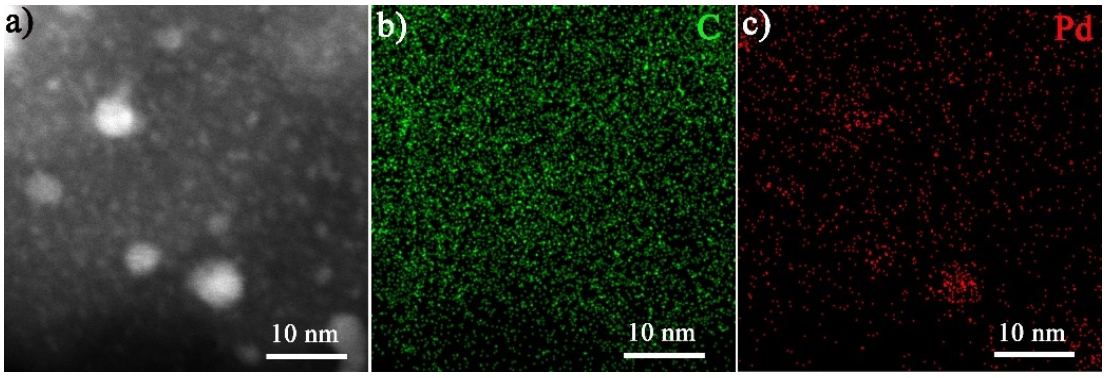


Figure S4. HRTEM image and corresponding elemental mapping analysis of Pd^{NP1}-GDY.

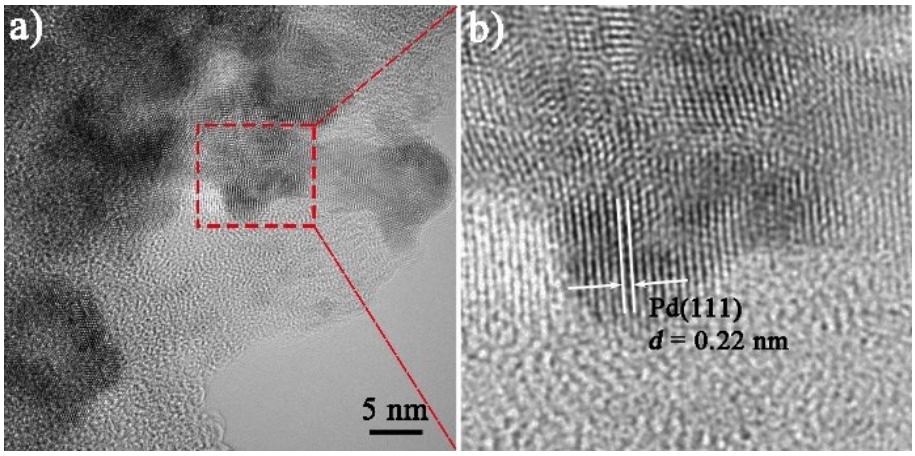


Figure S5. HRTEM images of Pd^{NP2}-GDY.

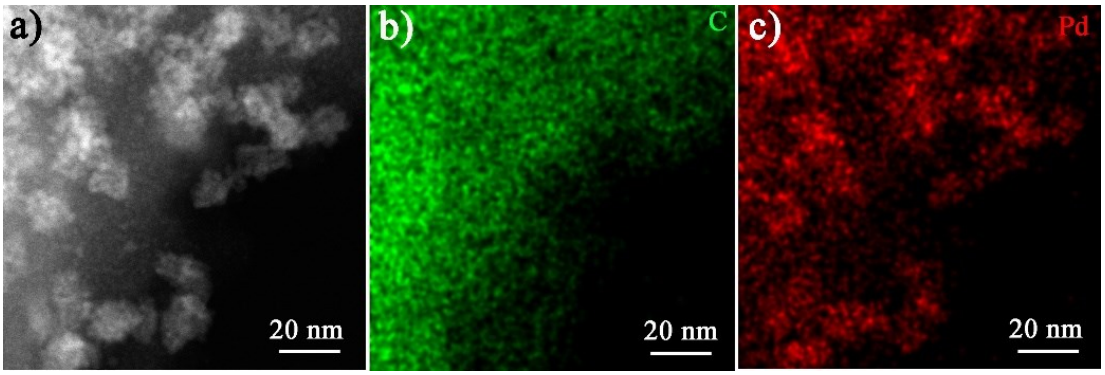


Figure S6. HRTEM image and corresponding elemental mapping analysis of Pd^{NP2}-GDY.

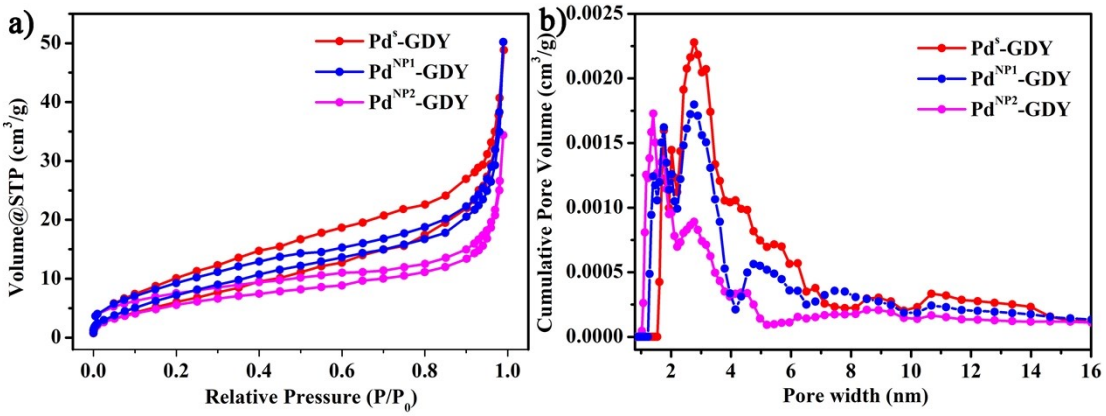


Figure S7. Nitrogen adsorption–desorption isotherms (a) and Corresponding pore size distribution (b) of Pds-GDY, Pd^{NP1}-GDY and Pd^{NP2}-GDY.

Table S1. Surface Area, Pore Volume, and Pore Size of Pds-GDY, Pd^{NP1}-GDY and Pd^{NP2}-GDY.

Sample	Surface area (m^2/g)	Pore volume (cm^3/g)	Pore size (nm)
Pd^{s}-GDY	25.0	0.049	2.77
Pd^{NP1}-GDY	21.5	0.043	2.77
Pd^{NP2}-GDY	21.0	0.029	1.41

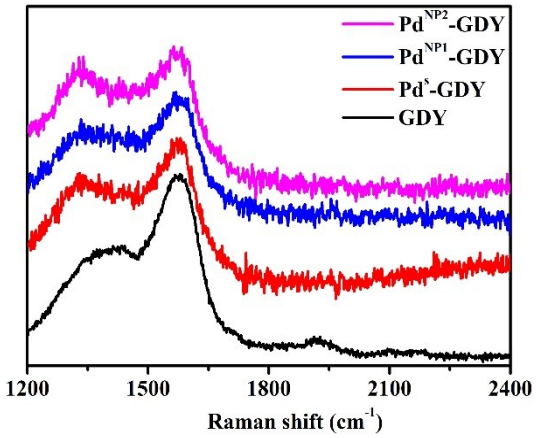


Figure S8. Raman spectra of GDY, Pd^{s}-GDY, Pd^{NP1}-GDY, and Pd^{NP2}-GDY.

Table S2. Pd K-edge EXAFS fitting results (*R*: distance; *CN*: coordination number; σ^2: Debye-Waller factor; ΔE_0: inner potential correction) of Pd foil and Pd^{s}-GDY.

Sample	Pd-C		Pd-Cl		Pd-Pd		σ^2 (Å^2)	ΔE_0 (eV)
	R (Å)	*CN*	*R* (Å)	*CN*	*R* (Å)	*CN*		
Pd foil	—	—	—	—	2.740± 0.002	12	0.0055±0.0003	2.9±0.4
Pd^{s}-GDY	1.98± 0.02	1.4±0.3	2.28± 0.02	1.8±0.5	—	—	0.003±0.001(O) 0.005±0.002(Cl)	5.6±1.7

Table S3. The Pd content in Pd^{s}-GDY, Pd^{NP1}-GDY, and Pd^{NP2}-GDY.

Catalyst	Pd loading (wt%)
Pd^{s}-GDY	0.42
Pd^{NP1}-GDY	0.56
Pd^{NP2}-GDY	0.65

Table S4. Catalytic performance of Pd^{s}-GDY, Pd^{NP1}-GDY, and Pd^{NP2}-GDY in phenylacetylene semihydrogenation.

Catalyst	Time (h)	Conv. /%	Alkene Sel. /%	TOF (h^{-1})
Pd^{s}-GDY	2	100	99.3	6290
Pd^{NP1}-GDY	2	100	95.8	4551
Pd^{NP2}-GDY	2.5	100	38.8	1270

TOF was calculated by the mole number of target product·(mole number of total Pd)$^{-1}$·h^{-1}.

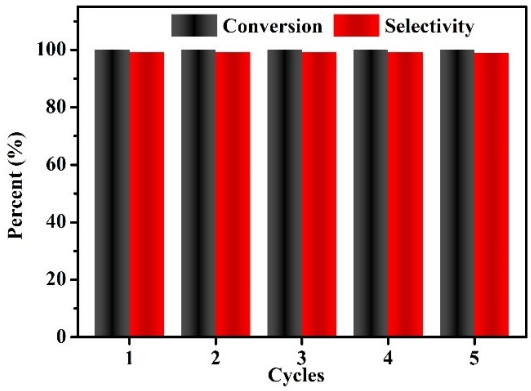


Figure S9. Recyclability of the Pd^{s}-GDY catalyst.

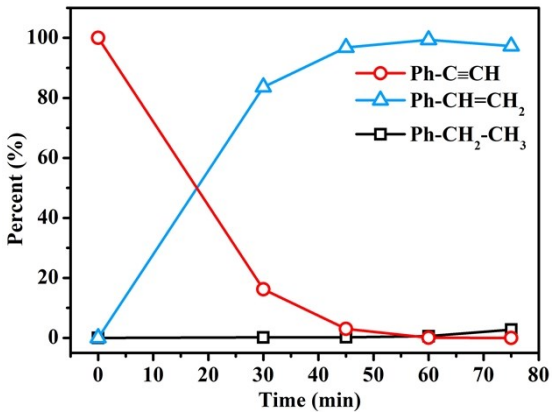


Figure S10. The conversion of phenylacetylene and the selectivity toward styrene and phenylethane as a function of reaction time over Pd^{s}-GDY. Reaction conditions: 2 mg catalyst, 1.0 mmol phenylacetylene, 2 mL ethanol, 50 °C, 0.2 MPa H_2.

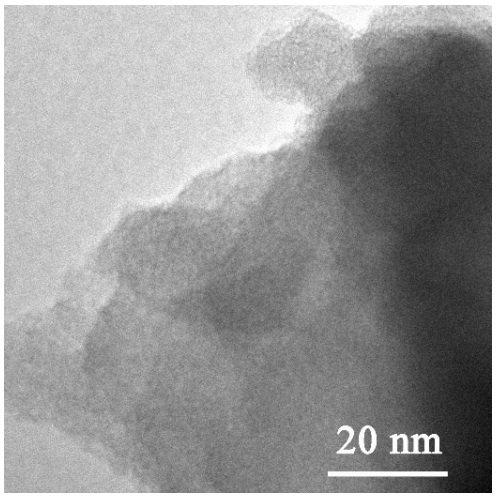


Figure S11. TEM image of Pd^{s}-GDY after simihydrogenation of phenylacetylene.

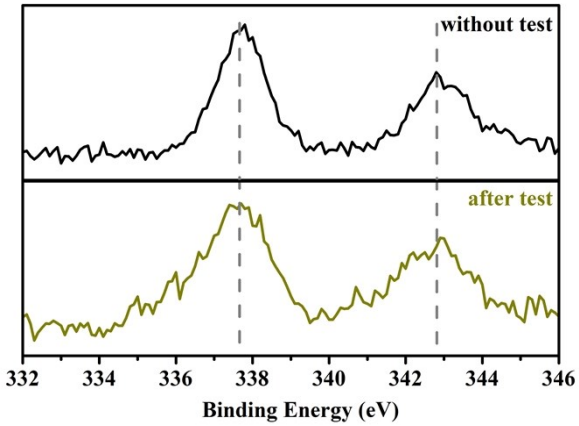


Figure S12. Pd 3d XPS spectra for Pd^{s}-GDY before and after semihydrogenation of phenylacetylene.

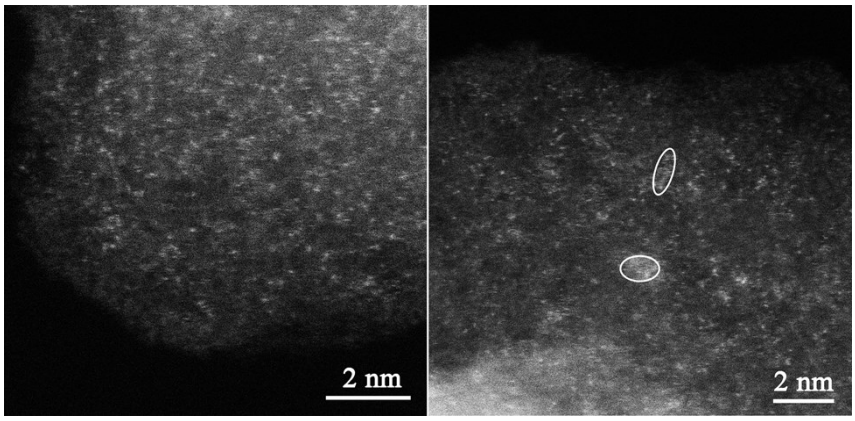


Figure S13. The atomic-resolution HAADF-STEM images for Pd^{s}-GDY after semihydrogenation of phenylacetylene.

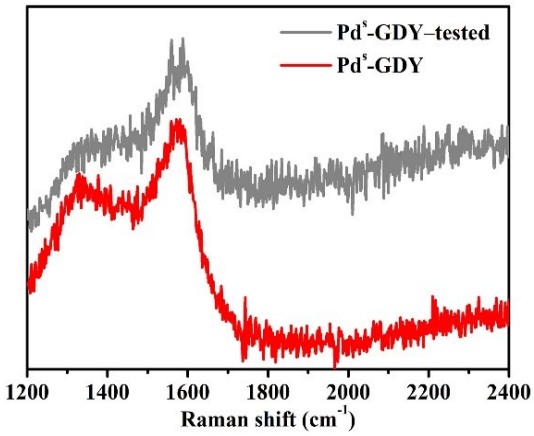


Figure S14. Raman spectra for Pd^s-GDY before and after simihydrogenation of phenylacetylene.

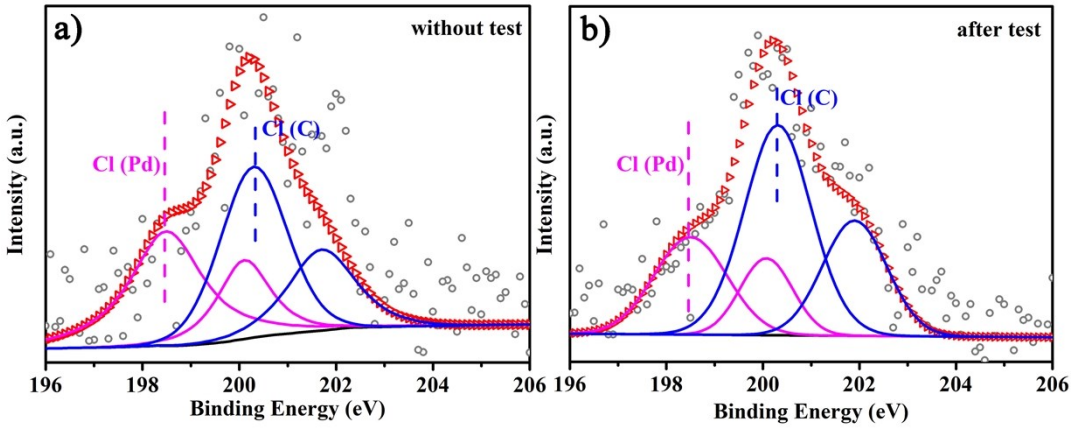
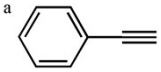
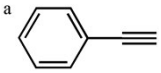
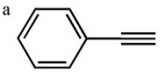
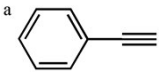
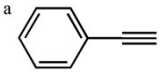
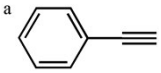
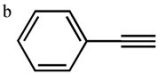
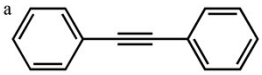
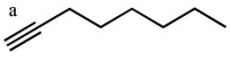
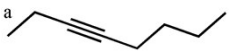


Figure S15. Cl 2p XPS patterns of Pd^s-GDY after semihydrogenation of phenylacetylene.

Table S5. The Pd content in Pd^s-GDY before and after semihydrogenation of phenylacetylene determined by EDS.

Pd^s-GDY	Atomic (%)
Without test	1.23
After test	1.20

Table S6. Liquid-phase semihydrogenation of alkyne on different catalysts.

Catalyst	Reagent	Time (h)	Conv. /%	Alkene Sel. /%
Pd^{NP1}-GDY	a 	2	100	95.8
		3	100	66.6
Pd^{NP2}-GDY	a 	2	86.4	59.7
		3	100	8.5
Pd/C-D	a 	1	100	91.4
		2	100	0
Pd/C	a 	2	100	0
GDY	a 	2	0	0
Pd^{S}-GDY	a 	2	100	99.3
		3	100	98.9
Pd^{S}-GDY	b 	1/3	100	99.9
Pd^{S}-GDY	a 	3	100	99.0
Pd^{S}-GDY	a 	2.5	100	97.6
Pd^{S}-GDY	a 	2.5	100	98.3

Reaction conditions: 1.0 mmol alkyne (a), 0.1 mmol alkyne and 0.9 mmol alkene (b), 2 mL ethanol, 0.2 MPa H_2, 25 °C.

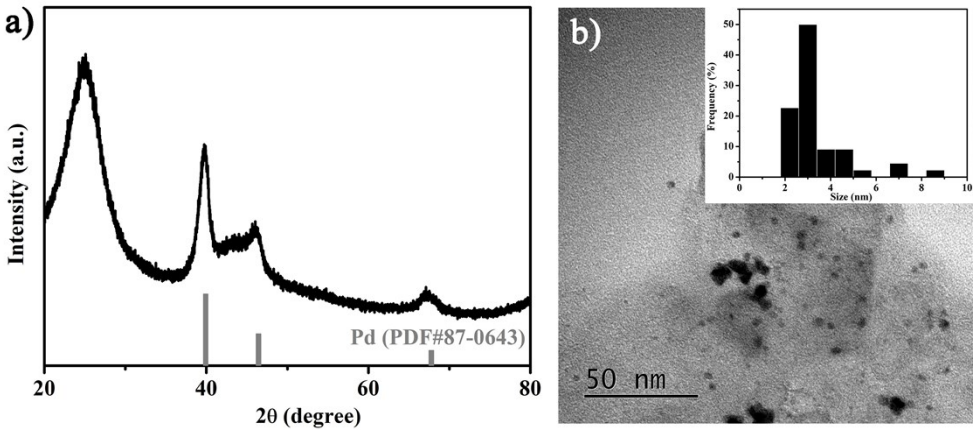


Figure S16. XRD pattern and TEM image for the prepared Pd/C-D.

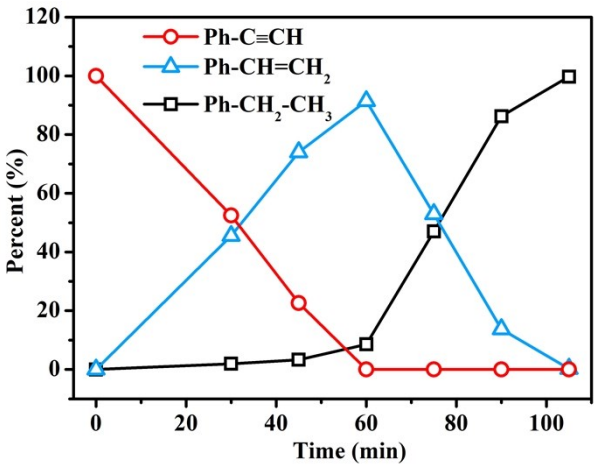


Figure S17. The conversion of phenylacetylene and the selectivity toward styrene and phenylethane as a function of reaction time over Pd/C-D.

As shown in Figure S16a, the XRD pattern shows peaks assigned to metallic Pd (PDF 87-0643), indicating the formation of Pd nanoparticles. The TEM (Figure S16b) image exhibits that the size of Pd nanoparticles in Pd/C-D was about 3 nm. The catalytic performance for the Pd/C-D catalysts was also measured. As shown in Figure S17, Pd/C-D shows a 100% conversion of phenylacetylene with 91.4% selectivity to after reacting for 1h. Then, Pd/C-D subsequently catalyzes the hydrogenation of styrene to phenylethane completely after 2h reaction. The hydrogenation properties on Pd/C-D are similar to that on Pd^{NP1}-GDY.

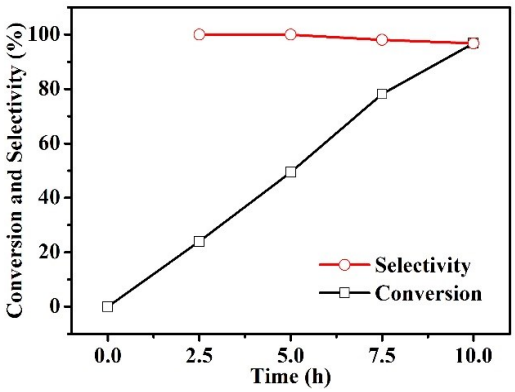


Figure S18. Performance testing of amplified substrates.

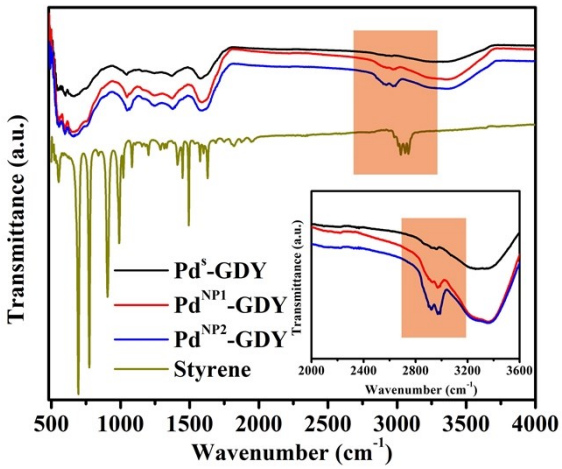


Figure S19. FT-IR spectra of pure styrene and Pd^{s}-GDY, Pd^{NP1}-GDY, Pd^{NP2}-GDY treated with styrene, respectively.