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Novel solid-state synthesis of surfactant- and solvent-free Pd tetrahedron nanocatalysts

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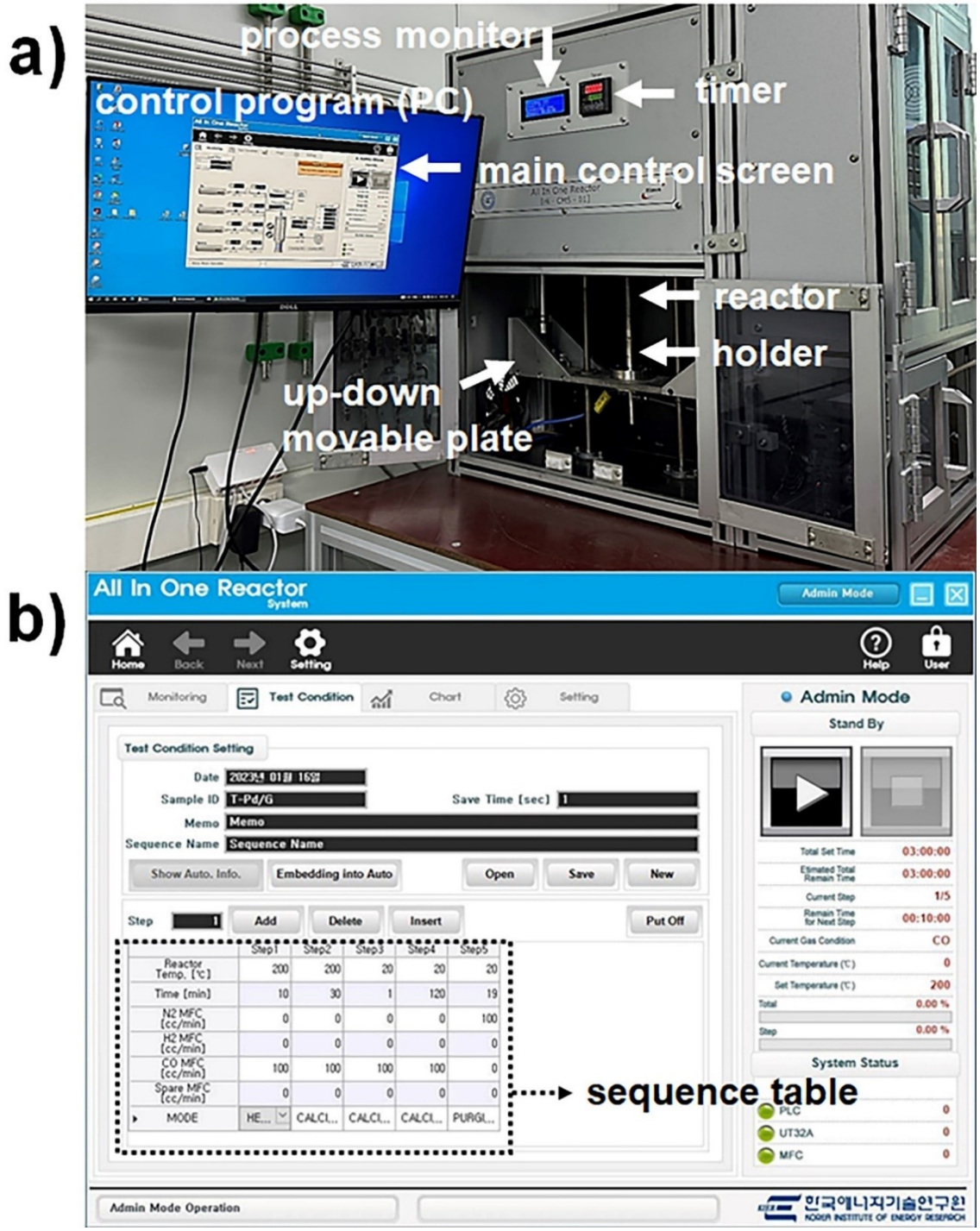

Figure S1. (a) A picture of the AIO reactor system and (b) the sequence table for T-Pd/G in the software program.

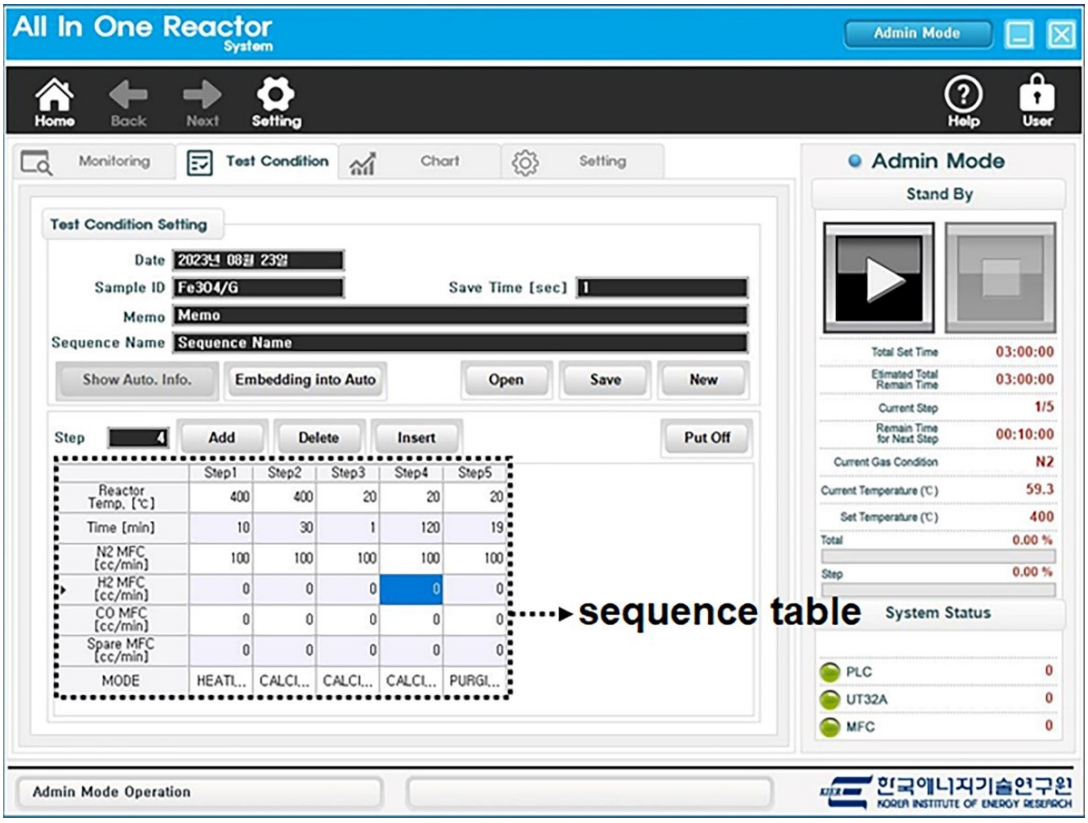

Figure S2. Sequence table for Fe_3O_4-G synthesis in the software program of the AIO reactor system.

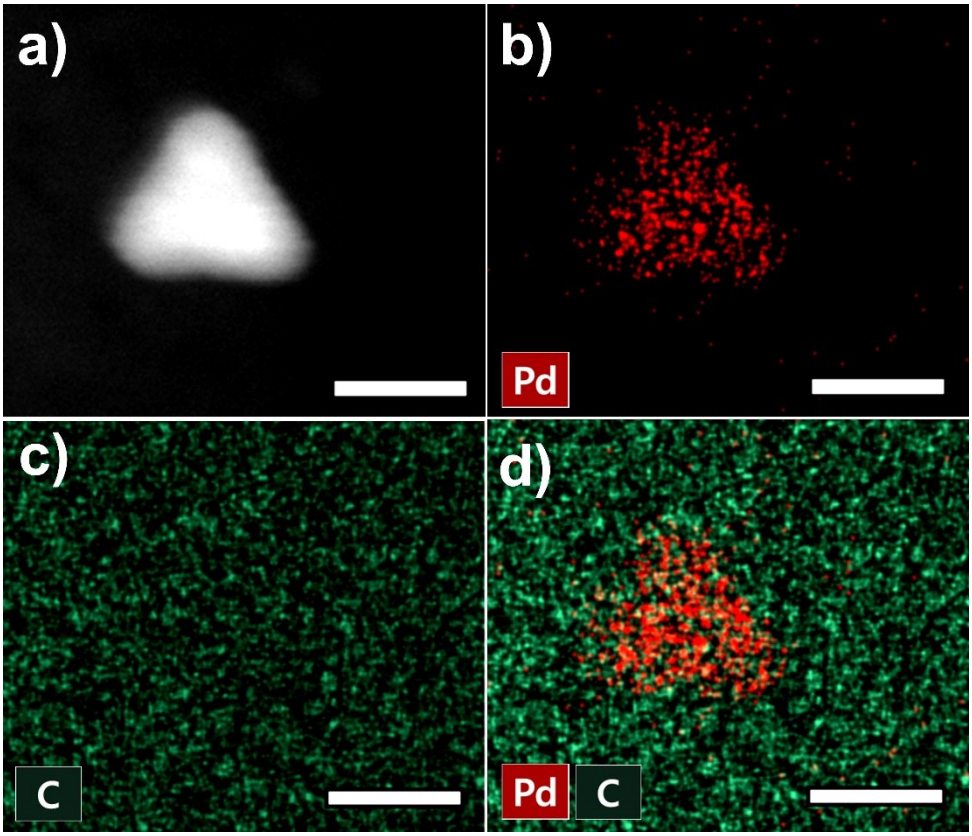

Figure S3. (a) HAADF-TEM image and (b-d) elemental mapping images of single Pd nanoparticle in T-Pd/G. All bars represent 10 nm.

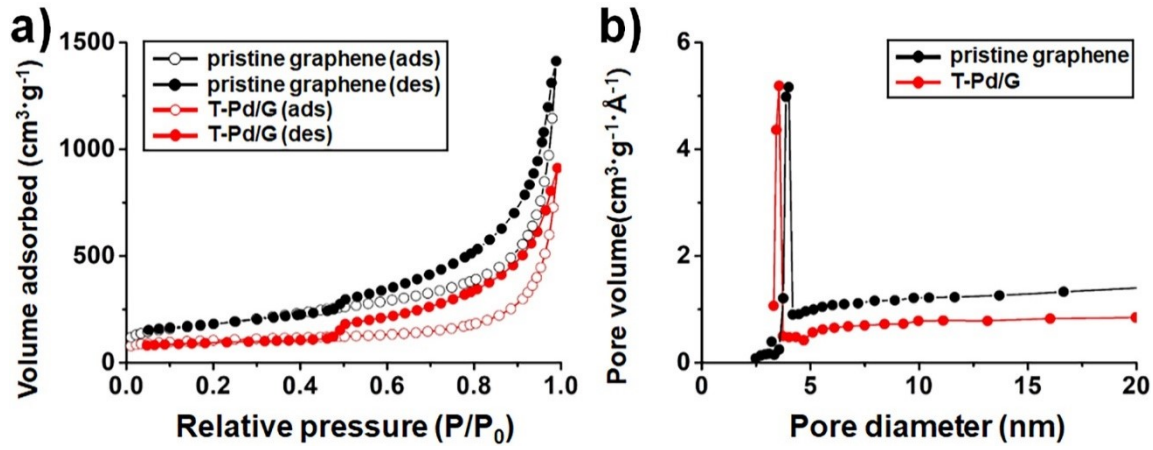

Figure S4. (a) N_2 sorption isotherms and (b) pore size distribution diagrams by desorption branches of pristine graphene and T-Pd/G.

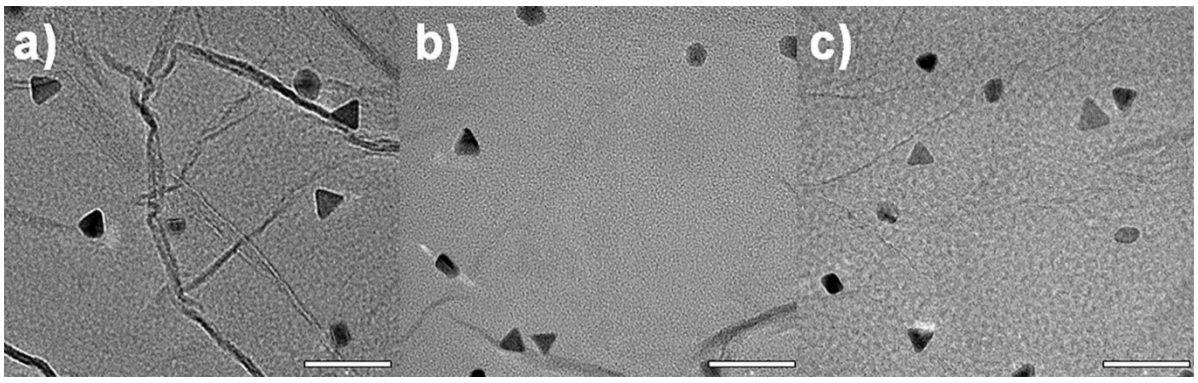

Figure S5. (a-c) TEM images of the T-Pd/G at different batches. All bars represent 50 nm.

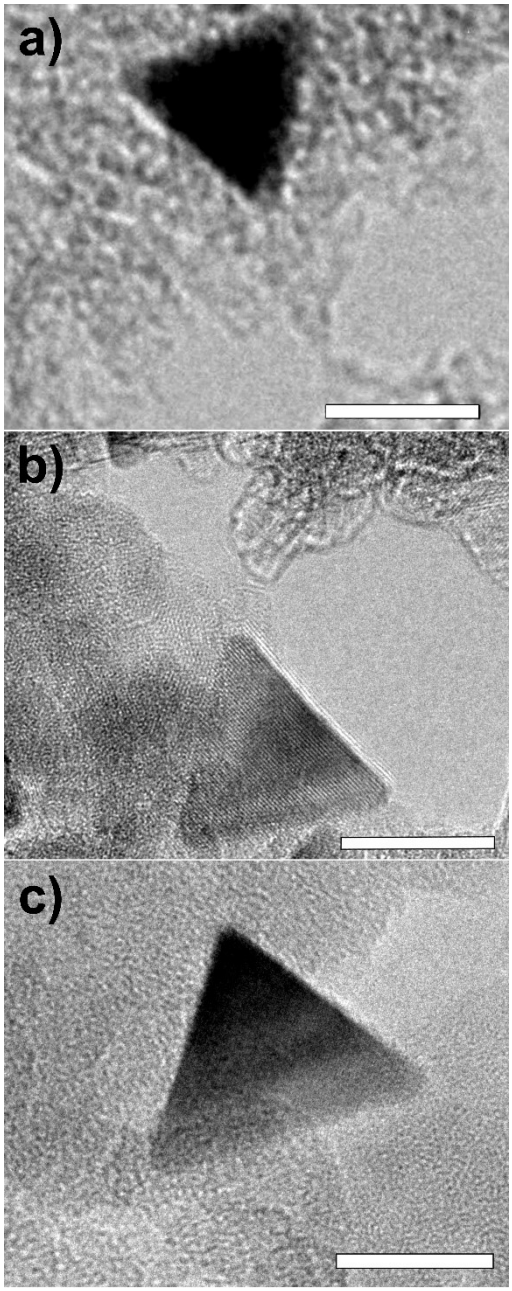

Figure S6. HRTEM images of (a) T-Pd/AC, (b) T-Pd/Al_2O_3, and (c) T-Pd/SiO_2. All bars represent 10 nm.

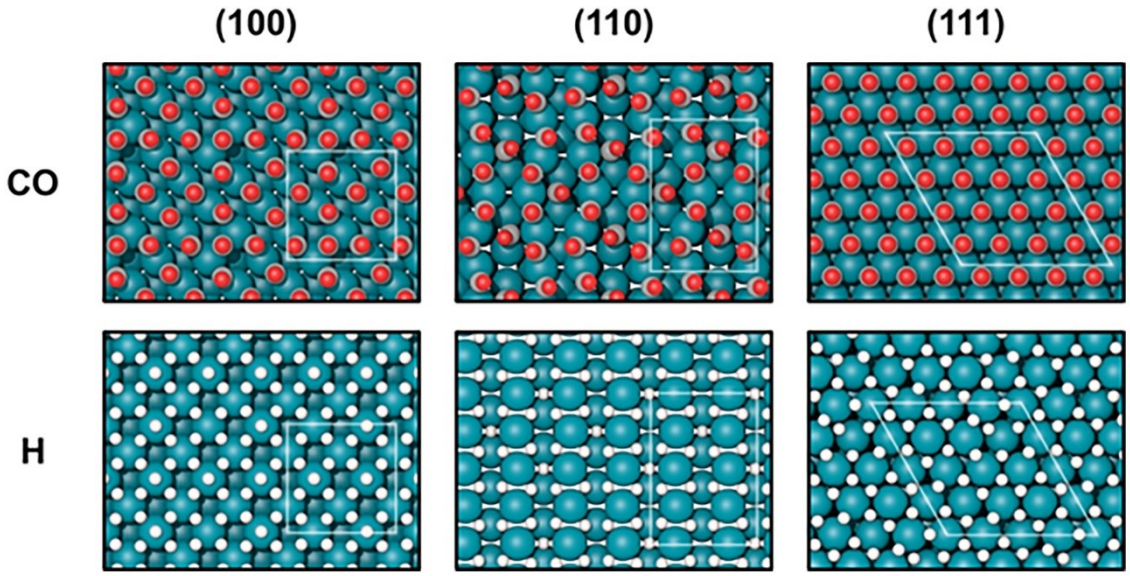

Figure S7. Atomic configurations of Pd slab models with full coverage of molecules.

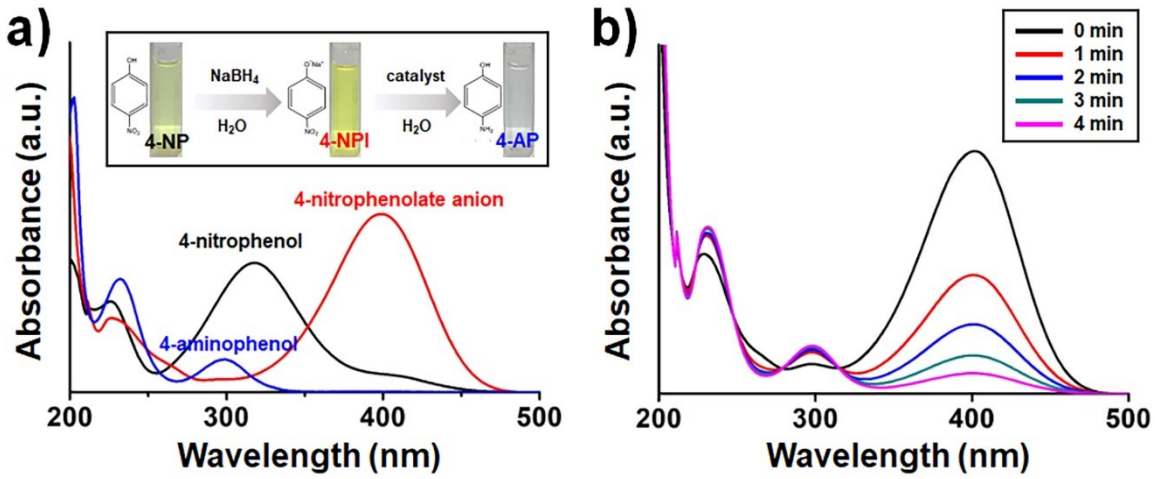

Figure S8. (a) UV–vis spectra and photographs of 4-nitrophenol (4-NP), 4-nitrophenolate anion (4-NPI), and 4-aminophenol (4-AP). (b) UV-vis spectra of the catalytic 4-NP reduction reaction at 30 °C for 4 min using T-Pd/G catalyst.

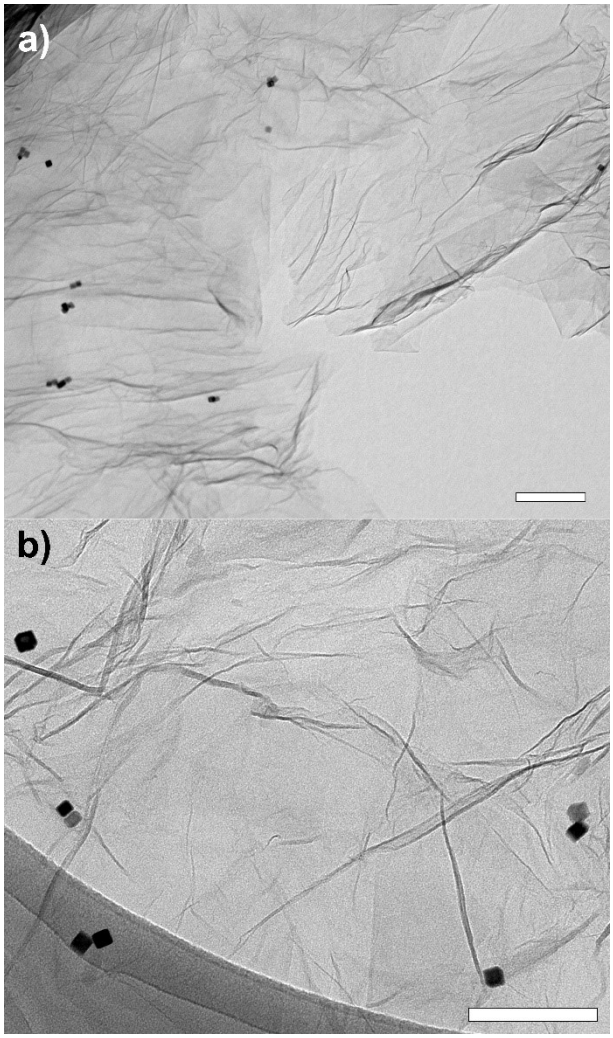

Figure S9. (a,b) Low-resolution TEM images of C-Pd/G. The bars represent 200 nm (a) and 100 nm (b).

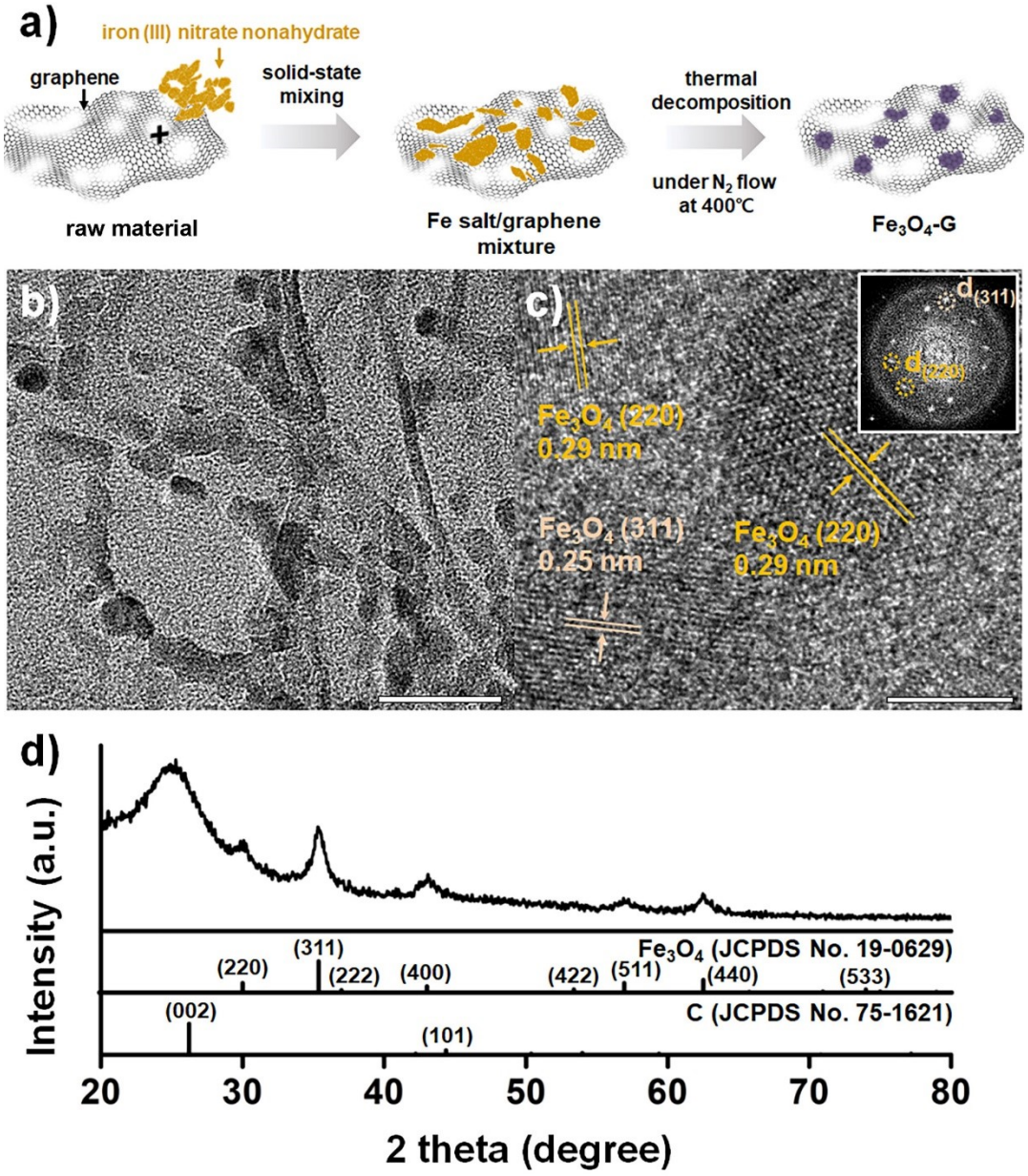

Figure S10. (a) A brief scheme of magnetically separable Fe_3O_4-G support. (b) TEM image, (c) HRTEM image with the corresponding FT pattern (inset of c), (d) XRD spectrum of Fe_3O_4-G. The bars represent 50 nm (b) and 5 nm (c), respectively.

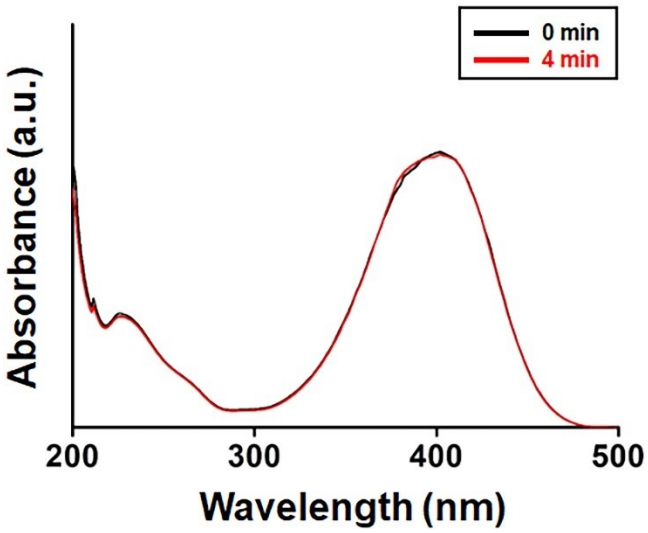

Figure S11. UV-vis spectra by the 4-NP reduction reaction at the initial point (0 min) and after reaction (4 min) using Fe_3O_4-G at 30 °C.

Table S1. Comparison of the lattice constant of Pd with those in the recently reported literature.

Method	Lattice constant (Å)	Ref.
GGA-PBE	3.94	This work
GGA-PBE	3.98	[1]
GGA-PBE	3.95	[2]
EXPT	3.88	[3]
EXPT	3.89	[4]

Table S2. Comparison of the surface energy of the low-index Pd slab model with those found in the literature.

	Surface energy ($J \cdot m^{-2}$)			
Method	(100)	(110)	(111)	Ref.
GGA-PBE	1.54	1.58	1.30	This work
GGA-PBE	1.54	1.60	1.36	[5]
GGA-PBE	1.49	1.55	1.31	[2]
GGA-PBE	1.51	1.60	1.33	[6]

Table S3. The adsorption energies of CO and H on different Pd facets calculated for both a single molecule and at full coverage.

Molecule	Facet	# of adsorbate	Adsorption energy (eV)
CO	(100)	1	–1.86
		9 (full coverage)	–0.74
	(110)	1	–1.88
		11 (full coverage)	–0.99
	(111)	1	–2.03
		16 (full coverage)	–0.85
H	(100)	1	–0.48
		19 (full coverage)	–0.02
	(110)	1	–0.50
		19 (full coverage)	–0.22
	(111)	1	–0.58
		27 (full coverage)	–0.06

Table S4. Rate constant data for each catalyst in 4-NP reduction at different reaction temperatures.

Catalyst	Reaction conditions	Temperature (℃)	Rate constant k ($x10^{-3}·s^{-1}$)
T-Pd/G	Catalyst amount: 2.0 mg C/N ratio = 2.0 reaction time: 4 min	5	6.4
		10	7.2
		20	9.2
		30	10.1
		40	11.2
		50	15.3
S-Pd/G		5	3.4
		10	3.6
		20	5.0
		30	6.2
		40	8.0
		50	9.5
commercial Pd/C		5	1.0
		10	1.2
		20	1.8
		30	2.9
		40	4.2
		50	5.9

*C/N ratio = used catalyst weight (g)/4-NP (mol).

Table S5. Comparison of rate constant and activation energies of Pd-based catalysts found in the literature for catalysts used in 4-NP reduction.

Catalyst	Reaction condition	Rate constant k ($x10^{-3}\cdot s^{-1}$)	E_a ($kJ\cdot mol^{-1}$)	Ref.
T-Pd/G	Catalyst amount: 2.0 mg C/N ratio = 2.0 reaction time: 4 min reaction temp.: 30 ℃	10.12	13.2	This work
S-Pd/G		6.23	17.8	
commercial Pd/C		2.90	30.3	
Pd NPs	Catalyst amount: 1.3 μg C/N ratio = 3.3 reaction time: 6 min reaction temp.: 25 ℃	8.7	14.1	[7]
PEI-Pd24	Catalyst amount: 20 mg C/N ratio = 166.7 reaction time: 13 min reaction temp.: room temp.	4	35.3	[8]
Pd/BGO	Catalyst amount: 50 mg C/N ratio = 5 reaction time: 2 min reaction temp.: room temp.	52	37.2	[9]
Pd/GNS-NH_2	Catalyst amount: 5.0 mg C/N ratio = 250 reaction time: 1 min reaction temp.: room temp.	N.A.	20.8	[10]
Pd/NCB	Catalyst amount: 85 μg C/N ratio = 1.8 Reaction time: 6 min reaction temp.: 30 ℃	6.4	38.9	[11]
Pd-1	Catalyst amount: 1.3 μg C/N ratio = 3.3 reaction time: 6 min reaction temp.: 25 ℃	8.57	22.2	[12]
Pd nanocubes	Catalyst amount: 2.4 mg C/N ratio = 750 reaction time: 45 min reaction temp.: 30 ℃	0.52	94.6	[13]

*C/N ratio = used catalyst weight (g)/4-NP (mol).

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