Supporting Information (SI)

Protein Particles Decorated with Pd Nanoparticles for the Catalytic Reduction of p-Nitrophenol to p-Aminophenol

Yeonhwa Yu,[1,†] Euiyoung Jung,[2,3,†] Hyun Jin Kim,[1] Ahyoung Cho,[2] Jinheung Kim,[3] Taekyung Yu[2,] and Jeewon Lee[1,*]*

[1]Department of Chemical and Biological Engineering, College of Engineering, Korea University, Anam-Ro 145, Seoul 136-713, Republic of Korea

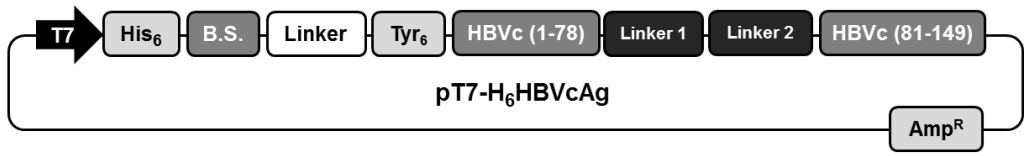
[2] Department of Chemical Engineering, College of Engineering, Kyung Hee University, Yongin 17104, Republic of Korea

[3]Department of Chemistry and Nano Science, Ewha Womans University, Seoul 03760, Republic of Korea

*Correspondence to: leejw@korea.ac.kr (J.L.), tkyu@khu.ac.kr (T.Y.).

†These authors contributed equally.

a



b

Protein	Primary structure
H_6HBVcAg	HHHHHHMASSLRQILDSQKMEWRSNAGGSGGGSGGGTGGGSG GGYYYYYYDIDPYKEFGASVELLSFLPSDFFPSIRDLLDTASALYREALE SPEHCSPHHTALRQAILCWGELMNLATWVGSNLEDGGGGSGGGG TLEAPKADNKFNKEQQNAFYEILHLPNLNEEQRNGFIQSLKDDPSQ SANLLAEAKKLNDAQAPKADEFNKFNKEQQNAFYEILHLPNLNEE QRNGFIQSLKDDPSQSANLLAEAKKLNDAQALKADGSGGGGSGG GGSRELVVSYVNVNMGLKIRQLLWFHISCLTFGRETVLEYLVSFGVW IRTPPAYRPPNAPILSTLPETTVV

c

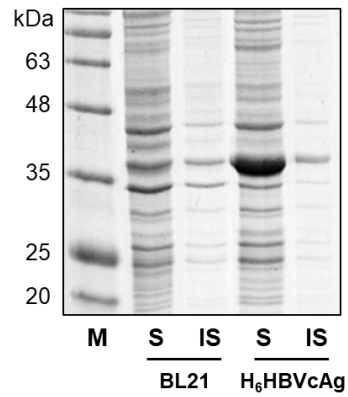


Figure S1. Plasmid expression vector (a) and coding sequence (b) for H_6HBVcAg and (c) result of SDS-PAGE analysis of soluble (S) and insoluble fraction (IS) recombinant *E. coli* cell lysates producing H_6HBVcAg.

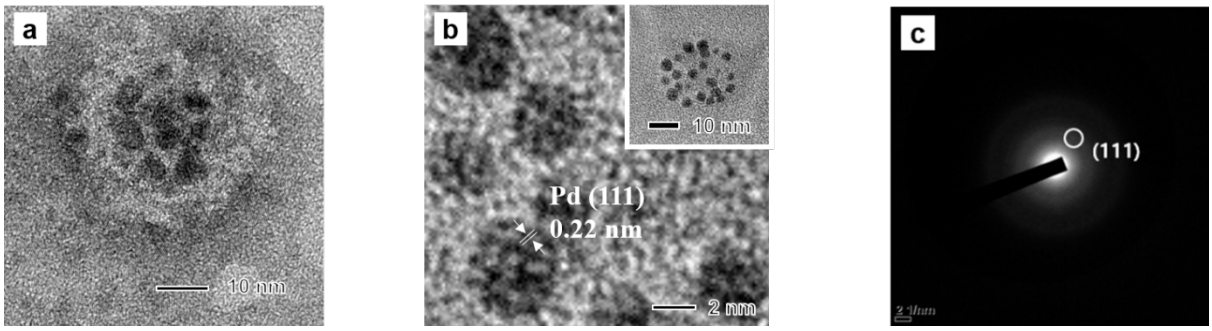


Figure S2. (a) Stained TEM image, (b) unstained HRTEM image (inset : unstained TEM image), and (c) ED pattern of PdNP-PPs.

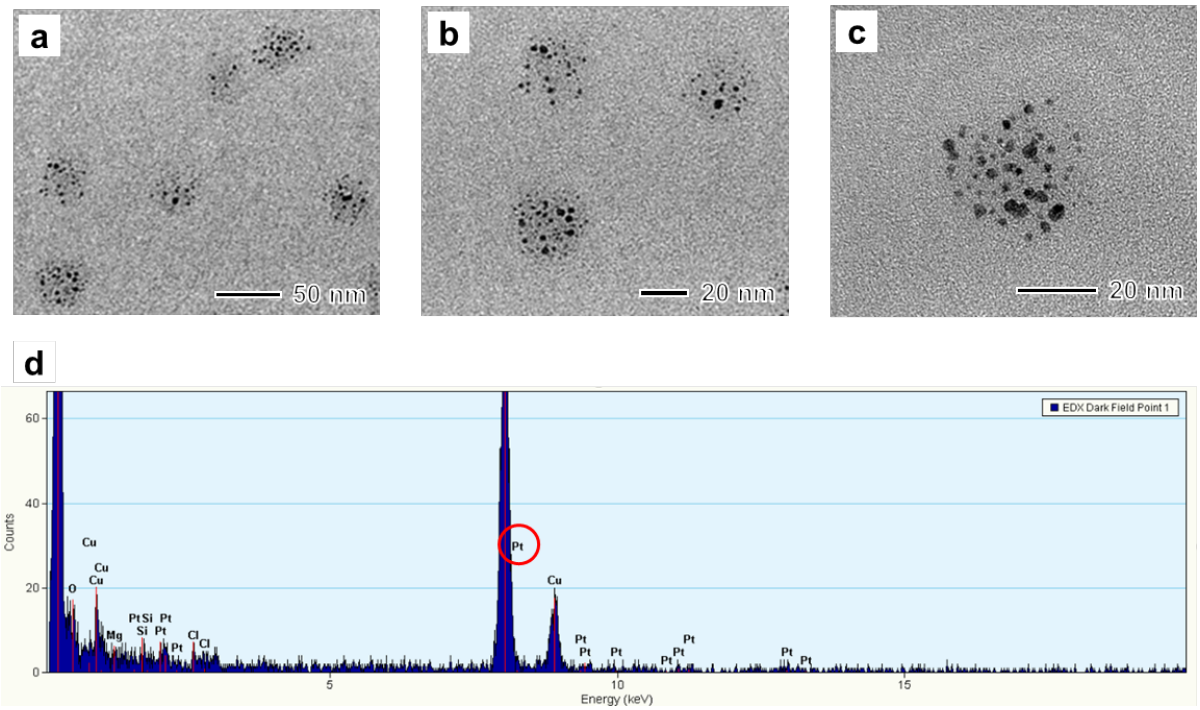


Figure S3. (a-c) TEM images and (d) EDX spectrum of samples synthesized by sequential addition of Pt precursor and Pd precursor.

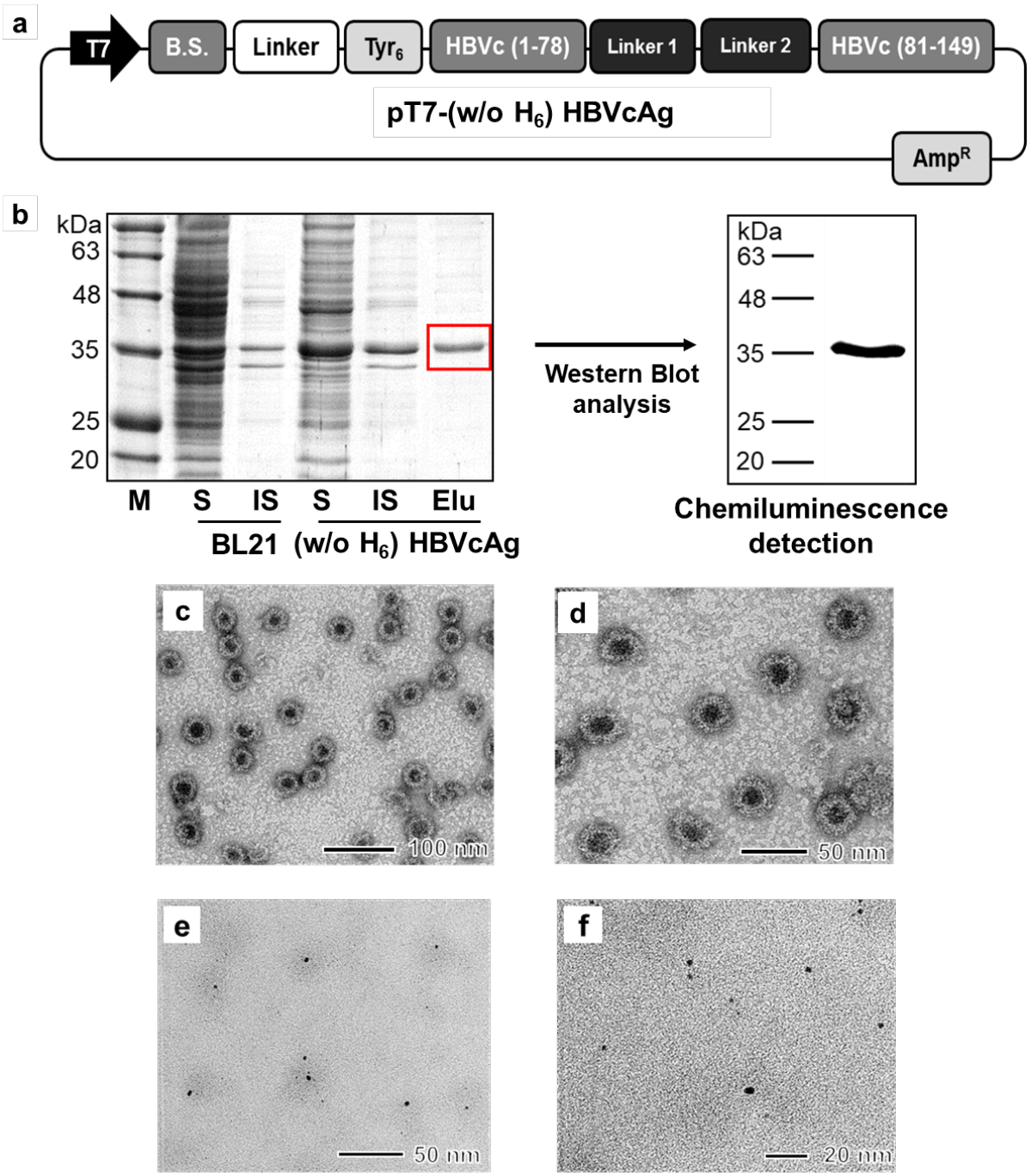


Figure S4. (a) Plasmid expression vector for (w/o H_6) HBVcAg, (b) result of SDS-PAGE analysis and Western blot analysis, (c-d) TEM images of (w/o H_6) HBVcAg PPs and (e-f) TEM images of PdNP-PPs using the (w/o H_6) HBVcAg PPs.

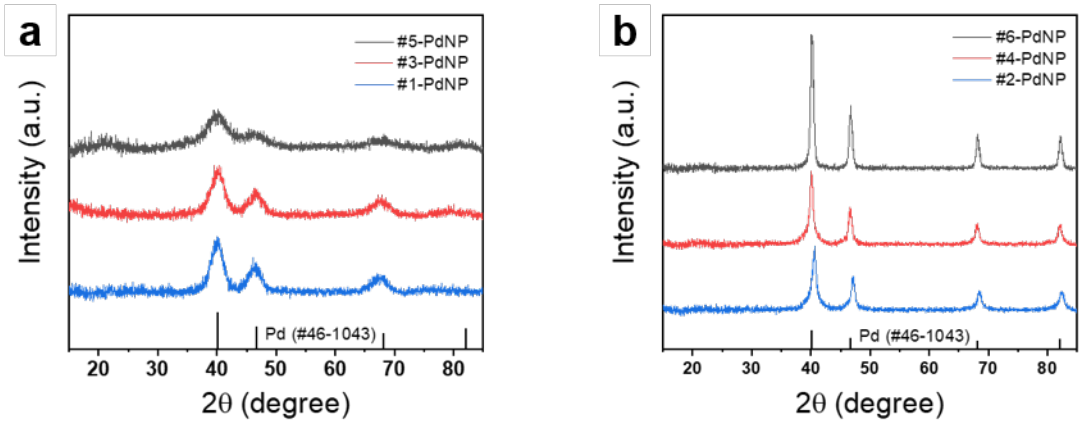


Figure S5. XRD diffraction patterns of (a) PdNPs (~ 3 nm) and (b) PdNPs (~ 30 nm).

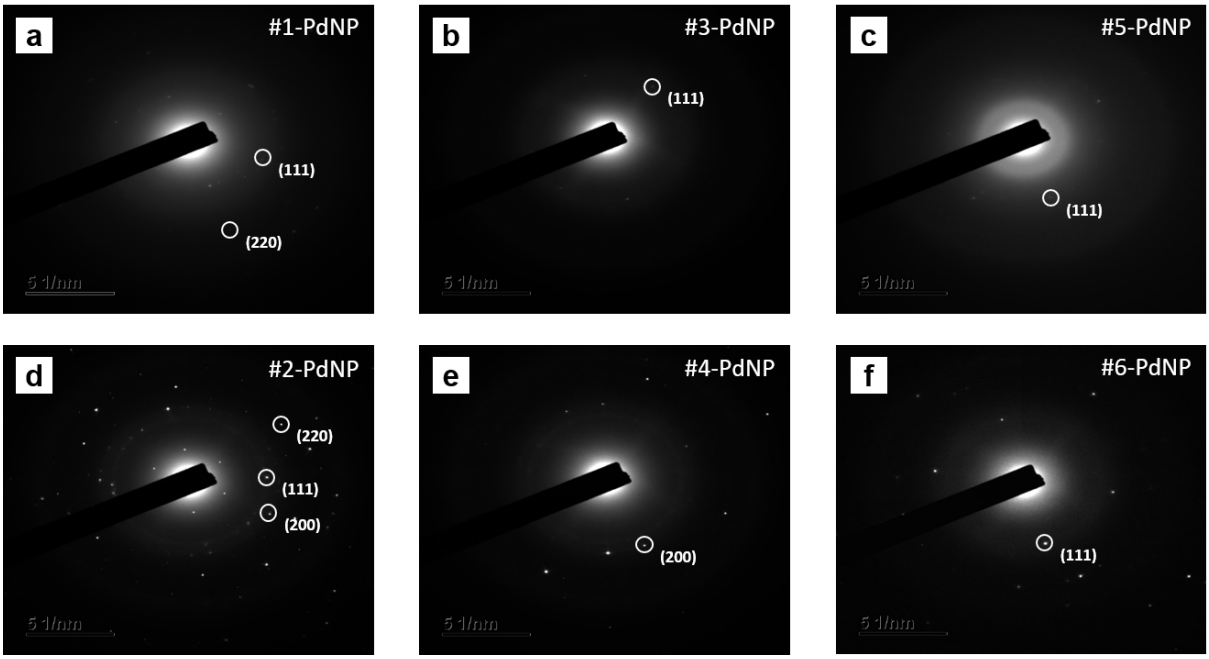
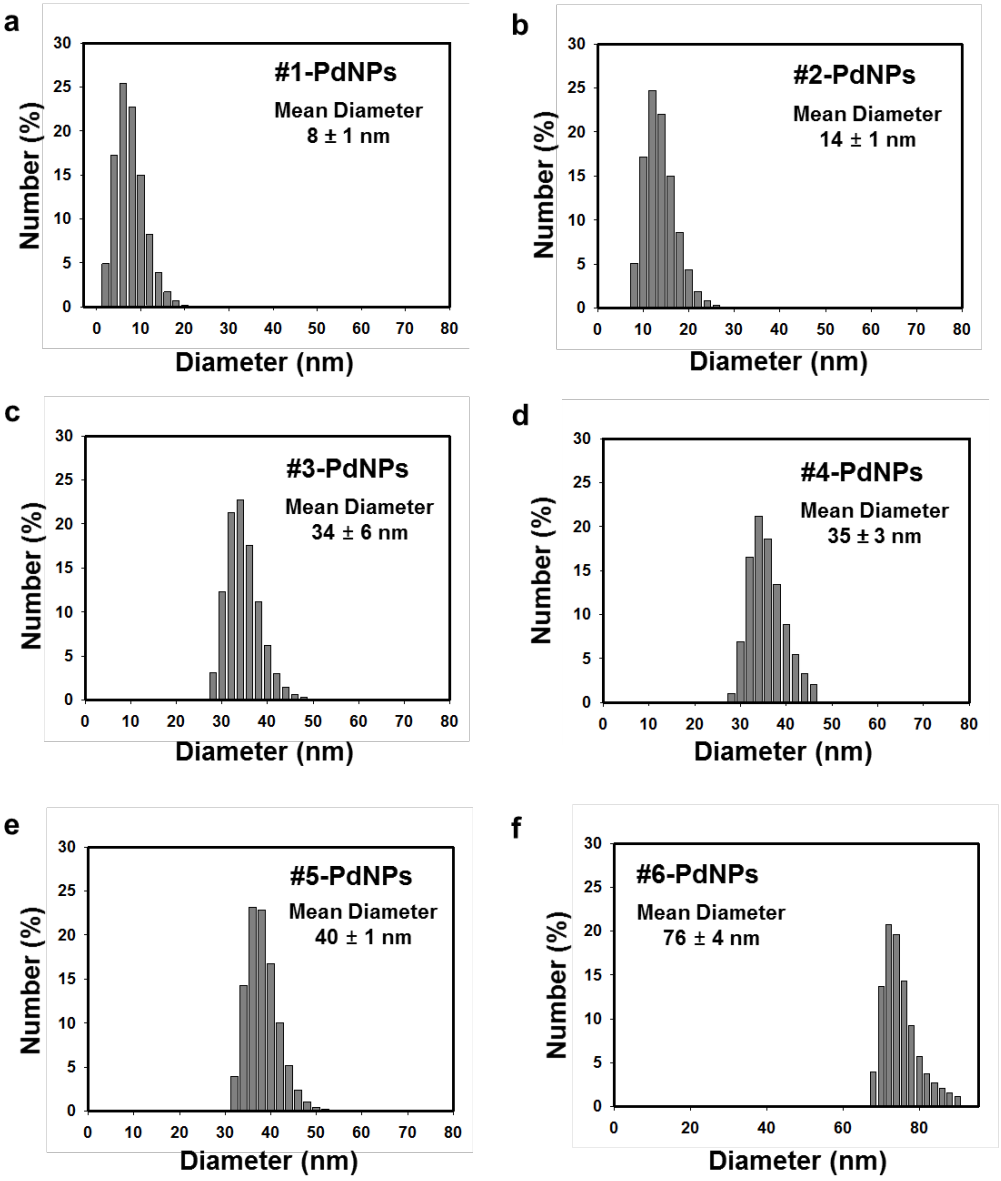


Figure S6. ED patterns of (a) #1-PdNP, (b) #3-PdNP, (c) #5-PdNP, (d) #2-PdNP, (e) #4-PdNP, and (f) #6-PdNP.



g

	#1-PdNPs	#2-PdNPs	#3-PdNPs	#4-PdNPs	#5-PdNPs	#6-PdNPs
Zeta potential (mV)	- 3.2 ± 3.1	- 5.5 ± 0.9	- 8.5 ± 0.4	- 3.0 ± 0.2	- 7.0 ± 0.3	- 11.0 ± 0.2

Figure S7. Results of DLS (a-f) and zeta potential (g) analyses of #1- to #6-PdNPs.

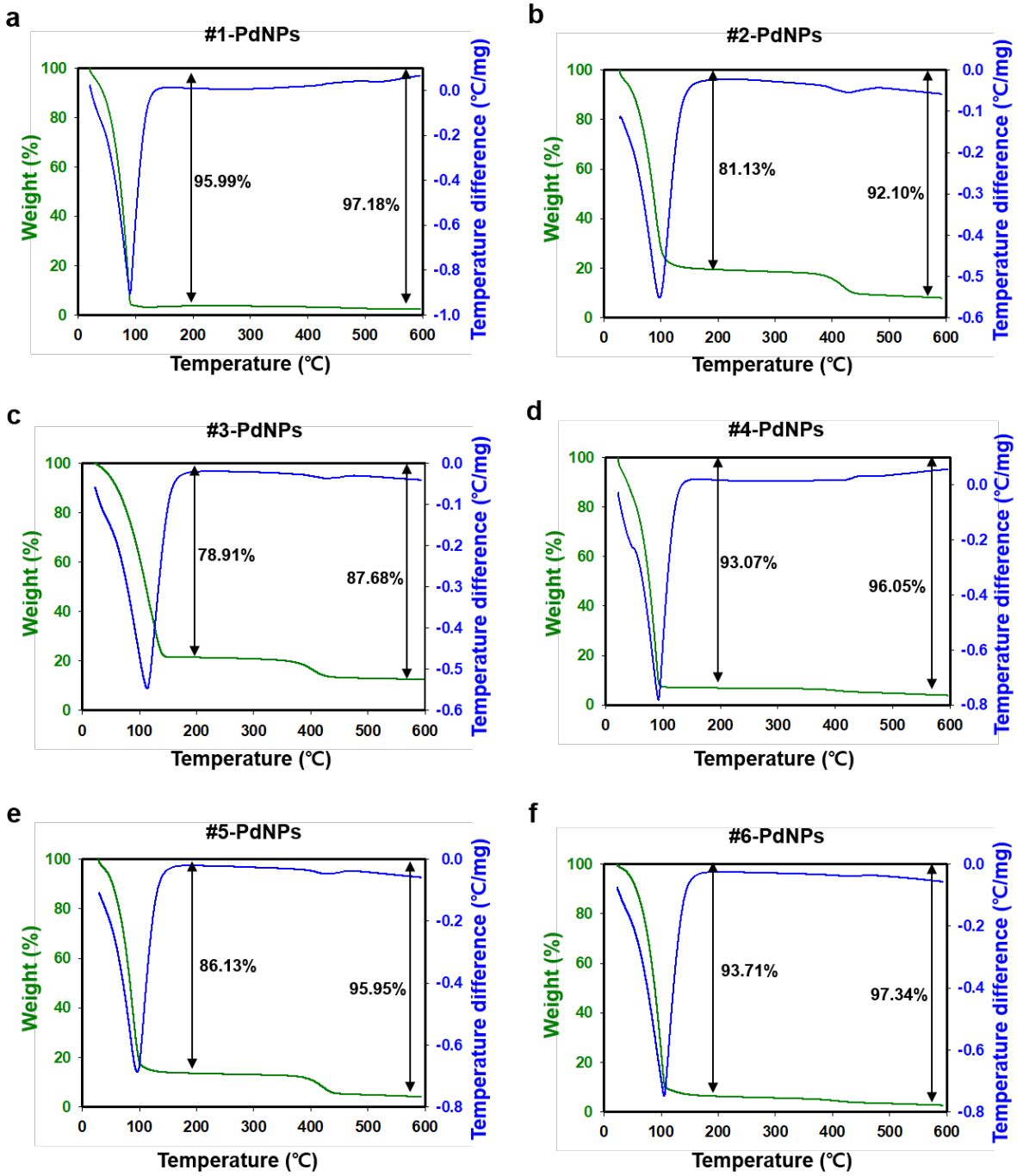


Figure S8. Results of TG-DTA analysis of PdNPs.

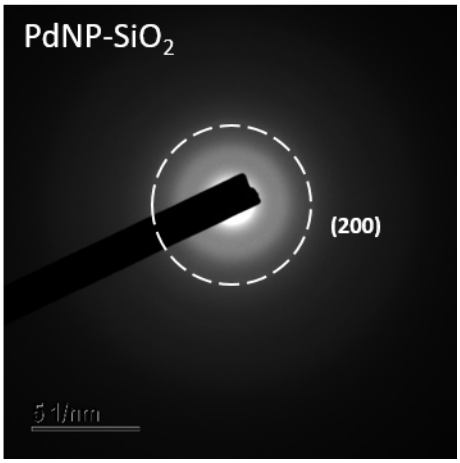


Figure S9. ED patterns of PdNP-SiO_2.

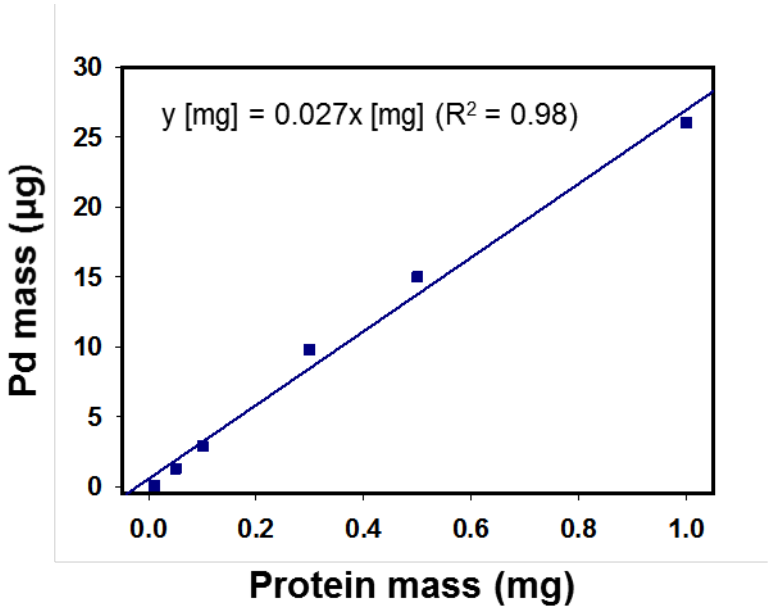
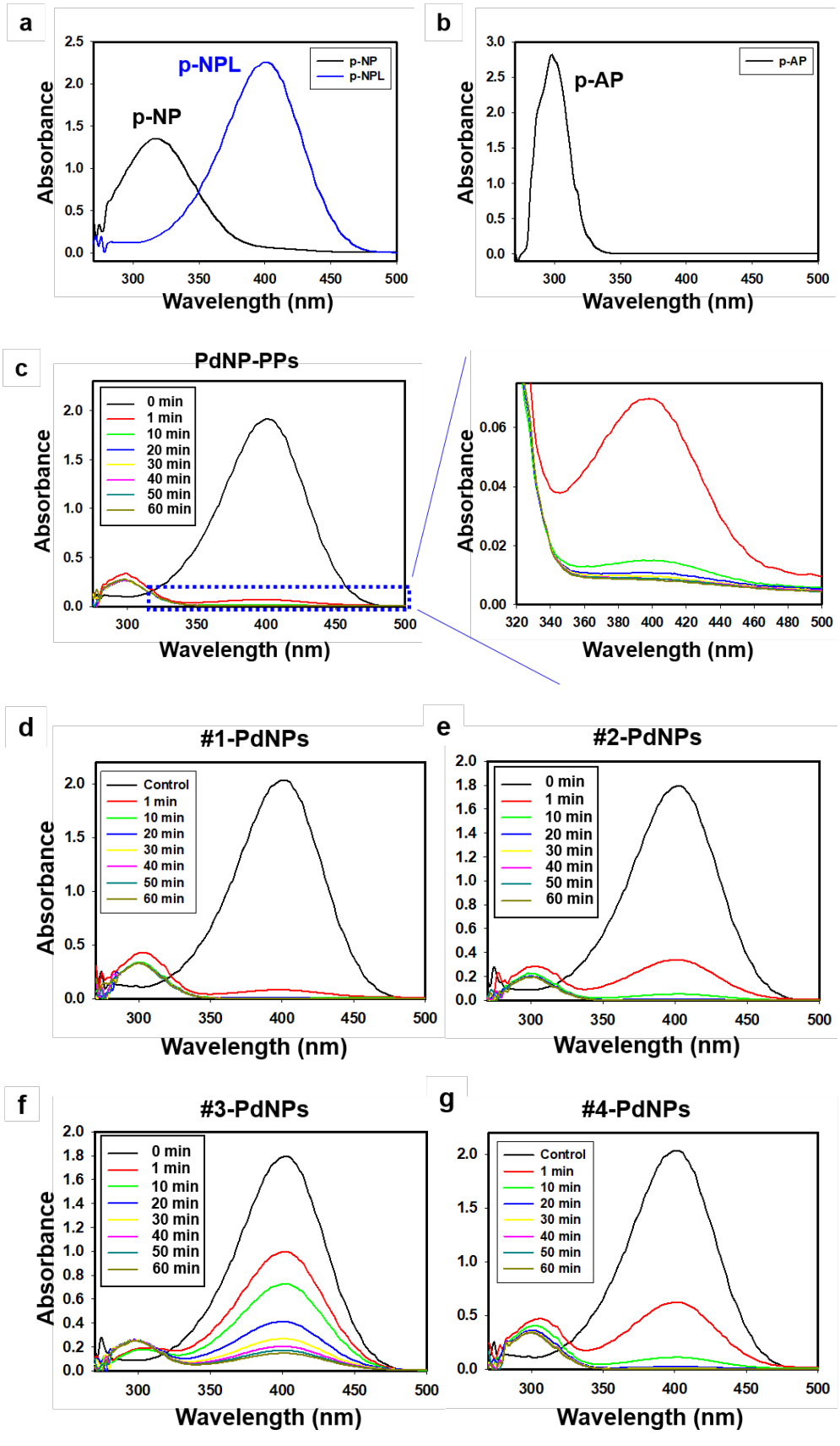


Figure S10. Correlation between Pd mass and protein mass in PdNP-PPs, determined by ICP-MS analysis.


a
p-NPL
p-NP
p-NP
p-NPL
Absorbance
Wavelength (nm)
b
p-AP
p-AP
Absorbance
Wavelength (nm)
c
PdNP-PPs
0 min
1 min
10 min
20 min
30 min
40 min
50 min
60 min
Absorbance
Wavelength (nm)
Absorbance
Wavelength (nm)
d
#1-PdNPs
Control
1 min
10 min
20 min
30 min
40 min
50 min
60 min
Absorbance
Wavelength (nm)
e
#2-PdNPs
0 min
1 min
10 min
20 min
30 min
40 min
50 min
60 min
Wavelength (nm)
f
#3-PdNPs
0 min
1 min
10 min
20 min
30 min
40 min
50 min
60 min
Absorbance
Wavelength (nm)
g
#4-PdNPs
Control
1 min
10 min
20 min
30 min
40 min
50 min
60 min
Wavelength (nm)

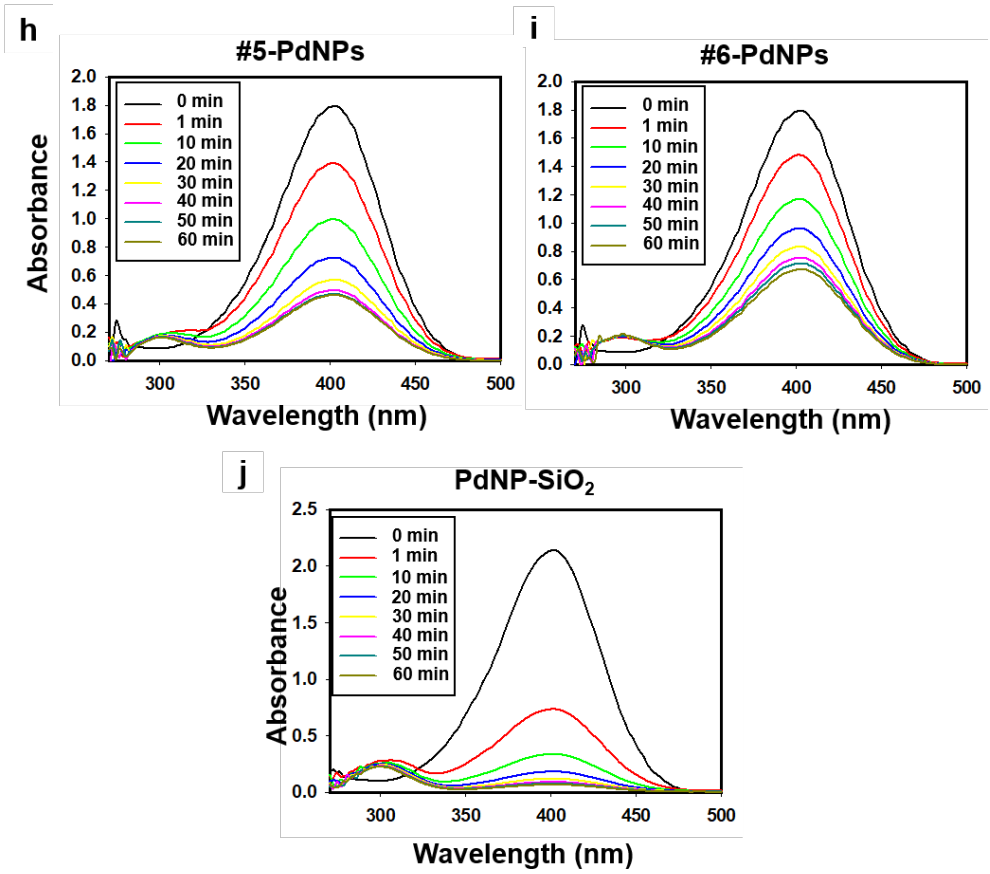


Figure S11. Maximum absorption peaks for (a) p-NP and p-NPL, (b) p-AP, and time-course changes in maximum absorption peaks for p-NPL and p-AP during the reduction of p-NPL to p-AP using various Pd nanocatalysts: (c) PdNP-PPs, (d) #1-PdNPs, (e) #2-PdNPs, (f) #3-PdNPs, (g) #4-PdNPs, (h) #5-PdNPs, (i) #6-PdNPs, and (j) PdNP-SiO_2.

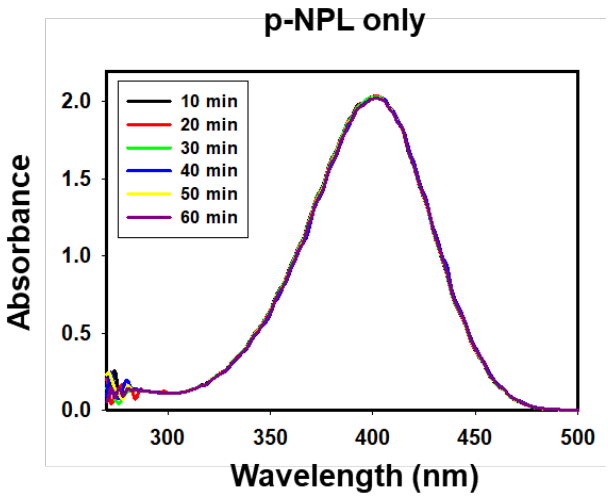


Figure S12. UV-vis spectra of an aqueous solution containing p-nitrophenol and $NaBH_4$ without the Pd catalysts during 60 min.

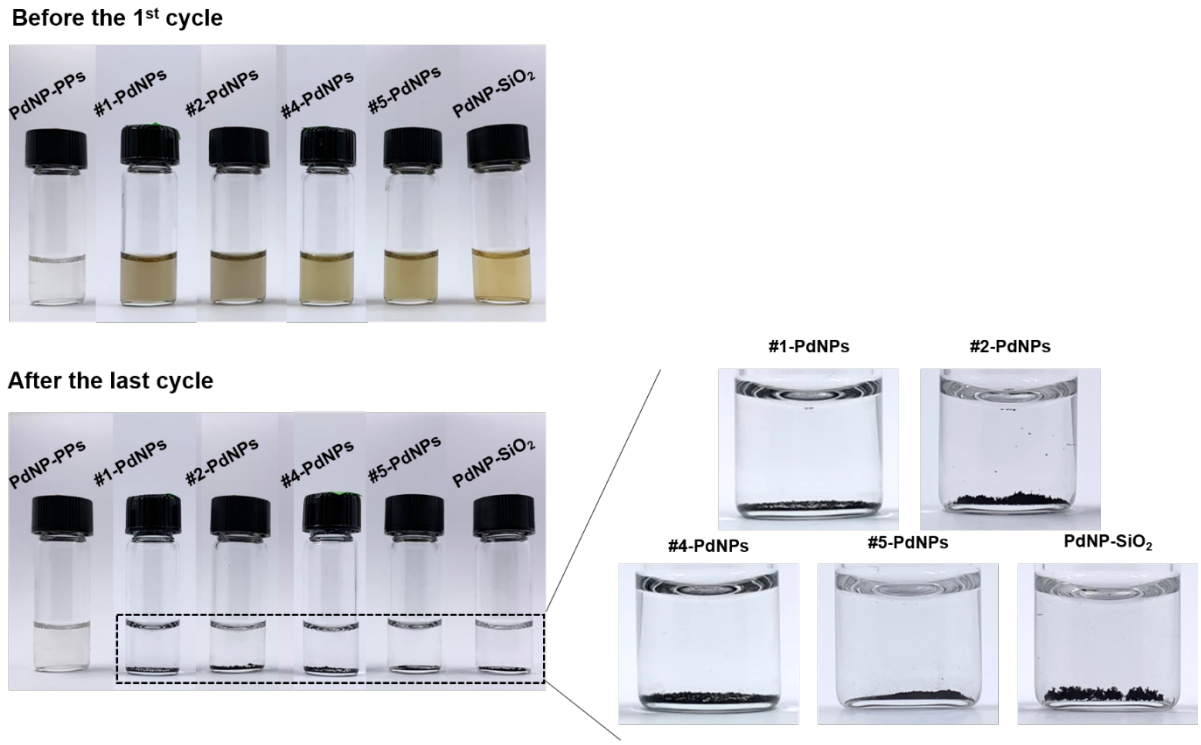


Figure S13. Photographic images of various Pd nanocatalysts solutions, collected before the 1st cycle and after the last cycle of multi-cyclic reactions.

Table S1. The TON and TOF values of Pd nanocatalysts during the recyclability tests.

	Cycle	1	2	3	4	5
PdNP-PPs	TON	57.7	56.4	55.5	52.2	47.2
	TOF(min^{-1})	5.8	5.6	5.5	5.2	4.7
PdNP-SiO_2	TON	35.7	18.2	10.3	6.9	9.5
	TOF(min^{-1})	3.6	1.8	1.0	0.7	0.9
#3-PdNPs (Pd 3 nm w/ 40000 MW PVP)	TON	55.5	6.5	4.1	4.6	3.0
	TOF(min^{-1})	5.6	0.6	0.4	0.5	0.3
#4-PdNPs (Pd 30 nm w/ 40000 MW PVP)	TON	39.4	3.9	3.8	3.0	2.5
	TOF(min^{-1})	3.9	0.4	0.4	0.3	0.3
#5-PdNPs (Pd 3 nm w/ 10000 MW PVP)	TON	57.4	56.1	22.3	22.4	8.6
	TOF(min^{-1})	5.7	5.6	2.2	2.2	0.9
#6-PdNPs (Pd 30 nm w/ 10000 MW PVP)	TON	53.9	29.9	30.2	7.2	6.9
	TOF(min^{-1})	5.4	3.0	3.0	0.7	0.7

Table S2. Amino acids and their binding metal ions.

Amino acid	Metal ions	Reference
Histidine	Pd^{2+}, Zn^{2+}, Cd^{2+}, Cu^{2+}, Ni^{2+}, Ag^{+}	1-6
Cysteine	Hg^{2+}, Pb^{2+}, Zn^{2+}, Cd^{2+}	6-8
Tryptophan	Cu^{2+}	6, 9
Tyrosine	$Fe^{3+}>Co^{2+}>Ni^{2+}>Cu^{2+}$ (binding affinity)	10

Table S3. Catalytic activity comparison of PdNP-PPs with other Pd catalysts.

Catalyst	Metal size (nm)	Mass of catalyst (mg)	Concentration of p-NP(mM)	Concentration of $NABH_4$ (mM)	TOF (mmol p-NP/ mmol metal min)	Reference
PdNP-PPs	3				5.8	
PVP(10000 MW)-Pd	3 / 30	0.81×10^{-4}	0.2	33.3	5.7 / 5.4	This study
PdNP-SiO_2	3				3.6	
Pd@h-mSiO_2-4.9%		0.05	0.1	8.3	1.56	11
CNT/PiHP/Pd	2.1 - 31.6	0.3×10^{-5}	0.2	16.5	1.5	12
RGO@Pd@C	4	5	0.1	19.4	4.6	13
Pd-rGO-CNT	4	5	0.1	9.7	1.2	14

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