

Electronic Supplementary Information

**Influence of Graphene Oxide Supports on Solution-Phase Catalysis of
Thiolate-Protected Palladium Nanoparticles in Water**

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I.	Spectroscopic and Microscopic Characterization of Pd Nanoparticles and Pd Nanoparticle-Graphene Oxide Hybrids	2
II.	Heat Treatments of Palladium Nanoparticle-Graphene Oxide Hybrids	4
III.	Catalysis Studies Comparing PdNP, PdNP/GO, and Heated PdNP/GO	6
IV.	Recyclability and Colloidal Stability of PdNP, PdNP/GO, and Heated PdNP/GO	8

I. Spectroscopic and Microscopic Characterization of Pd Nanoparticles and Pd Nanoparticle-Graphene Oxide Hybrids

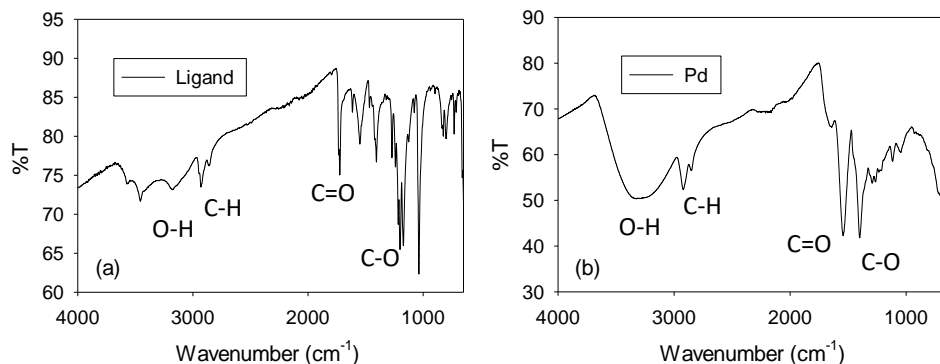


Figure S1. IR spectra of (a) sodium ω -carboxyl-S-hexanethiosulfate (the ligand precursor) and (b) ω -carboxylate-1-hexanethiolate-capped palladium nanoparticles. The peaks at $>3400\text{ cm}^{-1}$ in spectrum (a) is due to C=O overtone. The presence of O-H, C-H, C=O, and C-O stretching vibrations are clearly seen on both spectra.

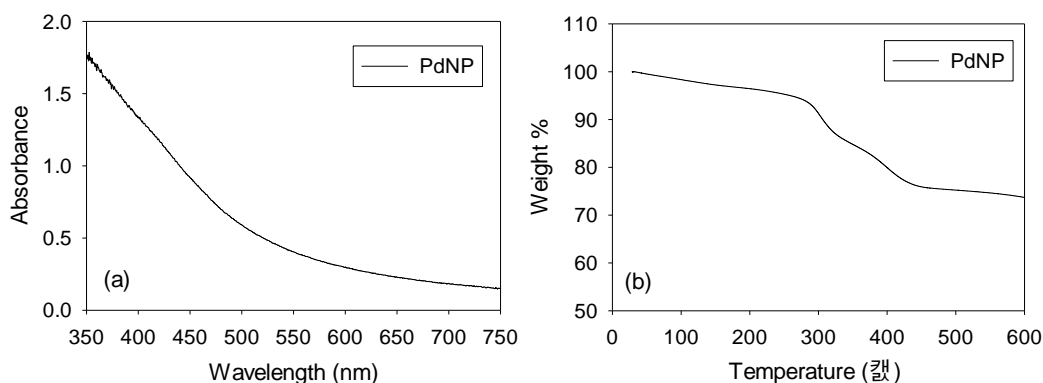


Figure S2. (a) UV-Vis spectrum and (b) TGA graph of ω -carboxylate-1-hexanethiolate-capped palladium nanoparticles. No absorption or plasmon bands are seen in UV-vis spectrum. TGA plot shows a $\sim 10\%$ weight loss by $300\text{ }^{\circ}\text{C}$ and an additional 15% by $400\text{ }^{\circ}\text{C}$.

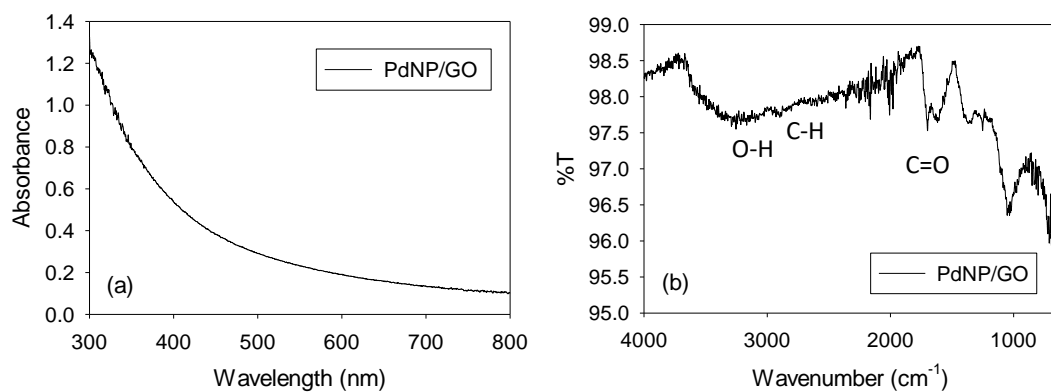


Figure S3. (a) UV-vis and (b) IR spectra of PdNP/GO hybrids. Only an exponential decay with increasing wavelength is shown in spectra (a). Stretching vibrations corresponding to the IR characteristics of ω -carboxylate-1-hexanethiolate ligands and GO are shown in spectra (b).

II. Heat Treatments of Palladium Nanoparticle-Graphene Oxide

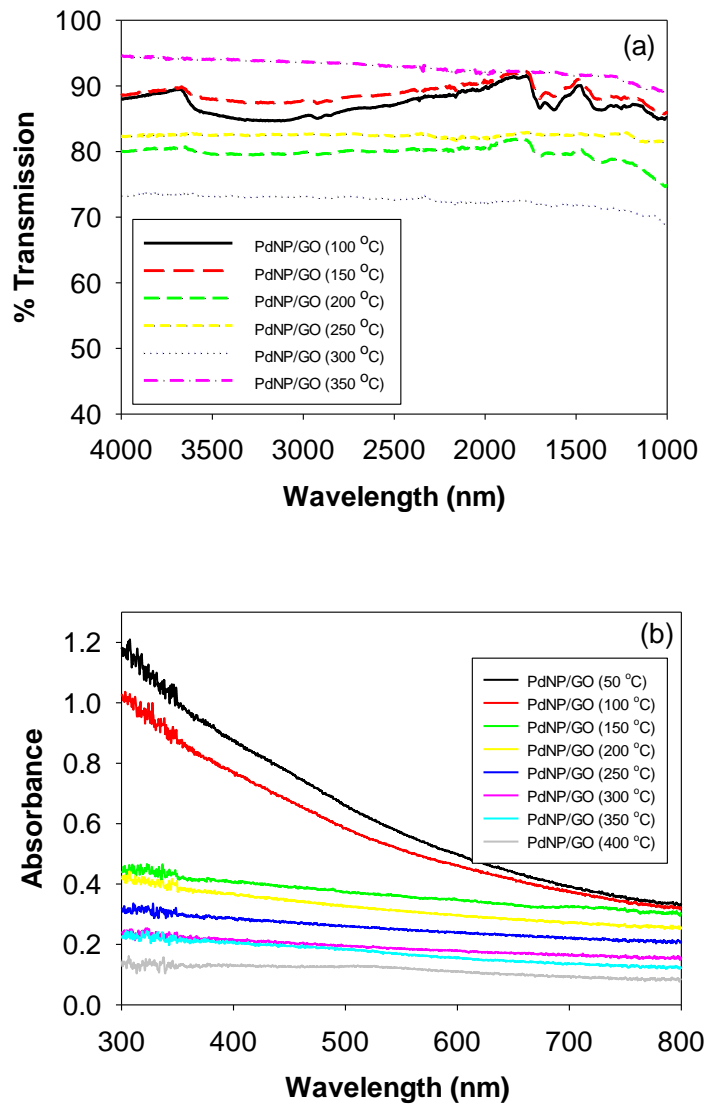


Figure S4. a) IR and b) UV-Vis spectra of PdNP/GO hybrids heated at 50-400 °C.

Table S1. The transitions of the average core size and dispersity of heated PdNP/GO.

Temperature (°C)	Particles
	PdNP/GO
50	2.03 ± 0.81
100	2.07 ± 0.96
150	2.38 ± 1.58
200	2.41 ± 1.21
250	2.46 ± 1.34
300	7.06 ± 2.85

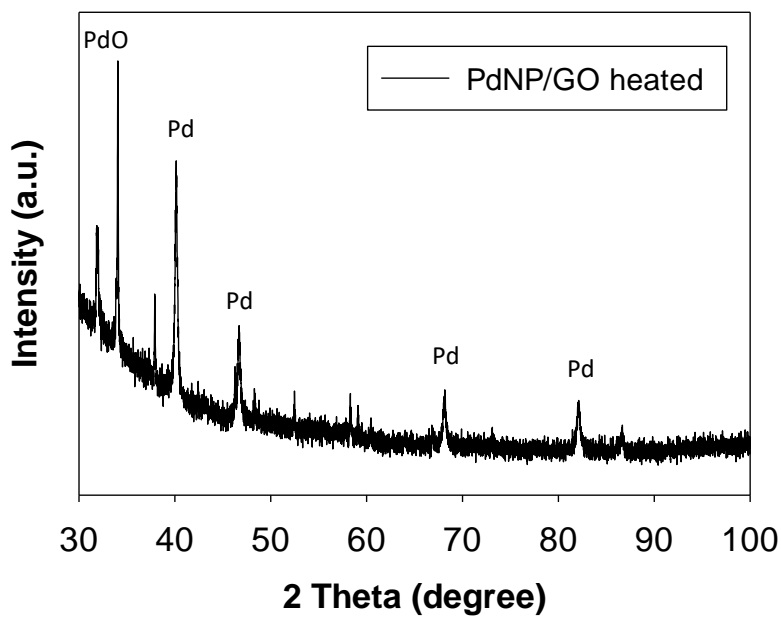


Figure S5. Powder XRD pattern of PdNP/GO hybrids heated at 300 °C.

III. Catalysis Studies Comparing PdNP, PdNP/GO, and Heated PdNP/GO

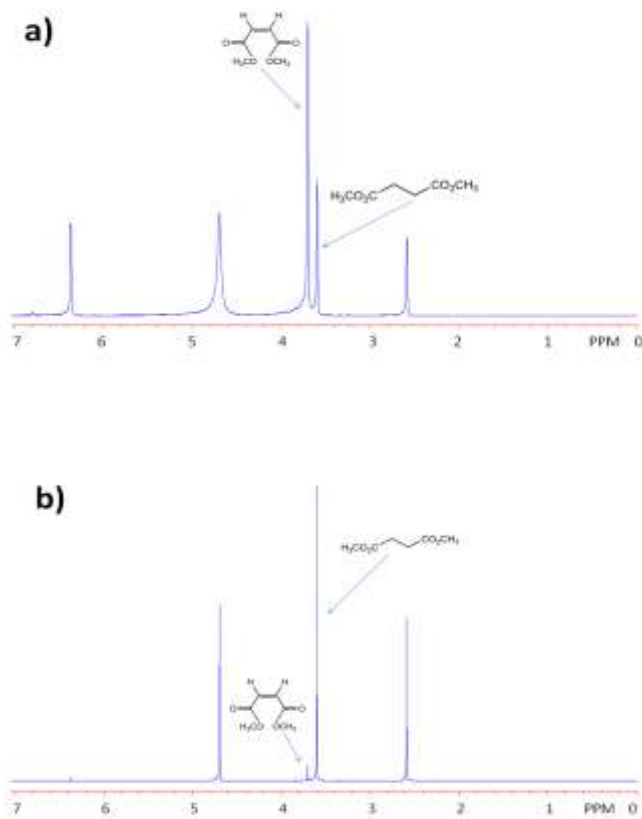


Figure S6. Examples of NMR spectra of DMAD hydrogenation showing the signals for semi- and full-hydrogenation products. The semi-hydrogenation product has two distinct hydrogens at δ 3.80 ppm ($-\text{OCH}_3$) and δ 6.50 ppm ($\text{C}=\text{C}-\text{H}$). The full-hydrogenation product also has two distinct hydrogens at δ 3.70 ppm ($-\text{CO}_2\text{CH}_3$) and δ 2.69 ppm (CH_2-CH_2).

Table S2. Summary of turn-over-frequency (TOF) for semi- and full-hydrogenation products with PdNP, PdNP/GO, and PdNP/GO heated at 300 °C.

PdNP ^a		PdNP/GO ^a		PdNP/GO 300 °C ^b	
TOF _{semi}	TOF _{full}	TOF _{semi}	TOF _{full}	TOF _{semi}	TOF _{full}
916	201	871	156	48	321

^a TOF (site⁻¹hour⁻¹) was calculated based on the model of Pd₂₂₅ (2.0 nm) with 140 surface Pd atoms after 3 h reaction. ^b TOF (site⁻¹hour⁻¹) was calculated based on the model of Pd₆₂₆₆ (5.5 nm) with 1472 surface Pd atoms after 24 h reaction.

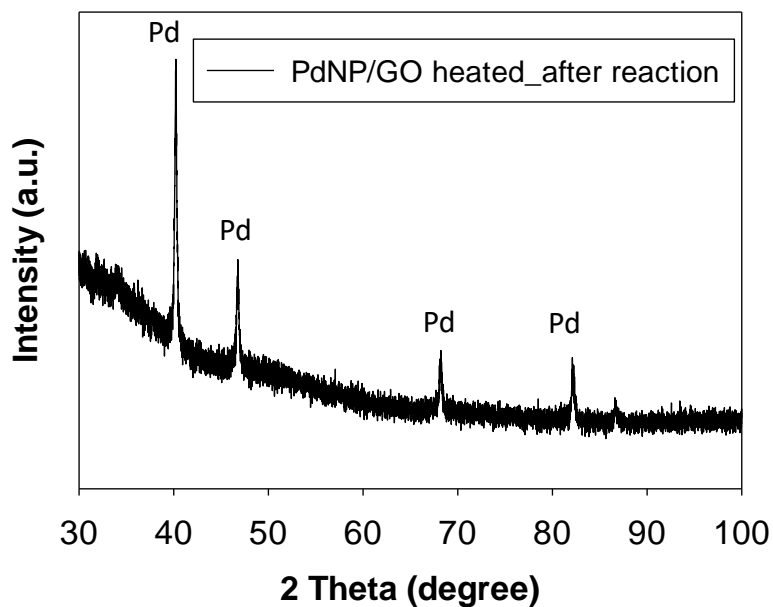
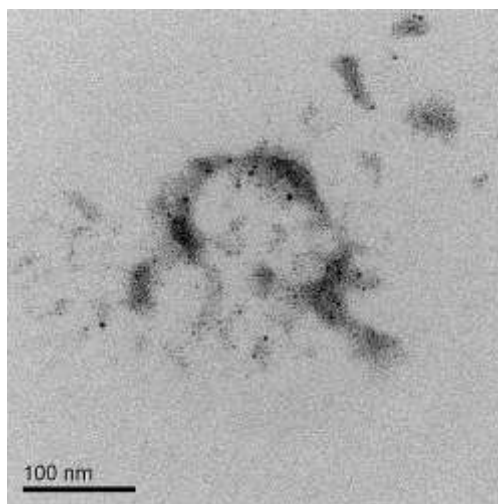
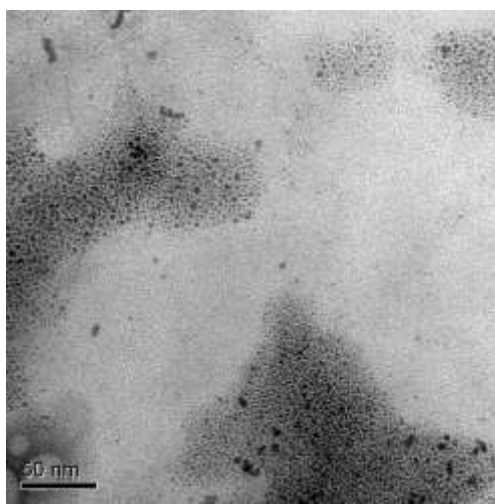


Figure S7. Powder XRD pattern of heated PdNP/GO hybrids after catalytic reaction.

IV. Recyclability and Stability of PdNP, PdNP/GO, and Heated PdNP/GO



(a)



(b)

Figure S8. TEM images of (a) PdNP and (b) PdNP/GO after the recycled uses.