Supporting Information

Iodine Activation: A General Method for Catalytic Enhancement of Thiolate Monolayer-Protected Metal Clusters

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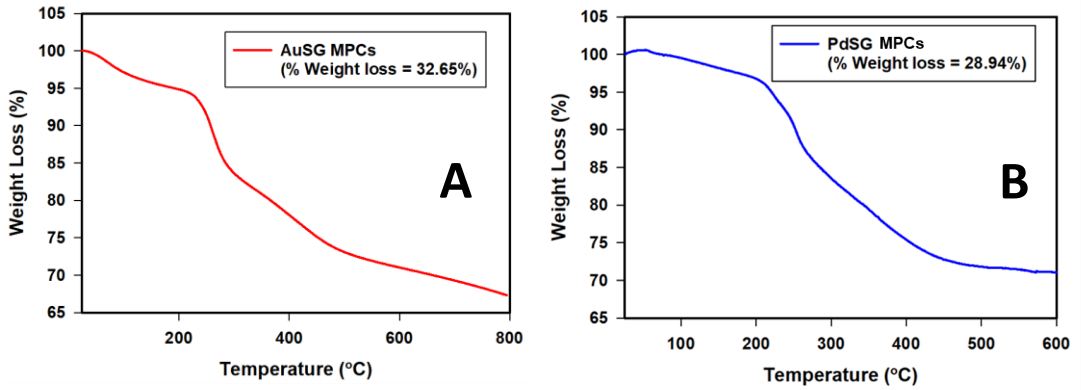

Figure S1: TGA of (A) AuSG MPCs and (B) PdSG MPCs.

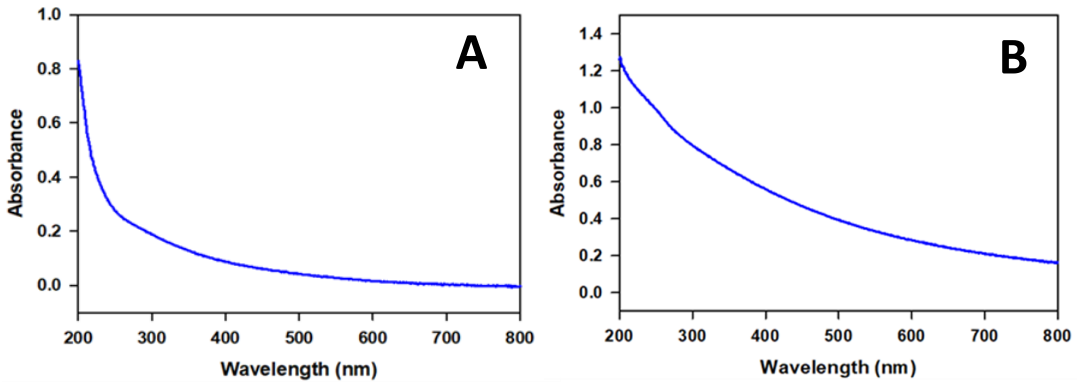

Figure S2: UV-Vis of (A) AuSG MPCs and (B) PdSG MPCs.

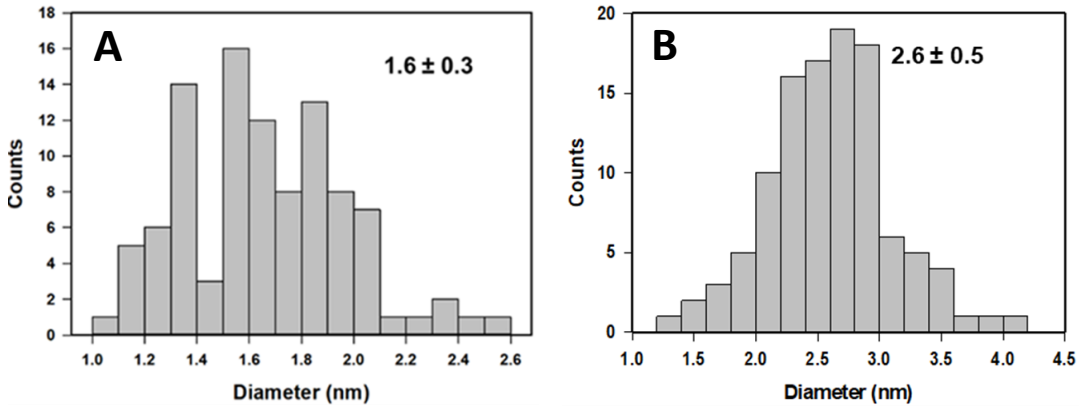

Figure S3: Particle size histograms of (A) AuSG MPCs and (B) PdSG MPCs.

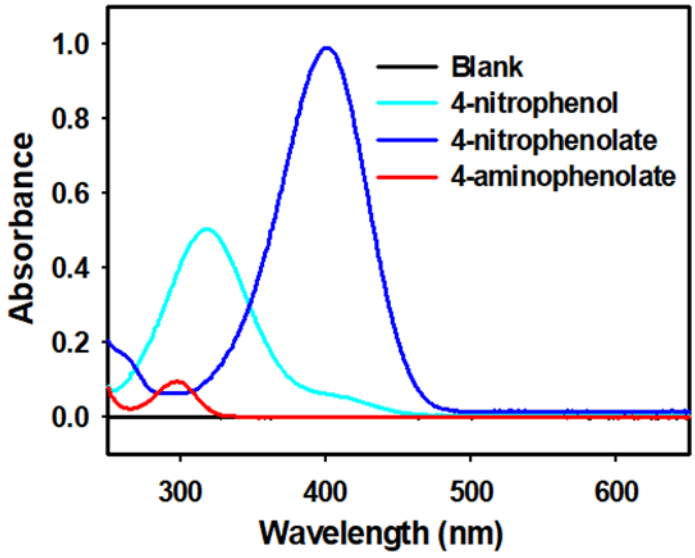

Figure S4: UV-Vis absorption spectra of 4-nitrophenol, 4-nitrophenolate (4-NP) and 4-aminophenolate (4-AP), each at a concentration of 3×10^{-5} M.

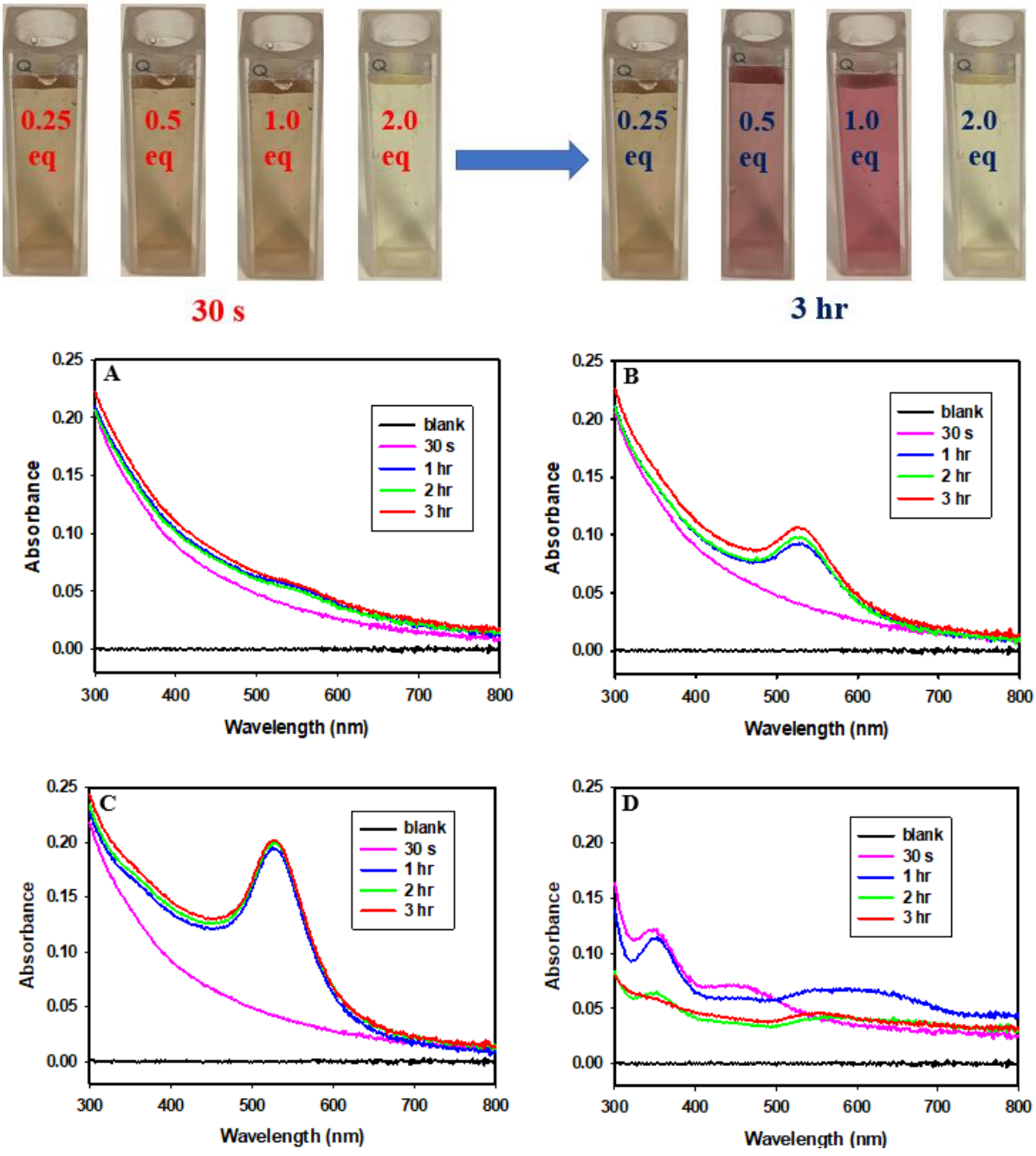

Figure S5: (Top) Digital image of aqueous solutions of AuSG MPCs after reaction with I_2 for 30 seconds and 3 hours. The change to red color and then disappearance of the color is consistent with aggregation or increased size by ripening followed by dissolution at higher equivalents of I_2. (Bottom) UV-Vis absorption spectra of aqueous solutions of AuSG MPCs treated with **A**: 0.25 eq, **B**: 0.5 eq, **C**: 1.0 eq, and **D**: 2.0 eq of I_2 for the times indicated.

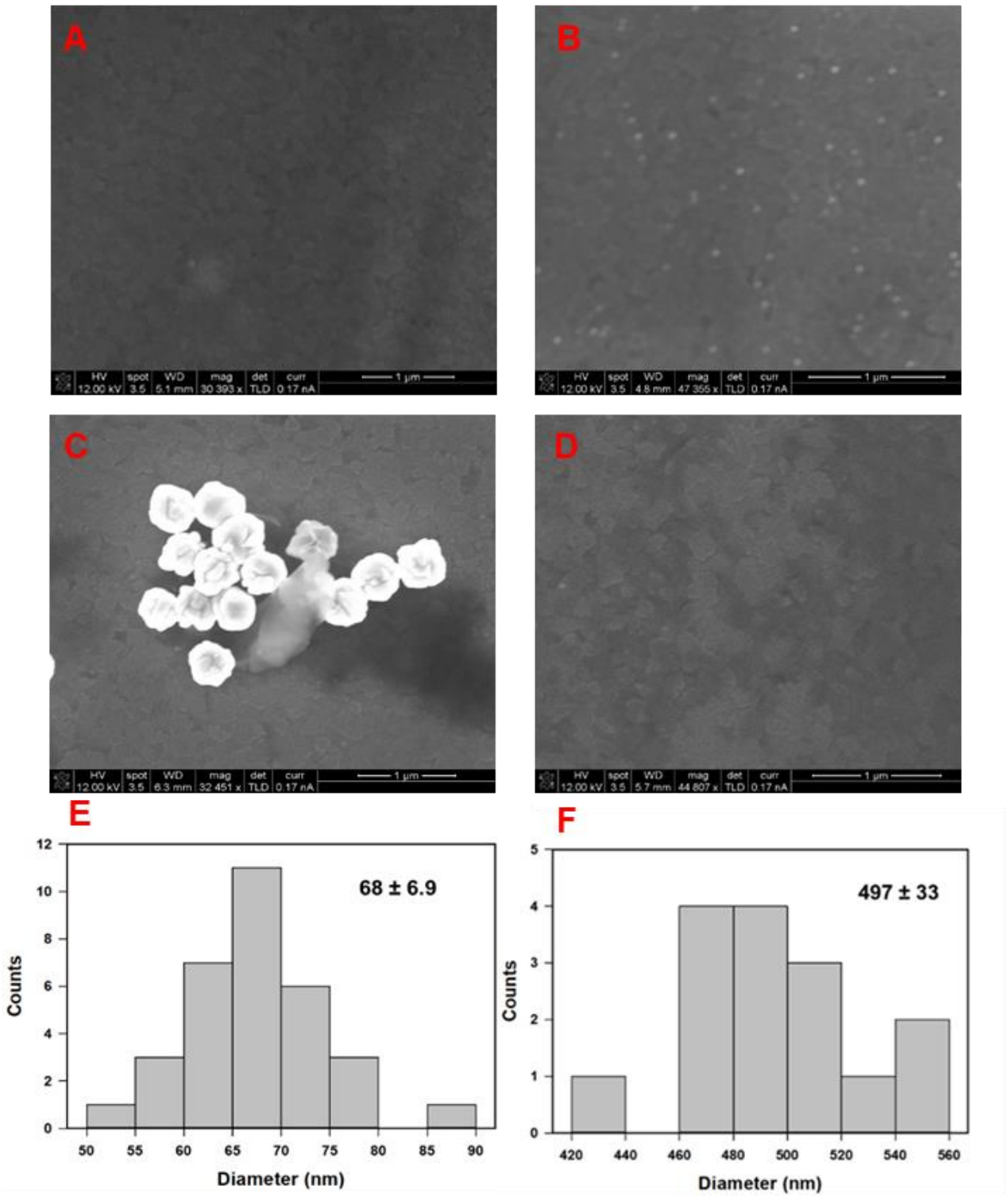

Figure S6: SEM images of iodine activated AuSG MPCs; **A.** 0.25 eq I_2 (cannot be observed in SEM), **B.** 0.5 eq I_2 (68 ± 7 nm), **C.** 1.0 eq I_2 (497 ± 33 nm), **D.** 2.0 eq I_2 (Au dissolved, only ITO observed), **E.** Histogram of AuSG MPCs with 0.5 eq I_2, and **F.** Histogram of AuSG MPCs with 1.0 eq I_2.

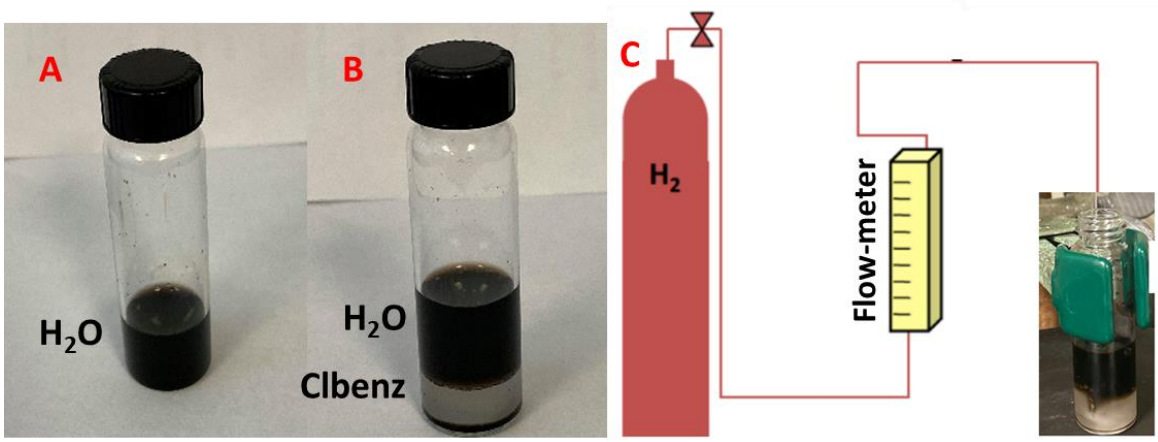

Figure S7: PdSG MPCs in water (**A**), after adding chlorobenzene (**B**), reaction set-up for isomerization/hydrogenation of allyl alcohol (**C**).

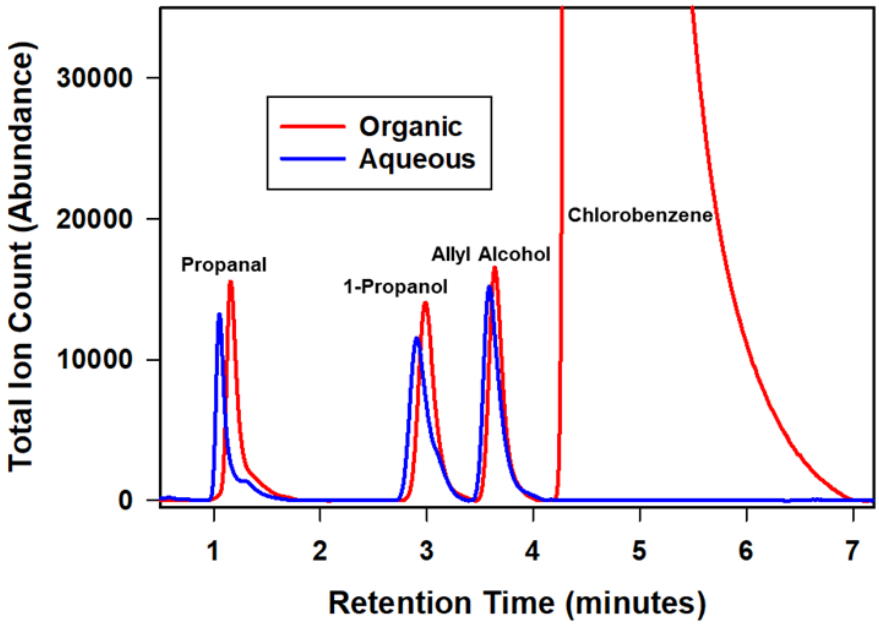

Figure S8: Gas chromatogram of a standard solution containing a mixture of 10 mM each of reactant (allyl alcohol), and products (propanal, 1-propanol) in organic phase (chlorobenzene), and aqueous phase. Three chromatograms were averaged to determine the response factor (R_f) in order to calculate final TOF values.

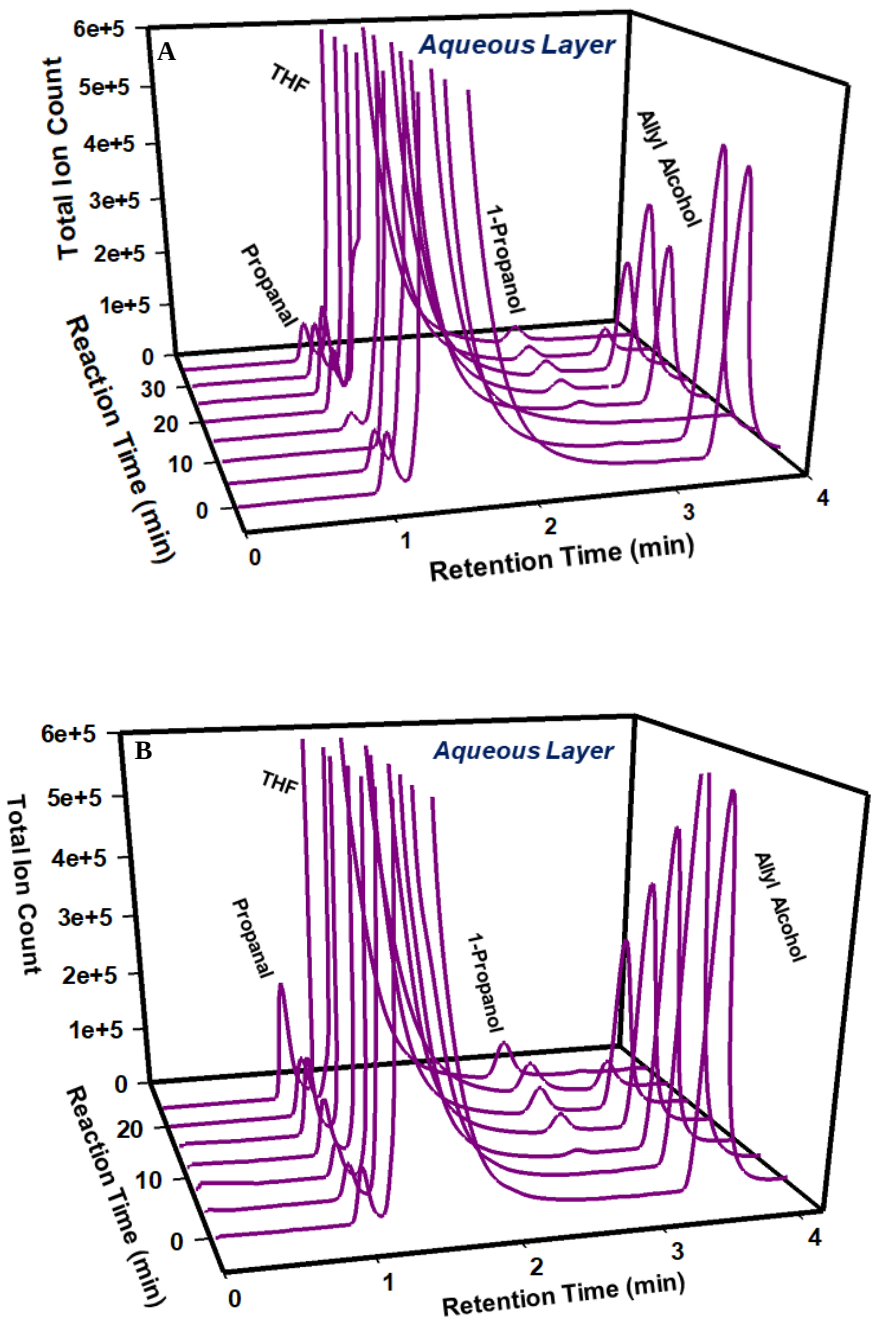

Figure S9: GC-FID chromatograms of allyl alcohol hydrogenation/isomerization using PdSG MPCs in 1:1 chlorobenzene:water with a H_2 flow rate of 20.0 ± 0.5 mL/min. **A:** aqueous phase, in absence of I_2, and **B**: aqueous phase, with 0.05 eq I_2.

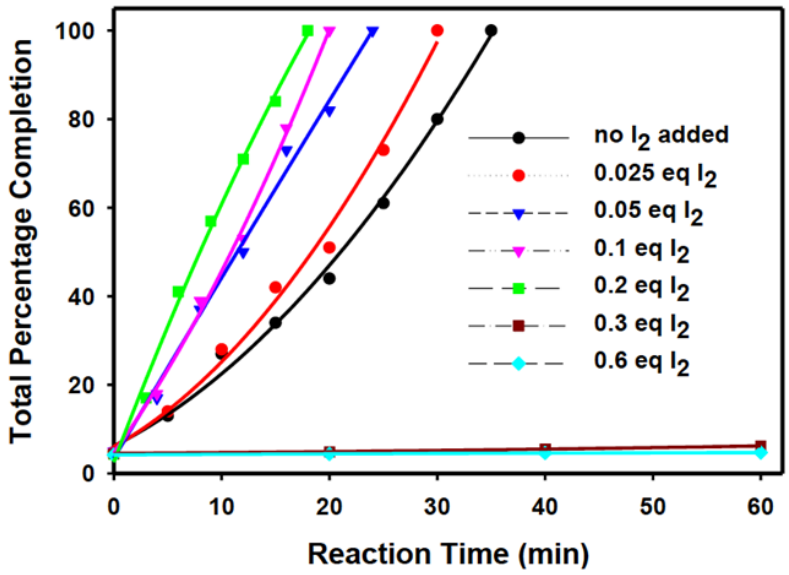

Figure S10: Reaction completion percentage (hydrogenated plus isomerized) for the PdSG MPC-catalyzed hydrogenation/isomerization of allyl alcohol in relation to added I_2. H_2 flow rate = 20.0 ± 0.5 mL/min.

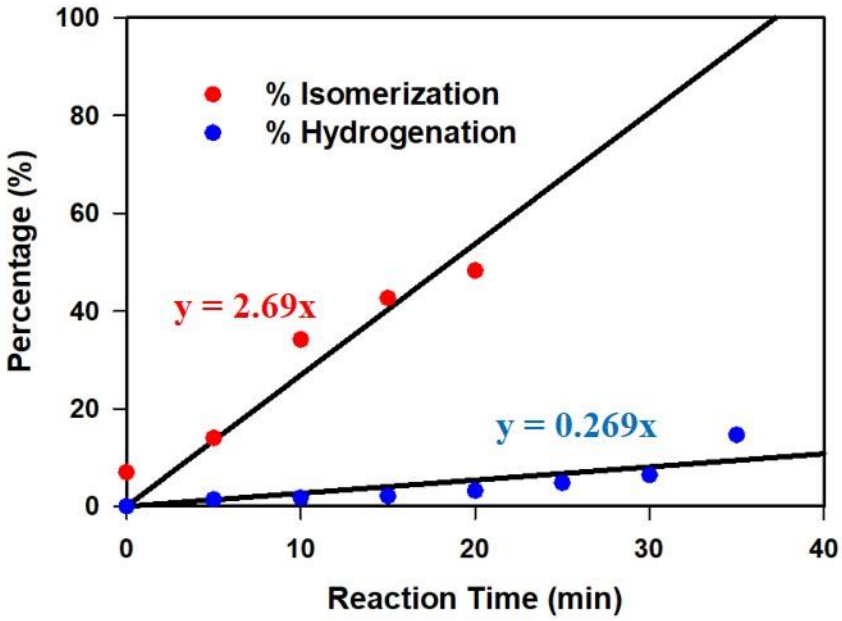

Figure S11: Plot of the %hydrogenation and %isomerization of allyl alcohol versus reaction time with the intercept of the line forced through zero, using PdSG MPCs as a catalyst (no I_2 added). The slopes for the points up to 60% isomerization and all of the points for hydrogenation were used to determine the TOF values.

Calculation of TOF values

Final TOF values were calculated based on the procedure reported in the literature.[1, 2, 3]

100% hydrogenation/isomerization = 200 µL allyl alcohol = 2.94 x 10^{-3} moles

Mass of Pd in the 6.0 mg of catalyst (PdSG MPCs) used for the reaction was calculated based on organic composition (glutathiolate determined by TGA of 29%, this gives 71% of Pd metal)

Mass Pd = 71% of 6.0 mg = 4.26 mg

moles Pd = (4.26 mg) / (106.42 mg/mmol) = 4.0 x 10^{-5} mol Pd

For example, PdSG MPCs (without I_2 added) as a catalyst:

TOF = {slope (% hydrogenated or isomerized/min)/100} * [{2.94 x 10^{-3} moles * 60 (min/h)} / 4.0 x 10^{-5} moles Pd]

TOF Hydrogenation = 0.002690 (fraction hydrogenated/min) * [{2.94 x 10^{-3} moles * 60 (min/h)} / 4.0 x 10^{-5} moles Pd]

TOF Hydrogenation = 12 moles hydrogenated/moles Pd/h

TOF Isomerization = 0.0269 (fraction isomerized/min) * [{2.94 x 10^{-3} moles * 60 (min/h)} / 4.0 x 10^{-5} moles Pd]

TOF Isomerization = 119 moles isomerized/moles Pd/h

Overall Conversion TOF = TOF Hydrogenation + TOF Isomerization

Total TOF = 12 + 119

Total TOF =131 moles products/moles Pd/h

% hydrogenation = $[(S_H * k_2) / (S_H * k_2 + S_R * k_1 * k_2 + S_I * k_1)]$ x 100%

% isomerization = $[(S_I * k_1) / (S_H * k_2 + S_R * k_1 * k_2 + S_I * k_1)]$ x 100%

Where, S_H = Peak area corresponding to hydrogenated product (1-Propanol)

S_I = Peak area corresponding to isomerized product (propanal)

S_R= Peak area corresponding to reactant (allyl alcohol)

k_1 = Response factor for hydrogenated product to reactant

k_2= Response factor for isomerized product to reactant

$k_1 = (S_H * C_R) / (S_R * C_H)$

$k_2 = (S_I * C_R) / (S_R * C_I)$

Where, C_R= Concentration of reactant, C_H= Concentration of hydrogenated product and C_I= Concentration of isomerized product (10 mM each)

The TOFs were determined from the slope of the points for <60% isomerization and for all of the points for hydrogenation. The TOFs were added to get total TOF of both products.

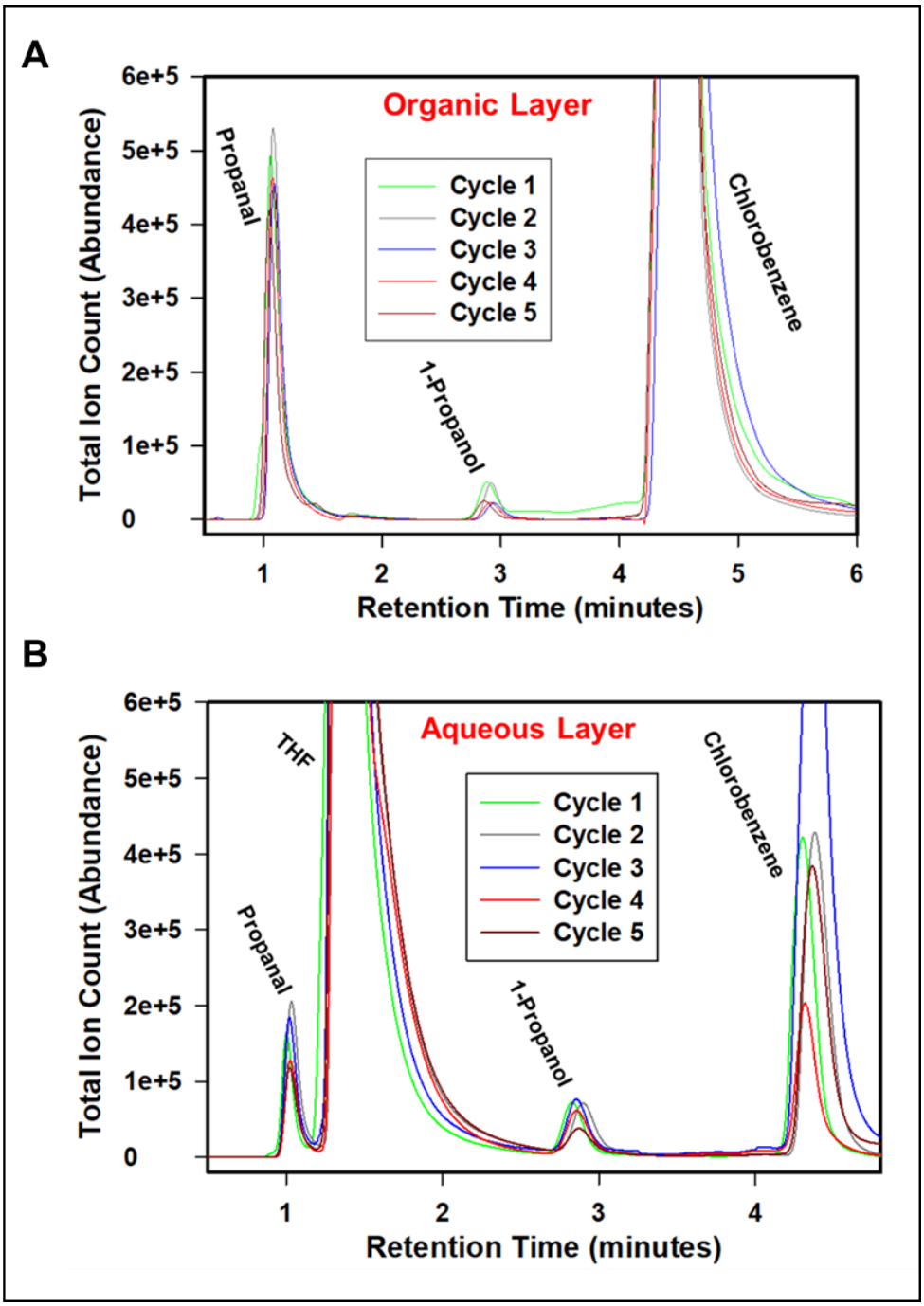

Figure S12: Gas chromatograms of cycle 1 to cycle 5 using PdSG MPCs as a catalyst for allyl alcohol hydrogenation/isomerization (no I_2 added); **A**. organic layer, and **B**. aqueous layer.

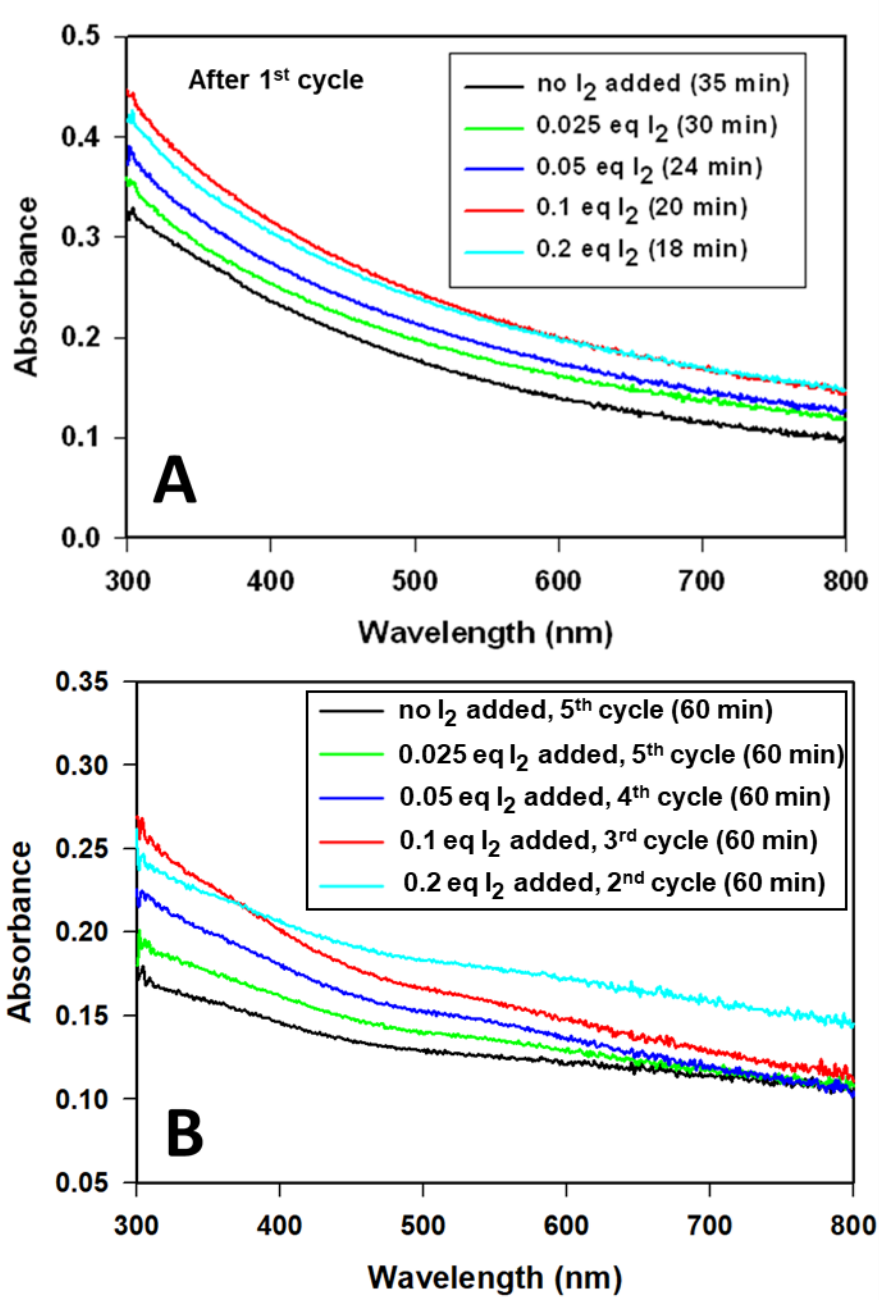

Figure S13: UV-Vis spectra showing the stability of PdSG MPCs after (A) completion of the first cycle and (B) completion of the last cycle (with no I_2 and different equivalents of I_2 addition) in the hydrogenation/isomerization of allyl alcohol (# cycles shown in B).

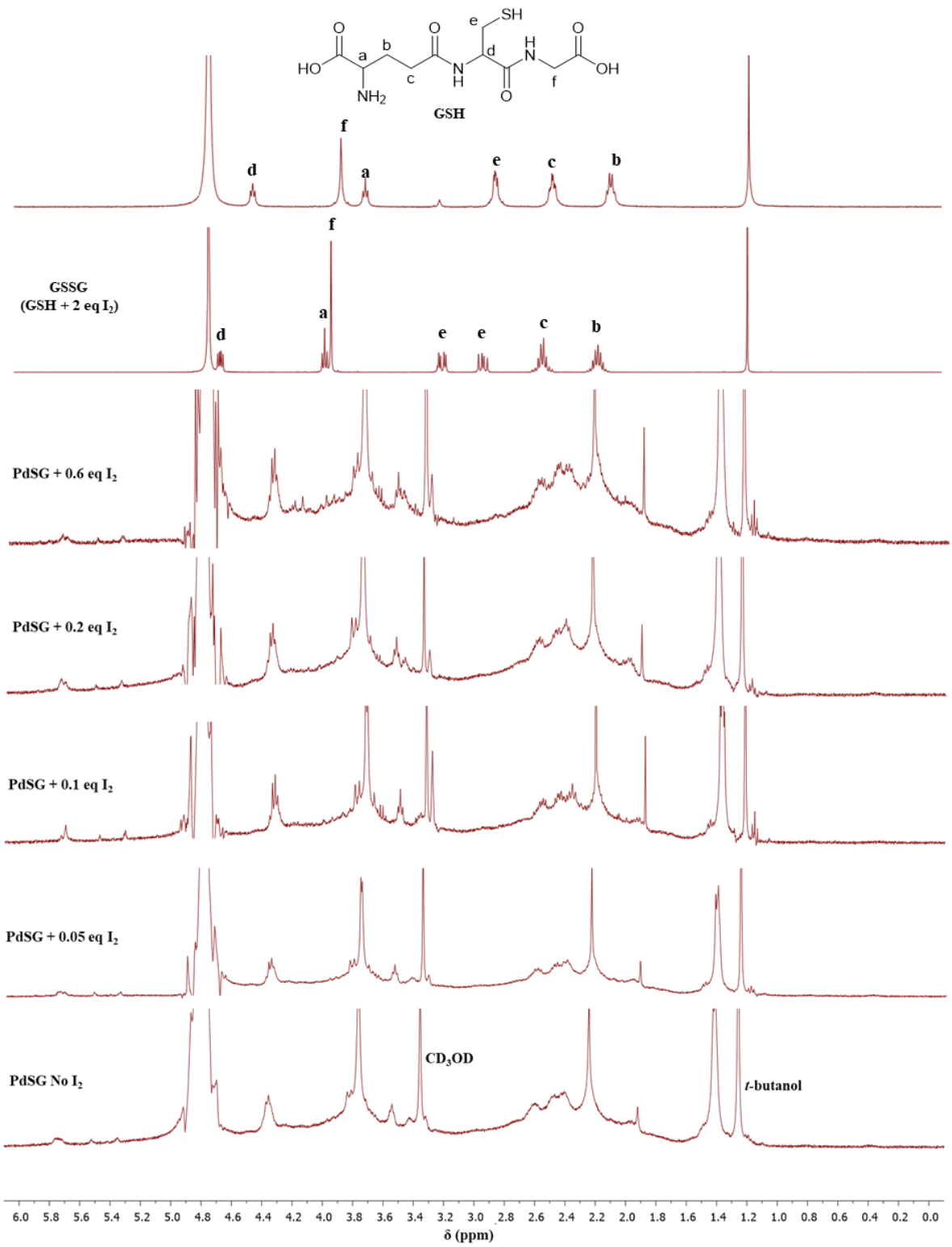

Figure S14: ^{1}H NMR (400 MHz, D_2O) spectra of PdSG MPCs upon I_2 activation. Each spectrum was obtained on a separate sample after 40 minutes of reaction with I_2 except for 0.1 equivalents I_2, which was obtained on the sample with 0.05 equivalents I_2 after adding a second 0.05 equivalents (0.1 total) and obtaining the spectrum after another 40 minutes.

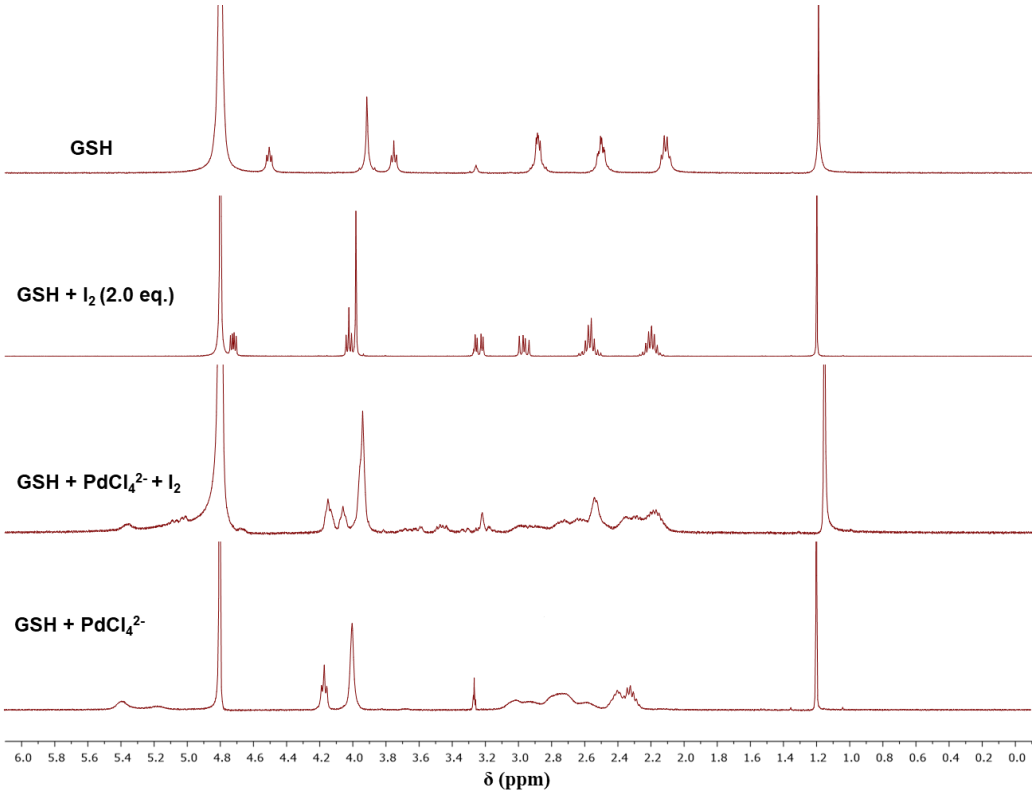

Figure S15: ^{1}H NMR spectra of GSH only and GSH treated with 2.0 equivalents I_2, 1 equivalent of K_2PdCl_4, and both I_2 and K_2PdCl_4 after 40 min.

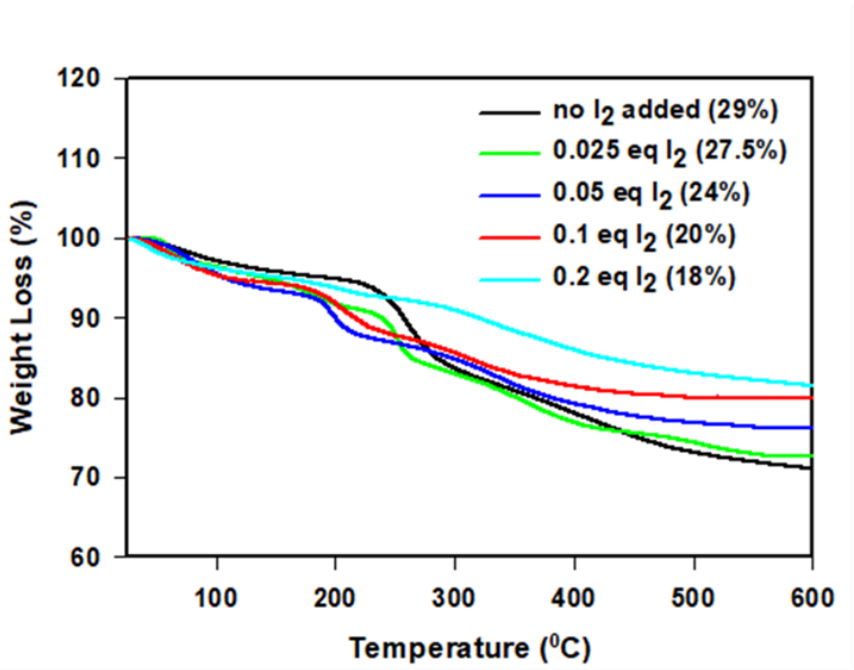

Figure S16: TGA of PdSG MPCs obtained after reaction with varying equivalents of I_2 addition for 60 min. There is less organic weight percent as the amount of I_2 increased. The estimated ligand loss is 5, 17, 31, and 38% for the 0.025 eq, 0.05 eq, 0.1 eq, and 0.2 eq, respectively.

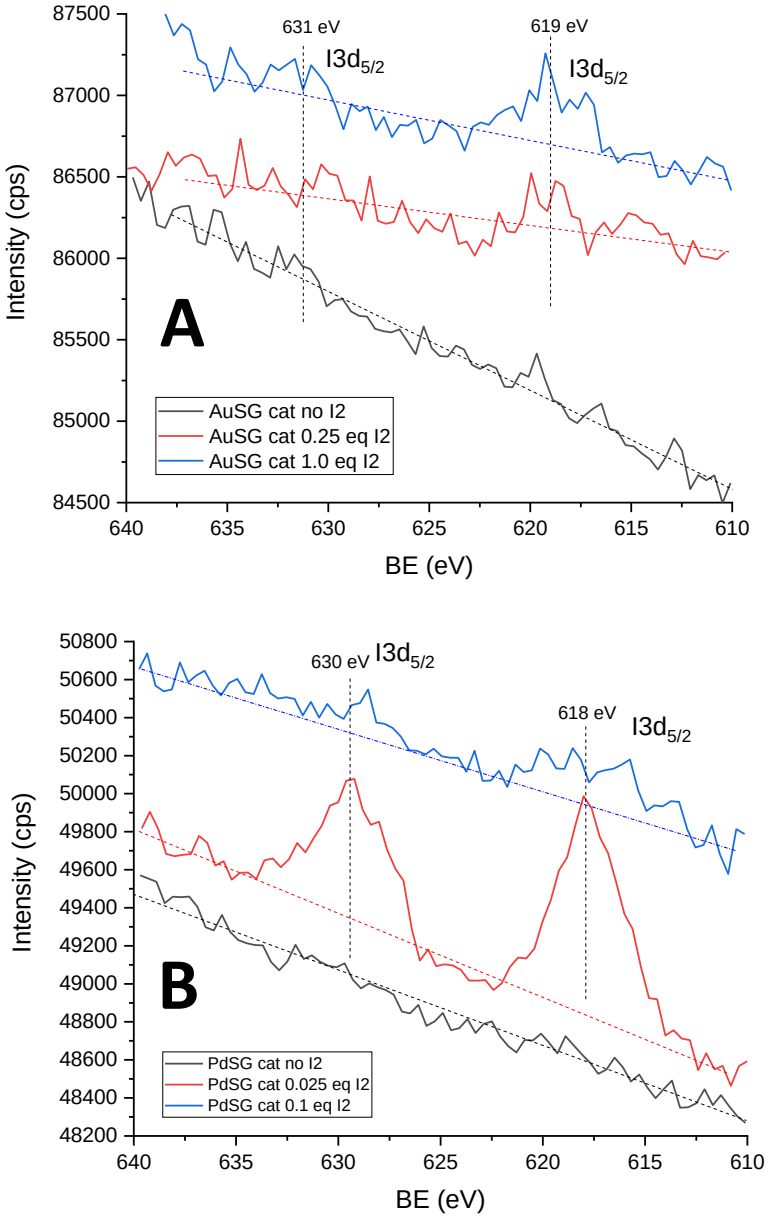

Figure S17: XPS survey spectra of the iodide region (BE 610-640 eV) of a sample of (A) AuSG MPCs and (B) PdSG MPCs after one reaction cycle with no I_2 and various I_2 additions as indicated.

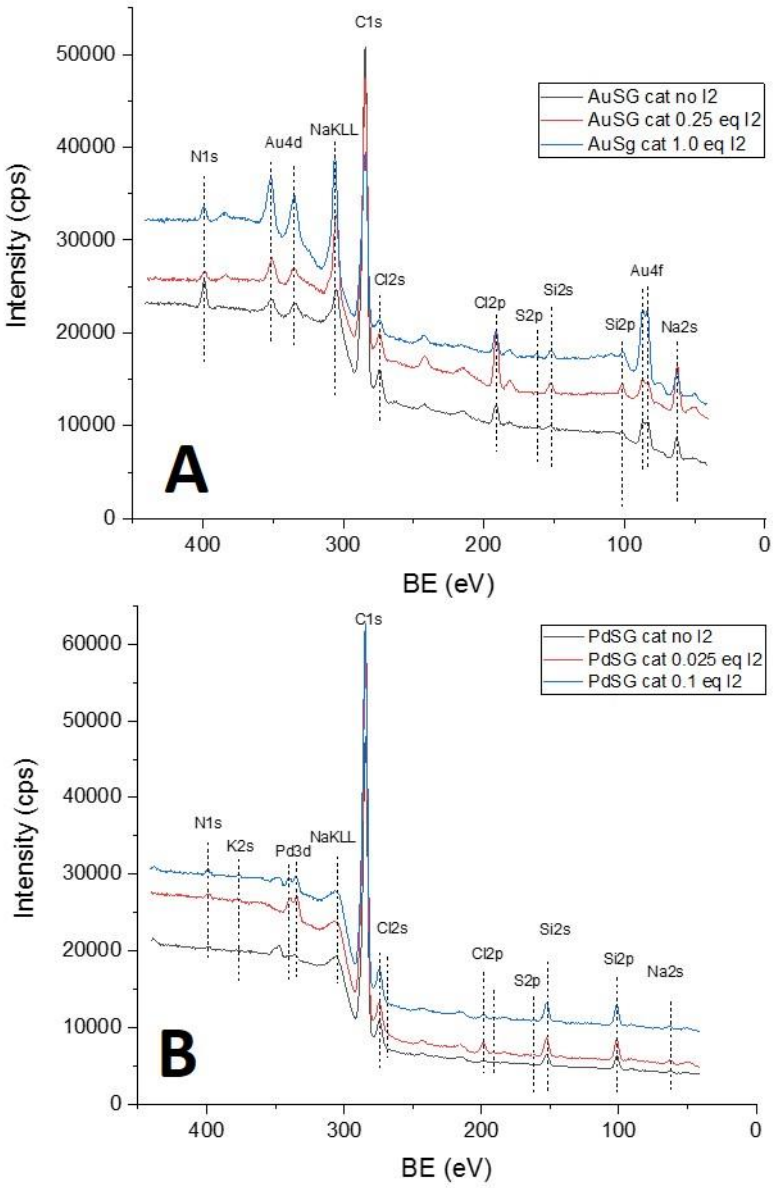

Figure S18: XPS survey spectra from 50-450 eV BE of a sample of (A) AuSG MPCs and (B) PdSG MPCs after one reaction cycle with no I_2 and various I_2 additions as indicated.

References

1. S. Bhattacharjee and M. Bruening, *Langmuir*, 2008, **24**, 2916–2920.
2. M. Moreno, L. N. Kissell, J. B. Jasinski and F. P. Zamborini, *ACS Catal.*, 2012, **2**, 2602–2613.
3. S. Bhama, T. R. Sibakoti, J. B. Jasinski and F. P. Zamborini, *Chem. Cat. Chem*., 2020, **12**, 2253-2261.