

Supporting Information

Manipulating Ligand-Nanoparticle Interactions and Catalytic Activity through Organic-Aqueous Tunable Solvents Recovery

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Schematic of in situ UV-Vis Pressure Vessel	2
Schematic of High Pressure Apparatus.....	3
Calculation of %NP Recovery	4
Extinction Spectra for LSPR.....	5
Nanoparticle Histograms for the Effect on Size of Thermal Treatments.....	6
TEM Micrographs of Nanoparticles having undergone Thermal Treatment.....	7
Nile Red Absorbance Spectra.....	8
Nanoparticle Sizes and Shapes Before and After OATS Processing.....	9
2-MBI Adsorption Before and After OATS Separation.....	10
Activation Energy	11
Kinetic Evaluation Before and After Pressurization Without Acetonitrile.....	12

Schematic of *in situ* UV-Vis Pressure Vessel

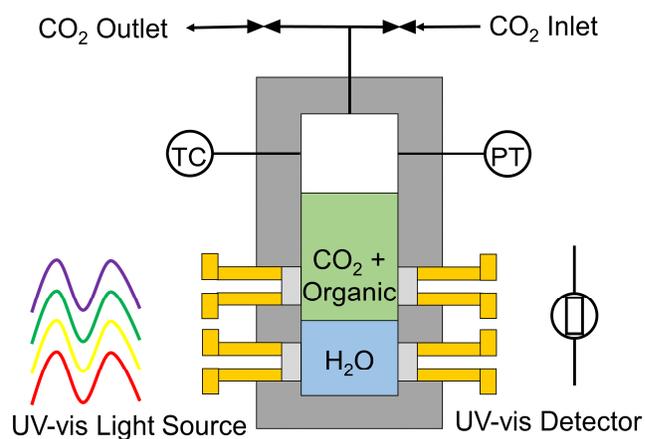


Figure S1. Schematic of *in situ* stainless steel UV-vis pressure vessel. The vessel is fitted with two sets of vertically oriented quartz windows and a thermocouple. CO₂ is introduced through the top of the vessel and the overhead pressure is measured with a pressure transducer.

Schematic of High Pressure Apparatus

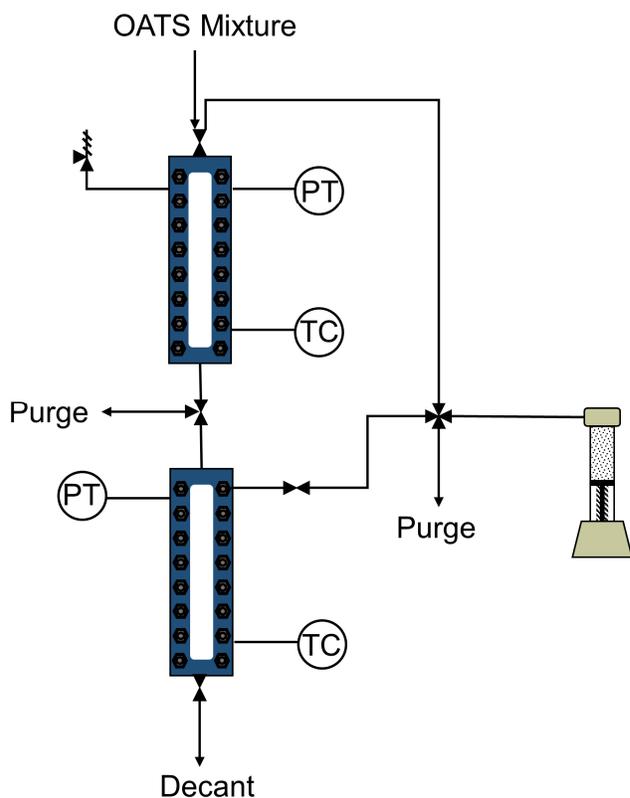


Figure S2. High pressure apparatus to perform nanoparticle separations and extractions. Two Jerguson gauges (17R20) are oriented vertically and separated by isolation valves. An OATS mixture is introduced into the top vessel and CO₂ pressurization is delivered via cylinder pump into both vessels simultaneously to allow easy decantation. When the phase separation has reached equilibrium at ~11.3 bar, the bottom aqueous phase is removed from the organic phase via decantation into the bottom vessel. Both vessels are relieved of pressure slowly overnight and each phase is collected individually.

Calculation of %NP Recovery

Nanoparticle recovery was calculated starting with the Beer-Lambert Law shown in Equation 1:

$$A = \epsilon l C_{Au} \quad (1)$$

where A is the total light absorbance, ϵ is the extinction coefficient, l is the path length through the cuvette, and C_{Au} is the concentration of gold nanoparticles. After pressure has been applied, nanoparticle dispersion can be calculated by a concentration ratio presented in Equation 2:

$$\frac{A_1}{A_0} = \frac{\epsilon l C_{Au_1}}{\epsilon l C_{Au_0}} = \frac{C_{Au_1}}{C_{Au_0}} \quad (2)$$

Path length and the extinction coefficient can be eliminated as constants because the extinction coefficient is not a function of the solvent or ligand it is constant for nanoparticles of constant size.³⁶ After rearranging Equation 2 and further reducing concentration, the amount of dispersed gold at any applied pressure can be calculated via a mass balance using Equation 3:

$$\%NP \text{ Recovery} = \frac{m_{Au_1}}{m_{Au_0}} * 100 = \frac{A_1 V_1}{A_0 V_0} * 100 \quad (3)$$

where m_{Au} is the number of moles of gold dispersed in solution, and V is the volume based off of the measurements presented in Figure 3.

Extinction Spectra for LSPR

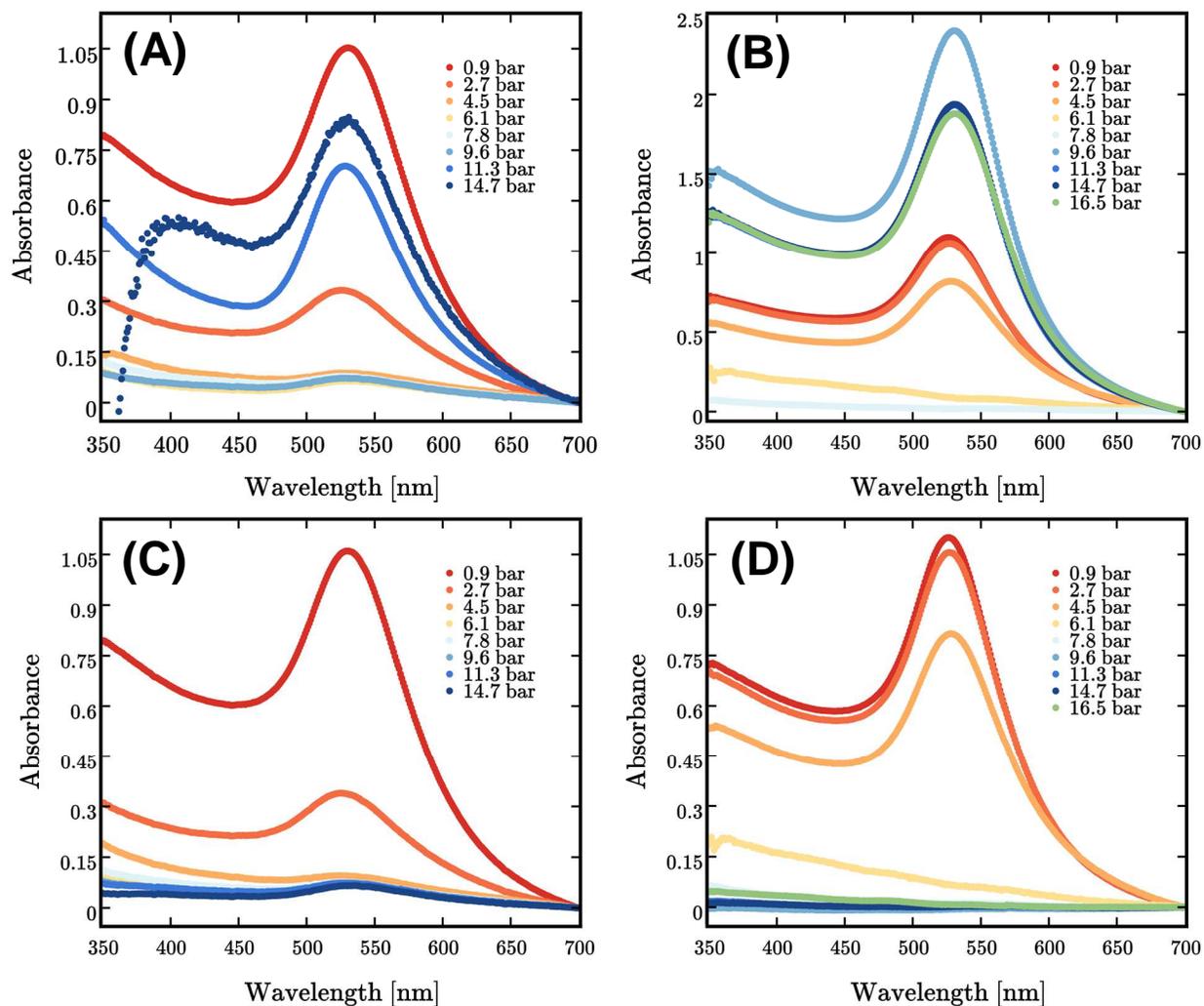


Figure S3. Localized surface plasmon resonance extinction spectra for gold nanoparticles measured at various absolute pressures of CO₂. (A) Aqueous phase for the non-thermally treated nanoparticles, (B) aqueous phase for the 40°C thermally treated nanoparticles, (C) organic phase for the non-thermally treated nanoparticles, (D) organic phase for the 40°C thermally treated nanoparticles. Slight red-shifts in peak wavelength were observed during both experiments, but no additional broadening or peaks formed throughout the experiment.

Nanoparticle Histograms for the Effect on Size of Thermal Treatments

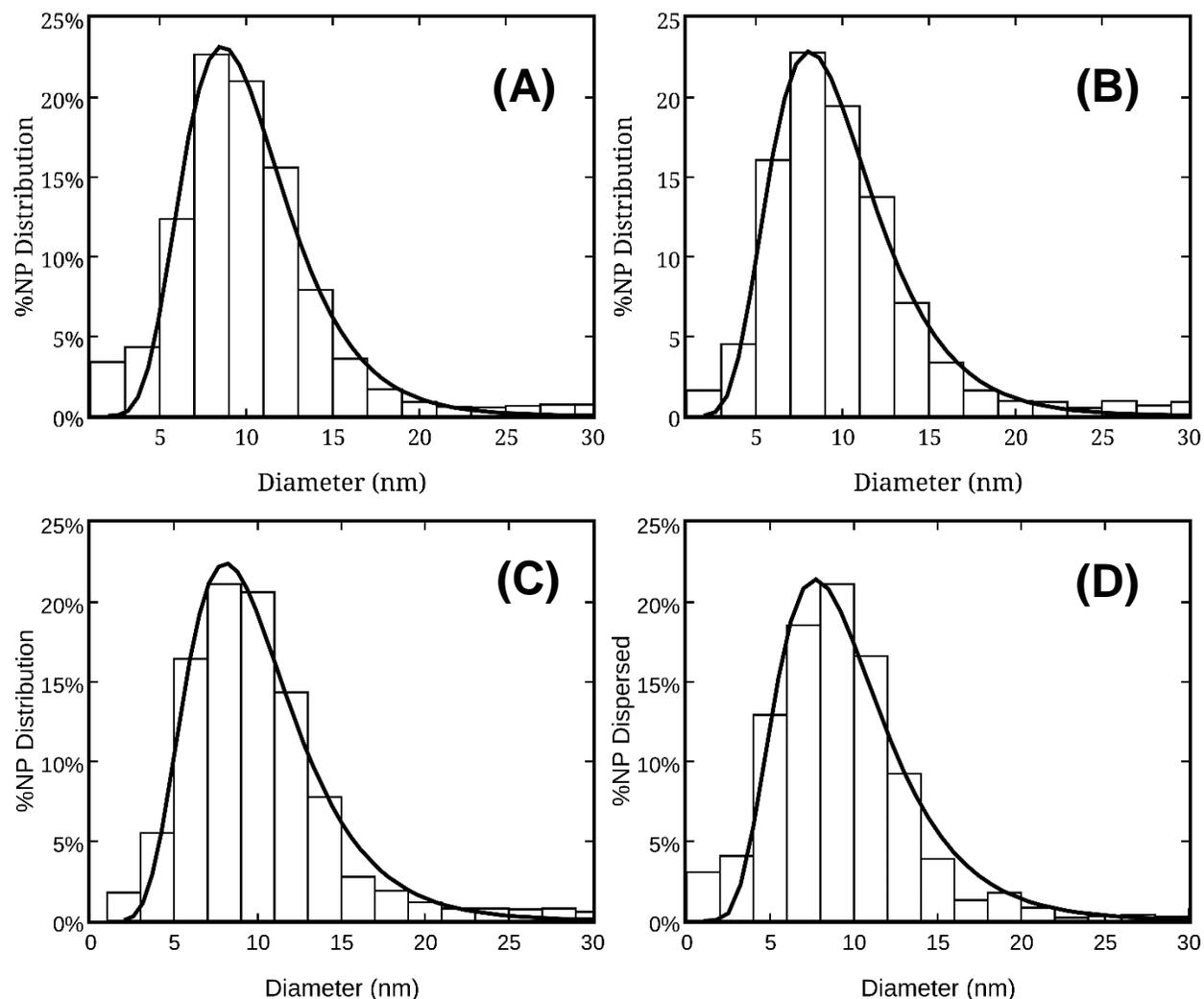


Figure S4. Histograms for the size effects from the thermal treatments. (A) Represents the nanoparticle mixture that underwent no thermal treatment, (B) 40°C thermal treatment, (C) 50°C thermal treatment, (D) 60°C thermal treatment. Histograms show that thermal treatments have no effect on nanoparticle size.

TEM Micrographs of Nanoparticles having undergone Thermal Treatment

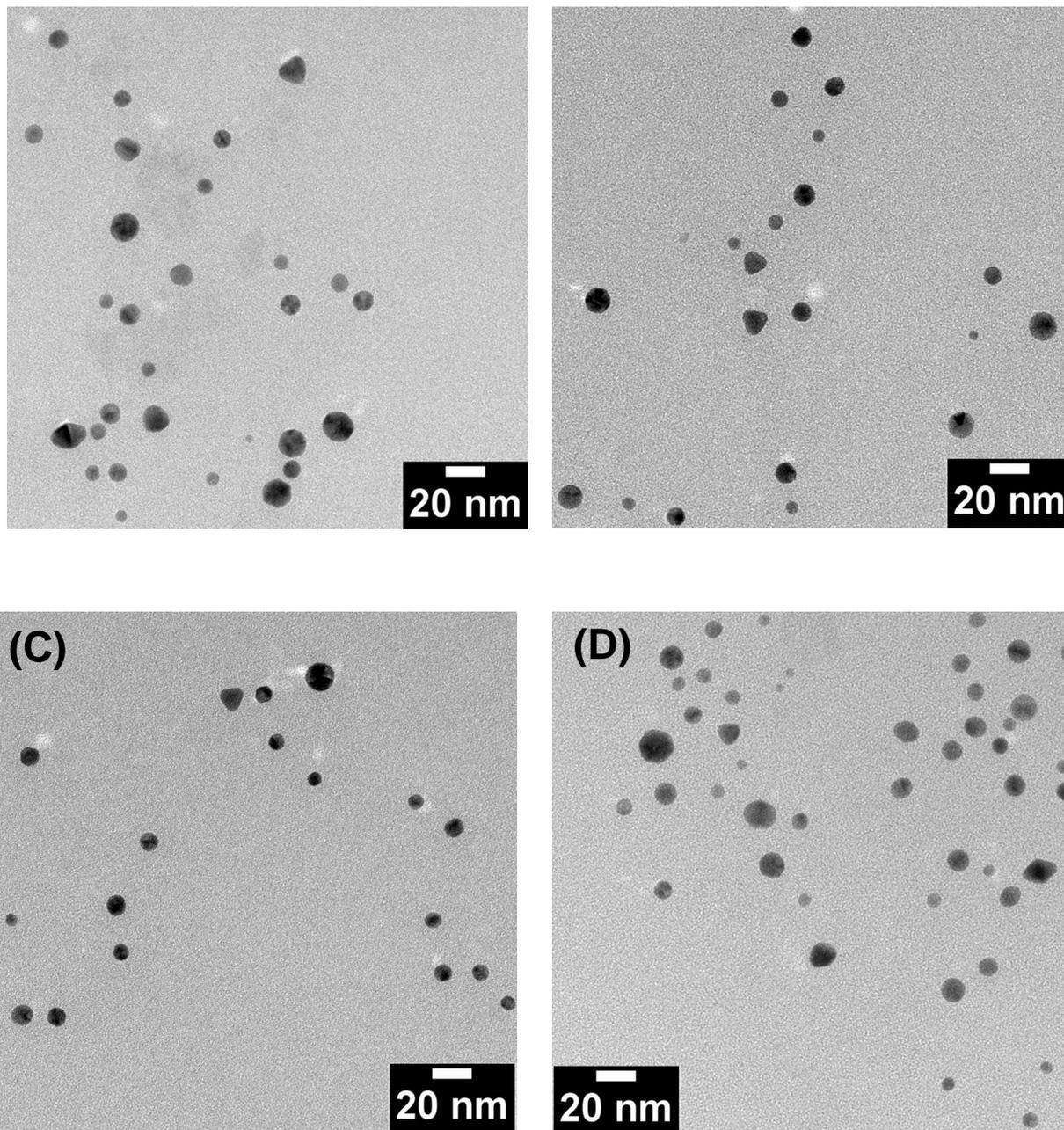


Figure S5. TEM micrographs for nanoparticles after application of the four thermal treatments (A) no treatment, (B) 40°C, (C) 50°C, (D) 60°C. No effect on shape of the nanoparticles from the thermal treatments was observed.

Nile Red Absorbance Spectra

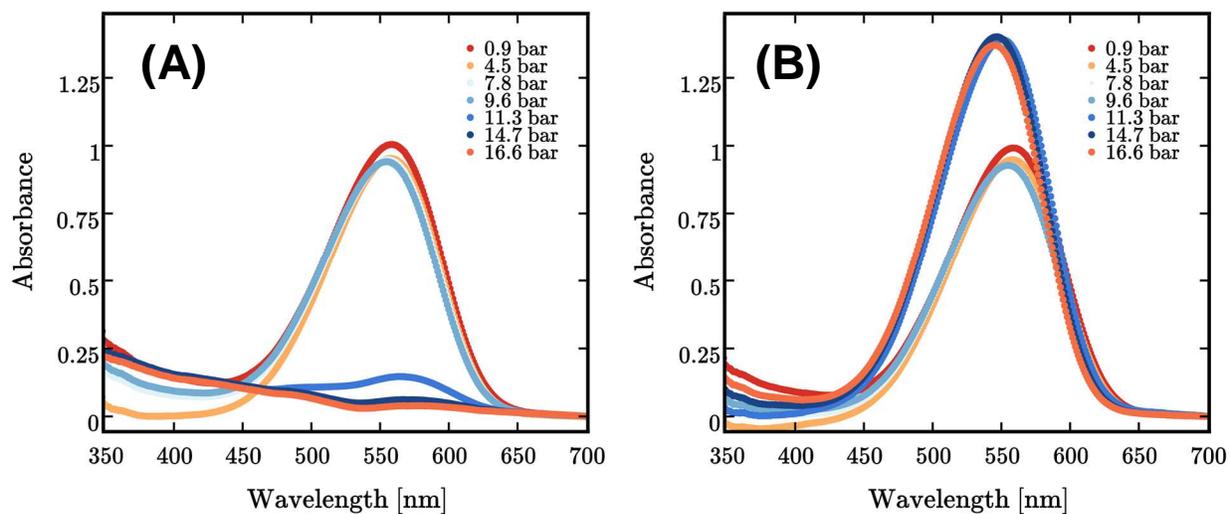


Figure S6. Nile Red absorbance spectra collected at various absolute pressures of CO₂. The experiment was carried out in the UV-vis pressure vessel shown by the schematic in Figure S1. (A) The spectra of the aqueous phase as collected through the bottom window, (B) the spectra of the organic phase as collected through the top window.

Nanoparticle Sizes and Shapes Before and After OATS Processing

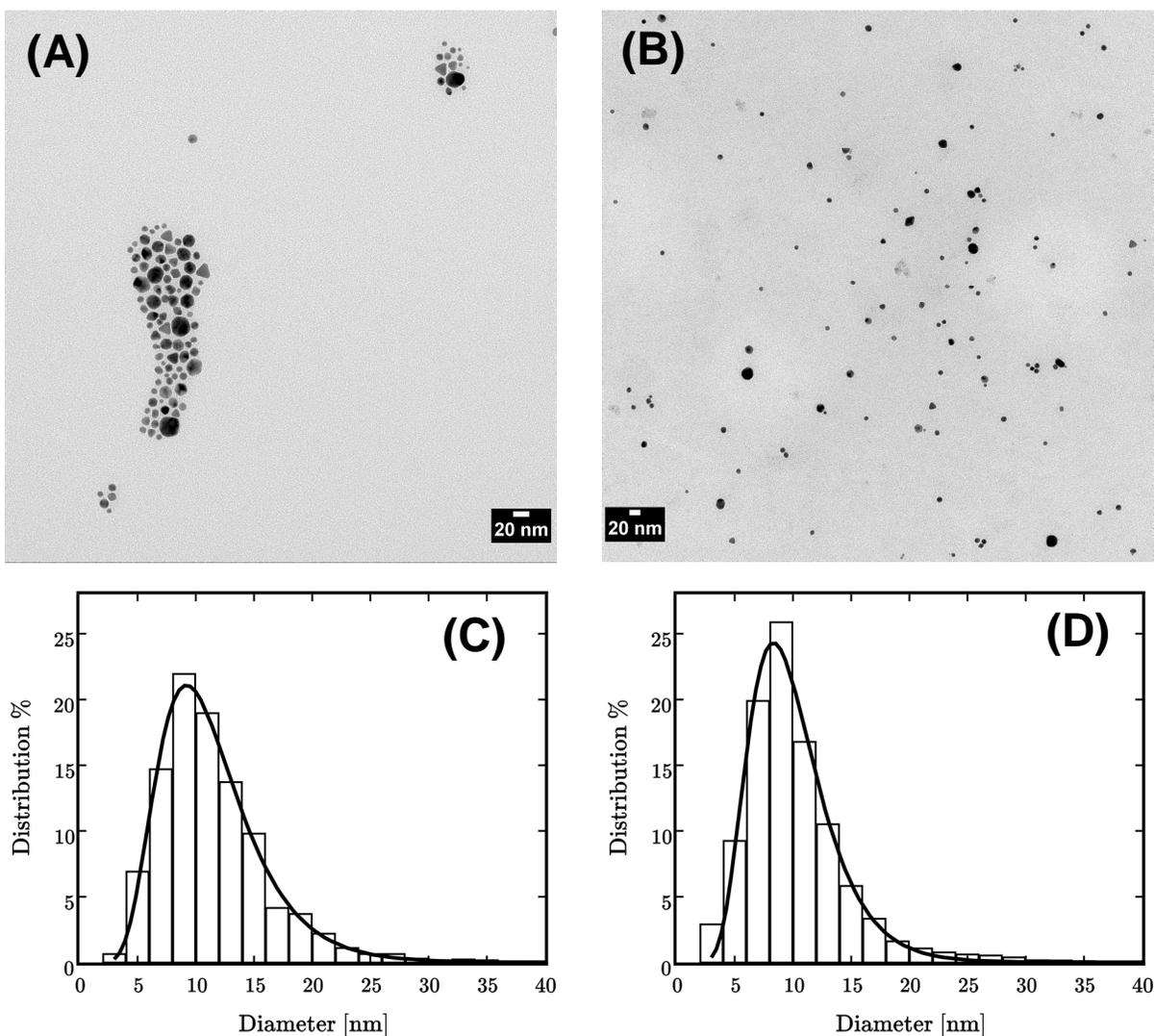


Figure S7. (A) TEM micrographic image of non-thermal treated gold nanoparticles prior to OATS processing, (B) TEM micrograph of gold nanoparticles after OATS processing. (C) Histogram of non-thermal treated gold nanoparticles prior to OATS processing, (D) histogram of gold nanoparticles after OATS processing. The narrowing of the histogram in (D) demonstrates that OATS processing likely caused the largest nanoparticles to precipitate, reducing the average size of the population.

2-MBI Adsorption Before and After OATS Separation

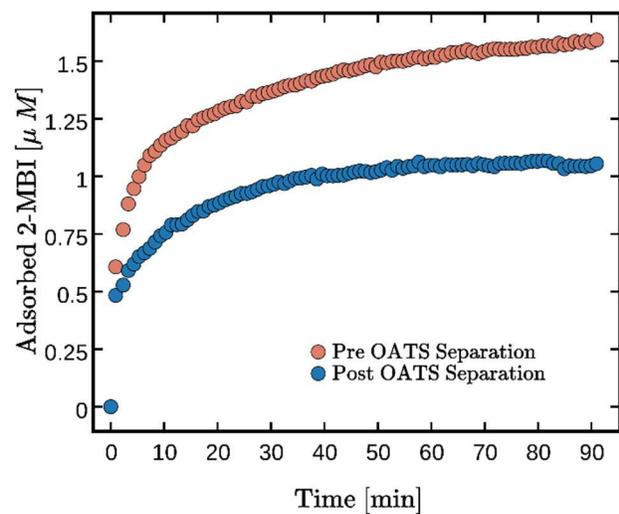


Figure S8. Surface volume concentration of adsorbed 2-MBI versus time before and after the OATS was performed on the nanoparticles. The decrease in surface availability after the OATS separation is likely caused by additional PVP reaching the surface, as demonstrated with the thermal treated nanoparticles. The likely cause is that both the separation and coordination of surface atoms are functions of free energy and will occur simultaneously. Therefore, the separation process causes more PVP carbonyl to reach the surface of the nanoparticle, decreasing the number of available active sites

Activation Energy

Activation energy is a measure of the fundamental reaction kinetics on the surface of the nanoparticles and is related to the rate of reaction by the Arrhenius equation.

$$k_{app} = A e^{\frac{-E_a}{RT}} \quad (2)$$

Where k_{app} is the apparent rate constant, A is the pre-exponential factor, E_a is the activation energy, R is the gas constant, and T is the temperature.

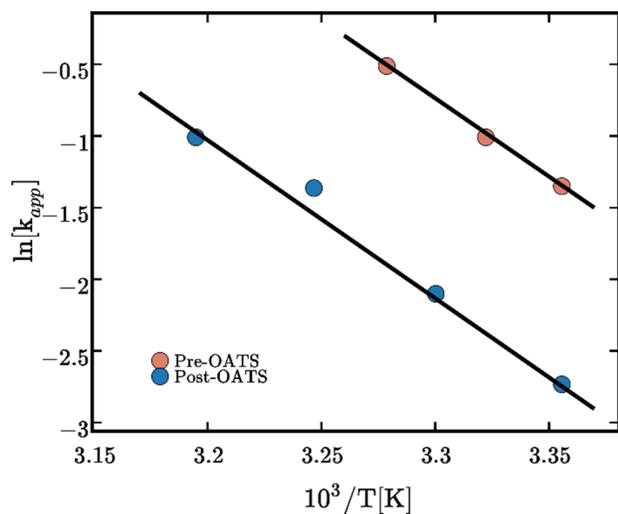


Figure S9 The effect of OATS separation on activation energy of the nanoparticles. Data is plotted as described by the linearization of the Arrhenius Equation. Activation energy before and after the OATS separation are the same, indicating the fundamental kinetics of the nanoparticles are unchanged. This indicates that we can recover the nanoparticles without changing the reaction kinetics, but surface availability is reduced.

Kinetic Evaluation Before and After Pressurization Without Acetonitrile

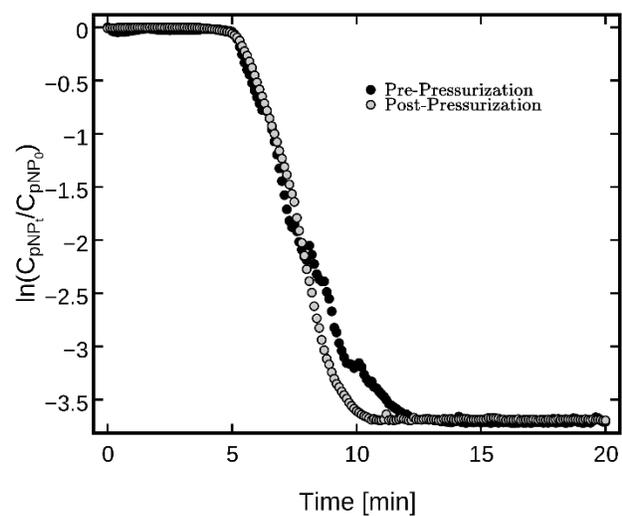


Figure S10. Hydrogenation of 4-nitrophenol to 4-aminophenol using a nanoparticle solution containing no acetonitrile test before and after pressurization to the typical mixed solvent separation pressure.