Electronic Supplementary Information

Mesoporous Silica-encapsulated Gold Core-Shell Nanoparticles for Active Solvent-free Benzyl Alcohol Oxidation

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Materials for the Synthesis of 3-aminopropyltriethylsilane

Allylamine ($C_3H_5NH_2$; 98%), triethylsilane ($C_6H_{16}Si$; 99%), and platinum (0)-1,3-divinyl-1,1,3,3tetramethyldisiloxne (Pt-DVDS; ~2% platinum) were obtained from Sigma-Aldrich. Toluene (C_7H_8 ; >99.5%) was obtained from J.T Baker. Toluene was dried over molecular sieves prior to use. All other materials were used without further purification.

Synthesis of 3-aminopropyltriethylsilane reversible ionic liquid

3-aminopropyltriethylsilane (APTES) was synthesized via a hydrosilylation reaction following a literature procedure.¹ Triethylsilane (1 eq), Pt-DVDS (0.001 eq), allylamine (2 eq), and 50 mL of anhydrous toluene were added to a sealed round bottom flask through a septum under a nitrogen atmosphere. The flask was connected to a reflux column and the temperature was brought to reflux conditions (~110°C) while stirring at 400 rpm. The reaction continued under refluxing toluene for 24 hours. The APTES was then distilled under vacuum at 2 torr and ~65°C. The molecular APTES was then converted to the APTES ionic liquid via addition of CO₂. The molecular APTES was sparged with CO₂ in a sealed and nitrogen purged vial until there was no mass changed of the vial for three consecutive measurements (~30 min).

HeXRD Analysis and Methods

The size of the gold core and the density of the silica shell are compared at three timepoints in the synthesis: (1) before the etching step, which corresponds with the micrograph in Figure 1A, (2) following the etching step prior to calcination of the catalyst, corresponding with Figure 1B, and (3) following calcination, corresponding with Figure 1C. The diffractogram is shown in Figure S1, where the SiO₂ scattering contribution appears between 1.2 and 1.7 Å⁻¹, well resolved from the first Au Bragg peak at q = 2.67 Å⁻¹.



Figure S1. (A) HeXRD patterns collected with $\lambda = 0.2114$ Å for all samples. Tick marks delineate the expected reflections for Au, with the corresponding Miller indices included. (B) PDF for the 3 samples: Signal from the gold nanoparticles dominate the PDF, however, the Si-O bond is present at 1.6 Å in the PDF profile.

Rietveld refinement of the heXRD data for proto and as-synthesized Au@SiO₂ revealed an enlarged gold *a* lattice parameter, shifted to larger values by 0.07 Å relative to bulk gold, which is expected at 4.07 Å for bulk gold, a face-centered-cubic structure.² An increase in unit cell volume is expected for nanoparticle samples due to the large percentage of near-surface atoms. Crystal

domain sizes of gold nanoparticles were found to vary insignificantly between the nanoparticles harvested in a truncated synthesis and the complete synthesis (9 versus 8 nm crystal domain diameter, respectively). However, following calcination, the crystal domain size was determined to increase to 15 nm. A summary of the parameters acquired with Rietveld refinement is presented in Table S1.

sample	a (Å)	Diameter (nm)	µ-strain	Rel. Intensity	R _{wp} (%)
Proto-CSNPs	4.07719	9	794.6	20.2594	7.714
As synthesized CSNPs	4.07804	8	1183.5	2.86652	4.554
Calcined CSNPs	4.07968	15	2182.2	3.03092	5.157

Table S1. Rietveld fit for the gold nanoparticle core of $Au@SiO_2$ samples. Fit residuals, R_{wp} , are reported for the total fit, including the background polynomial.

Methods: Total x-ray scattering and high-energy x-ray diffraction

Data for high energy x-ray diffraction and total x-ray scattering for PDF analysis was collected at beamline 11 ID-B of the Advanced Photon Source,³ Argonne National Laboratory (Argonne, IL, USA) during top-up mode. X-rays (86.7 keV, $\lambda = 0.143$ Å and 58.66 keV, $\lambda = 0.2113$ Å) are delivered via two individual in-line, bent Laue brilliance-preserving monochromators, using symmetrically-cut Si(422) or Si(311) to select the energy. Acquisition utilized an amorphous silicon-based detector of resolution 2048x2048 pixel with 200x200 µm⁴ pixel size, Perkin-ElmerTM.

Instrument parameters (sample-detector distance, beam energy, beam center, and nonorthogonality) were determined from the scattering of a cerium dioxide standard (CeO₂, NIST diffraction intensity standard set 674a, diluted 1:25 with glassy carbon). Powder samples were loaded into 2.1 mm inner diameter polyimide (Kapton[®]) capillaries and sealed with general purpose epoxy (Devcon, 5 Minute[®] Rapid-Curing). Total scattering scans are the summation of 150 exposures of 2 sec length at 86.7 keV and 230 mm sample to detector distance. High-energy x-ray diffraction was measured at 58.66 keV and 800 mm sample to detector distance by summing 30 exposures of 2 sec duration. Dark images matching the data acquisition frame rate were acquired between each sample and subtracted from the data in 5 min intervals to remove detector noise without x-ray delivery. Dead and overexposed pixels on the detector were masked in General Structural Analysis System II (GSAS-II), with typical 2D diffractograms shown in Figure S2.⁴



Figure S2. Typical 2D detector images acquired at beamline 11 ID-B of as-synthesized $Au@SiO_2$ used for creation of (A) X-ray total scattering pairwise distributions and (B) X-ray diffractograms. In these images, the high q integration limit is marked in green, the low q integration limit is marked in orange, and the radial origin is marked in purple. The masked pixels and the area including the beam stop are marked with red pixels and lines, respectively, and both are not included in the analysis.

Rietveld refinement of heXRD data was performed in GSAS-II using the chebyschev-1 algorithm with 3 terms to fit a background polynomial. Instrument parameters were refined using

diffraction of the CeO₂ NIST diffraction intensity standard set 674a. Gold heXRD was fit with a previously published structure⁵ and only the 1) pattern intensity, 2) unit cell a parameter, 3) particle size, and 4) particle strain were refined in successive order.

To calculate Pair Distribution Function (PDF) profiles from the total scattering signal, the contribution of an empty polyimide capillary was subtracted from sample data in the reciprocal-space signal. PDF profiles, G(r), were evaluated in PDFgetX3 (Columbia Technology Ventures), assuming an SiO₂ to Au ratio of 2:1 for the fully synthesized catalyst.





Figure S3. GC-FID calibration curves for biphenyl, benzyl alcohol, benzyl benzoate, and benzaldehyde over ranges spanning expected concentrations.

Surface Atom Calculation Method

The surface atom calculation method was first published in a paper by Bryant et al.⁶ Using the gold nanoparticle size distributions for each catalyst, a random starting guess for the number of nanoparticles per gram of catalyst was chosen and applied to the size distribution:

$$\left(\frac{\# NPs}{g}\right)_{i} = (\% frequency)_{i} * \left(\frac{\# NPs}{g}\right)_{guess}$$
(1)

The volume and surface area of each bin were then calculated assuming spherical nanoparticles:

$$V_{NP,i} = \frac{4}{3} \pi \left(\frac{D_{NP}}{2}\right)_i^3 \tag{2}$$

$$SA_{NP,i} = 4\pi \left(\frac{D_{NP,i}}{2}\right)_{i}^{2}$$
(3)

The total surface area per gram for each bin was calculated applying the size distribution to the individual nanoparticle surface areas:

$$SA_i = SA_{NP,i} \left(\frac{\# NPs}{g}\right)_i \tag{4}$$

Assuming each gold atom occupies surface area equal to its cross-sectional area (r = 0.166 nm), the number of surface atoms per gram for each bin was calculated:

$$\left(\frac{\#Surface\ Atoms}{g}\right)_i = \frac{SA_i}{\pi (0.166)^2} \tag{5}$$

To set up a system of equations to solve for the actual number of nanoparticles per gram, the mass per gram of each bin was calculated using gold density ($\rho = 19.32 \ g/cm^3$) and then summed, resulting in the gold loading according to the guessed value:

$$m_{i} = \left(\frac{\# NPs}{g}\right)_{i} V_{NP,i} \left(1.932 * 10^{-20} \frac{g}{nm^{3}}\right)$$
(6)

$$(gold \ loading)_{guess} = \sum_{i=0}^{n} m_i \tag{7}$$

This value can then be compared to the known gold loading from ICP-MS studies for each catalyst. The squared error between the two was minimized by changing the guess for total number of nanoparticles per gram using Microsoft Excel's solver package:

$$Error parameter = ((gold \ loading)_{guess} - (gold \ loading)_{ICP-MS})^2 * (10^8)$$
(8)

Note: the error was multiplied by 10^8 to improve the solver algorithm's precision.

The surface fraction of gold for each catalyst can then be calculated using the surface atoms per gram catalyst, the gold loading, and the moles gold used in a given reaction ($n = 0.5 \mu mol Au$):

$$Surface Atom Fraction = \left(\frac{Surface atoms}{m_{catalyst}}\right) * \left(\frac{m_{catalyst}}{reaction}\right) * \left(\frac{3.011 * 10^{17} Au \ atoms}{reaction}\right)^{-1}$$
(9)

S8

Bin	Frequency	%freq	# NPs/g	V _{NP,i} (nm ³)	SA _{NP,i} (nm ²)	SA _i (nm²)	Surface Atoms	Au mass (g)
0	0	0.0%	0.00E+00	0.00	0.00	0.00E+00	0.00E+00	0.00E+00
1	0	0.0%	0.00E+00	0.52	3.14	0.00E+00	0.00E+00	0.00E+00
2	0	0.0%	0.00E+00	4.19	12.57	0.00E+00	0.00E+00	0.00E+00
3	0	0.0%	0.00E+00	14.14	28.27	0.00E+00	0.00E+00	0.00E+00
4	1	0.8%	5.18E+11	33.51	50.27	2.60E+13	3.01E+14	3.35E-07
5	3	2.5%	1.55E+12	65.45	78.54	1.22E+14	1.41E+15	1.97E-06
6	15	12.4%	7.77E+12	113.10	113.10	8.79E+14	1.02E+16	1.70E-05
7	22	18.2%	1.14E+13	179.59	153.94	1.75E+15	2.03E+16	3.95E-05
8	27	22.3%	1.40E+13	268.08	201.06	2.81E+15	3.25E+16	7.25E-05
9	8	6.6%	4.14E+12	381.70	254.47	1.05E+15	1.22E+16	3.06E-05
10	18	14.9%	9.33E+12	523.60	314.16	2.93E+15	3.38E+16	9.43E-05
11	12	9.9%	6.22E+12	696.91	380.13	2.36E+15	2.73E+16	8.37E-05
12	7	5.8%	3.63E+12	904.78	452.39	1.64E+15	1.90E+16	6.34E-05
13	4	3.3%	2.07E+12	1150.35	530.93	1.10E+15	1.27E+16	4.61E-05
14	2	1.7%	1.04E+12	1436.76	615.75	6.38E+14	7.37E+15	2.88E-05
15	0	0.0%	0.00E+00	1767.15	706.86	0.00E+00	0.00E+00	0.00E+00
16	0	0.0%	0.00E+00	2144.66	804.25	0.00E+00	0.00E+00	0.00E+00
17	0	0.0%	0.00E+00	2572.44	907.92	0.00E+00	0.00E+00	0.00E+00
18	0	0.0%	0.00E+00	3053.63	1017.88	0.00E+00	0.00E+00	0.00E+00
19	2	1.7%	1.04E+12	3591.36	1134.11	1.18E+15	1.36E+16	7.19E-05
20	0	0.0%	0.00E+00	4188.79	1256.64	0.00E+00	0.00E+00	0.00E+00

Au-SiO₂ Control Catalyst Surface Atom Calculation Table

GUESS 6.27E+13 NPs /g cat.

Total Surface Au	1.91E+17	atoms / g cat.
Error Parameter	4.70E-30	
actual mass	0.00055	g Au / g CSNP
total mass	5.50E-04	g Au / g CSNP

First-Order Approximation Verification Curve



Figure S4. Verification of first-order approximation accuracy at t = 0.5 hours. Conversion after 1 hour does not fit the approximation.



Nanoparticle Gold Core & Silica Shell Size Analysis Histograms

Figure S5. Histogram plots of CSNP core diameter and shell thickness at various states.



Figure S6. (a) DSC-TGA of as-synthesized nanoparticles, (b) DSC-TGA of once-used nanoparticles, (c) mass spectra of as-synthesized nanoparticles, (d) mass spectra of once-used nanoparticles.

Low Conversion Control Catalyst Parity



Figure S7. Benzaldehyde selectivity of benzyl alcohol oxidation catalyzed by CSNPs and supported Au nanoparticles, in the presence of K_2CO_3 , reacted for increasing times to match conversion on CSNPs. Ceria-supported NPs were unable to match CSNP conversions within 24 hours.

Sample Calculations of Effective Diffusion, Knudsen Diffusion, and Thiele Modulus

$$D_{eff}(T) = \frac{D_{AB}(T) \phi_p \sigma_c}{\tau}$$

(1) Substitute morphology constants with empirical silica parameters from literature⁸

$$D_{eff_{R}}(T) = D_{AB}(T) \left(\frac{\phi_p \sigma_c}{\tau}\right)$$
$$D_{eff_{R}}(T) = (0.668) D_{AB}(T)$$

(2) Calculate effective diffusion coefficient at a given temperature

$$D_{eff}(373 K) = 0.668 D_{AB}(373 K)$$
$$D_{eff}(373 K) = 0.668 \left(4.51 * 10^{-10} \frac{m^2}{s}\right)$$
$$D_{eff}(373 K) = 3.01 * 10^{-10} \frac{m^2}{s}$$

(3) Calculate Knudsen diffusion coefficient at a given temperature

$$D_{KA} = \frac{d_P}{3} \sqrt{\frac{8RT}{\pi \cdot MW}}$$
$$D_{KA} = \frac{2.55 * 10^{-9}m}{3} \sqrt{\frac{8 \left(8.314 \frac{J}{mol \cdot K}\right) (364 \, K)}{\pi \left(0.10814 \frac{kg}{mol}\right)}}$$
$$D_{KA} = 2.27 * 10^{-7} \frac{m^2}{s}$$

(4) Calculate Thiele moduli using the lowest calculated diffusion coefficient (effective diffusivity)

$$\phi_{eff} = R \sqrt{\frac{k}{D_{eff}}}$$

$$\phi_{eff} = 2.74 * 10^{-8} m \sqrt{\frac{6.38 * 10^{-5} s^{-1}}{3.01 * 10^{-10} \frac{m^2}{s}}}$$

$$\phi_{eff} = 1.26 * 10^{-5}$$

Sample Calculation of Weisz-Prater Parameter

(1) To calculate the Weisz-Prater criterion, the solid catalyst density was determined:

$$\rho_c = \frac{m_{CSNPs}}{V'_{CSNPs}} = \frac{m_{CSNPs}}{V_{CSNPs,dry} - V_{void}}$$

(2) A known mass and volume of dry powder catalyst was added to sufficient benzyl alcohol to completely wet the silica support (benzyl alcohol, roughly double the volume of the dry catalyst). The final volume of the mixture was measured and the solid catalyst volume was calculated:

$$\rho_c = \frac{m_{CSNPs}}{V_{mixture} - V_{BnOH}}$$

$$\rho_c = \frac{0.1243 g}{(2.2 mL - 2.0 mL)}$$

$$\rho_c = 0.622 \frac{g}{cm^3}$$

(3) With this value the Weisz-Prater criterion was calculated, using effective diffusivity at 100 °C and assuming benzyl alcohol concentration at the catalyst surface was equal to bulk concentration at 1000 rpm stirring:^{9,10}

$$C_{WP} = \frac{-r'_A(obs)\rho_c R^2}{D_{eff}C_{As}}$$

$$C_{WP} = \frac{\left(48.17\frac{mol\ A}{kg\ \bullet\ hr}\right)\left(622\frac{kg}{m^3}\right)(2.74*10^{-8}m)^2}{\left(1.08*10^{-6}\frac{m^2}{hr}\right)\left(9617\frac{mol\ A}{m^3}\right)}$$

$$C_{WP} = 2.16*10^{-9}$$

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