

Supplementary Material

Au₉ clusters deposited as Co-Catalysts on S-Modified Mesoporous TiO₂ for Photocatalytic Degradation of Methyl Orange

Anahita Motamedisade,¹ Amir Heydari,^{1,2} D. J. Osborn,³ Abdulrahman S. Alotabi^{1,4} and
Gunther G. Andersson^{1*}

1 Institute for Nanoscale Science and Technology, Flinders University, Adelaide 5042, Australia

2 Chemical Engineering Department, Faculty of Engineering, University of Mohaghegh Ardabili, Ardabil 56199-11367, Iran

3 Department of Chemistry, University of Adelaide, Adelaide, South Australia, Australia

4 Department of Physics, Faculty of Science and Arts in Baljurashi, Albaha University, Baljurashi 65655, Saudi Arabia

* Corresponding author, E-mail: gunther.andersson@flinders.edu.au

1. The phosphine ligand stabilised Au clusters preparation method:

1.1. Au(PPh₃)Cl:

The protocol used in this study was adapted from Malatesta et al^[1]. A stirred (500 rpm) solution of tetrachloroauric acid (2.010 g, 5.102 mmol) in absolute ethanol (10 mL) was added rapidly to triphenylphosphine (2.65 g, 10.10 mmol) in absolute ethanol (75 mL). Upon adding triphenylphosphine, the yellow colour of the solution disappeared, and a white precipitate formed. For 15 minutes, the resulting solution was vigorously stirred (1000 rpm) to ensure a complete reaction. In order to collect the solid white product, the reaction mixture was centrifuged (5 minutes, 5000 rpm). It was washed three times in hot ethanol (3 × 20 mL) on a sintered glass funnel filter (porosity 3). The solution was filtered after dissolving the solid product in chloroform (30 mL), and then the solvent was removed under reduced pressure. A vacuum desiccator was used to dry the crude product. Through the use of vapour diffusion, the product was recrystallized from a mixture of dichloromethane and methanol to form needle-like white crystals.

Yield: 3.11 g, 92 %. ³¹P NMR (CDCl₃, 25 °C); δ 33.16 ppm referenced to H₃PO₄.

1.2. AuPPh₃(NO₃):

It was prepared as a powder sample according to synthesis procedure reported by Mueting et al[2]. An Au(PPh₃)Cl (3.973 g, 8.042 mmol) solution in chloroform (50 mL) was rapidly mixed with an AgNO₃ (3.430 g, 20.191 mmol) solution in 130 mL of ethanol and stirred

for one hour in a covered reaction vessel by aluminium foil. In order to remove the AgCl precipitate, a sintered glass funnel filter was used (porosity 3), and the filtrate was slowly dried at room temperature in a rotary evaporator. 50 mL of ethanol was used three times to wash the crude product. In 50 mL of dichloromethane, the product was dissolved, followed by 150 mL of ethanol. Dichloromethane was then removed by bubbling the solution for a few hours with nitrogen flow. Filtered white crystals were washed with cold ethanol (3 x 5 mL) and cold diethyl ether (3 x 5 mL).

Yield: 3.75 g, 88 %. ^{31}P NMR (CDCl_3 , 25 °C); δ 25.2 ppm referenced to H_3PO_4 .

1.3. $\text{Au}_9(\text{PPh}_3)_8(\text{NO}_3)_3$:

Triphenyl phosphine stabilized Au_9 clusters, $\text{Au}_9(\text{PPh}_3)_8(\text{NO}_3)_3$, were prepared according to the synthesis procedure reported by Wen et al^[31]. 92 mL of ethanol solution of 0.072 g NaBH_4 (1.92 mmol) was mixed with 160 mL of ethanol solution of $\text{Au}(\text{PPh}_3)\text{NO}_3$ (4.0 g, 7.6 mmol). With the help of a rotary evaporator, the solvent was removed from the solution after it was filtered to remove insoluble impurities and the solution was transformed into a deep red solution within two hours. Solids obtained this way were dissolved in 20 mL CH_2Cl_2 and filtered through a sintered glass filter funnel (porosity 3). A rotary evaporator was used to remove the solvent, resulting in a black precipitate washed with 50 mL of THF. Dark green was the colour of the solid after washing. A further wash of the solid was carried out with THF (3 x 50 mL) and hexanes (3 x 50 mL). Crystallization of the precipitate from methanol was achieved through slow diffusion of diethyl ether at 4°C. Around a five-day period, it led to the formation of dark green crystals.

Yield 1.32 g, 37 %. ^{31}P NMR (CD_3OD , 25 °C); δ 57.77 ppm referenced to H_3PO_4 .

2. Characterisation methods of Au clusters:

2.1. ^{31}P NMR

Particular cluster species in solution can be identified using the chemical shifts of the phosphorous peak associated with the ligands. ^{31}P NMR chemical shifts of the different types of Au clusters synthesized in this work with different size and counter ion were summarised in Table S1 (Figure S1). They are consistent with the references listed in the same Table S1.

Table S1. Experimental ^{31}P NMR isotropic chemical shifts and solvents

Clusters	Solvent	Chemical shift (^{31}P), ppm	Reference
$\text{AuPPh}_3(\text{Cl})$	CDCl_3	33.16	[4]

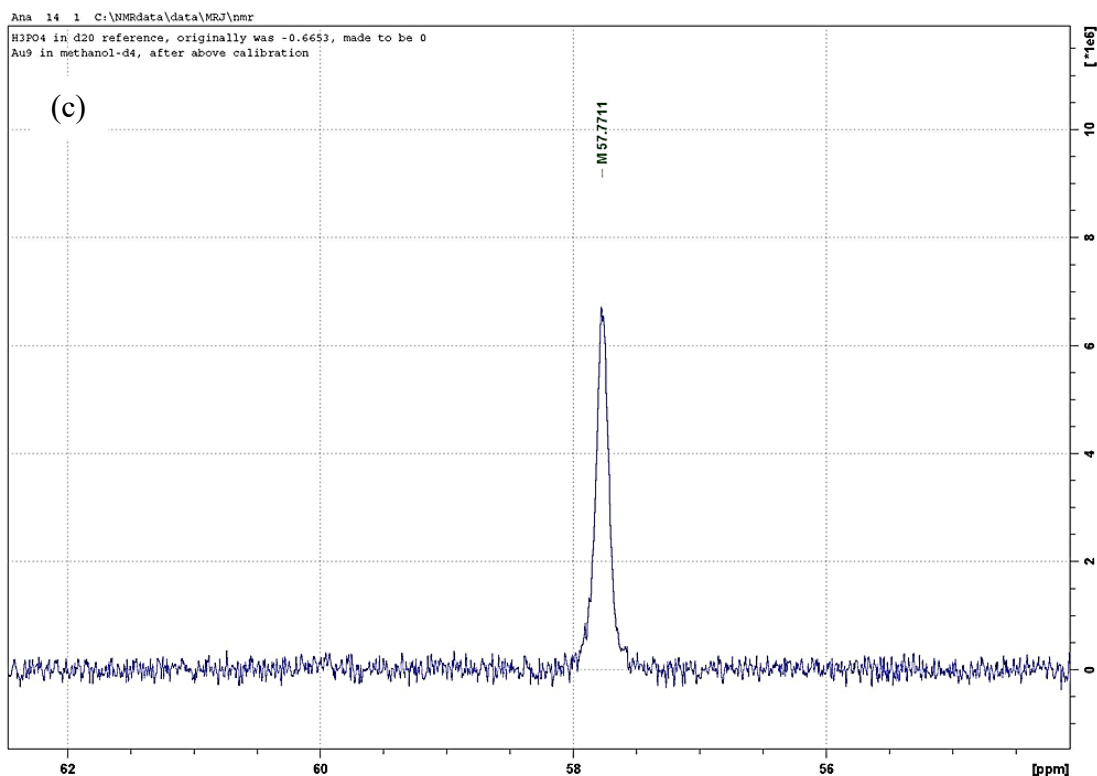


Figure S1. ^{31}P NMR of a) $\text{AuPPh}_3(\text{Cl})$ b) $\text{AuPPh}_3(\text{NO}_3)$ c) $\text{Au}_9(\text{PPh}_3)_8(\text{NO}_3)_3$

2.2. UV-Vis:

The absorption spectra were collected from 230 to 800 nm. The molecular-like optical properties of Au_9 clusters display distinct peaks.

Figure S2 shows a UV-vis spectrum observed in methanol solution exhibit three faint shoulders, centered in 354, 384 and 450 nm and one sharp peak centered in 319, that are consistent with the reference sample confirming successful preparation of Au_9 clusters^[3].

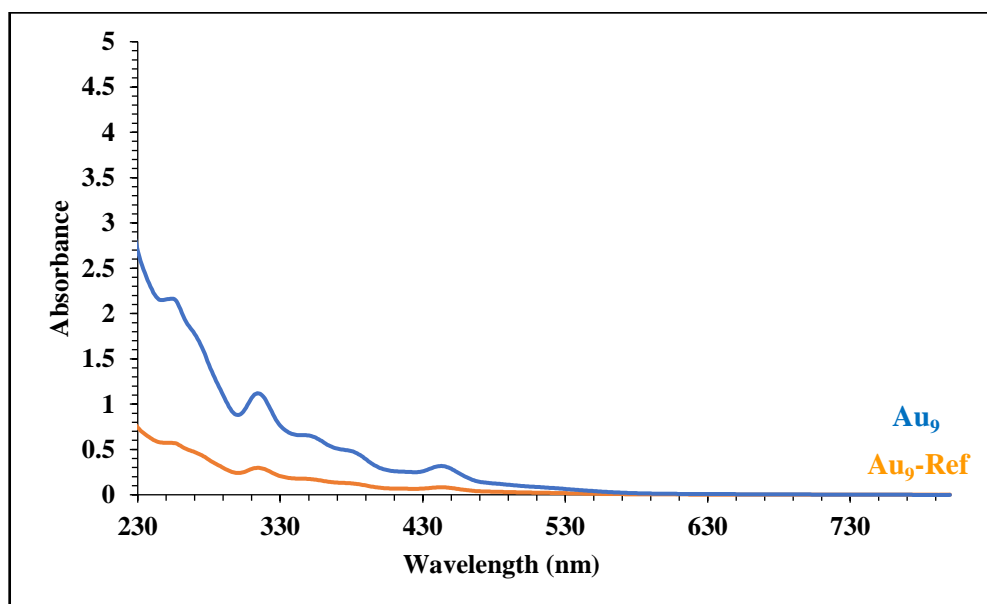


Figure S2. UV-vis spectra of prepared Au₉ cluster and reference sample

2.3. Positive ESI-TOF Mass Spectrometry.

The most challenging part of this study was establishing an appropriate solvent and condition for MS analysis that produced reasonable data, since this type of MS spectrometer has not yet been reported for Au cluster characterisation.

In this successful procedure, mass range was 500-4000 m/z. The heater on the source inlet was maintained at 80°C but desolvation temperature was set on 150°C. Ions were sprayed at 2.25 kV using Ar carrier gas. Solutions of the raw synthetic mixture of Au₉ nanoclusters were prepared using UHPLC grade methanol and analysed at a concentration of 100 g/mL. External mass calibration was performed via injection of sodium iodide (2 µg/µL). Values of m/z, and intensity for the simulated high-resolution MS for Au₉ NCs were summarised in Table S2. The data in Table S2 and a pattern for molecular ion peak for the [Au₉(PPh₃)₈]₃⁺ in Figure S3 show the Au₉ clusters has been successfully synthesised as they are consistent with ones already reported^[3].

Table S2. Values of m/z, and intensity for the simulated high-resolution mass spectrometry for Au₉.

Mass/ Charge	Intensity
1289.8	63
1290.13	100
1290.47	73
1290.81	35
1291.16	16
1291.5	6
1291.81	4
1292.13	4
1292.48	5
1292.81	5.5

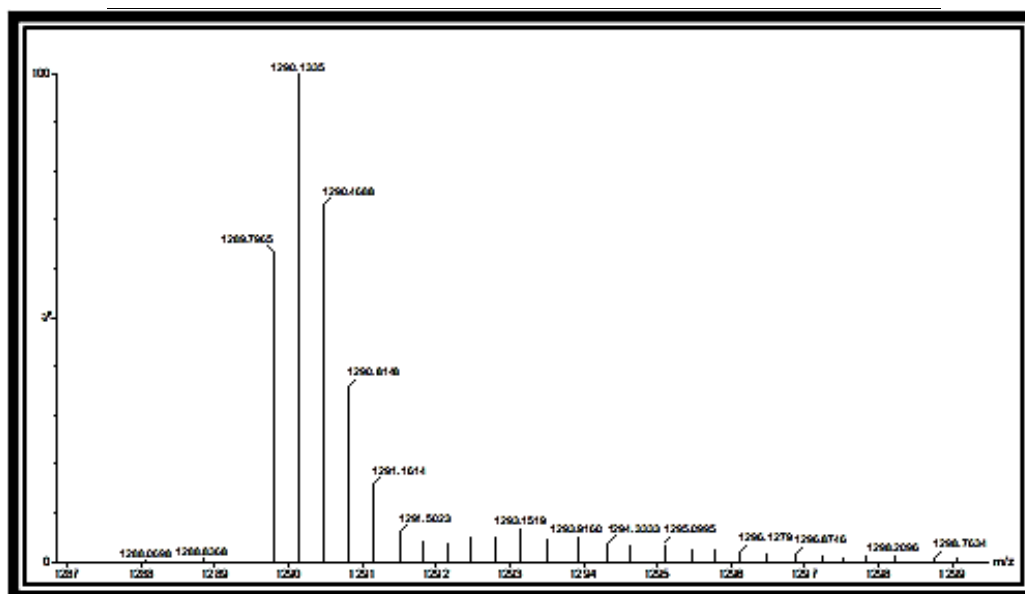


Figure S3. Molecular ion peak for the $[Au_9(PPh_3)_8]^{3+}$

3. Scherrer's equation:

$$\text{Particle Size} = (0.9 \times \lambda) / (d \cos \theta)$$

$$\lambda = 1.79 \text{ \AA} \text{ (in the case of Co K}\alpha\text{1)}$$

$$\Theta = 2\theta/2$$

d = the full width at half maximum intensity of the peak (in Rad)

To convert from angle to rad

$$\text{Rad} = (22 \times \text{angle}) / (7 \times 180) = \text{angle} \times 0.01746$$

$$\text{MTiO}_2 \quad \tau = \frac{0.9 \times 1.79 \text{ \AA}}{\left(\frac{22 \times 0.5 \text{ angle}}{7 \times 180} = 0.00873 \text{ rad}\right) \cos 29.6/2} = 190.87 \text{ \AA} = 19.09 \pm 0.1 \text{ nm}$$

$$\text{SMTiO}_2 \quad \tau = \frac{0.9 \times 1.79 \text{ \AA}}{\left(\frac{22 \times 0.5 \text{ angle}}{7 \times 180} = 0.00873 \text{ rad}\right) \cos 29.7/2} = 190.91 \text{ \AA} = 19.09 \pm 0.1 \text{ nm}$$

4. NEXAFS analysis:

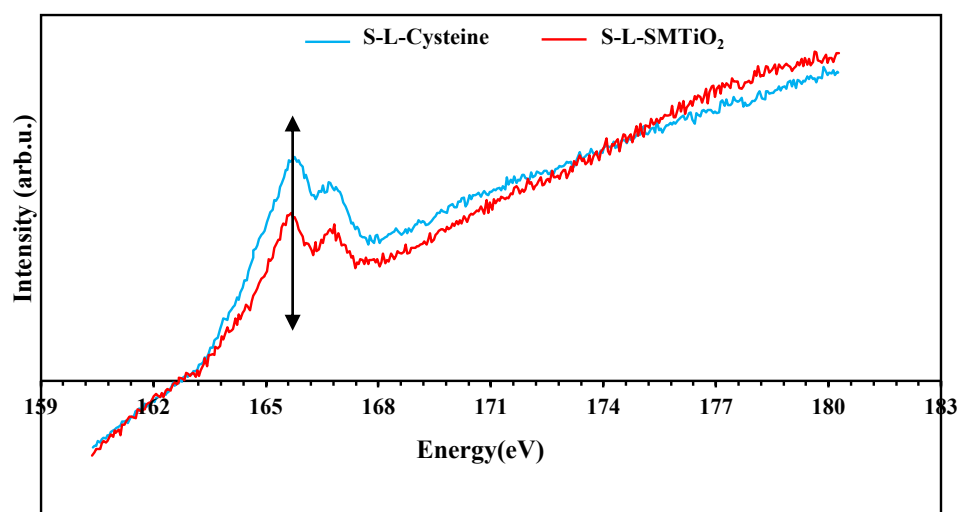


Figure S4. NEXAFS spectra at the S L-edge Cysteine as a reference, and SMTiO₂ sample.

5. XPS analysis:

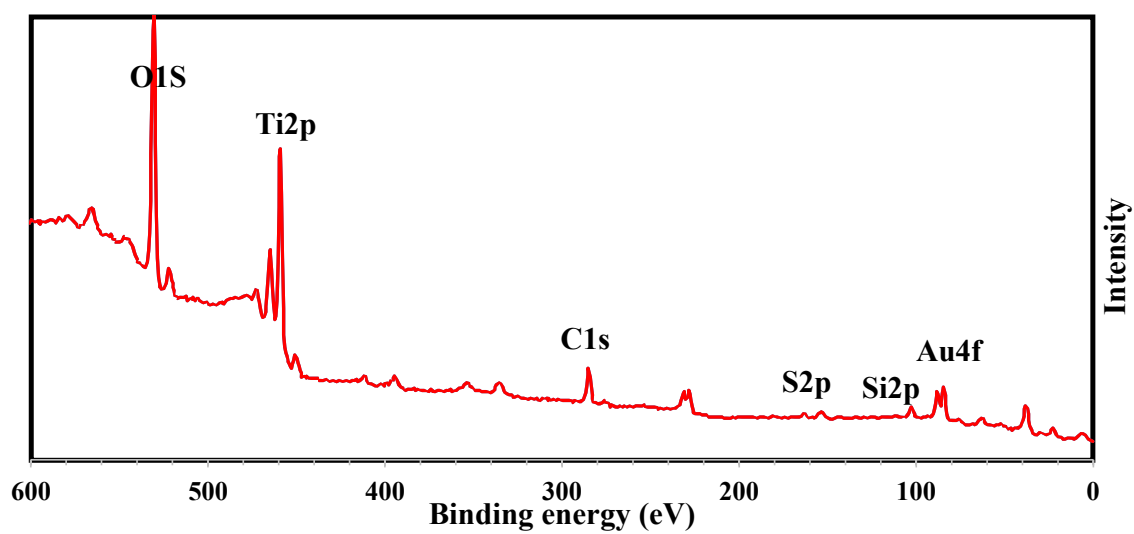


Figure S5. XPS survey of Au₉ NCs/SMTiO₂ nanocomposites

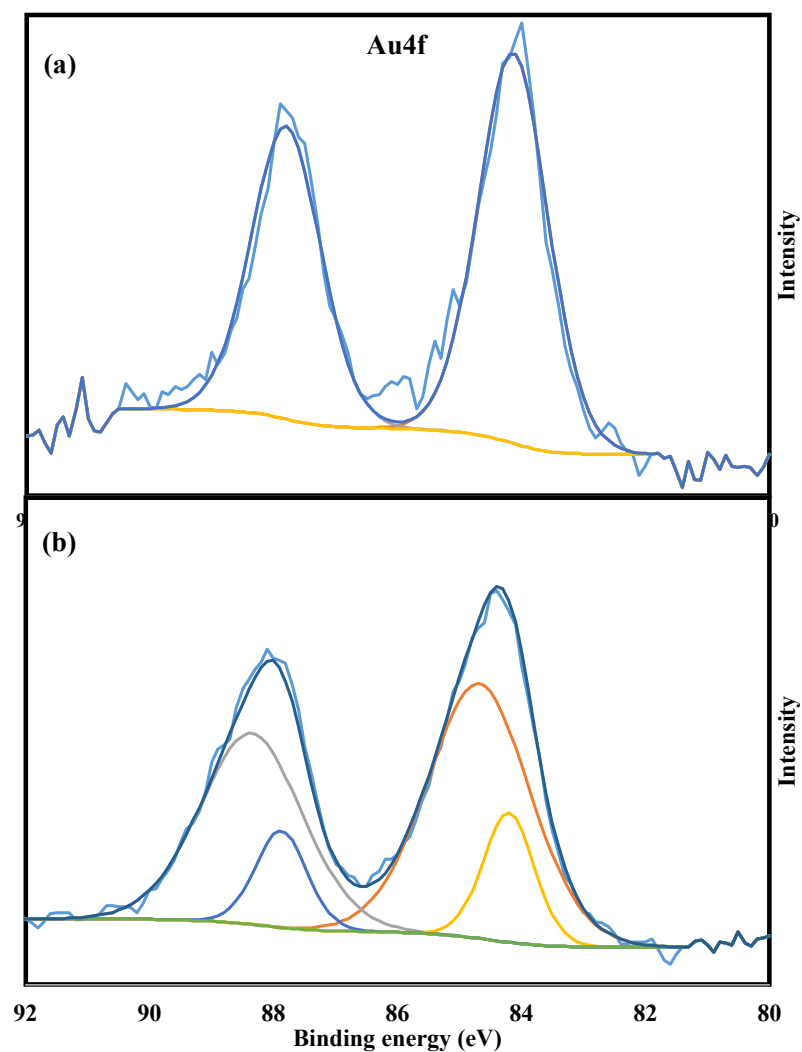


Figure S6. High resolution XPS of Au4f in (a) Au₉ NCs/MTiO₂ and (b) Au₉ NCs/SMTiO₂ nanocomposites after annealing treatment to remove the ligands.

6. STEM section notes

4 – LP (Ligated Au₉ clusters, mesoporous TiO₂)

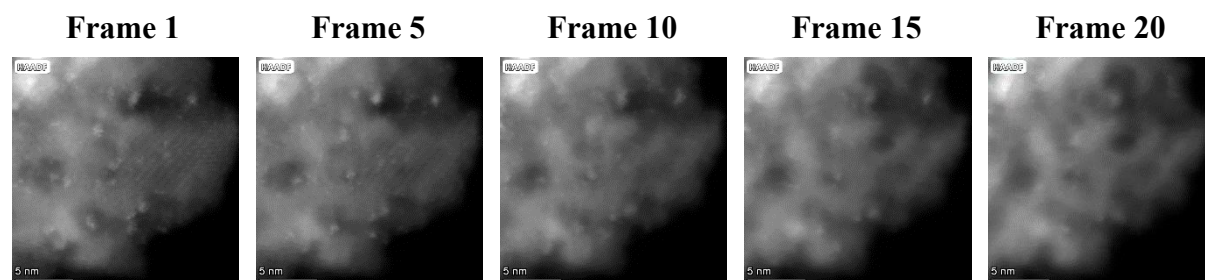


Figure S7. HAADF frames from EDS mapping of MTiO_2 after deposition of Au_9 clusters showing migration of Au during the scanning of the scanning of the electron beam across the surface. The sample was not heated to remove the ligands on the Au_9 clusters.

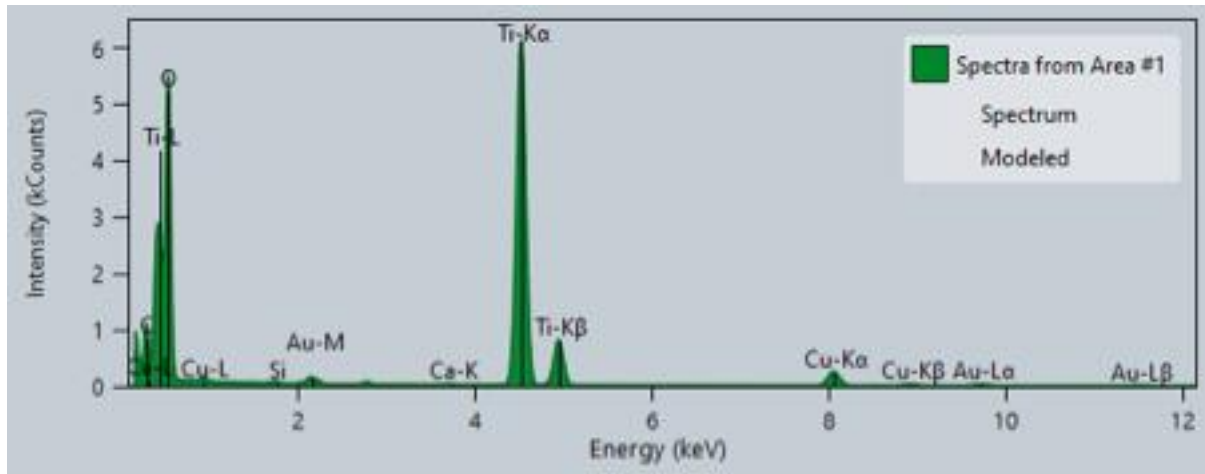


Figure S8. Integrated spectrum from EDS mapping of MTiO_2 after deposition of Au_9 clusters showing the presence of Au, Ti, and O. The sample was not heated to remove the ligands on the Au_9 clusters.

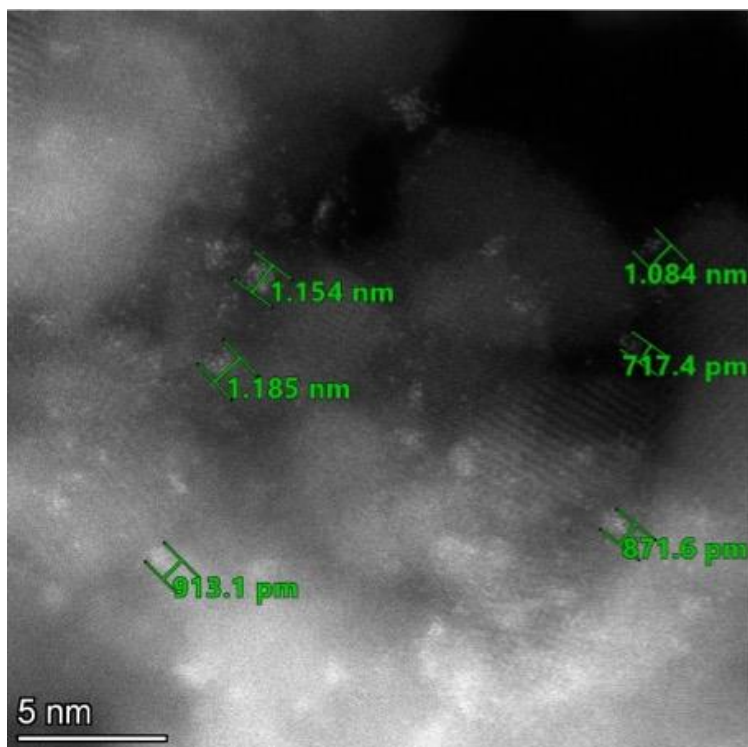


Figure S9. HAADF image of MTiO_2 after deposition of Au_9 clusters showing measurements of some of the Au nanoclusters. The sample was not heated to remove the ligands on the Au_9 clusters.

5 – CP (Au_9 core, mesoporous TiO_2)

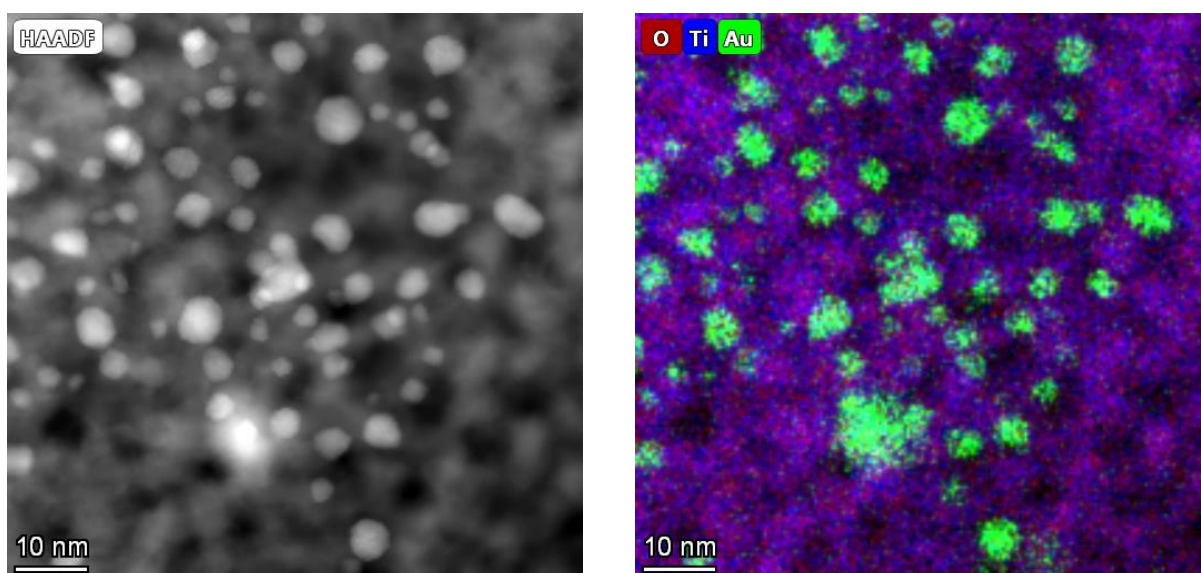


Figure S10. EDS maps of MTiO_2 after deposition of Au_9 clusters after heating to remove ligands showing presence of O, Ti, and Au.

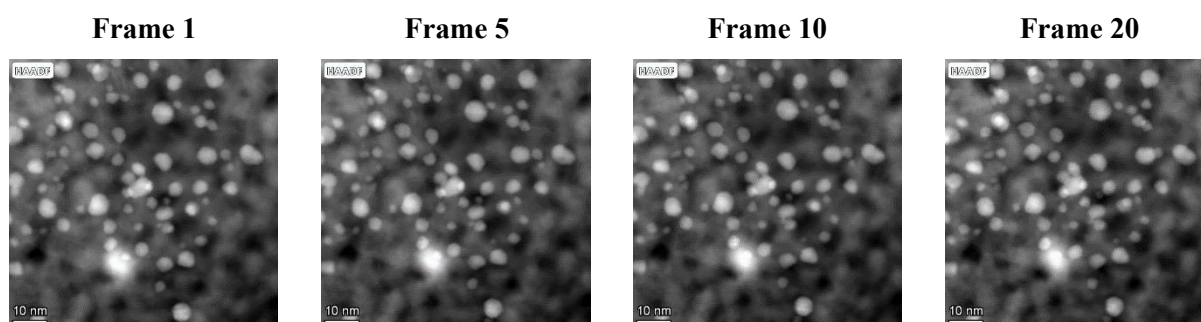


Figure S11. HAADF frames from EDS mapping of MTiO_2 after deposition of Au_9 clusters and heating to remove ligands showing very little migration of Au during the scanning of the scanning of the electron beam across the surface.

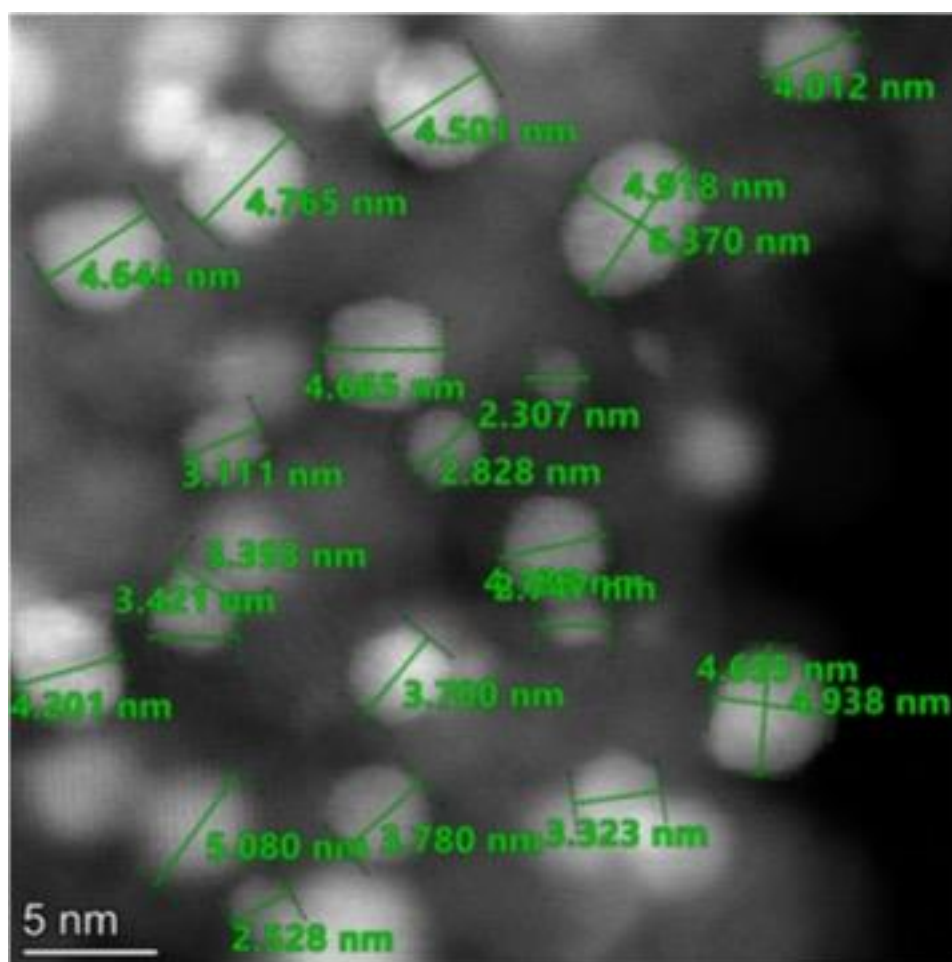


Figure S12. HAADF image of MTiO_2 after deposition of Au_9 clusters and heating to remove ligands showing measurements of some of the Au nanoclusters.

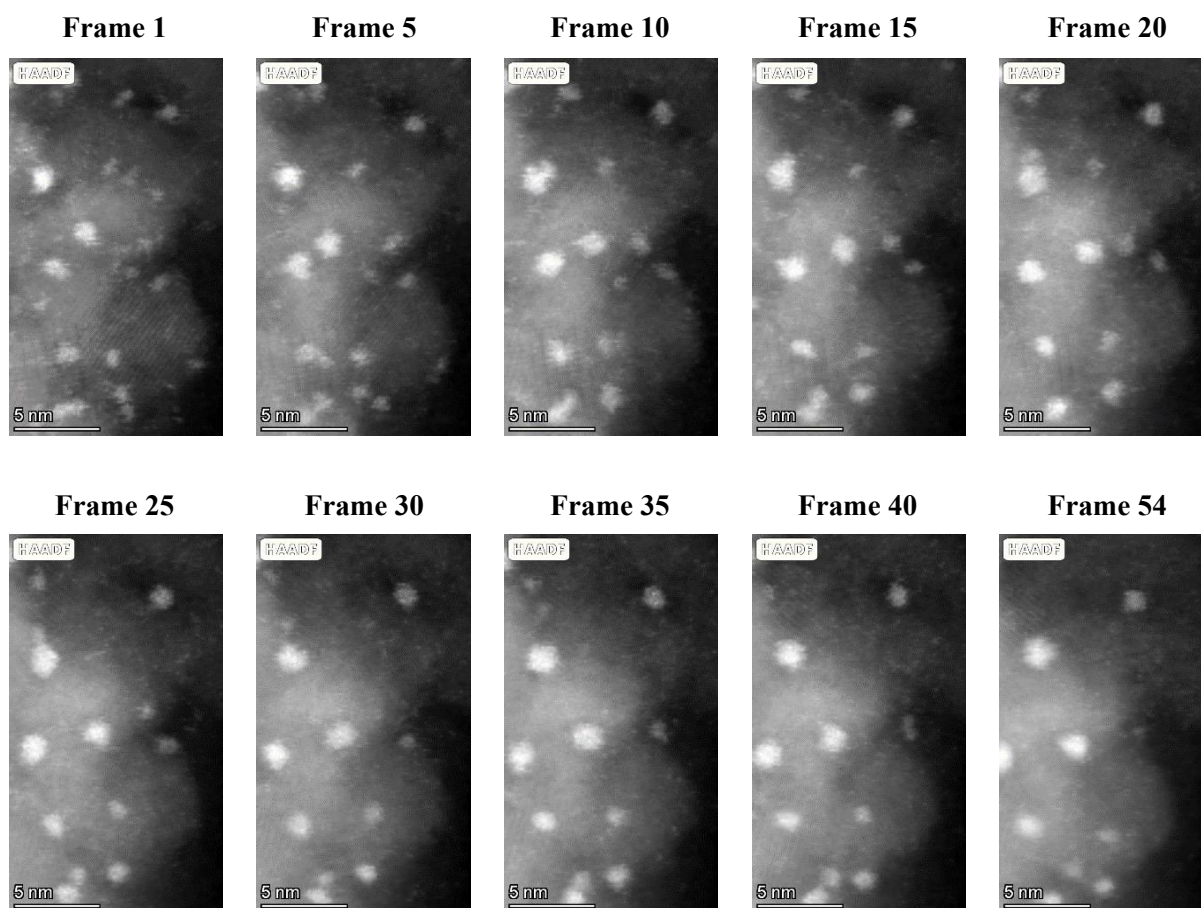


Figure S13. HAADF frames from EDS mapping of SMTiO_2 after deposition of Au_9 clusters showing migration of Au during the scanning of the scanning of the electron beam across the surface. The sample was not heated to remove the ligands on the Au_9 clusters.

SPL (Ligated Au_9 clusters/ SMTiO_2 nanocomposite)

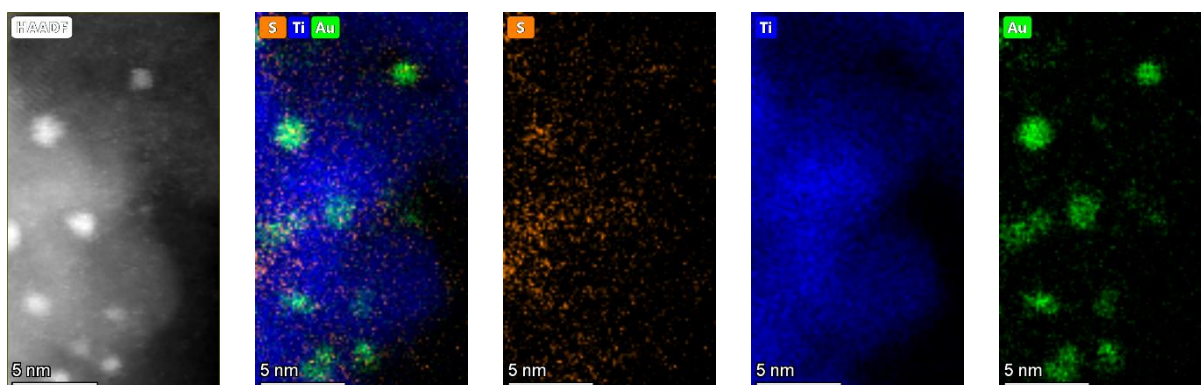


Figure S14. EDS maps of SMTiO_2 after deposition of Au_9 clusters showing presence of S, Ti, and Au. The sample was not heated to remove the ligands on the Au_9 clusters. Note that significant agglomeration of Au atoms has occurred due to interaction with the electron beam.

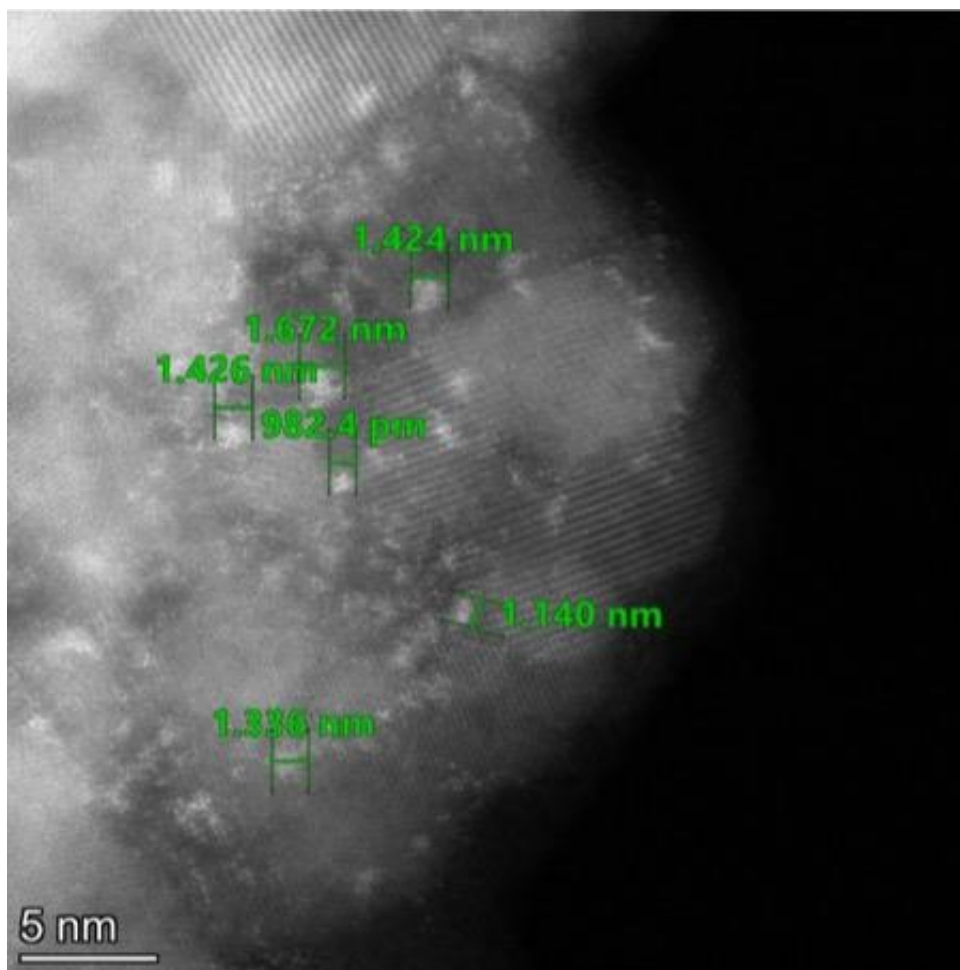


Figure S15. HAADF image of SMTiO₂ after deposition of Au₉ clusters showing measurements of some of the Au nanoclusters. The sample was not heated to remove the ligands on the Au₉ clusters.

SPC (Au₉ core /SMTiO₂ nanocomposite after heating to remove ligands)

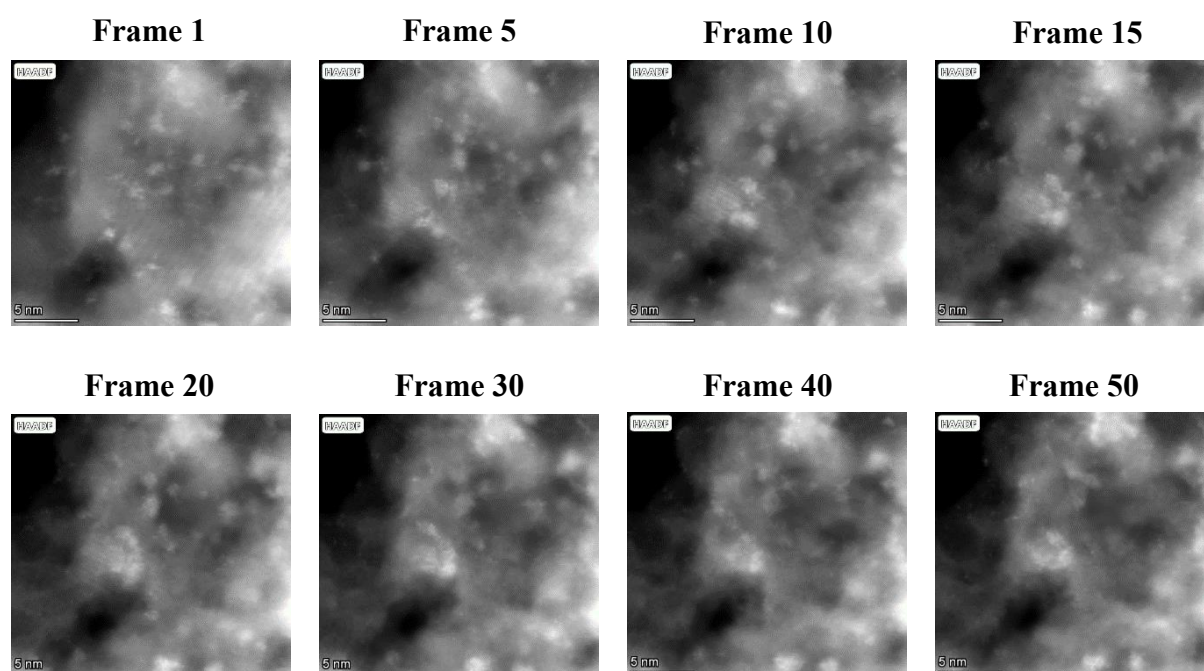


Figure S16. HAADF frames from EDS mapping of SMTiO₂ after deposition of Au₉ clusters and heating to remove ligands showing migration of Au during the scanning of the scanning of the electron beam across the surface.

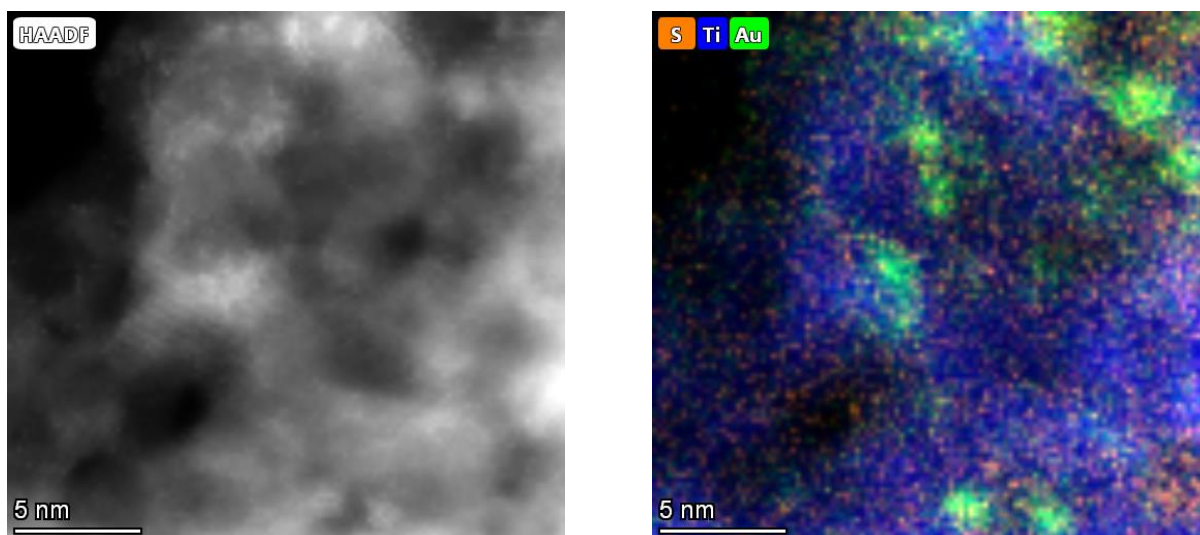


Figure S17. EDS maps of SMTiO₂ after deposition of Au₉ clusters after heating to remove ligands showing the presence of S, Ti, and Au. Note that significant agglomeration of Au atoms has occurred due to interaction with the electron beam.

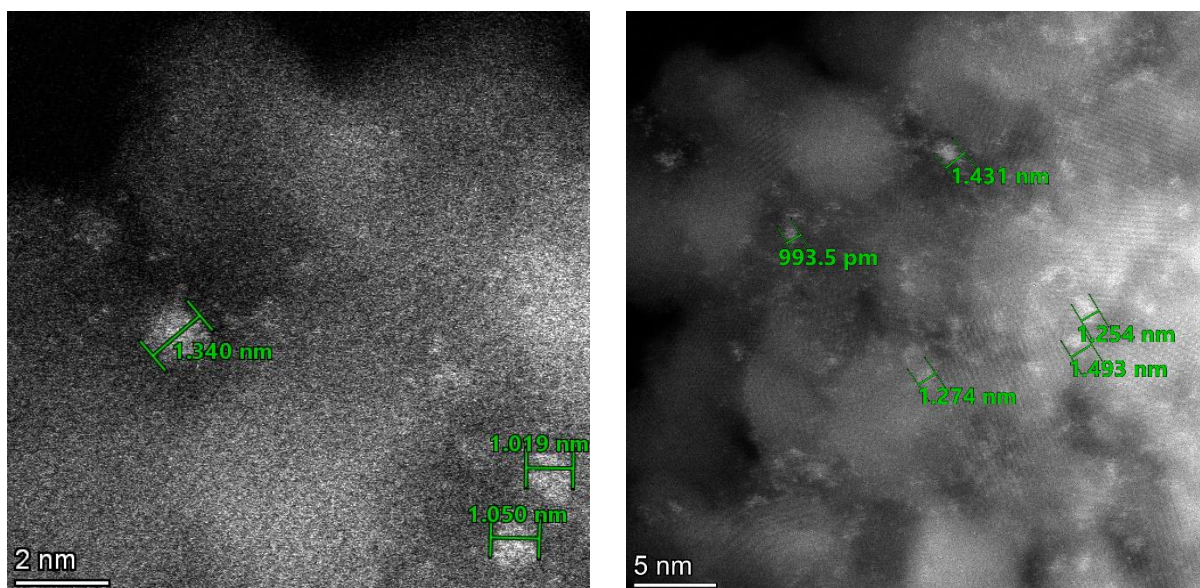
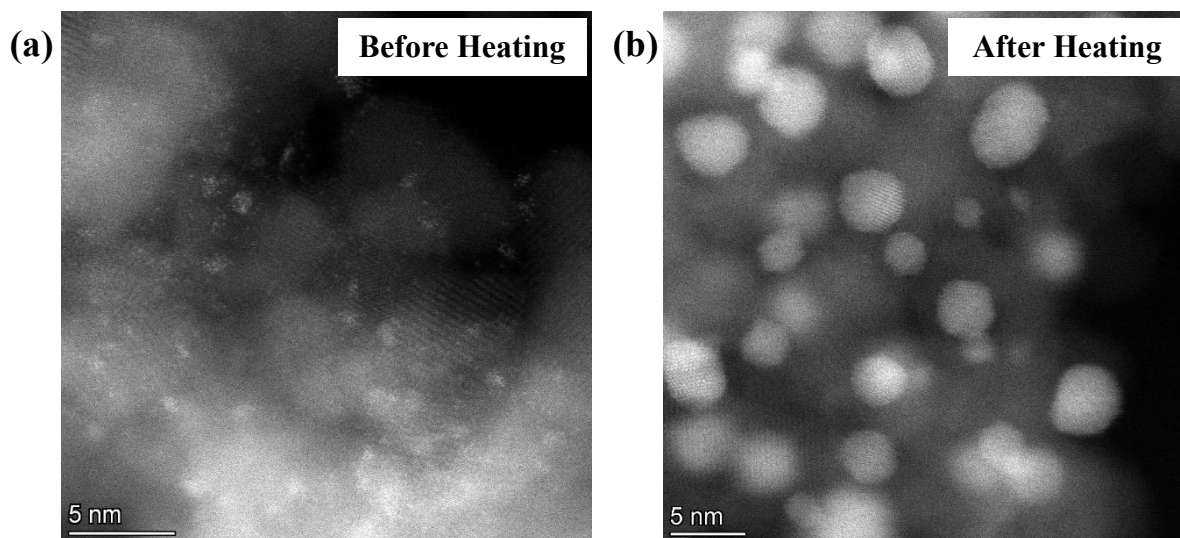


Figure S18. HAADF image of SMTiO₂ after deposition of Au₉ clusters and heating to remove ligands showing measurements of some of the Au nanoclusters.

Au₉ deposited on MTiO₂



Au₉ deposited on SMTiO₂

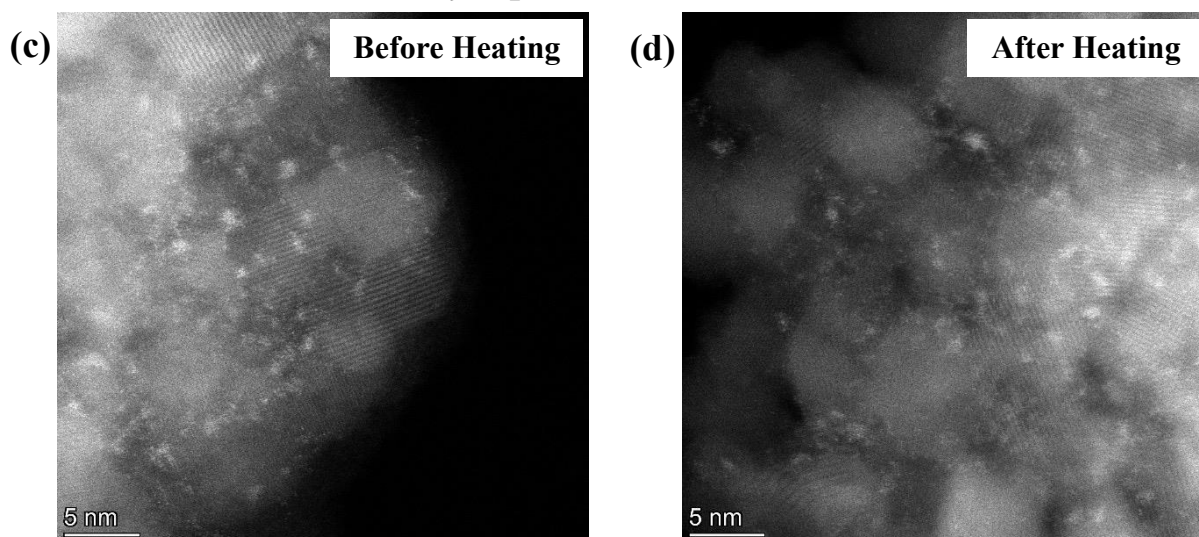
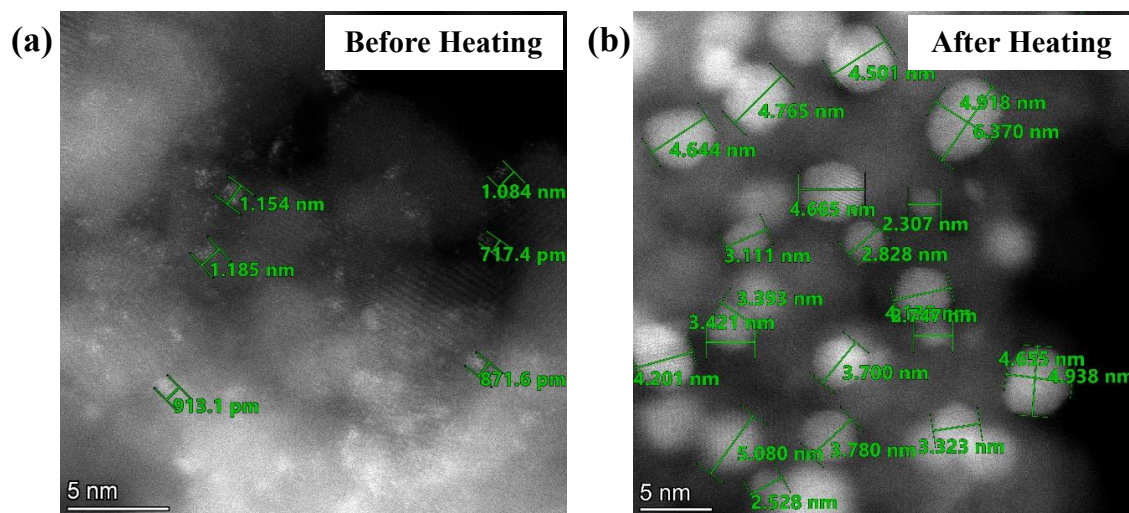


Figure S19. HAADF images of Au₉ deposited on photocatalyst substrates before and after heating to remove ligands from Au₉. Image a) Au₉ on MTiO₂ before heating, b) Au₉ on MTiO₂ after heating, c) Au₉ on SMTiO₂ before heating, and d) Au₉ on SMTiO₂ after heating. The images clearly show the reduction in agglomeration by heating is significantly.

Au₉ deposited on MTiO₂



Au₉ deposited on SMTiO₂

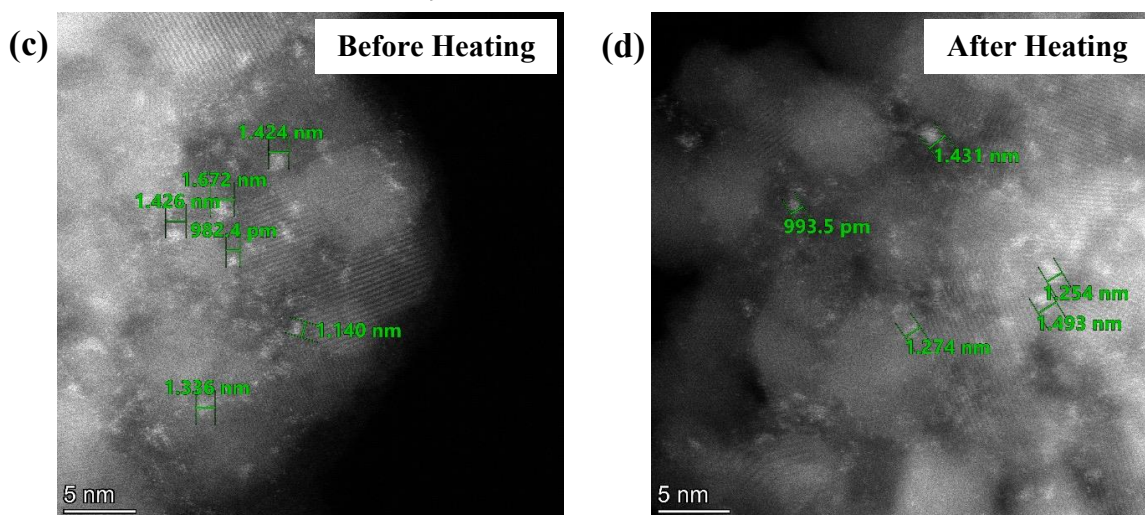


Figure S20. HAADF images of Au₉ deposited on photocatalyst substrates before and after heating to remove ligands from Au₉. Image a) Au₉ on MTiO₂ before heating, b) Au₉ on MTiO₂ after heating, c) Au₉ on SMTiO₂ before heating, and d) Au₉ on SMTiO₂ after heating. The images clearly show the reduction in agglomeration by heating is significantly.

References:

- [1] L. Malatesta, L. Naldini, G. Simonetta, F. Cariati, Triphenylphosphine-gold (0)/gold (I) compounds, *Coordination Chemistry Reviews*, 1 (1966) 255-262.
- [2] A. Mueting, B. Alexander, P. Boyle, A. Casalnuovo, L. Ito, B. Johnson, L. Pignolet, M. Leeaphon, K. Meyer, R. Walton, Mixed-Metal-Gold Phosphine Cluster Compounds, *Inorganic Syntheses*, (1992) 279-298.

- [3] F. Wen, U. Englert, B. Gutrath, U. Simon, Crystal structure, electrochemical and optical properties of $[\text{Au}_9(\text{PPh}_3)_8](\text{NO}_3)_3$, Wiley Online Library, 2008.
- [4] D.P. Anderson, J.F. Alvino, A. Gentleman, H. Al Qahtani, L. Thomsen, M.I. Polson, G.F. Metha, V.B. Golovko, G.G. Andersson, Chemically-synthesised, atomically-precise gold clusters deposited and activated on titania, *Physical chemistry chemical physics*, 15 (2013) 3917-3929.
- [5] R.H. Adnan, G.G. Andersson, M.I. Polson, G.F. Metha, V.B. Golovko, Factors influencing the catalytic oxidation of benzyl alcohol using supported phosphine-capped gold nanoparticles, *Catalysis Science & Technology*, 5 (2015) 1323-1333.