Synthesis of Sinter-Resistant Au@Silica Catalysts Derived from Au_{25} Clusters

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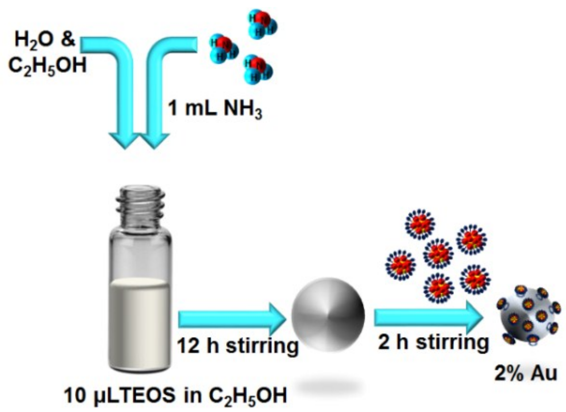


Scheme S1: General scheme for the synthesis of $Au_{25}(11\text{-}MUA)_{18}/SiO_2$ clusters

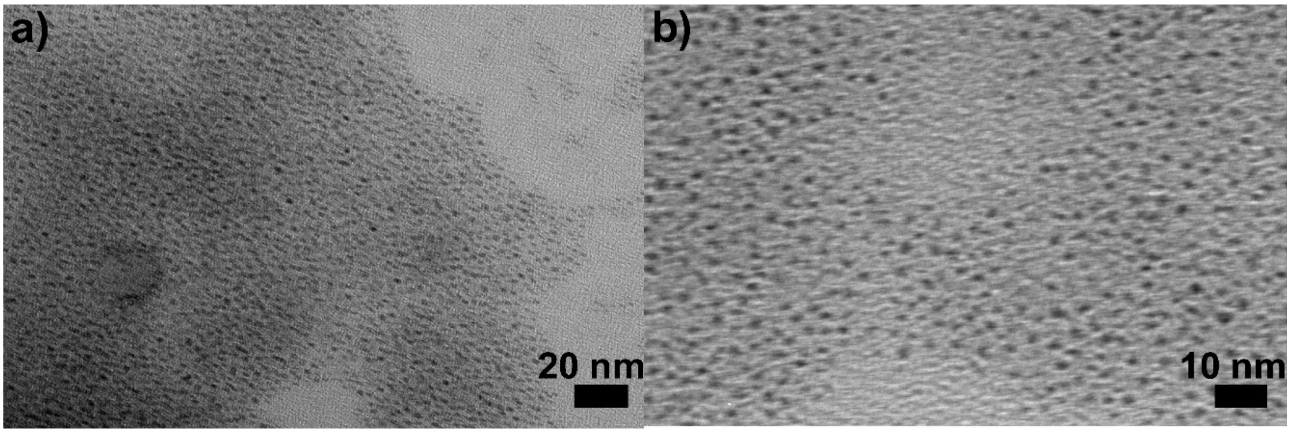


Figure S1: TEM images of as-synthesized $Au_{25}(11\text{-}MUA)_{18}$ clusters.

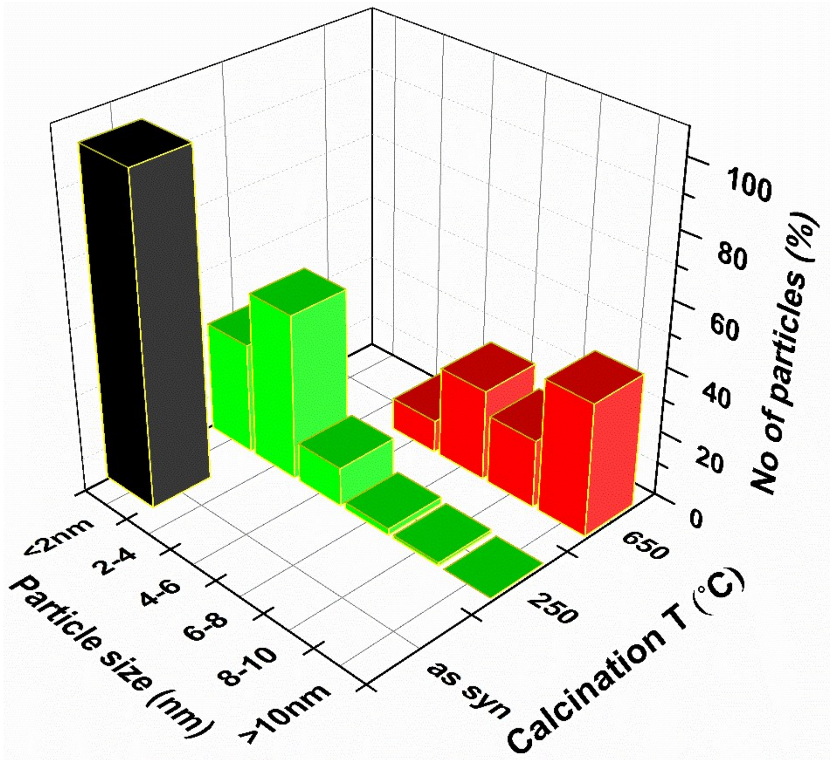


Figure S2: Histogram of Au_{25}/SiO_2 catalysts calcined at 250˚C and 650˚C

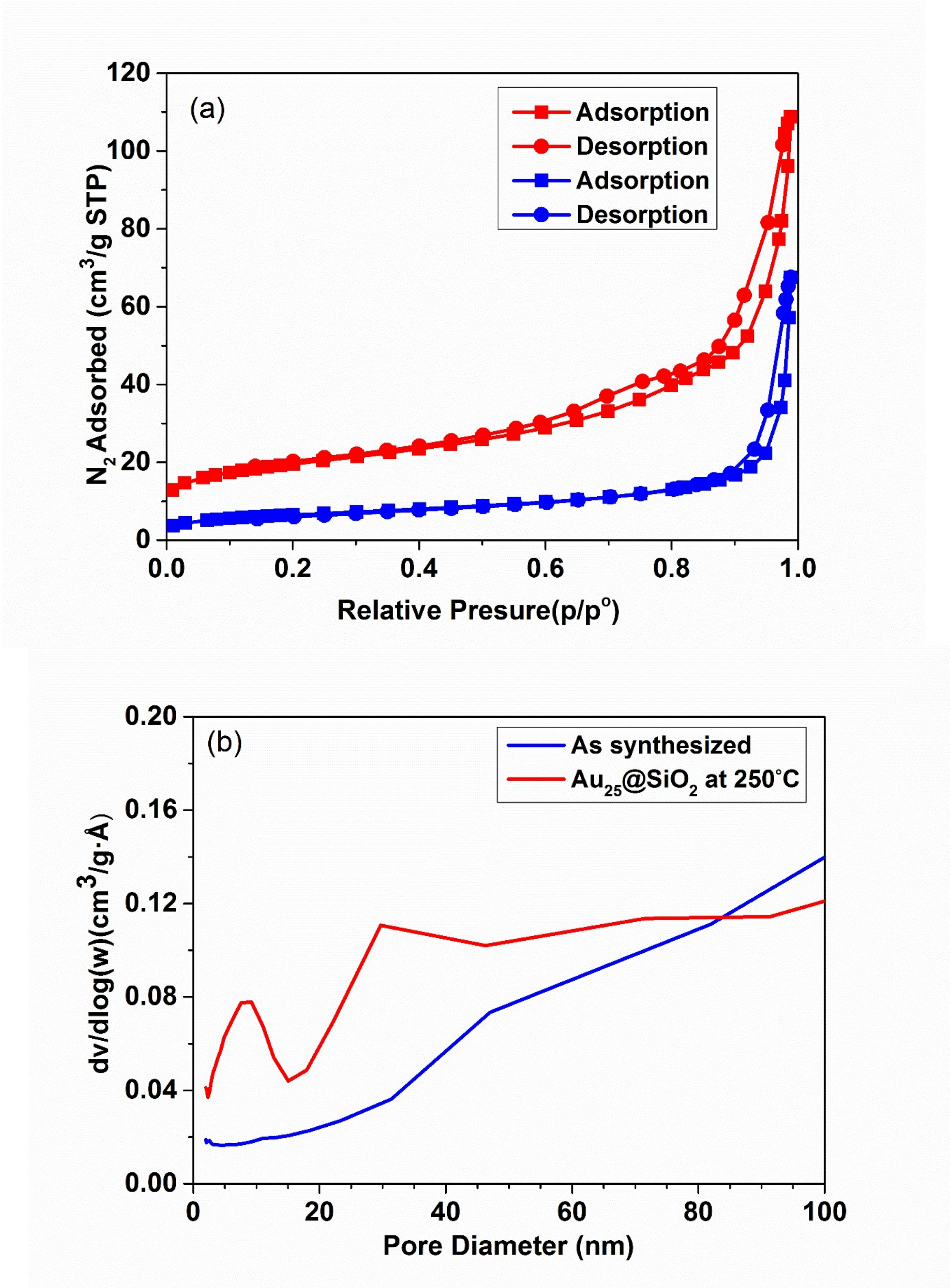


Figure S3: (a) N_2 Adsorption/Desorption isotherms and (b) BJH Pore Size Distributions of $Au_{25}@SiO_2$ catalysts as-synthesized (blue) and after calcination at 250˚C (red).

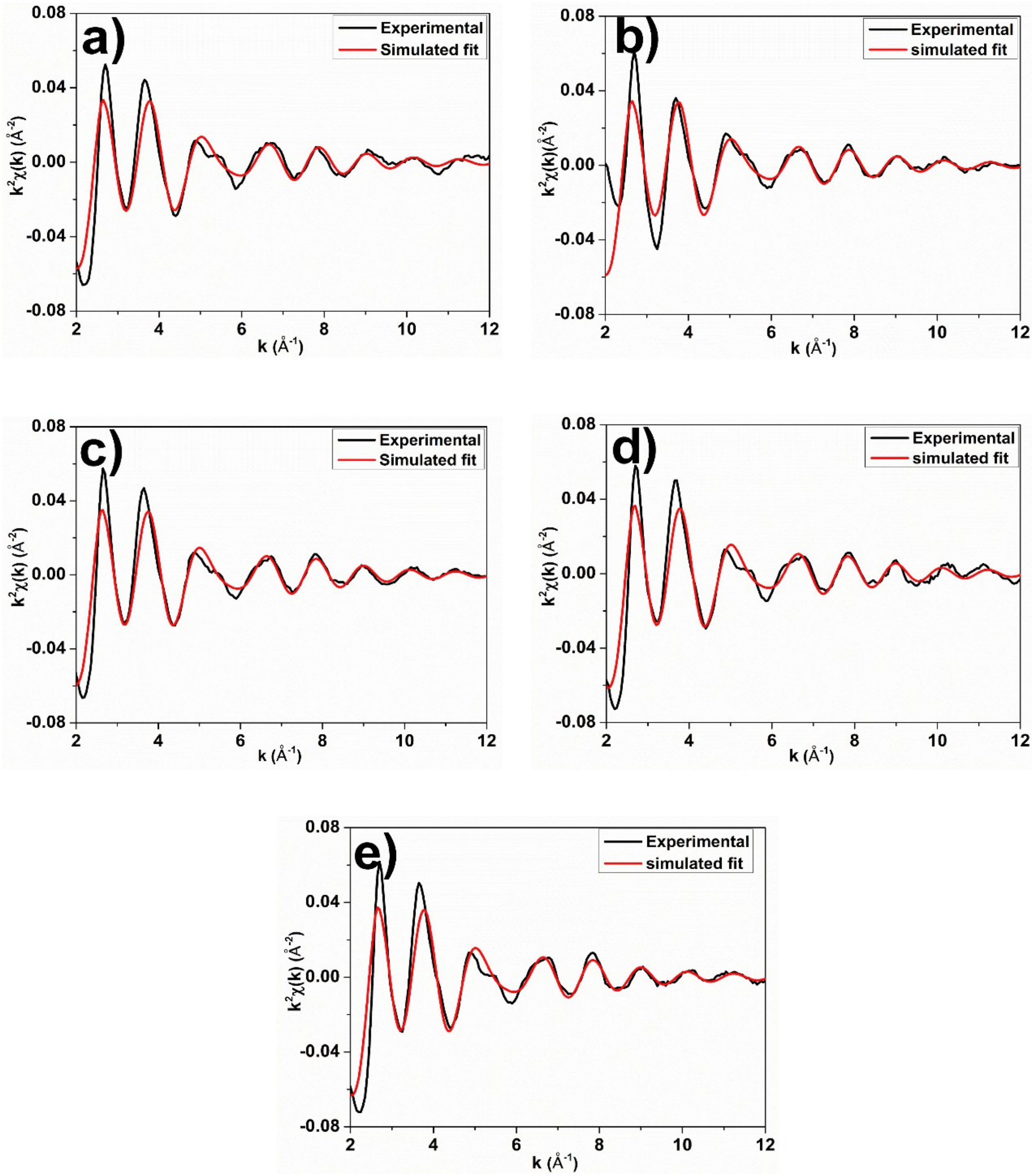


Figure S4: Au L_3 edege EXAFS fitting data in k space of Au@SiO_2 calcined at a) 250˚C, b) 350˚C c) 450˚C d) 550˚C and e) 650˚C.

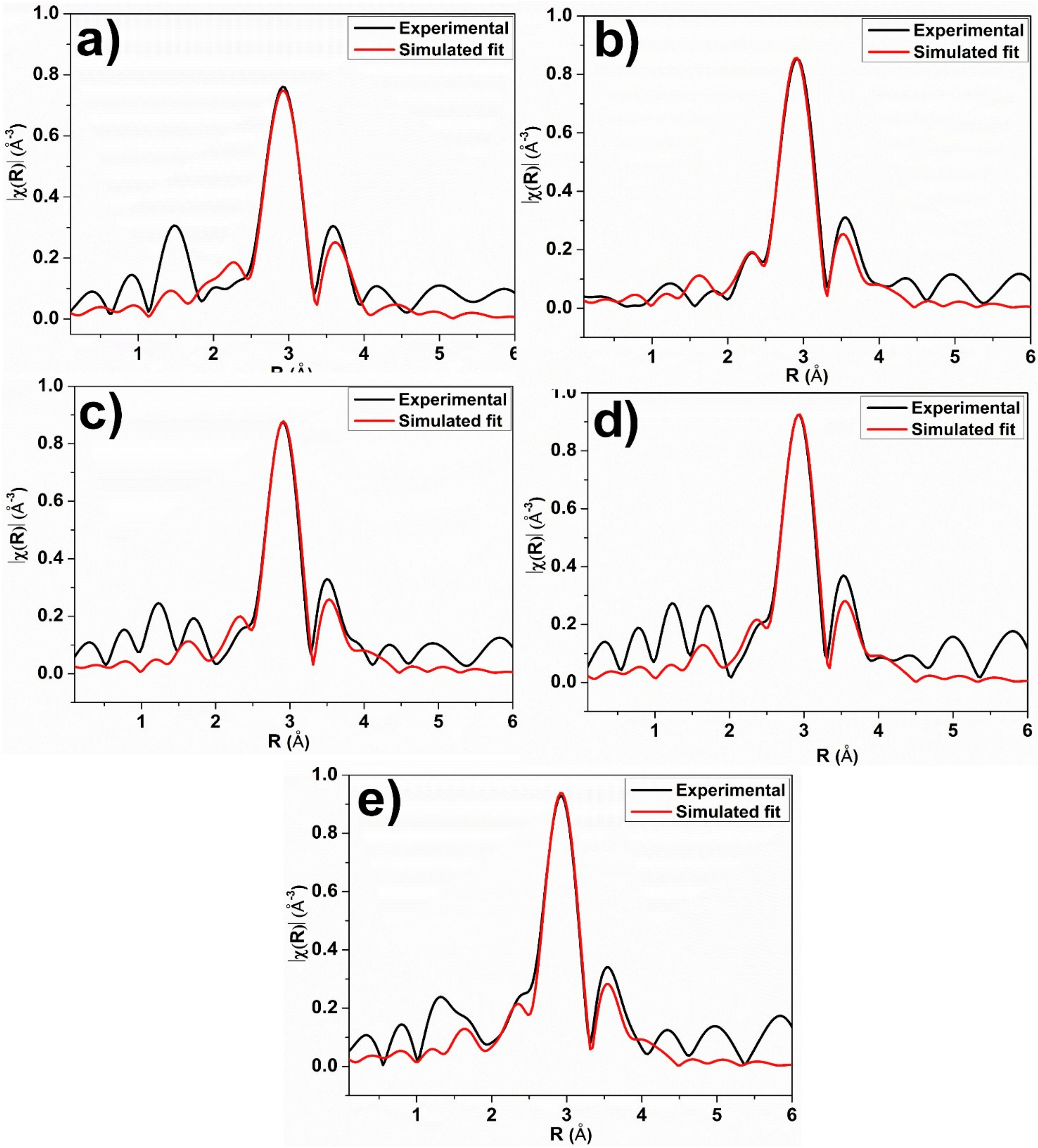


Figure S5: Au L_3 edge EXAFS fitting data in R space of Au@SiO_2 calcined at a) 250˚C, b) 350˚C c) 450˚C d) 550˚C and e) 650˚C.

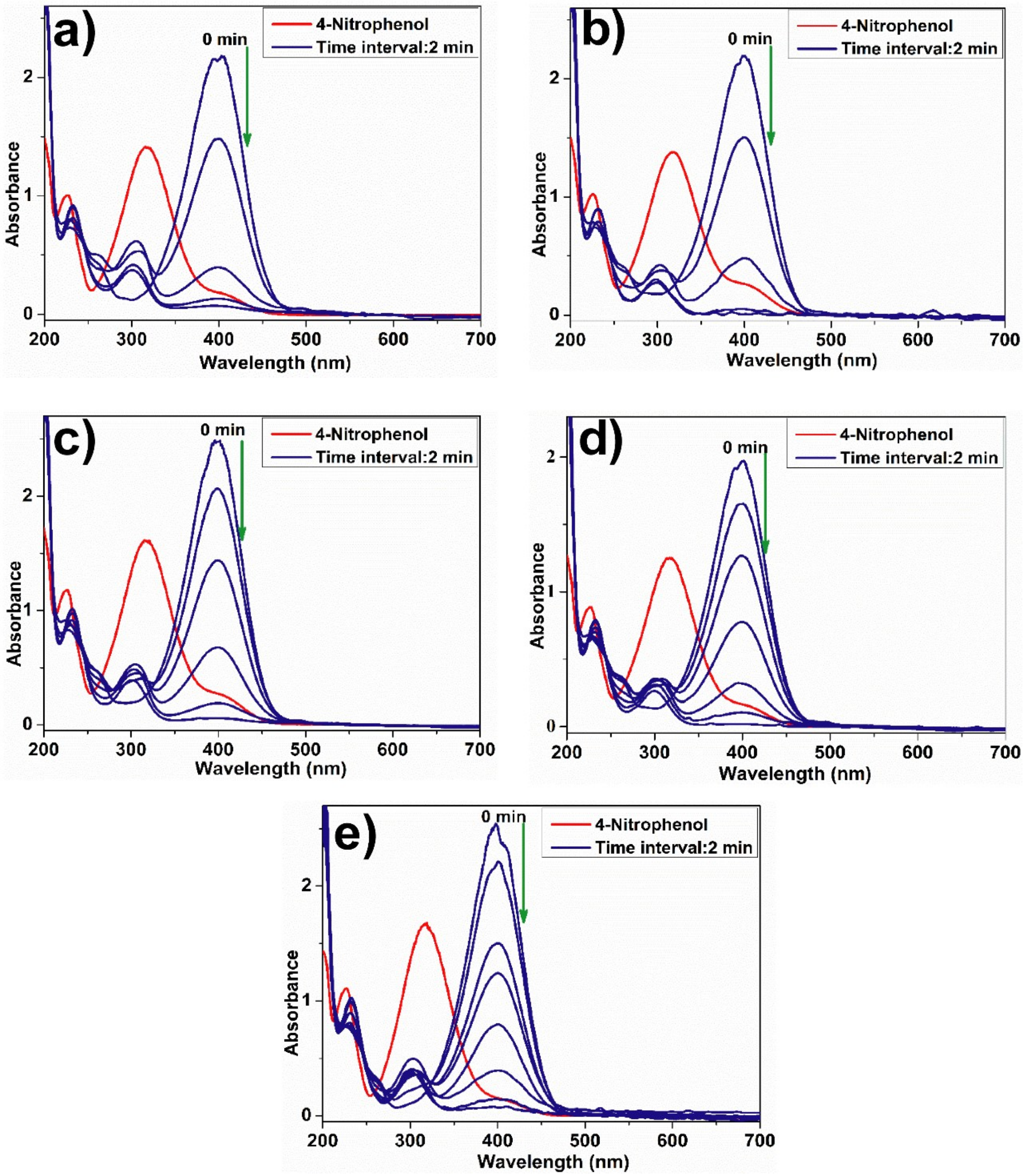


Figure S6: Catalytic activity for 4-nitrophenol reduction reaction over $Au@SiO_2$ calcined at a) 250˚C, b) 350˚C c) 450˚C d) 550˚C and e) 650˚C

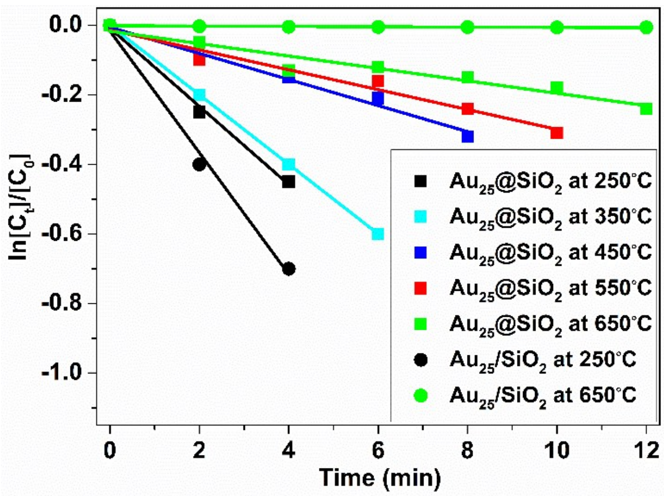
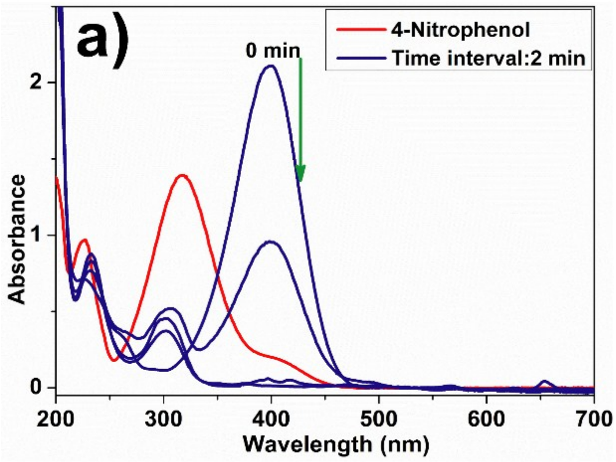


Figure S7: Plot of ln[Ct]/[C_o] as a function of reaction time in min for 4-nitrophenol reduction reaction over Au@SiO_2 catalysts calcined at different temperatures.



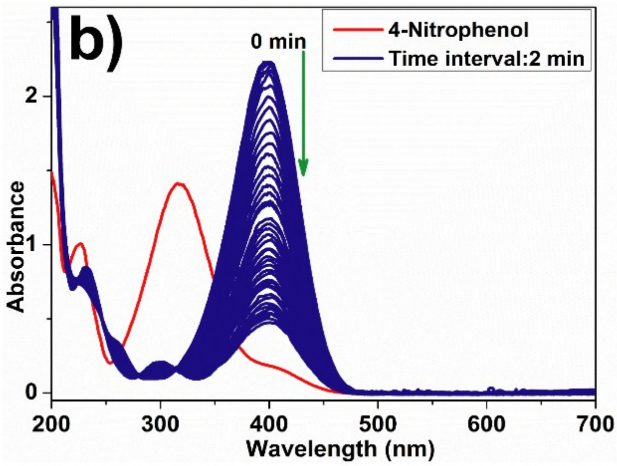


Figure S8: Conversion of 4-nitrophenol to 4-aminophenol over Au_{25}/SiO_2 catalysts calcined at 250˚C and 650˚C

Rate constant calculation:- 4-nitrophenol reduction follows pseudo-first-order kinetics

$$Ln\frac{[C_t]}{[C_0]} = -kt$$

C_t – Concentration of 4-nitrophenolate at time t

C_0 – Initial concentration of 4-nitrophenolate

k- First order rate constant

t- Time in minutes

Table S1: X-ray crystallographic information of $[N(C_8H_{17})_4]$ $[Au_{25}(SCH_2CH_2Ph)_{18}]$[1]

Type	**Coordination Number**	**Bond length (Å)**
Au-S		2.32 ± 0.01
Au-Au (core)	1.44	2.79 ± 0.01
Au-Au(surf)	1.92	2.93 ± 0.06
Au-Au(staple)	2.88	3.16 ± 0.08

Table S2: Recyclability for styrene epoxidation reaction over $Au_{25}@SiO_2$/250˚C catalyst

Cycle	Conversion (%)	Selectivity		TON
		SO (%)	BA (%)	
First	70.0	92.3	7.6	2800
Second	62.1	94.2	5.8	2500
Third	65.2	95.4	4.6	2600
Fourth	67.5	95.6	4.4	2700
Fifth	67.1	90.2	9.8	2700

TON: (Conversion* moles of styrene)/(moles of Au)

Calculation of number of surface atoms[2]

1) Average particle size of Au@SiO_2 calcined at 250˚C is 2.2nm

Volume of a sphere $V = \left(\frac{4}{3}\right)\pi r^3$

$$V = \left(\frac{4}{3}\right) * \pi * (1.1nm)^3 = 5.5nm^3$$

Au is F.C.C with lattice constant 0.4080nm

Volume of unit cell $V = a^3$

$$V = (0.4080nm)^3 = 0.0679nm^3$$

Each unit cell contains 4 Au atoms

Total Au atoms in a particle = $= \left(\frac{5.5nm^3}{0.0679nm^3}\right) * 4 = 324\ atoms$

Surface area of sphere $A = 4\pi r^2$

$$A = 4\pi(1.1nm)^2 = 15.2nm^2$$

Surface are of a unit cell $A = a^2$

$$A = (0.4080nm)^2 = 0.1664nm^2$$

Each unit cell on surface contains 2 Au atoms

Total Au surface atoms in a particle = $= \left(\frac{15.2nm^2}{0.1664nm^2}\right) * 2 = 182\ atoms$

Total no of Au atoms in 20mg catalyst =no of moles of Au* $6.02*10^{23}$ atoms

$$= 2.0 * 10^{-6} * 6.02 * 10^{23}\ atoms = 12 * 10^{17}\ \text{atoms}$$

Total no of particles in 20mg catalyst $= \frac{12 * 10^{17}\ atoms}{328atoms} = 3.7 * 10^{15}$

Total no of surface atoms in 20mg catalysts = No of particles * no of surface atoms in a particle

$3.7 * 10^{15} * 182\ atoms$ $= 6.7 * 10^{17}$ surface atoms

No of moles of surface atoms $= \frac{6.7 * 10^{17}}{6.02 * 10^{23}} = 11 * 10^{-7} moles$

2) Average particle size of Au@SiO_2 calcined at 650˚C is 3.2nm

Volume of a sphere $V = \left(\frac{4}{3}\right)\pi r^3$

$$V = \left(\frac{4}{3}\right) * \pi * (1.6nm)^3 = 17.14nm^3$$

Total Au atoms in a particle = $= \left(\frac{17.14nm^3}{0.0679nm^3}\right) * 4 = 1009\ atoms$

Surface area of sphere $A = 4\pi r^2$

$$A = 4\pi(1.6nm)^2 = 32.15nm^2$$

Total Au surface atoms in a particle = $= \left(\frac{32.15nm^2}{0.1664nm^2}\right) * 2 = 386\ atoms$

Total no of particles in 20mg catalyst $= \frac{12 * 10^{17}\ atoms}{1009\ atoms} = 1.2 * 10^{15}$

Total no of surface atoms in 20mg catalysts = No of particles * no of surface atoms in a particle

$1.2 * 10^{15} * 386\ atoms = 4.6 * 10^{17}$ surface atoms

No of moles of surface atoms $= \frac{4.6 * 10^{17}}{6.02 * 10^{23}} = 7.6 * 10^{-7} moles$

3) Average particle size of Au/SiO_2 calcined at 250˚C is 3.2nm

Volume of a sphere $V = \left(\frac{4}{3}\right)\pi r^3$

$$V = \left(\frac{4}{3}\right) * \pi * (1.6nm)^3 = 17.14nm^3$$

Total Au atoms in a particle = $= \left(\frac{17.14nm^3}{0.0679nm^3}\right) * 4 = 1009\ atoms$

Surface area of sphere $A = 4\pi r^2$

$$A = 4\pi(1.6nm)^2 = 32.15nm^2$$

Total Au surface atoms in a particle = $= \left(\frac{32.15nm^2}{0.1664nm^2}\right) * 2 = 386\ atoms$

Total no of particles in 20mg catalyst $= \frac{12 * 10^{17}\, atoms}{1009\, atoms} = 1.2 * 10^{15}$

Total no of surface atoms in 20mg catalysts = No of particles * no of surface atoms in a particle

$1.2 * 10^{15} * 386\, atoms$ = $4.6 * 10^{17}$ surface atoms

No of moles of surface atoms $= \frac{4.6 * 10^{17}}{6.02 * 10^{23}} = 7.6 * 10^{-7} moles$

4) Average particle size of Au/SiO_2 calcined at 650˚C is 15.5nm

Volume of a sphere $V = \left(\frac{4}{3}\right)\pi r^3$

$$V = \left(\frac{4}{3}\right) * \pi * (7.7nm)^3 = 1911nm^3$$

Total Au atoms in a particle = $= \left(\frac{1911nm^3}{0.0679nm^3}\right) * 4 = 112577\, atoms$

Surface area of sphere $A = 4\pi r^2$

$$A = 4\pi(7.7nm)^2 = 744.68nm^2$$

Total Au surface atoms in a particle = $= \left(\frac{744.68nm^2}{0.1664nm^2}\right) * 2 = 8950\, atoms$

Total no of particles in 20mg catalyst $= \frac{12 * 10^{17}\, atoms}{28149\, atoms} = 1.1 * 10^{13}$

Total no of surface atoms in 20mg catalysts = No of particles * no of surface atoms in a particle

$1.1 * 10^{13} * 8950\, atoms$ $= 0.98 * 10^{17}$ surface atoms

No of moles of surface atoms $= \frac{0.98 * 10^{17}}{6.02 * 10^{23}} = 1.6 * 10^{-7} moles$

References

1 M. W. Heaven, A. Dass, P. S. White, K. M. Hoh and R. W. Murray, *J. Am. Chem. Soc.*, 2008, **130**, 3754–3755.

2 M. Jin, H. Zhang, Z.Xie and Y. Xia, *Angew. Chem. Int. Ed.*, 2011, 50, 7050–7054