Electronic Supplementary Information

Controlled Growth and Catalytic Activity of Gold Monolayer Protected Clusters in Presence of Borohydride Salts

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Experimental

Materials: All organic solvents, hydrochloric acid, celite, magnesium sulfate and nitrobenzene were purchased from EMD chemicals; organic solvents were HPLC grade and distilled over drying agents before use. Tetraocytlammonium bromide (TOAB, 98%), 1-dodecanethiol ($C_{12}SH$, >98%), 11-mercaptoundecanoic acid (MUA), 4-nitrophenol (4-NP, 98%), 3-nitrophenol (3-NP, 99%), 2-nitrophenol (2-NP, 98%), Eosin Y (99%), 4-nitrotoluene (4-NT, 99%) and lithium borohydride ($LiBH_4$, 2M solution in THF) and sodium borohydride ($NaBH_4$, 99%) were purchased from Aldrich and used as received. Hydrogen tetrachloroaurate (III) trihydrate ($HAuCl_4.3H_2O$, 99.99%), polyvinylpyrrolidone (PVP, MW 40,000), 1-hexanethiol (C_6SH, 97%) and 1-octadecanethiol ($C_{18}SH$, 98%) were purchased from Alfa Aesar. Deuterated solvents were purchased from Cambridge Isotope Laboratories.

Synthesis of Au MPCs: Alkanethiolate (*i.e.* 1-hexanethiolate, 1-dodecanethiolate and 1-octadecanethiolate) protected Au MPCs were synthesized via a modified Brust-Schiffrin method using standard literature procedures.[1,2] All solvents were degassed with N_2 (Praxair) and reactions were kept under an N_2 atmosphere unless otherwise noted. A typical synthesis is as follows: 30 ml of an aqueous solution of $HAuCl_4.3H_2O$ (0.25 g, 0.63 mmol) was stirred with a solution of TOAB (1.38 g, 2.54 mmol) in 80 ml of toluene until all the $HAuCl_4$ was transferred to the organic layer and the water layer became colorless. 2.54 mmol of alkanethiol ligand was then added to the organic phase. After stirring for several minutes, a sodium borohydride (0.40 M, 25.0 mL) solution was added dropwise and the resulting solution was stirred for the next 24 h. Excess thiol, free disulfide and TOAB impurities were removed by sequential washing with ethanol, isopropanol, acetonitrile, and acetone.

11-mercaptoundecanoic acid (MUA) Au MPCs were synthesized using a one phase method.[3] $HAuCl_4.3H_2O$ (0.25 g, 0.63 mmol) in 20 mL was added to MUA (0.28 g, 1.26 mmol) solution in 25 mL ethanol. The solution was stirred until it turned cloudy white and then a freshly prepared sodium borohydride solution (0.40 M, 25.0 mL) was added dropwise. The mixture was stirred for the 3 h and then kept at $-20^{o}C$ for 3 h. The precipitate was collected by vacuum filtration and the particles were dissolved in deionized water and purified by dialysis. The beakers were recharged with fresh water every 12 h over the course of 120 h.

PVP-stabilized Au nanoparticles were synthesized in a one phase method. PVP (1.39 mM, 5.0 mL) in methanol was added to $HAuCl_4.3H_2O$ (10 mM, 1.1 mL) in methanol. After 30 min of stirring, a freshly prepared sodium borohydride solution (0.10 M, 1.0 mL) was added and the resulting solution was stirred until it turned deep red color.

Synthesis of Larger Au MPCs via $LiBH_4$ addition: For all the reactions, 1.0 mmol of Au MPCs (w.r.t Au) was used and was dissolved in 3.0 mL THF. Varying amounts of lithium borohydride solution in THF were added from 10 molar excess to 500 molar excess. The $LiBH_4$ was added dropwise over a period of 15 minutes. The reaction was stirred overnight and was purified via column chromatography with toluene as the mobile solvent.

Reduction Catalysis: The reduction of 4-nitrophenol (4-NP), 3-nitrophenol (3-NP), 2-nitrophenol (2-NP) and Eosin Y by $NaBH_4$ was studied using UV-Vis spectroscopy. All the solutions were purged with N_2 prior to use. In a typical catalytic reaction, 2.65 ml of THF was mixed with the Au MPCs solution in THF (1.0 mM in Au, 0.15 mL) and the substrate solution (1.5 mM, 0.10 mL, 4-NP in water and 3-NP, 2-NP and Eosin Y in THF), followed by the addition of a freshly prepared $NaBH_4$ aqueous solution (1.5 M, 0.10 mL). Immediately after the addition of $NaBH_4$, UV-Vis spectra of the sample were recorded in one minute intervals over the range of 250-550 nm until the yellow solution became colorless. The rate constant of the reduction process was determined by measuring the change in absorbance of the initially observed peak at 400 nm for the 4-nitrophenol, 274 nm for 3-nitrophenol, 365 nm for 2-nitrophenol and 523 nm for Eosin Y as a function of time. Control experiments were carried out under the same conditions without Au MPCs. Reactions with PVP-stabilized Au nanoparticles were carried out at a Au concentration of 0.10 mM.

The reduction of 4-nitrotoluene (4-NT) and nitrobenzene (NB) were monitored using ^1H NMR. All the solutions were purged with N_2 prior to use. In a typical reaction 20 solutions (per catalyst) of the following reaction mixtures were prepared in $CDCl_3$: Au MPCs solution in $CDCl_3$ (1-hexanethiolate, 1-dodecanethiolate and 1-octadecanethiolate Au MPCs, 1.5 M, 0.1 mL) or water (11-mercaptoundecanoic acid Au MPCs and PVP-stabilized Au nanoparticles,1.0 mM in Au, 0.15 mL), were added to the substrate solution in $CDCl_3$ (1.5 mM, 0.10 mL) along with additional $CDCl_3$ to give a final volume of 2.9 mL of $CDCl_{3.}$ Finally, finally a freshly prepared $NaBH_4$ aqueous solution (1.5 M, 0.10 mL) was added and stirred vigorously. The reactions were quenched with hydrochloric acid (10 M, 5 mL) at 1 min time intervals. The $CDCl_3$ layer was collected and passed through anhydrous magnesium sulfate column to remove the moisture and ^1H NMR spectra were obtained. The rate constant was measured by change in reactant concentration as a function of time. Control experiments were carried out at the same conditions without Au MPCs.

Characterization: Absorption spectra were recorded on a Varian Cary 50 Bio UV-Vis spectrometer with an optical path length of 1.0 cm. Transmission electron micrographs (TEM) were obtained with a Philips 410 microscope operating at 100 kV. Samples were prepared by placing a drop of solution on a holey-carbon-coated Cu TEM grid (400 mesh) and allowing the solvent to evaporate in air. ^1H NMR was recorded on a Bruker 500 MHz Avance spectrometer; chemical shifts were referenced to the residual protons of the deuterated solvent.

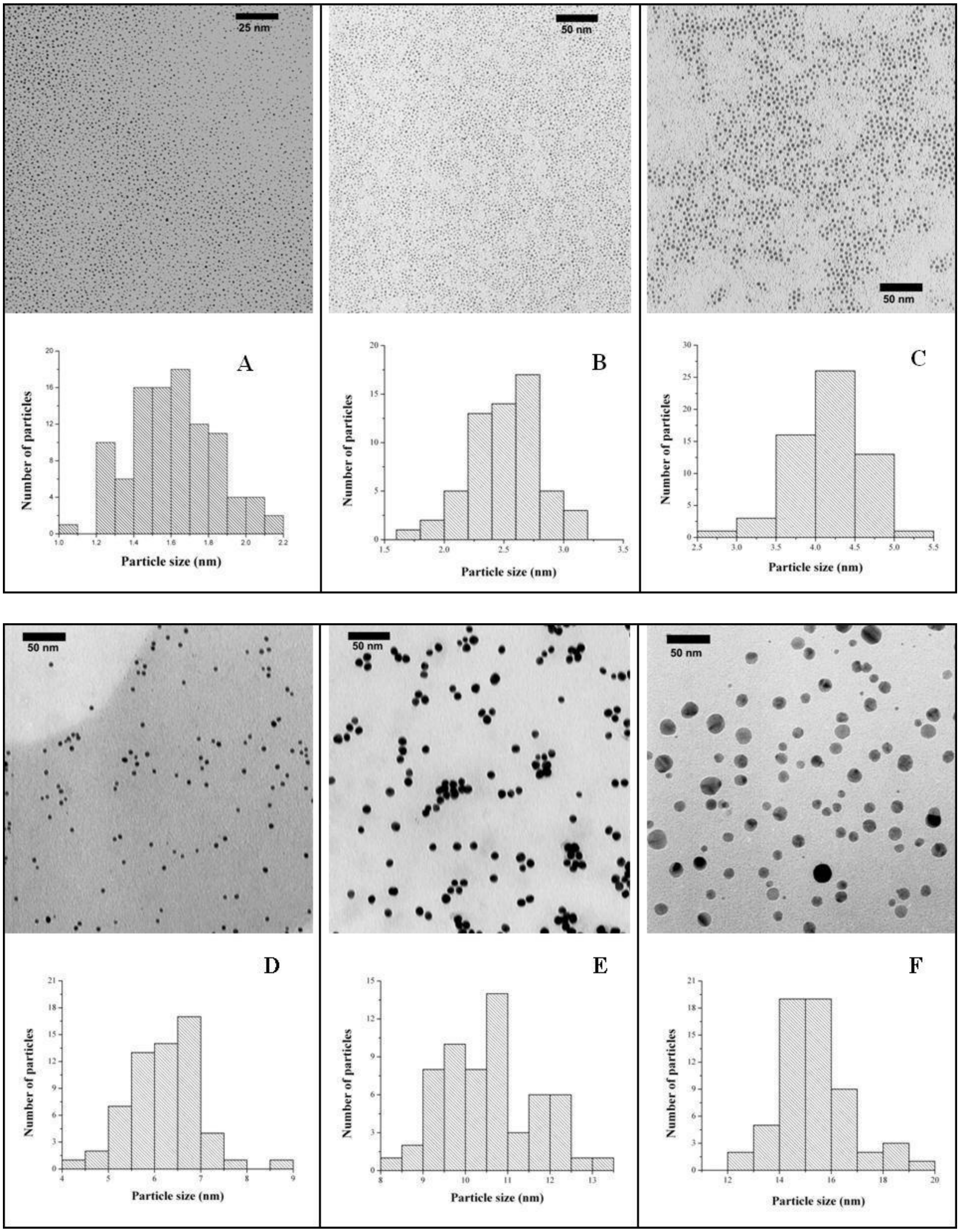
References:

1. Brust, M.; Walker, M.; Bethell, D.; Schiffrin, D. J. and Whyman, R., *J. Chem. Soc., Chem. Commun.* **1994**, 801-802.

2. Dasog, M. and Scott, R. W. J., *Langmuir*, **2007**, 23, 3381-3387.

3. Kang, S. Y. and Kim, K., *Langmuir*, **1998,** 14, 226-230.

Figure S1: TEM images and particle size histograms of dodecanethiolate Au MPCs (A) as synthesized and after the addition of (B) 10, (C) 20, (D) 30, (E) 60, and (F) 80, (G) 100, (H) 150, and (I) 500 equivalents of $LiBH_4$.



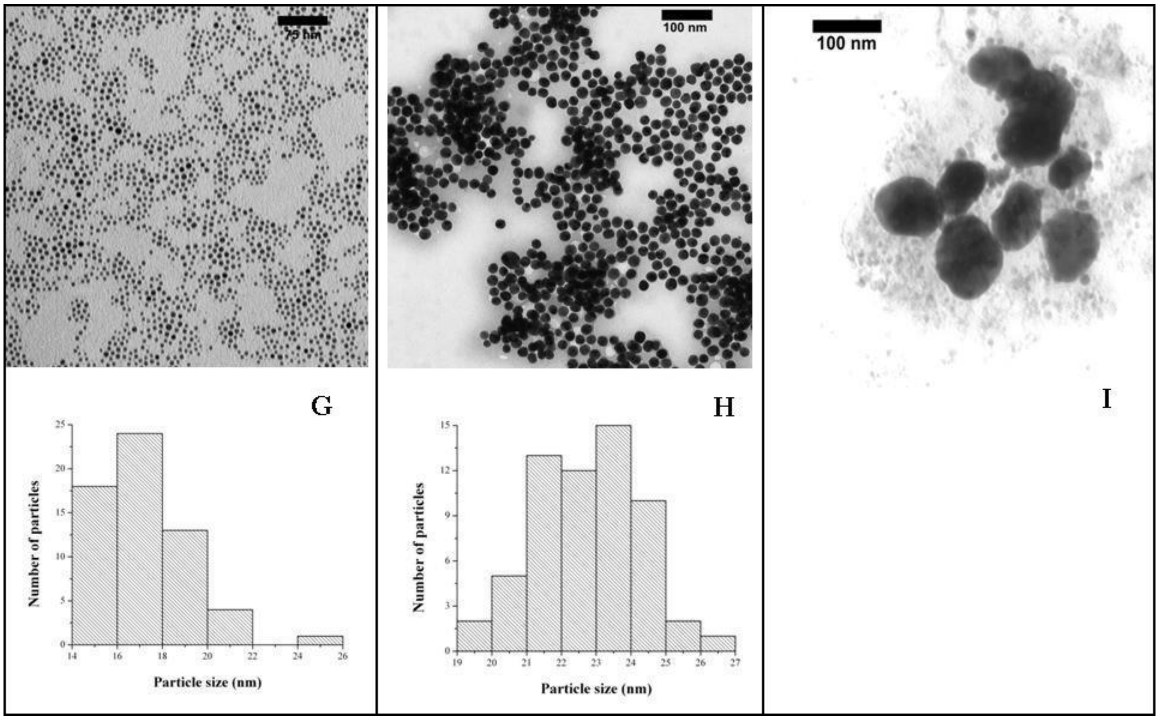

75 nm
100 nm
100 nm
G
H
I
Number of particles
0
5
10
15
20
25
14
16
18
20
22
24
26
Particle size (nm)
Number of particles
0
3
6
9
12
15
19
20
21
22
23
24
25
26
27
Particle size (nm)

Figure S2: Plot of TEM particle size vs. excess $LiBH_4$ added.

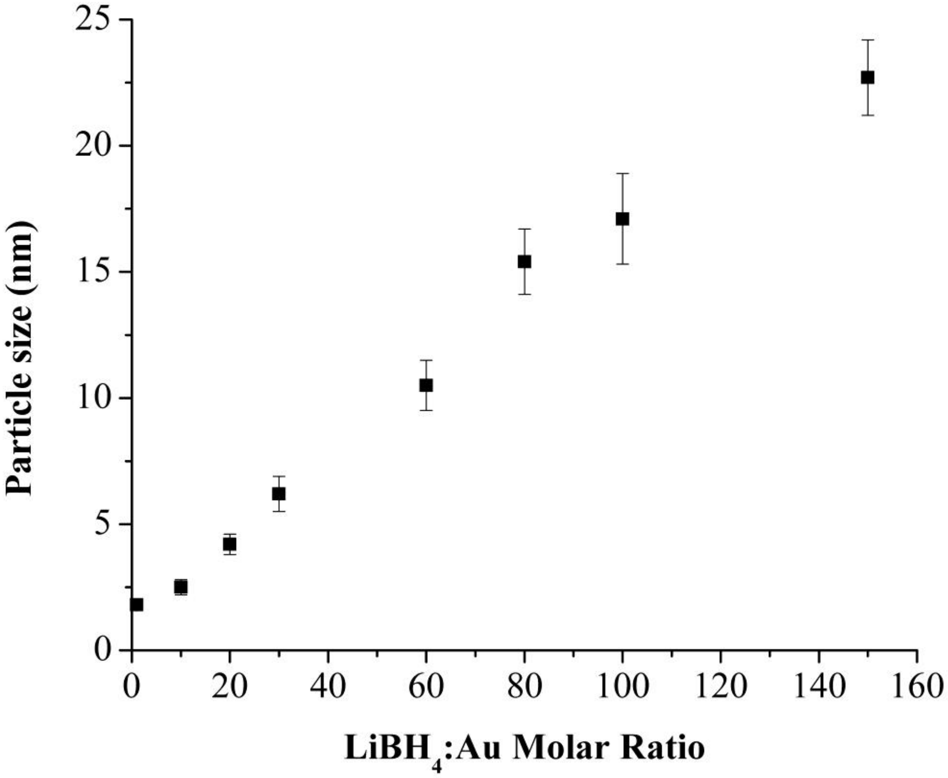


Figure S3: UV-Vis spectra of Au MPCs with increasing with increasing amounts of lithium borohydride); (from bottom) 10, 20, 60, 100, 150 and 500 molar equivalents of $LiBH_4$.

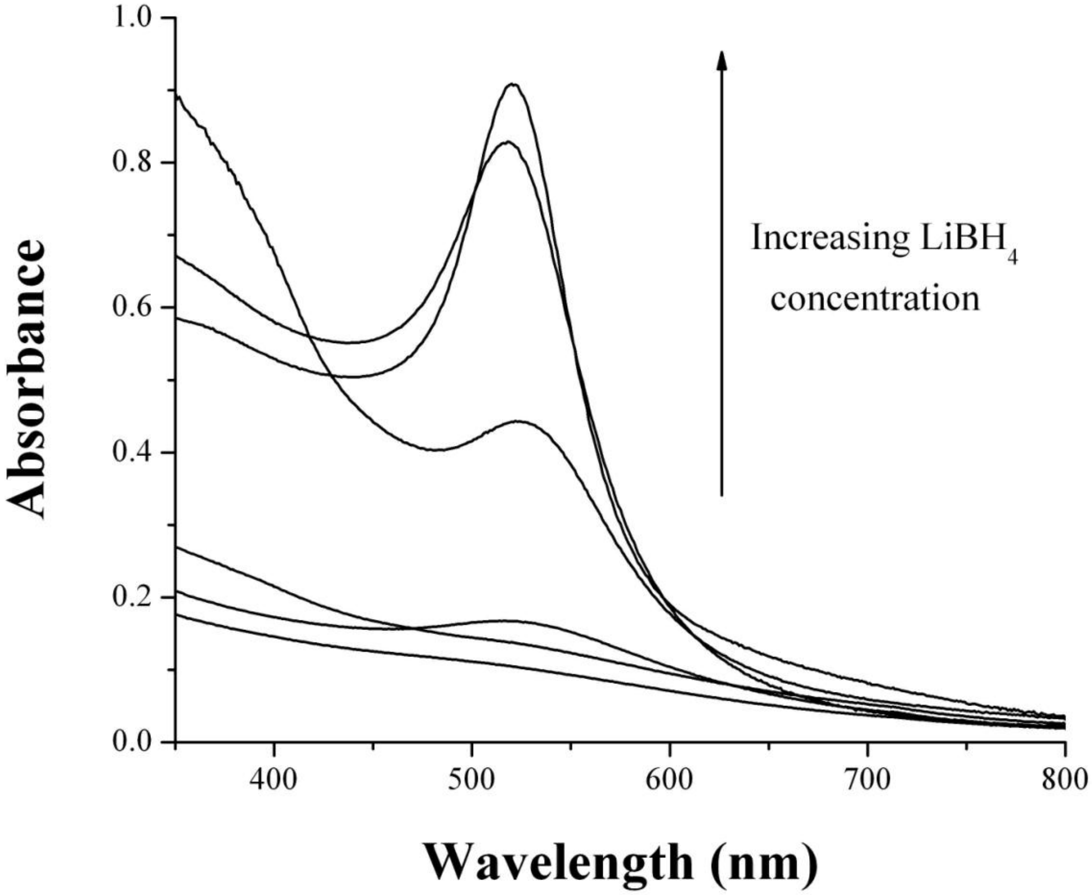


Figure S4: ^{1}H NMR spectrum of dodecanethiolate Au MPCs, (A) after purification and (B) after addition of 1000x excess of $NaBH_4$ and filtration of particles through celite.

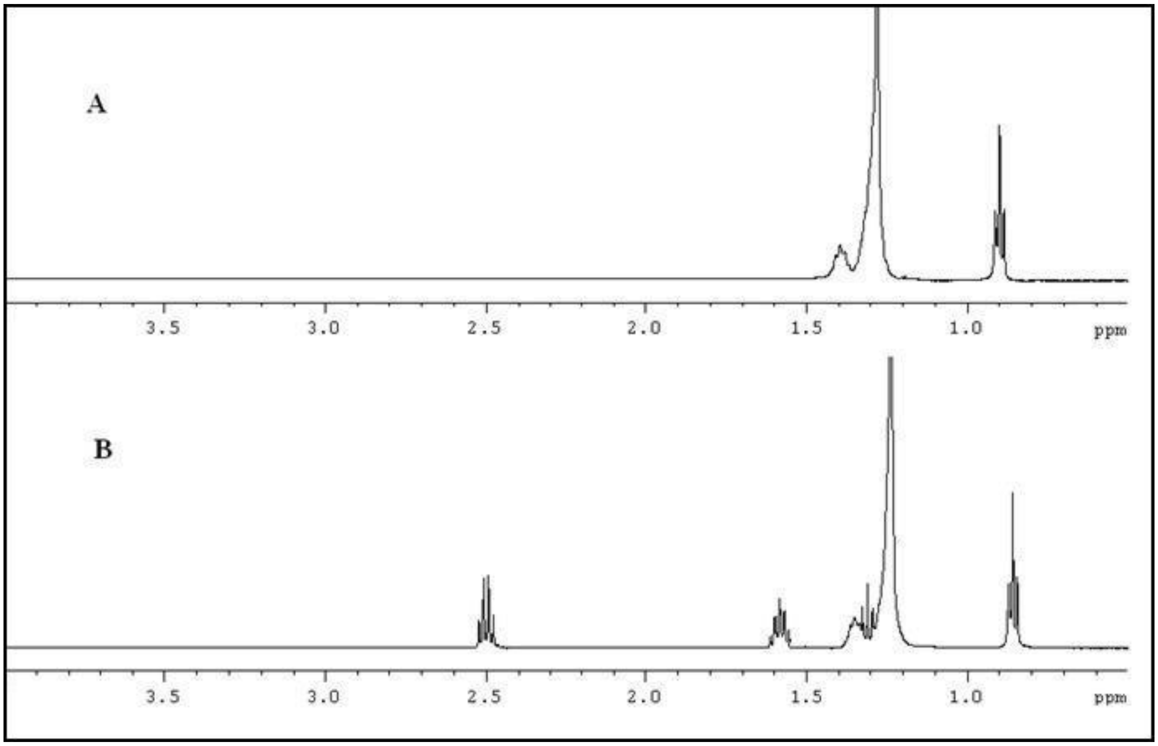


Figure S5. Representative UV-Vis spectra of the reduction of 4-nitrophenol to 4-aminophenol over dodecanethiolate Au MPCs. Conditions: $NaBH_4$: Au: substrate: 1000:1:1. (initial Au MPC size 1.6 ± 0.2 nm).

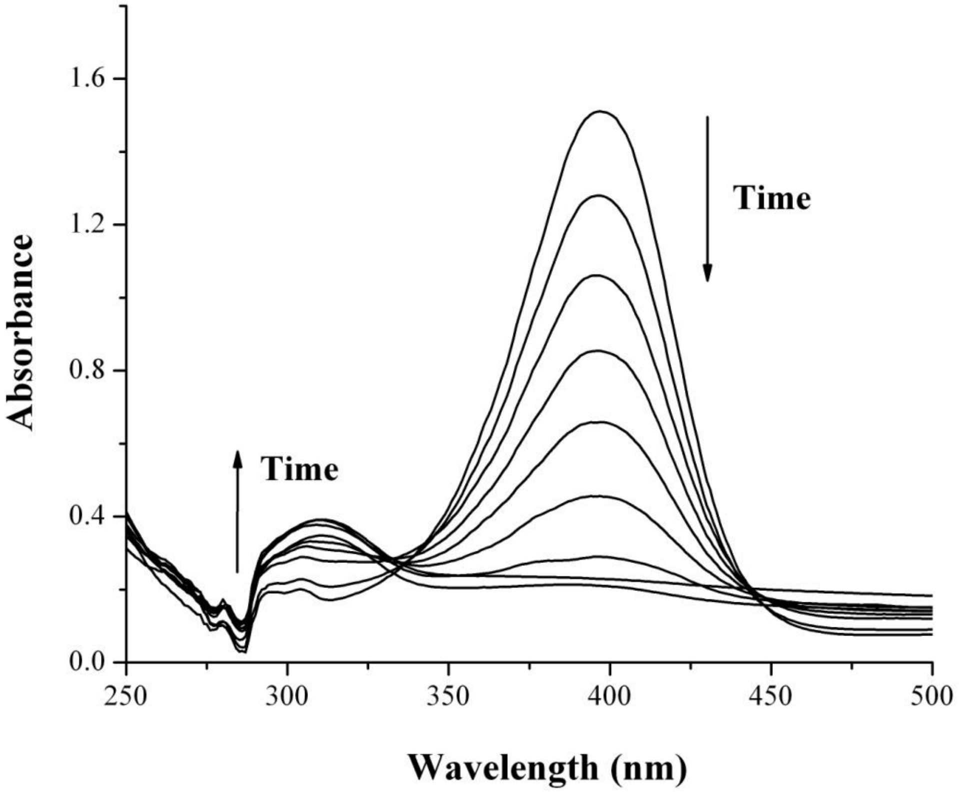


Figure S6. Kinetic pseudo-first order plots of nitrophenol absorption peak at 400 nm vs. time using different Au MPC catalyst concentrations (initial Au MPC size 1.6 ± 0.2 nm).

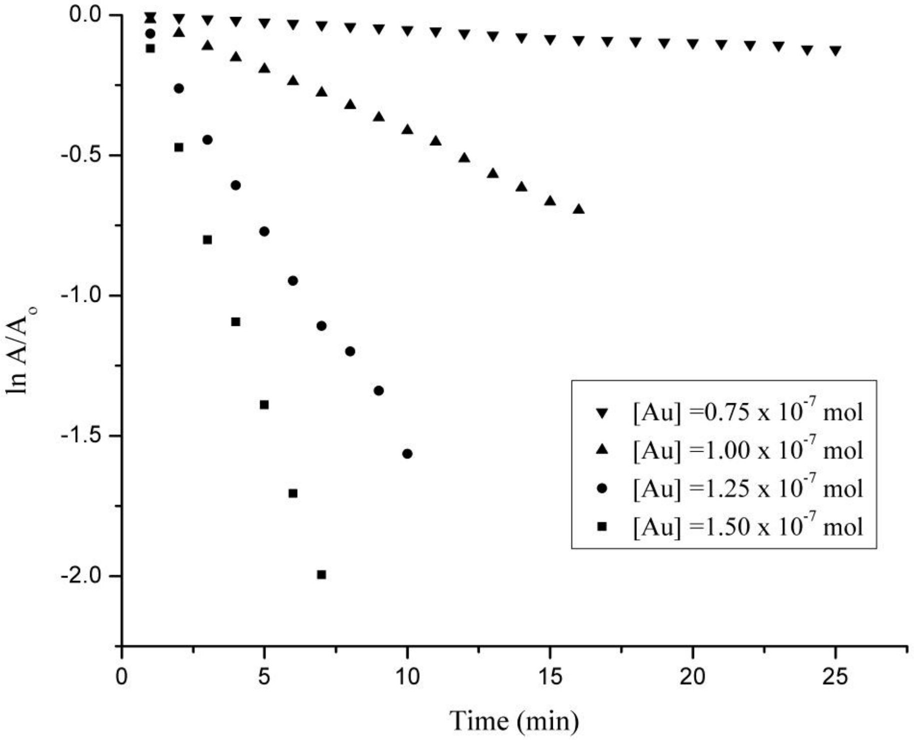


Figure S7: UV-Vis spectra of [A] C_6SH-Au MPCs, [B] C_{12}SH-Au MPCs, [C] C_{18}SH-Au MPCs, [D] MUA-Au MPCs and [E] PVP Au MPCs

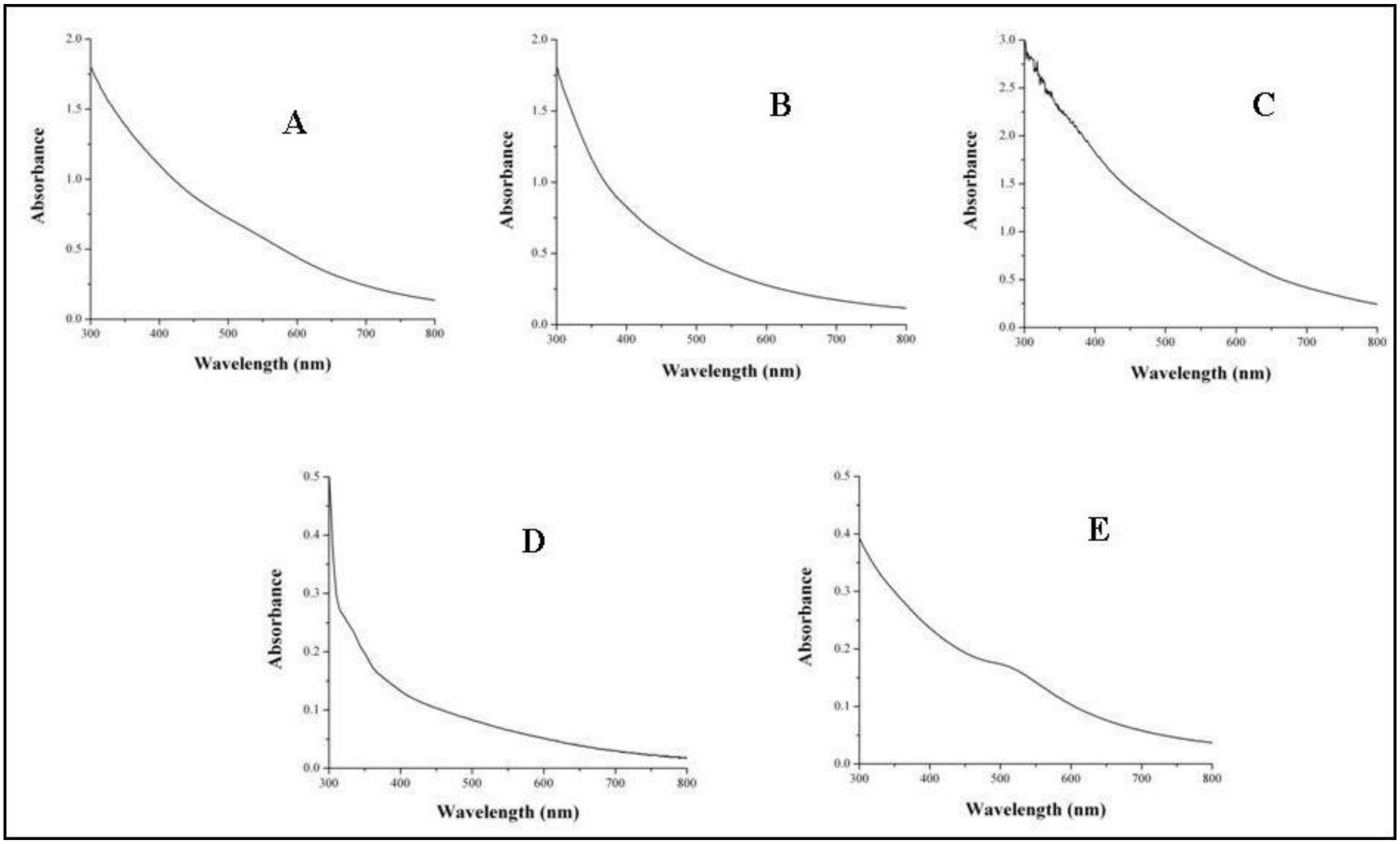


Figure S8: TEM images and particle size histograms of [A] C_6SH-Au MPCs (1.9 ± 0.2 nm), [B] C_{12}SH-Au MPCs (1.6 ± 0.2 nm), [C] C_{18}SH-Au MPCs (1.9 ± 0.2 nm), [D] MUA-Au MPCs (1.9 ± 0.2 nm) and [E] PVP Au nanoparticles (2.9 ± 0.3 nm).

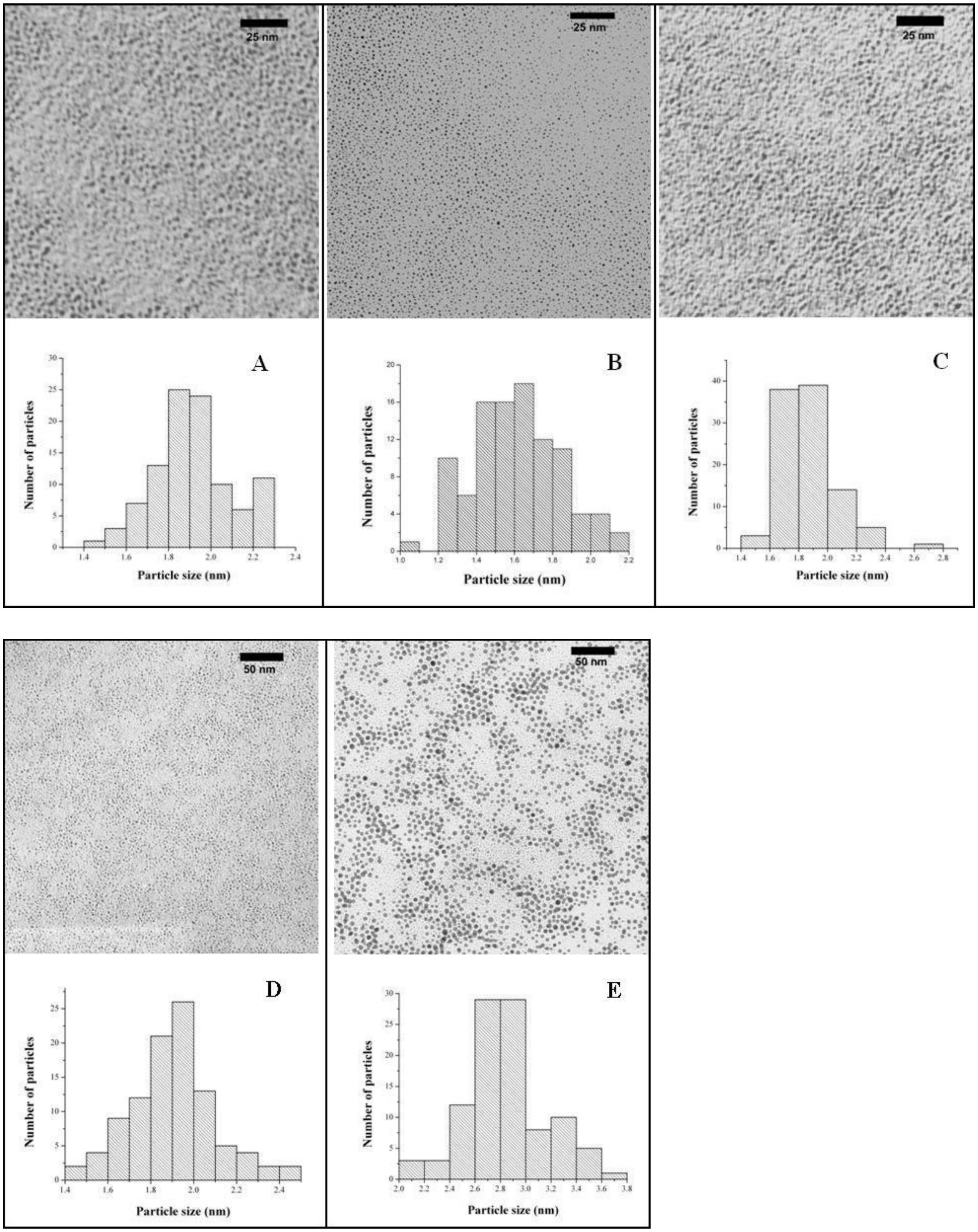


Figure S9: ^{1}H NMR spectrum of [A] C_6SH-Au MPCs, [B] C_{18}SH-Au MPCs and [C] MUA-Au MPCs

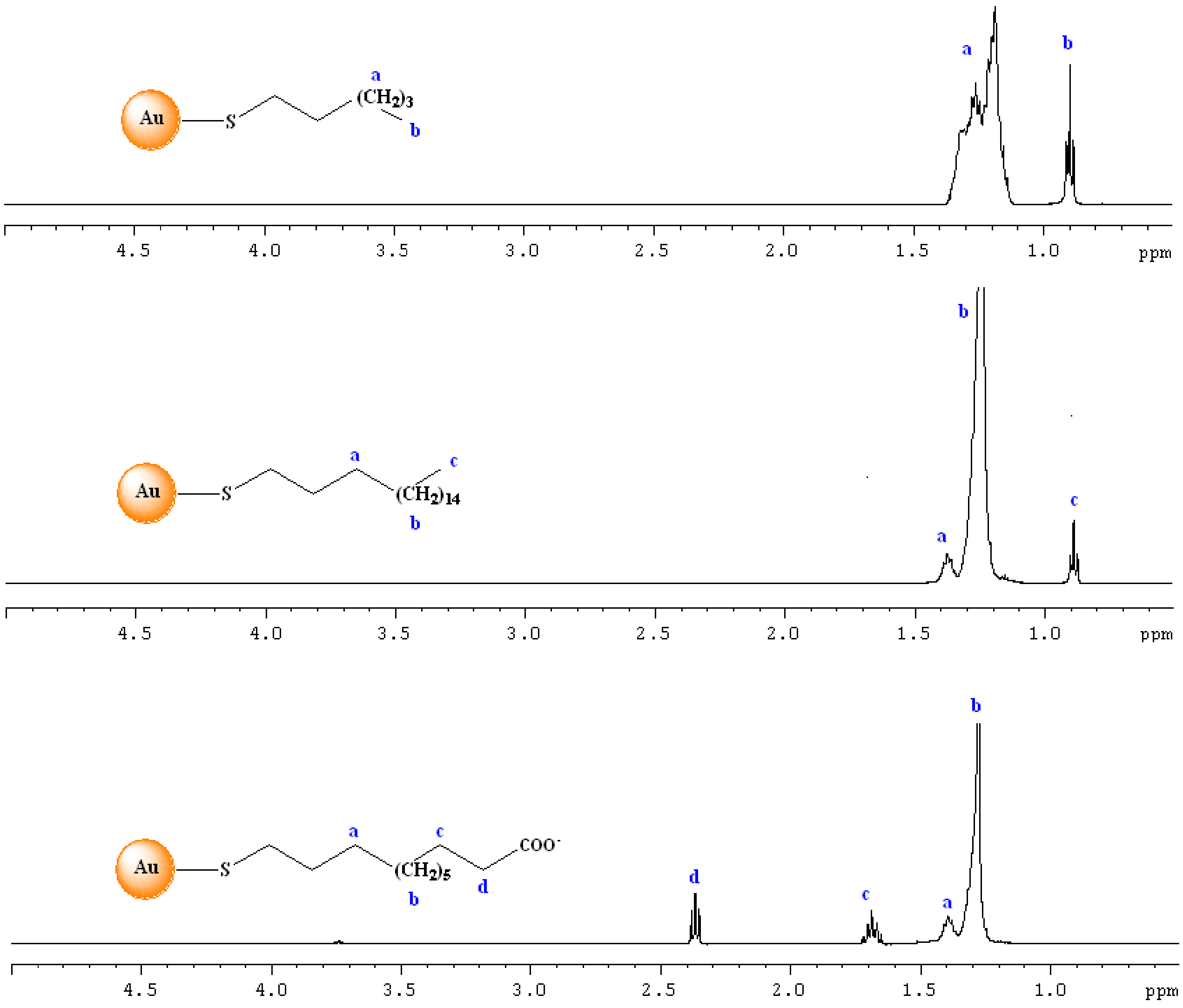


Figure S10: Plot of pseudo-first order rate constant for nitrophenol reduction vs. particle size of dodecanethiolate MPCs.