Electronic Supplementary Information

Fine control on nanoparticle sizes and size distributions: Temperature and ligand effects on the digestive ripening process

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Methods

Characterisation Instruments: TEM characterisation was carried out using FEI, TECNAI G2 TF 30 and FEI, TECNAI G2 TF 20 electron microscopes. UV-vis spectra of nanoparticle dispersion were taken on a JASCO V-570 UV-visible spectrophotometer.

Synthesis of nanoparticles: All the reactions were carried out in inert atmosphere and t-butyltoluene was degassed properly prior to use. 0.02M DDAB (didodecyldimethylammonium bromide) was prepared in 10 mL t-butyltoluene. $AuCl_3$ was added to this solution by sonication to make a 0.01M solution. The dark orange solution was reduced by drop wise addition of aqueous $NaBH_4$ (80 μL, 9.4M) under vigorous stirring. The stirring was continued for 3-4 hours to ensure complete reduction. Dodecanethiol was added to to this colloidal dispersion maintaining metal ligand molar ratio 1:30. Subsequently ligand coated nanoparticles were separated from excess ligand, DDAB and other reaction side products by precipitating with 30 mL ethanol addition. The precipitate was dried and again re-dispersed in 10 mL t-butyltoluene. Another dose of respective ligands were again added keeping 1:30 metal-ligand molar ratio.

The colloids are then refluxed for 90 minutes at 110 ºC and then slowly cooled down. Same reaction was carried out at higher temperature (at 180 ºC). Same protocol was followed to synthesize C8SH and C16SH capped Au nanoparticles.

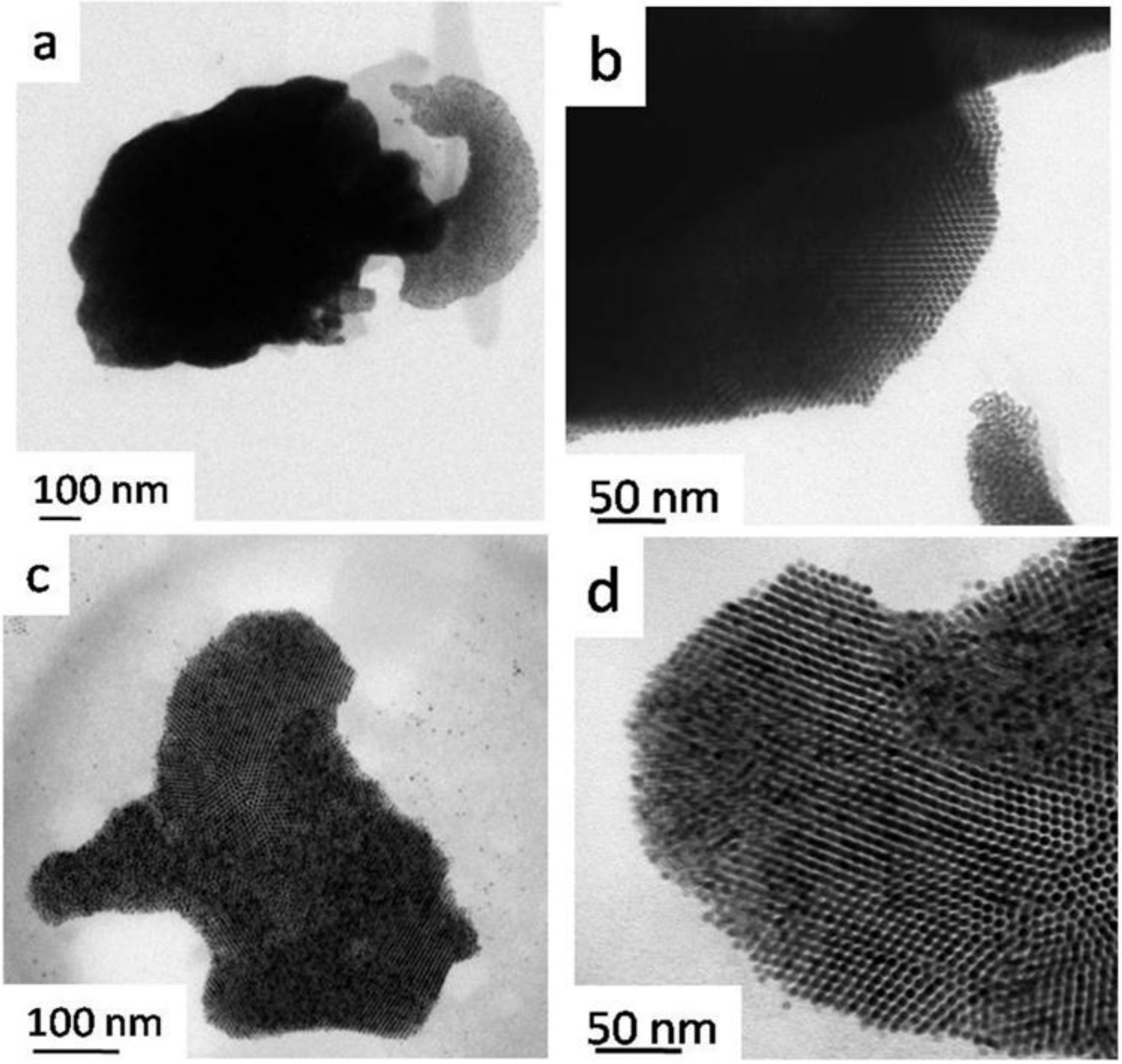

Fig-S1: TEM images of Au nanoparticles digestive ripened with octanethiol at 110 ºC (a,b) and 180 ºC (c,d) at different magnification.

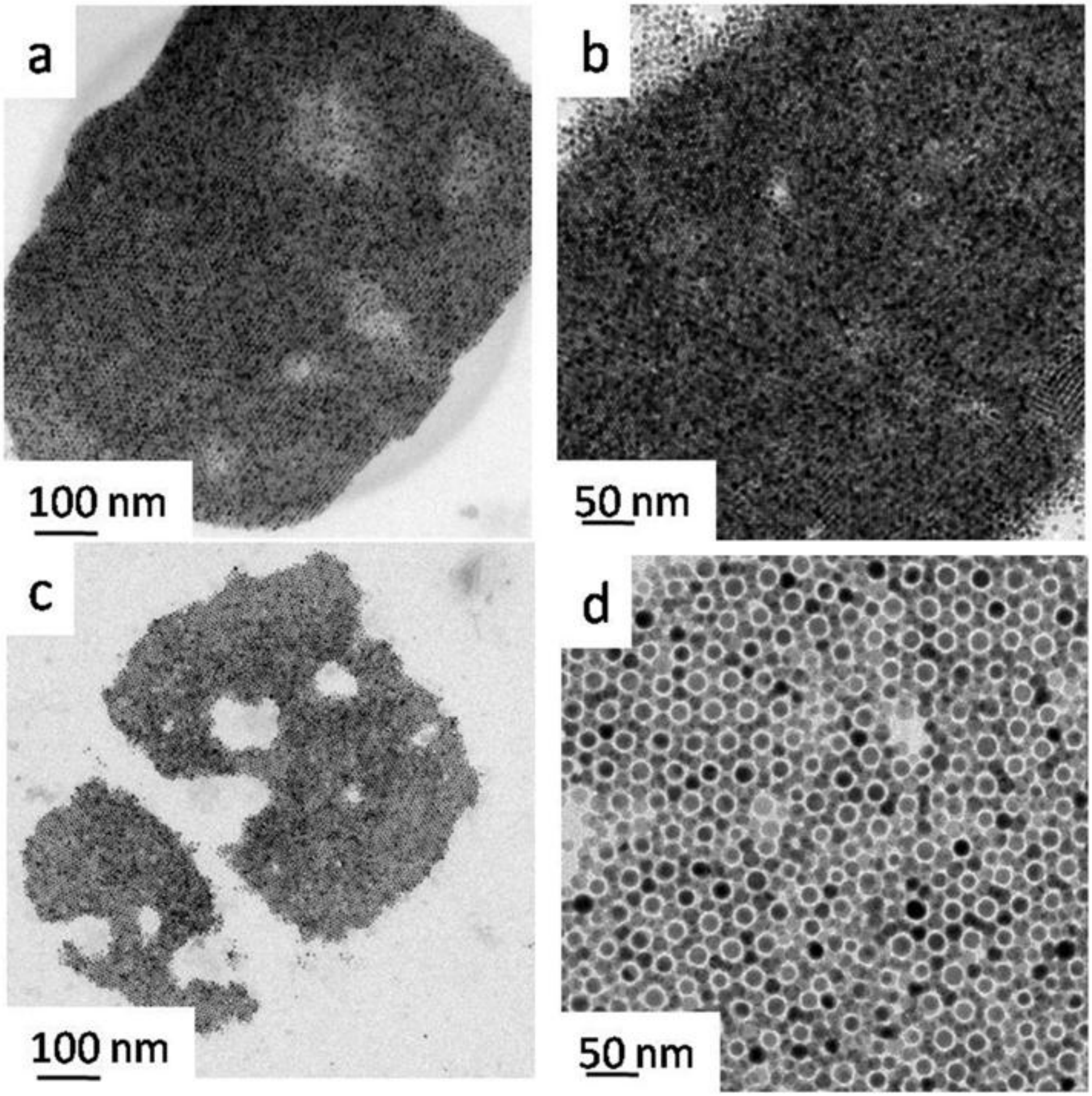

Fig-S2: TEM images Au nanoparticles digestive ripened with dodecanethiol at 110 ºC (a,b) and 180 ºC (c,d) at different magnification.

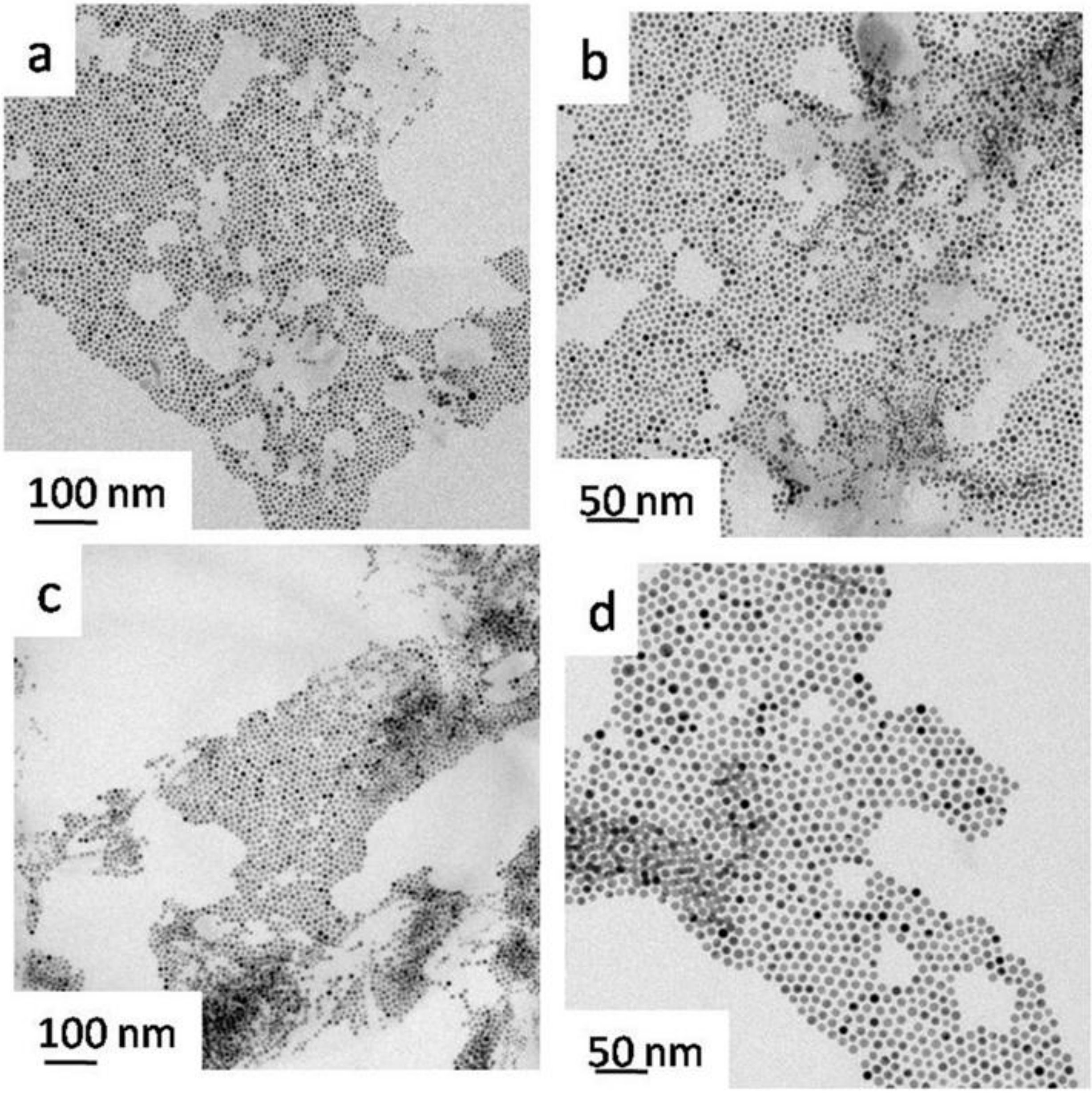

Fig-S3: TEM images Au nanoparticles digestive ripened with hexadecanethiol at 110 ºC (a,b) and 180 ºC (c,d) at different magnification.

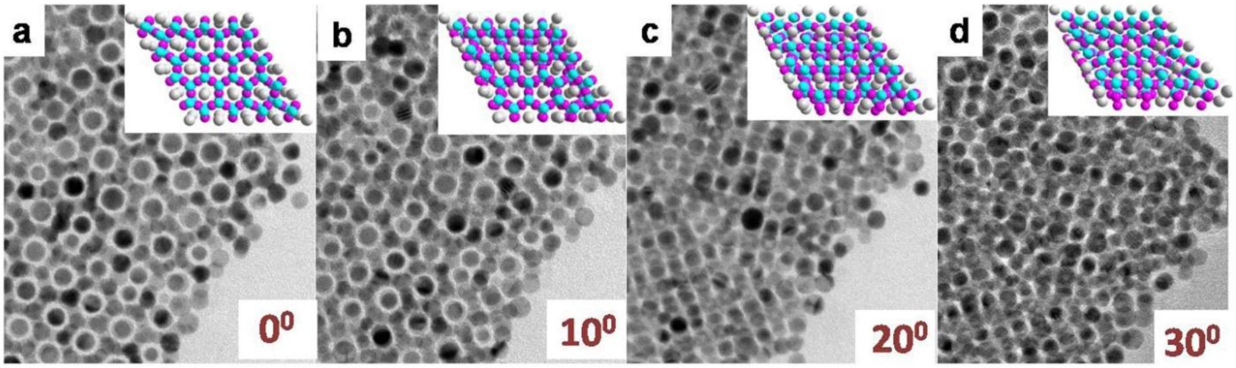

Fig-S4. TEM images obtained by tilting the grid (on which AB_5 structure was seen) in X-direction (α angle) at 10, 20 and 30° respectively. Inset represent corresponding structural model obtained by Diamond software (version 2.1.0.0).

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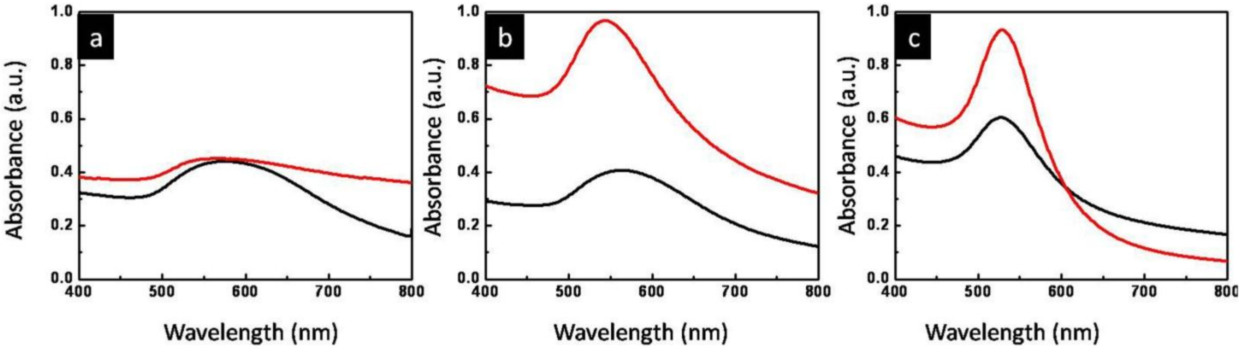

Fig-S5: Optical spectra of Au nanoparticles digestive ripened by octanethiol (a), dodecanethiol (b) and hexadecanethiol (c). Black and red lines represent spectra of particles synthesized at 110 ºC and 180 ºC respectively.

Although most of the reports indicate superlattice formation on drying we are convinced that nucleation of SLs happens in solution. This started with an observation of precipitate when nanoparticle dispersion was left standing for few days. C8SH capped particle seem to precipitate in much faster rate, leaving clear supernatant compared to light red colour supernatant for C12SH capped system. This signals greater degree of attraction in C8SH capped particles compared to C12SH capped ones. This result was further supported by UV-Visible measurement. Shifting of λ_{max} towards higher wavelength and greater extent of broadening for C8SH system compared to C12SH one corroborates the above mention prediction. Looking into magnitude of λ_{max} shift, we further predicted that, for C12SH system, synthesized at 110 ºC, there exists stronger interparticle attraction compared to the same system, synthesized at 180 ºC. This difference in attraction potential can be claimed for resulting fcc packing for the former one and a AB_5 packing for later, on TEM grid.