Kinetically Controlled Seeded Growth Synthesis of Citrate-Stabilized Gold Nanoparticles up to 200 nm: Size Focusing versus. Ostwald Ripening

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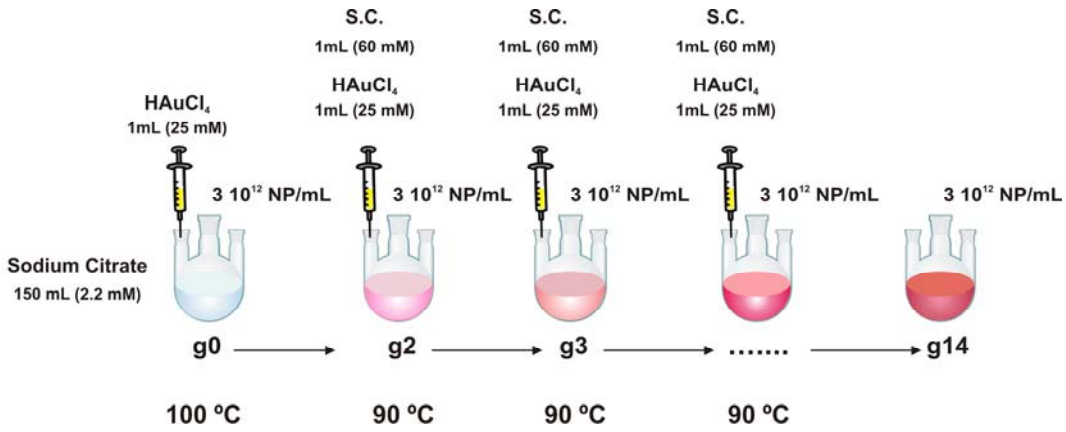
Additional Results

1. Synthesis of Au NPs up to 30 nm in diameter

1.1. Experimental



Scheme S1- Seeded growth of Au NPs up to 30 nm in diameter. Gold seeds (~ 10 nm, ~3 10^{12} NP/ml) were prepared by adding 1ml HAuCl4 [25 mM] into 150 ml sodium citrate 2.2 mM at 100 C. Once the synthesis was finished and in the same vessel, the reaction was cooled down until the temperature of the solution reached 90 °C. Then, 1 mL of sodium citrate (60 mM) and 1 mL of a HAuCl4 solution (25 mM) were sequentially injected (time delay ~ 2 min). After 30 min, aliquots of 2 mL were extracted for further characterization by Transmission Electron Microscopy (TEM) and UV-Vis spectroscopy. By repeating this process (sequential addition of 1mL of sodium citrate 60 mM and 1 mL of HAuCl4 25 mM), up to 14 generations of gold particles of progressively larger on sizes were grown. The concentration of each generation of particles is approximately the same than the original seed particles (~3 10^{12} NP/ ml).

1.2. Image Analysis

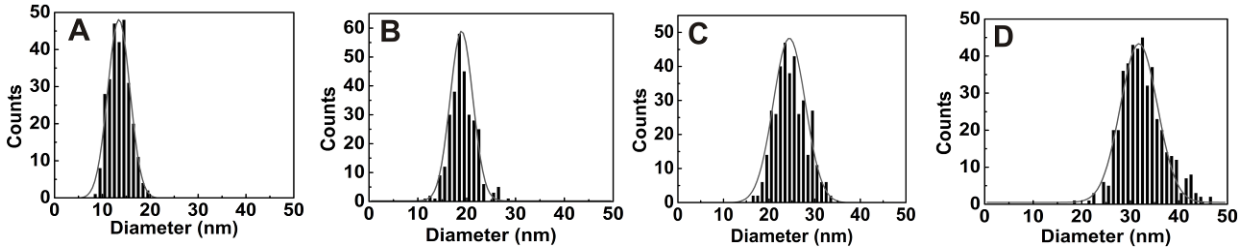


Figure S1- TEM image analysis of Au NPs shown in figure 1. Au seed diameter increases from 13.5 ± 2.1 nm (A), to 19.2 ± 2.6 nm after 3 growing steps (B), to 24.8 ± 3.4 nm after 7 growing steps (C) and to 30.5 ± 3.9 nm after 13 consecutive growth steps (D). In all cases, the concentration of the Au NP solution is the same (~ 3 10^{12} NPs/ml). At least, 100 NPs were counted in each case.

1.3. The effect of the Temperature

In order to evaluate the effects of temperature on the final Au NPs morphology, we prepared Au NPs under identical conditions (1 ml of HAuCl4 [25 mM] was injected into 150 ml of sodium citrate [2.2 mM]) while temperature of the solution was varied from 80 to 100˚C.

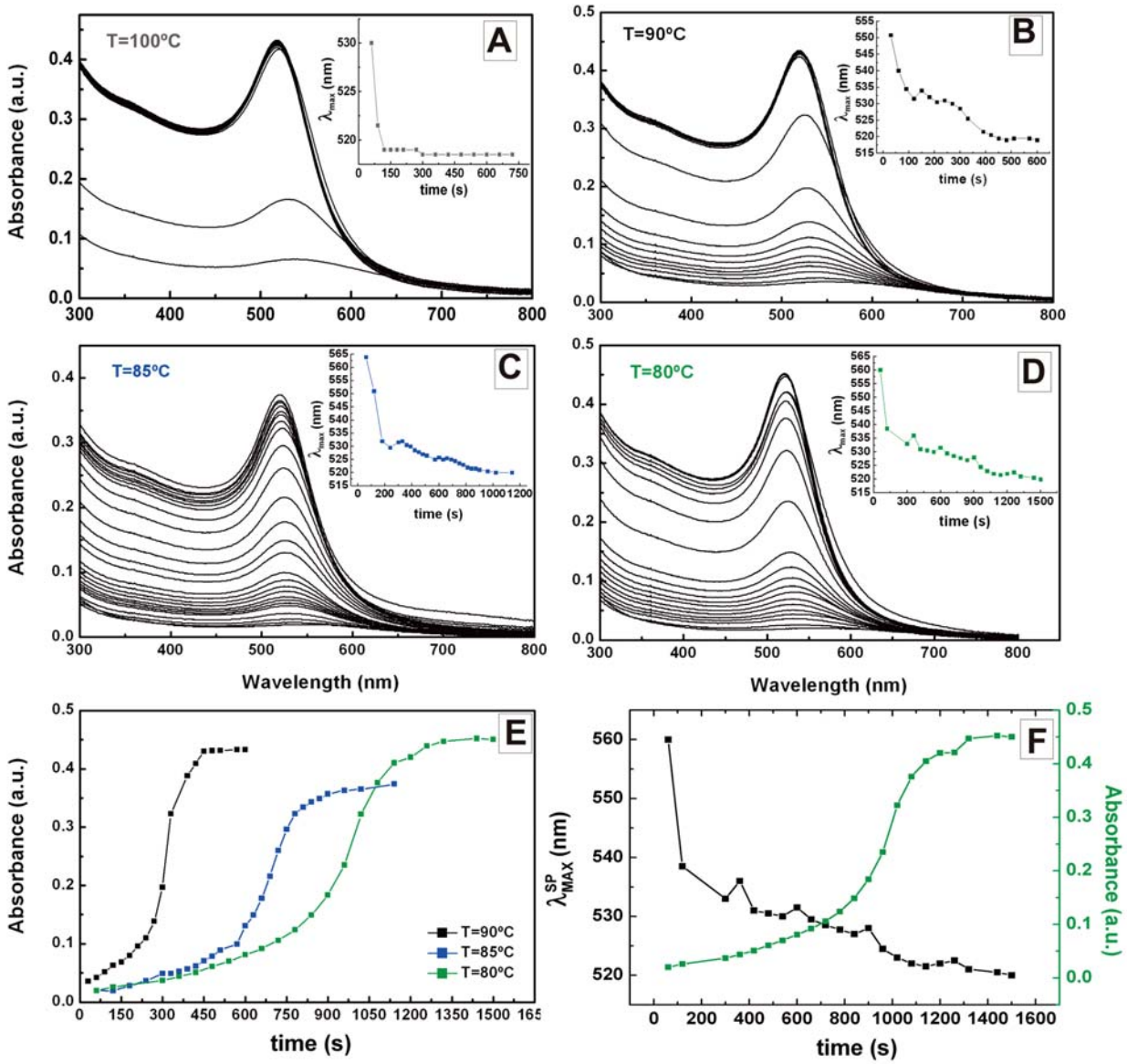


Figure S2- Time evolution UV-Vis spectra of Au NPs growth kinetics for different temperatures: 100 ˚C (A), 90 ˚C (B), 85 ˚C (C) and 80 ˚C (D). For all reaction temperatures, the temporal evolution kinetics is similar but time scale increases as the temperature decrease (E). Time evolution of the SPR band and the intensity maximum as a function of time for 80 C reaction temperature.

Temporal evolution of the particle formation has been recorded as a function of time after the initiation event, which is the addition of the $HAuCl_4$ to the reducing solution at different temperatures. Since the reaction rate is a strong function of the temperature, the reaction was quenched by cooling the samples in ice water. To verify that quenching does indeed provide sufficient delay for sampling, two samples were collected during the reaction in which one sample was quenched and later (about one hour) analyzed and other sample was analyzed immediately in all cases the spectra compared well.

Typical absorption spectra are shown in figure S2. Essentially, for all four reaction temperatures, the temporal evolution is similar but the time scale increases as the temperature decreases. As expected, samples at short times have relatively flat absorption profiles. Later, when the solution turns dark purple, SPR band begins to appear and initially appears near 560 nm. As the reaction progresses, the plasmon band intensity increases (Inset of Fig S2-A, B, C and D) and blue-shifts smoothly to a constant value around 520 nm, characteristic of spherical Au NPs. This blue-shift in the position of the SPR peak is clearly seen in the inset of the figures where they have been plotted vs. time.

Seed particles were prepared under identical conditions (1 ml of HAuCl4 [23.4 mM] was injected into 150 ml of sodium citrate [2.2 mM]) while temperature of the solution was kept at 100 °C.

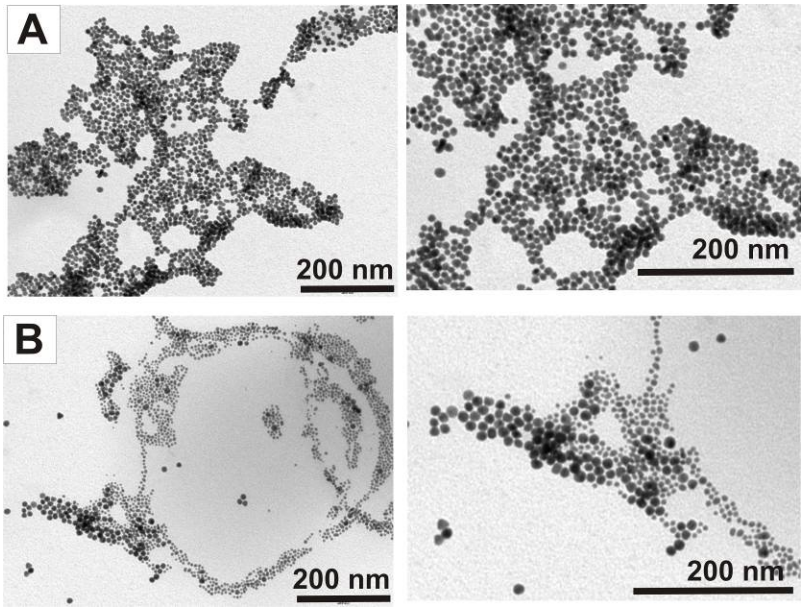


Figure S3- Transmission electron microscopy images of seed (A) and grown (B) Au NPs. The use of higher temperatures did not avoid the nucleation of a second population of particles

1.4. The Role of the sodium citrate

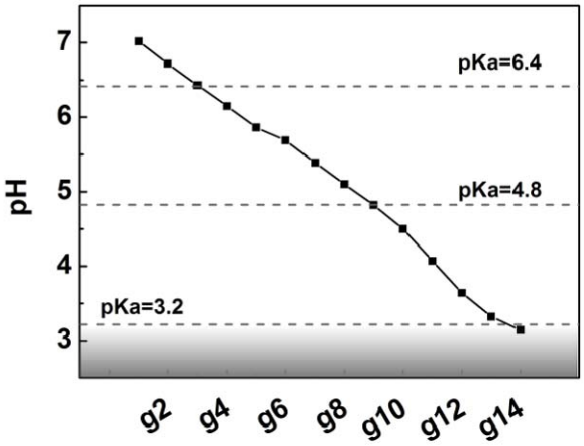


Figure S4- Plot of experimentally obtained pH values after each growing step and pKa values of sodium citrate (6.4, 4.8 and 3.2). When solution pH is lower than the 3rd pKa value of sodium citrate, all its carboxylic groups are deprotonated and hence electrostatic interactions cannot keep particles stable in solution, leading to immediate aggregation. In order to overcome this problem, we experimentally measured the amount of sodium citrate needed, as a buffer, to keep constant the pH of the solution (~7) during the whole process.

1.5. Injection of higher amounts of gold precursor (5x, 10x).

Gold seeds (~9 nm, $3x10^{12}$ NP/ml) were prepared by injecting 1 ml of $HAuCl_4$ [25 mM] into 150 ml of sodium citrate [2.2 mM] at 90 °C. Once the synthesis was finished, 4 ml of sodium citrate [60 mM] and 5 ml or 10 ml of $HAuCl_4$ [25 mM] were added and the solution was heated up. The amount of sodium citrate added is intending that the pH of the solution maintains around 7. Figure S4-A shows images of seed particles from a small region of a carbon grid. It can be seen the monodispersity of the seed particles which is reflected in to small standard deviation (8.7 ± 0.8 nm). Resultant particles are larger (Fig.S4-B,C); than the initial seeds and additional nucleation is observed. Moreover, grown particles are not spherical anymore.

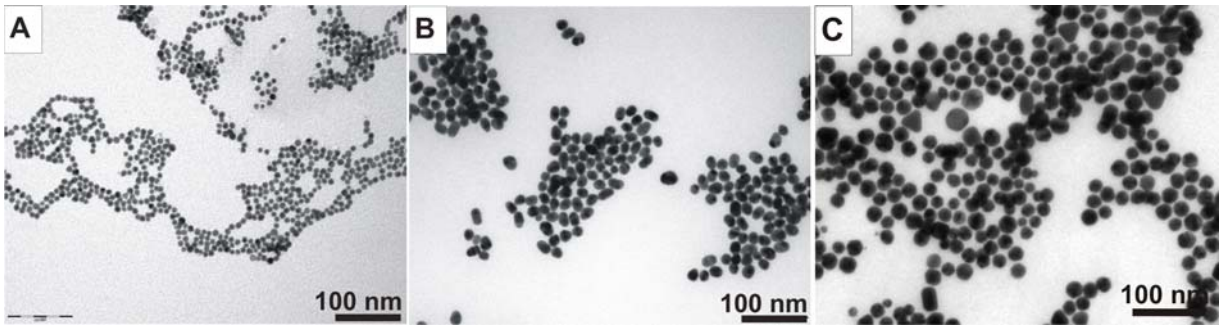
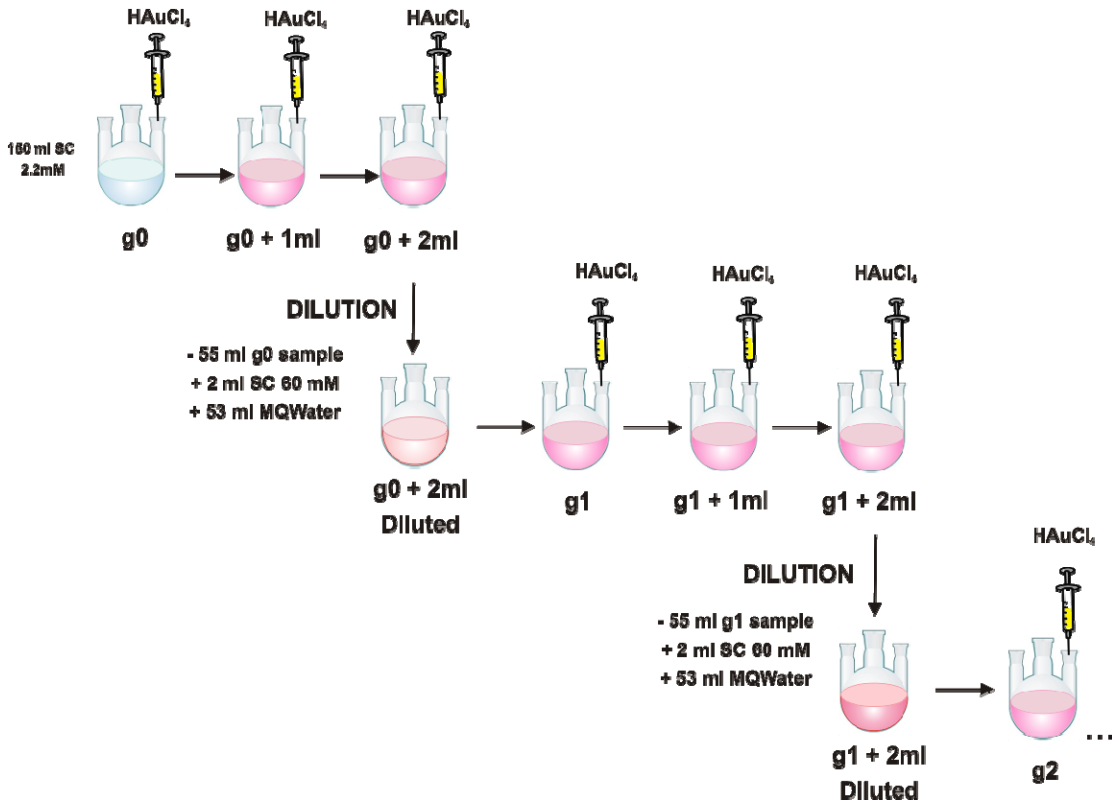


Figure S5- Growth of gold nanoparticles by fast injection of the metal salt: TEM characterization. Seed particles (A) and resultant particles (B and C).

2. Synthesis of Au NPs up to 180 nm in diameter

2.1. Experimental



Scheme S2. Gold seeds (~ 10 nm, ~$3x10^{12}$ NP/ml) were prepared by the standard method (1ml $HAuCl_4$ [25 mM], 150 ml sodium citrate [2.2 mM], 100 C). Once the synthesis was finished the solution was cooled down to 90 C and 1 ml of $HAuCl_4$ solution ([25 mM]) was injected. After 30 min the reaction was finished. This process was repeated twice. After that, the sample was diluted by extracting 55 ml of sample and adding 53 ml of MQ water and 2 ml of sodium citrate 60 mM. This solution was then used as seed solution and the process was repeated again.

2.2. Additional TEM Results

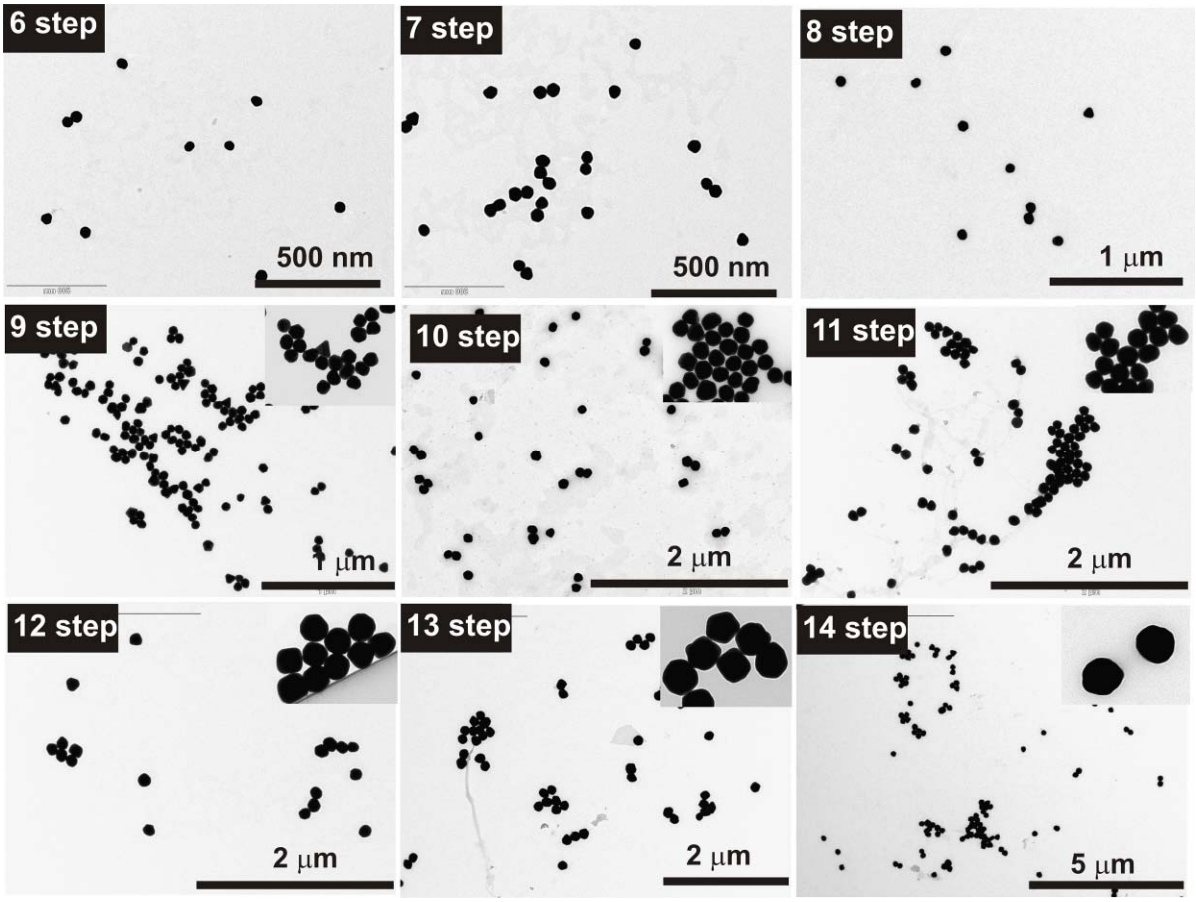


Figure S6- Supplementary transmission electron microscopy images of Au NPs synthesized by the seeded growth approach.

2.3. Image Analysis

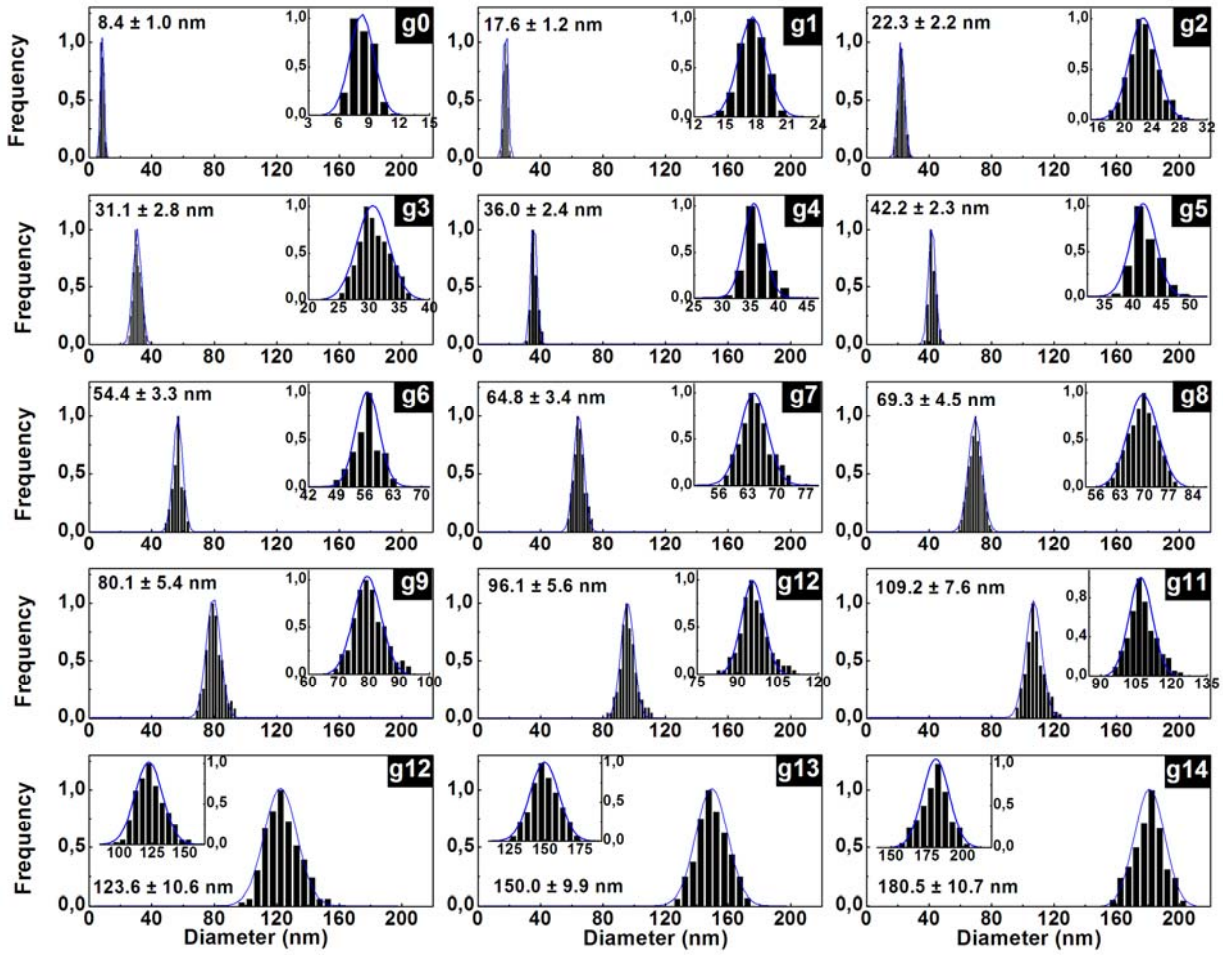


Figure S7- TEM image analysis of Au NPs shown in figure 2. At least, 100 NPs were counted in each case.

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3. The effect of seed concentration

3.1. Image Analysis

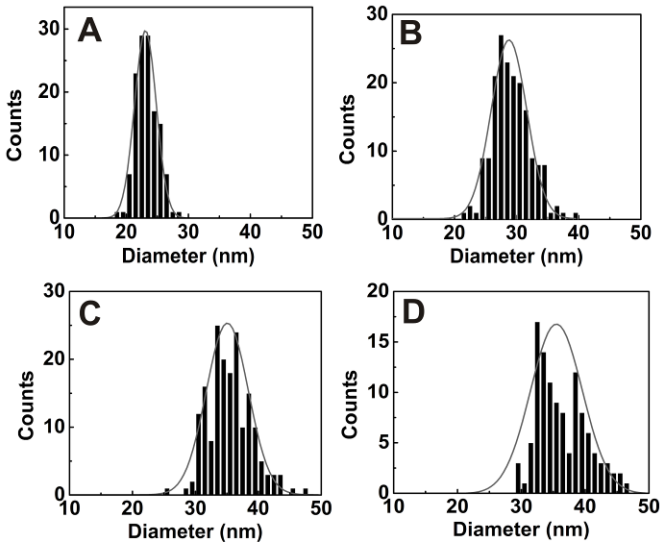

Figure S8- Size distribution of Au NPs obtained using different concentrations of seed solution (A) 23.3 ± 1.7 nm ($7.5x10^{11}$ Au NP/ml), (B) 29.2 ± 3.0 nm ($3x10^{11}$ Au NP/ml), (C) 35.5 ± 3.4 nm ($2x10^{11}$ Au NP/ml) and (D) 36.6 ± 4.3 nm ($1.5x10^{11}$ Au NP/ml).