

SUPPORTING INFORMATION

Hydroquinone Synthesis of Silver Nanoparticles: A simple Model Reaction to
Understand the Factors which Determine Their Growth and Nucleation.

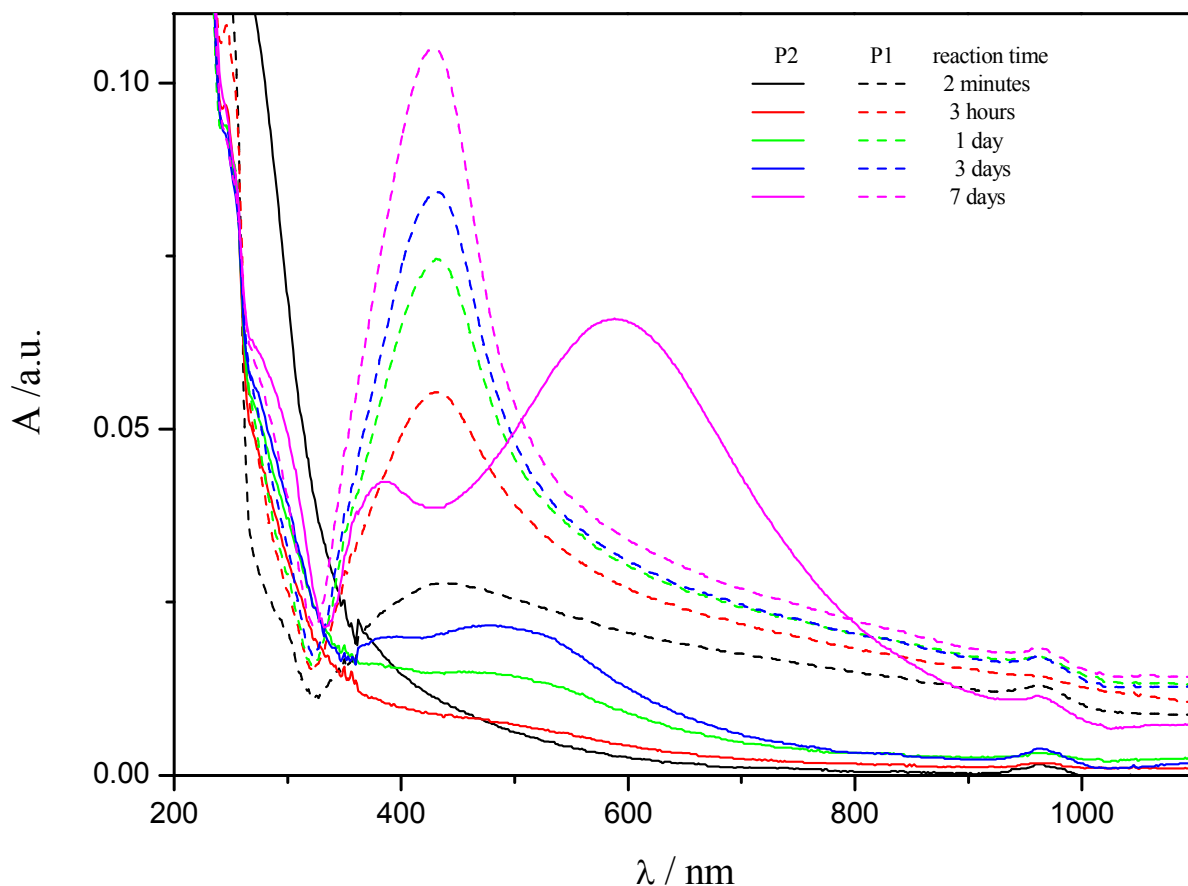
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A- The Early Stages of the Reaction with Different Mixing Protocols

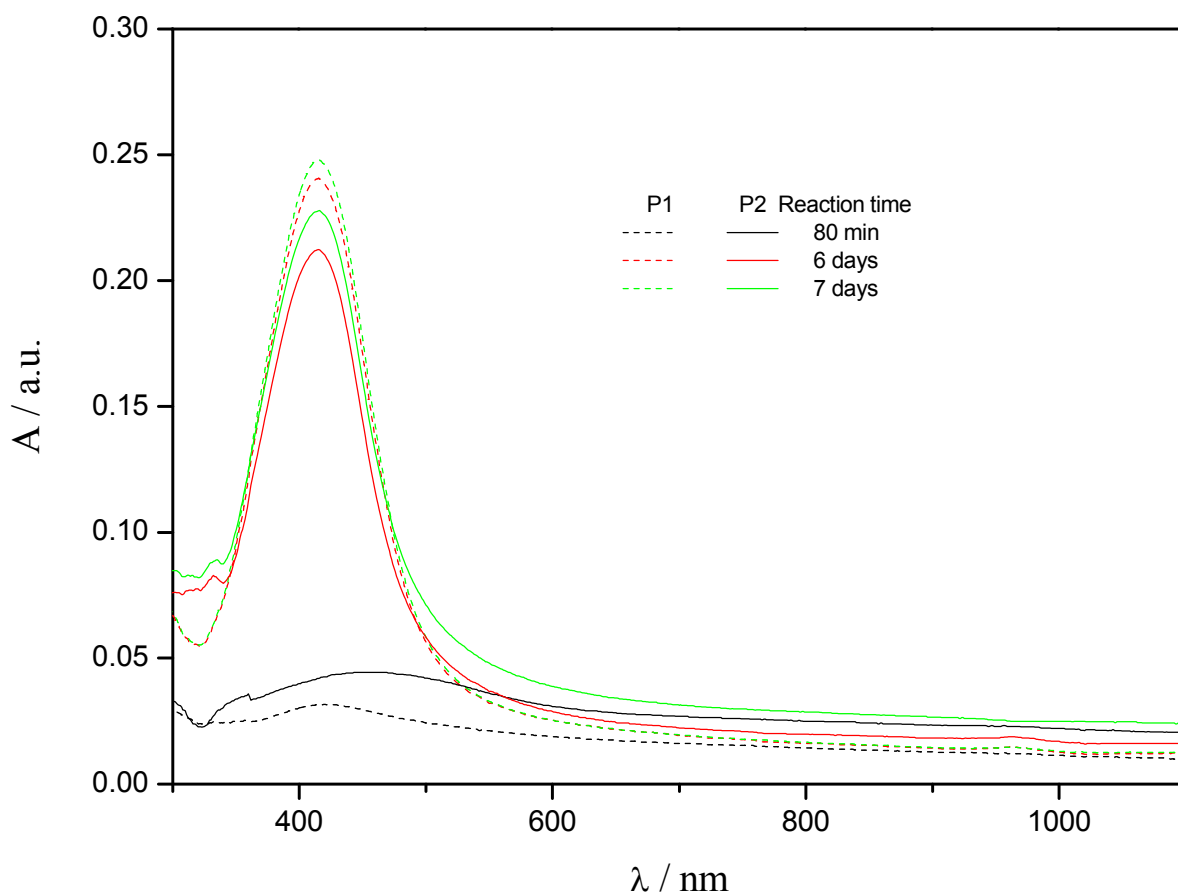
1) 100 μM AgNO_3 + 5 μM H_2Q + 100 μM $\text{TMA}(\text{OH})$



SA1. Evolution of the SPR's spectra of NP's prepared with **P1** (dashed lines) and **P2** (solid lines) for reaction time of: (black) 2 minutes immediately after the mixing of reactants, (red) 3 hours, (green) 1 day, (blue) 3 days, and (magenta) 7 days.

The spectra exhibit noticeable differences in their shapes, indicating that the NP's obtained under different mixing conditions present drastic differences in their size/shape distribution. Immediately after the mixing of reactants, **P1** leads to a spectrum with a peak around 435 nm and a long tail extended within the whole visible range. On the contrary, for **P2** the characteristic dipole SPR of small spheres is absent. As the reaction time elapses, the SPR peak of NP's prepared with **P1** increases continuously with no remarkable changes in the shape of the profile, indicating that the increase of the number of small spherical NP's generated by progressive nucleation constitutes the main process. In the case of the NP's obtained with **P2**, the SPR profile evolves to define a doubly-peaked spectrum. The peak at longer wavelength values red-shifts with the development of the reaction, indicating that NP's become larger.

2) $100 \mu\text{M AgNO}_3 + 5 \mu\text{M H}_2\text{Q} + 1000 \mu\text{M NH}_3 + 1000 \mu\text{M TMA(OH)}$

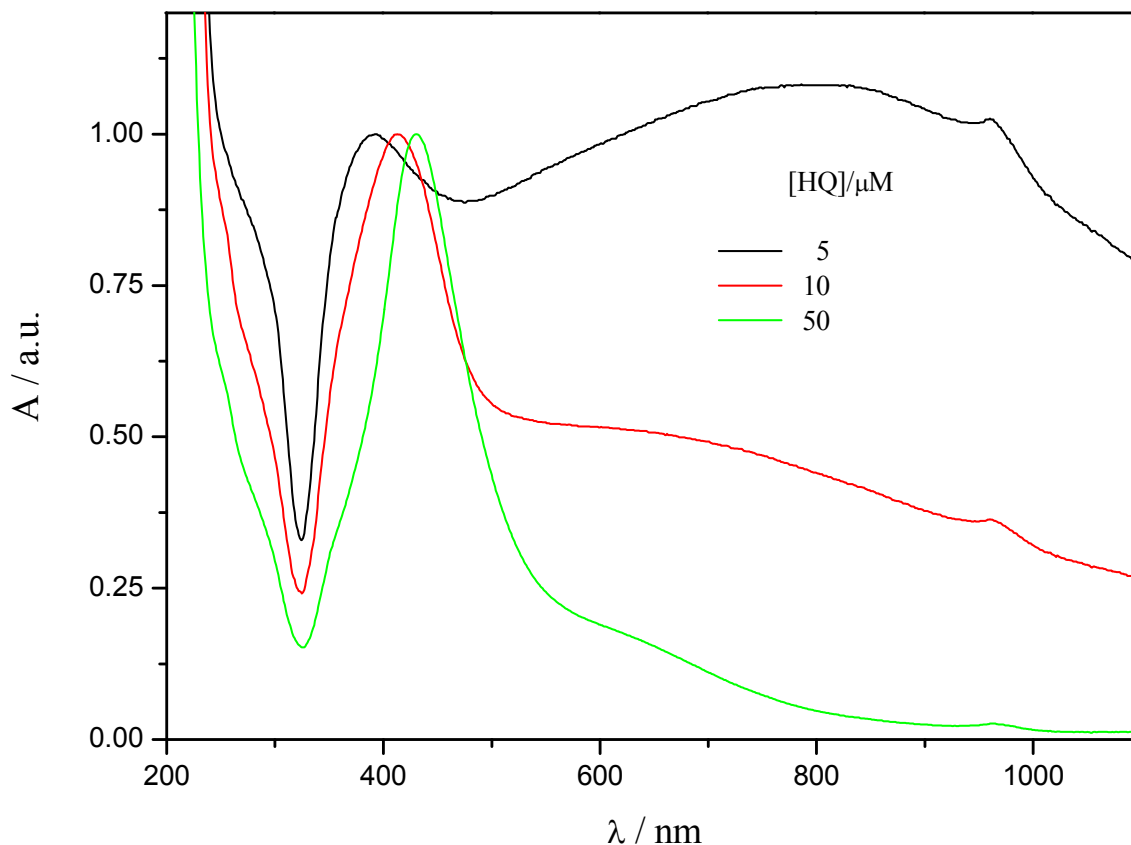


SA2. Evolution of the SPR's spectra of NP's prepared with **P1** (dashed lines) and **P2** (solid lines) for reaction time of: (black) 80 minutes immediately after the mixing of reactants, (red) 6 days, (green) 7 days.

Different mixing conditions lead during the early stages of the reaction to different spectra, however as the reaction time elapses the SPR profiles become similar. The uncontrolled events during the mixing that generate different shape/size distribution have a minor influence on the final morphology of the NP's. The continuous increase observed in the SPR peak at 414 nm is associated with the increment of the amount of small spherical NP's coming from the progressive nucleation.

B- Increase of the H₂Q Concentration

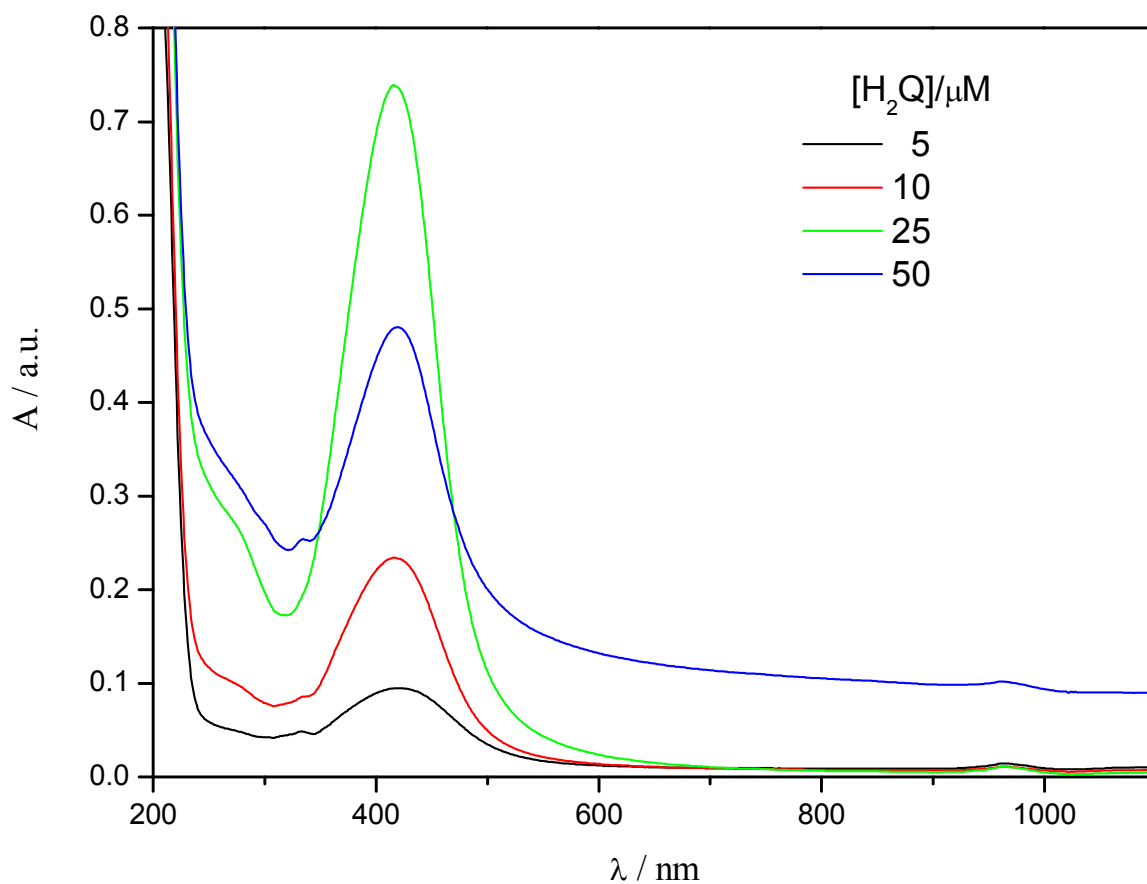
1) 100 μM AgNO₃ + 100 μM TMA(OH), *P2*



SB1. Normalized SPR's spectra of NP's prepared with *P2* for increasing H₂Q concentration.

The increase of H₂Q concentration leads to rise of the number of small spherical NP's which is evidenced by the red shift observed for the series of spectra around 400 nm. The characteristic dipole SPR maximum of large NP's (800 nm) also decreases becoming an ill defined peak and, finally, a shoulder of the main SPR peak at around 400 nm. Under the present conditions, the increase of H₂Q produces a large amount of small spherical NP's, however some large NP's coming from an uncontrolled growth are also obtained.

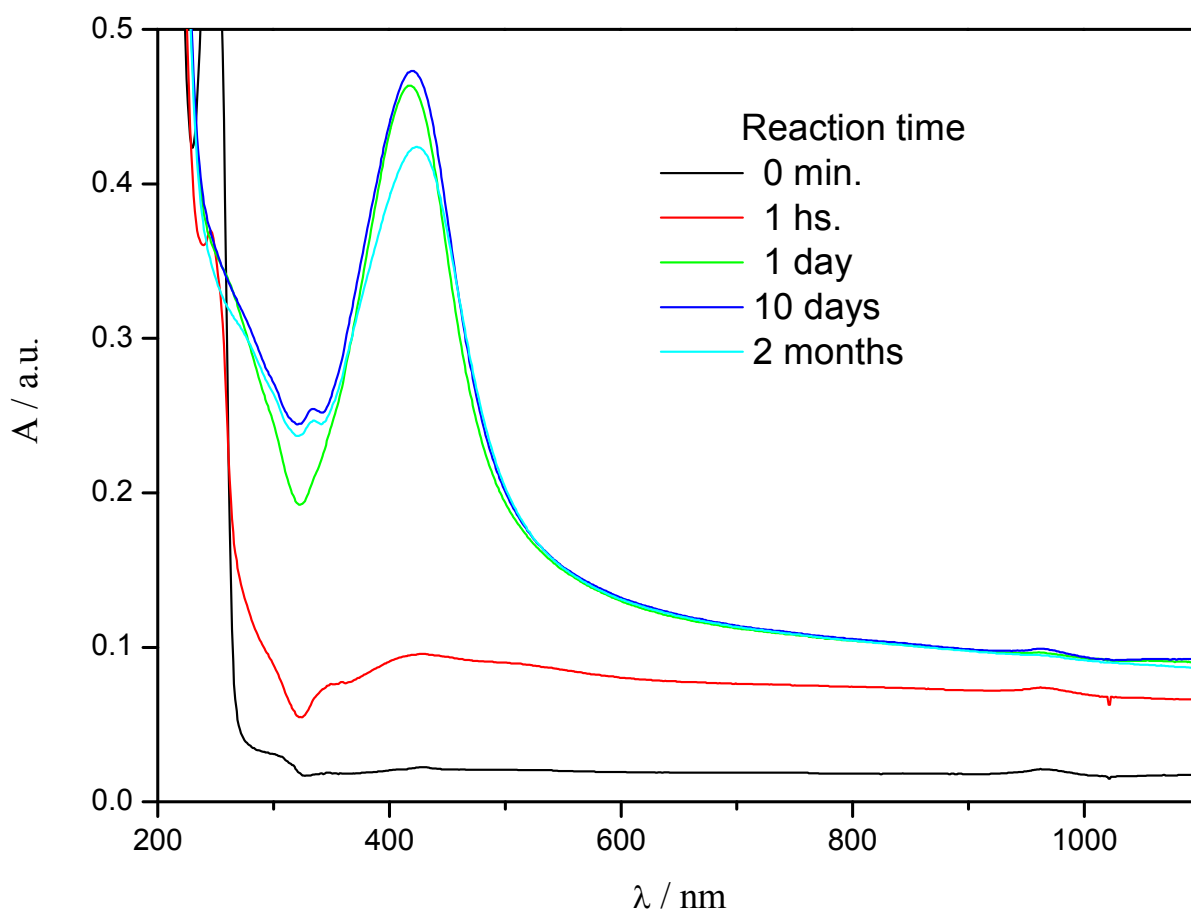
2) $100 \mu\text{M AgNO}_3 + 1 \mu\text{M NH}_4\text{Cl} + 1000 \mu\text{M NH}_3$, *P2*



SB2. SPR's spectra of NP's prepared with *P2* for increasing H_2Q concentration.

The rise of the number of small spherical NP's caused by the increase of H_2Q concentration is observed as an increase of the peak at around 400 nm, however a noticeable tail is observed for the highest concentration value. This last feature is a clear indication that the increase of H_2Q concentration does not always favour the formation of small spherical NP's, even for conditions under which the growth is quenched.

3) 100 μM AgNO_3 + 50 μM H_2Q + 1 μM NH_4Cl + 1000 μM NH_3 , *P2*



SB3. Evolution with the reaction time of the SPR's spectra of NP's prepared with *P2* for 100 μM AgNO_3 + 50 μM H_2Q + 1 μM NH_4Cl + 1000 μM NH_3 .

The changes of the SPR profile during the reaction indicates that NP's morphology is determined by a complex interplay between progressive nucleation and autocatalytic surface growth. At high concentration of H_2Q (50 mM), an uncontrolled growth is observed during the early stages of the reaction, as is evidenced by the SPR profiles extended in the whole visible range. The quenching effect of silver ammonia complex on the catalytic surface growth is limited under these conditions. As the reaction time elapses, the decrease of H_2Q concentration makes the quenching of the autocatalytic surface growth more important, leading again to an increase of the amount of small spherical NP's (evidenced by the SPR peak at around 400 nm).