

Supporting Informations

Ref	[HAuCl ₄] _{fixed} mM	V _{Au sol.} mL	V _{Citrate sol.} mL	t _{mix.} min	Reflux	Size
1	0.25	100	-	#	-	TEM
2	0.25	149	1	5	Yes	TEM
3	0.254	50	0.16-1	5-30	No	TEM
4	0.3	100	0.3-3	20-30	Yes	DLS
5	0.2	-	-	30	No	TEM, UV-Vis
6	0.25	199	1	15	Yes	TEM

Table 1. Experimental conditions for the different synthesis of AuNPs' considered for comparison in figure 1 and 7 of the present study. In all cases, the solution of citrate is added into the solution HAuCl₄ at 98 °C ± 2 °C without extra pH adjustment. The molar ratio X has been varied by playing on citrate concentration keeping a fixed gold concentration indicated in the table. We note “-“ when an information is not available.

In this article “The reaction was allowed to run until the solution reached a wine red color”.

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3. Frens, G. Controlled Nucleation for the Regulation of the Particle Size in Monodisperse Gold Suspensions, *Nature* **1973**, *241*, 20-22.
4. Zabetakis, K.; Ghann, W. E.; Kumar, S.; Daniel, M.-C. Effect of high gold salt concentrations on the size and polydispersity of gold nanoparticles prepared by an extended Turkevich-Frens method, *Gold Bull.* **2012**, *45*, 203-211.
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6. Wuihschick, M.; Birnbaum, A.; Witte, S.; Sztucki, M.; Vainio, U.; Pinna, N.; Rademann, K.; Emmerling, F.; Kraehnert, F.; Polte, J. *ACS Nano* **2015**, *9*, 7052-7071.

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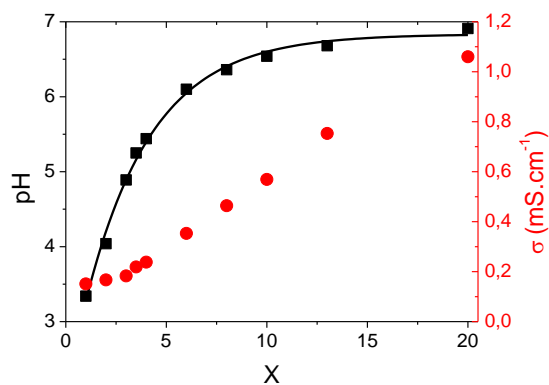


Figure 1. Evolution of pH (black square) and electrical conductivity (red disc) as a function of the molar ratio X for AuNPs prepared in this study by the ‘Inverse’ method. The black line is a fit of pH (X) with the following expression: $pH(X) = -4.8e^{-X/3.3} + 6.8$

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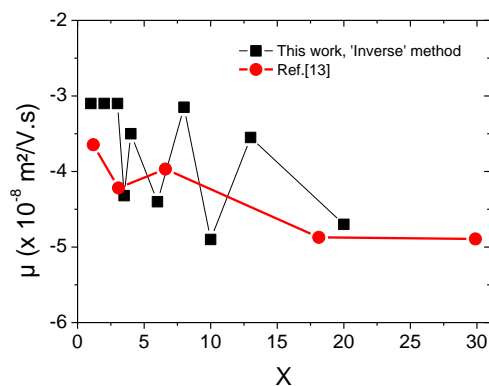


Figure 2. Evolution of the electrophoretic mobility (μ) as a function of the molar ratio X for AuNPs prepared in this study by the 'Inverse' method and for AuNPs prepared by Chow and Zukoski in [13].

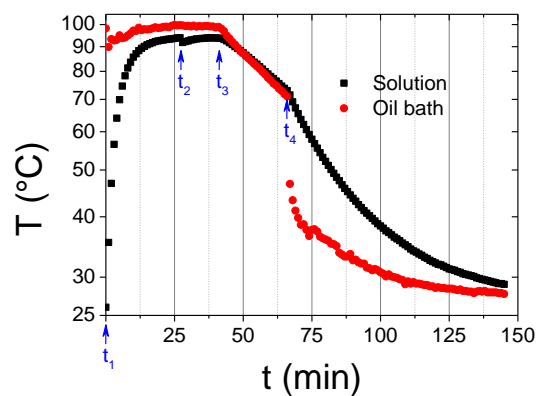


Figure 3. Time evolution of the oil bath' and solution' temperatures measured during a 'classical' synthesis. The different times indicated by blue arrows correspond to: $t_1 = 0$ min, the introduction of the flask containing the gold (III) solution inside the oil bath preheated at 96 °C; $t_2 = 27$ min, the injection of the citrate solution in the gold (III) solution; $t_3 = 42$ min, switch off stirring and heating; $t_4 = 66$ min, removal of the heating bath. Note that after t_4 , the temperature assigned to the oil bath is not correct because of partial immersion of the thermocouple in the oil bath due to movement of the bath at this time.

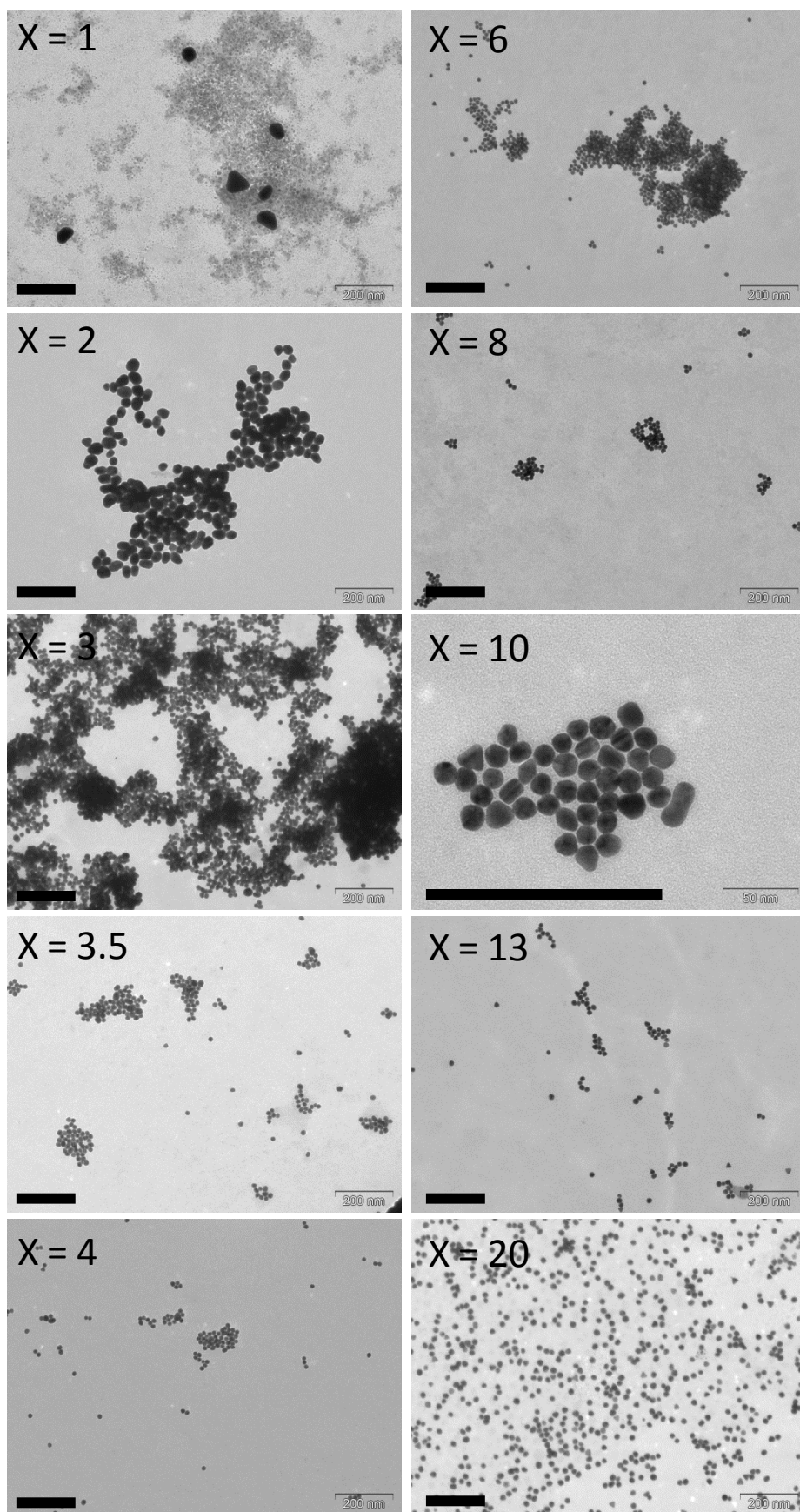


Figure 3. Typical TEM images of AuNPs prepared by the 'classical' method for different ratio X indicated on the images. All the black scale bars correspond to 200 nm.

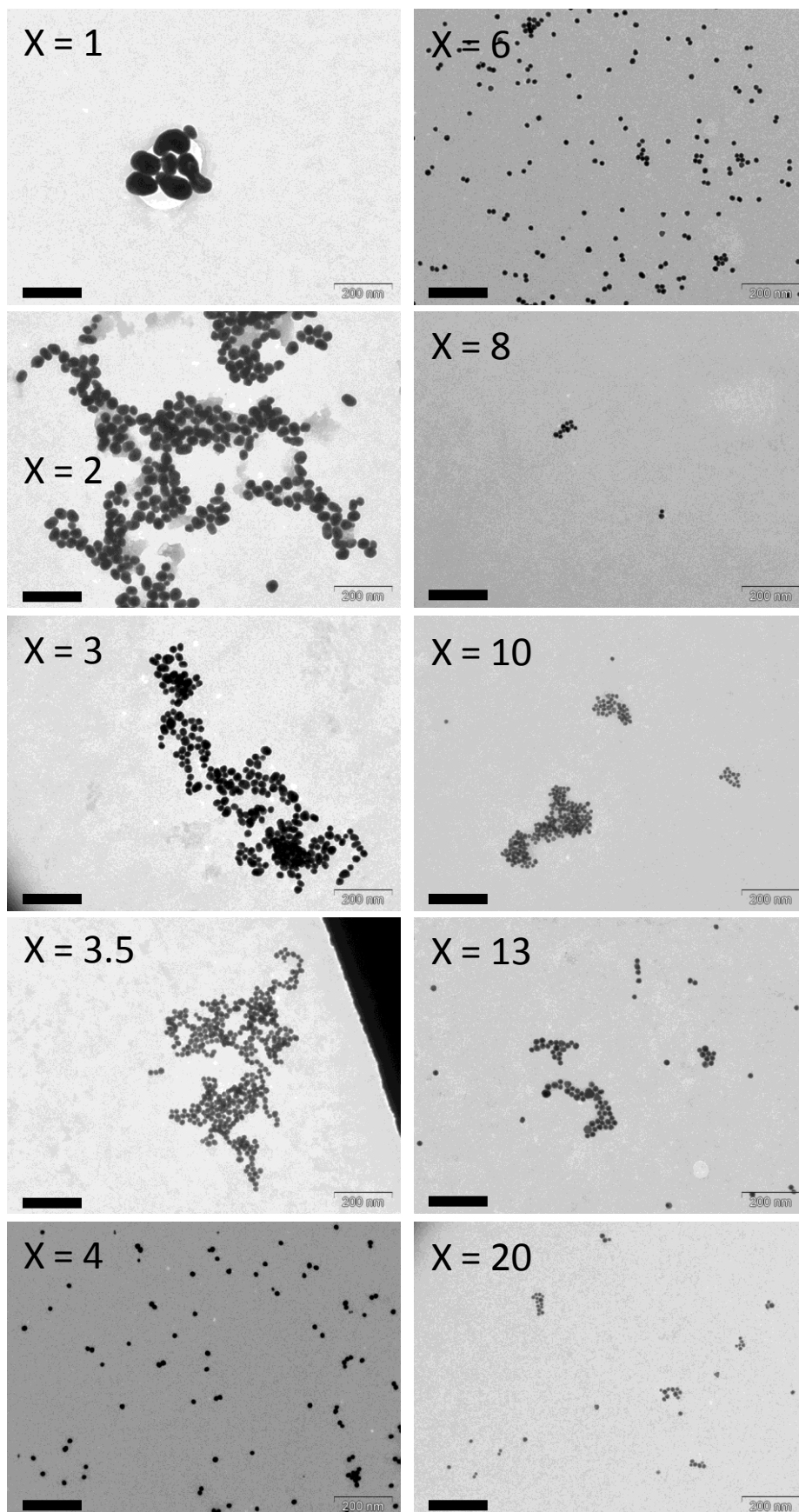


Figure 4. Typical TEM images of AuNPs prepared by the ‘inverse’ method for different ratio X indicated on the images. All the black scale bars correspond to 200 nm.