

Figure S1. (a, b) TEM images of 18 and 40 nm AuNPs respectively. (c, d) 18 and 40 nm AuNPs size distribution over at least 100 nanoparticles corresponding to the curve fit (Gaussian model) and values given are the center and the half-width of such curves. (e) absorption spectra; (f) DLS analyses. D_H : hydrodynamic diameter, PDI: polydispersity index.

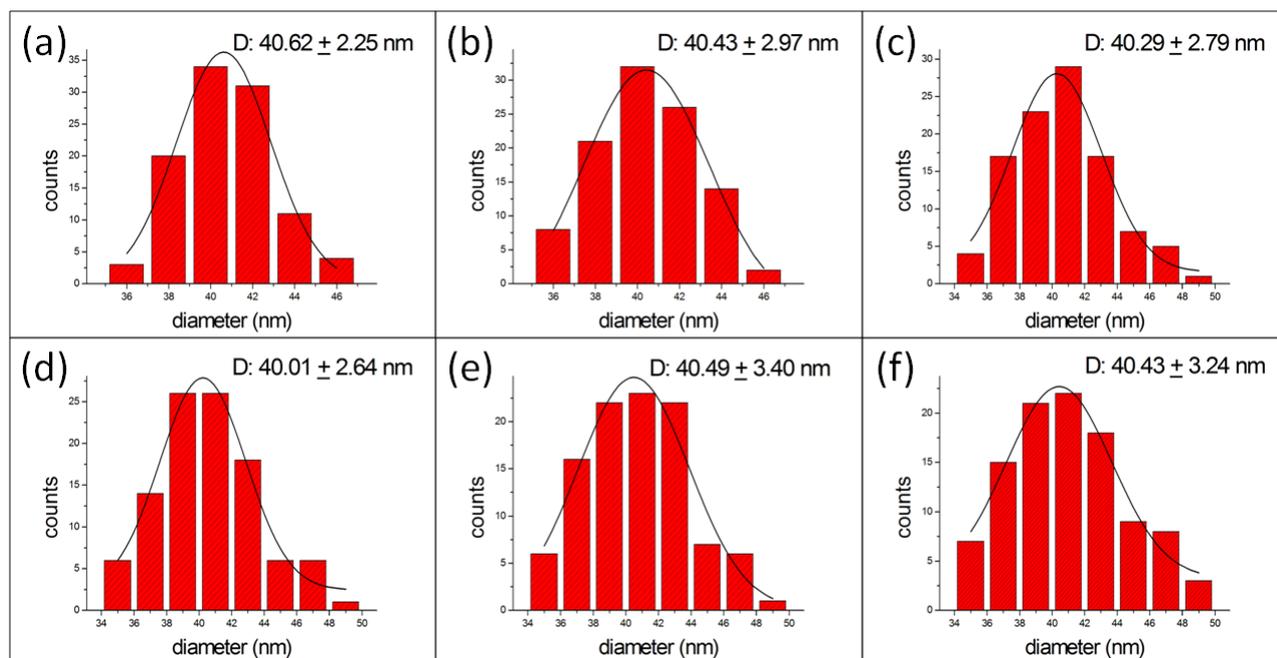


Figure S2. Size distribution analysis of 40 nm Au MBNPs synthesized at different HEPES concentration, namely 0 mM (a), 0.2 mM (b), 1 mM (c), 2.5 mM (d), 5 mM (e) and 25 mM (f). Resulting histograms were fitted using Gaussian distribution, mean diameter and half width coming from the Gaussian fits are reported. Statistical analysis of colloid diameter was evaluated from TEM imaging of more than one hundred nanoparticles.

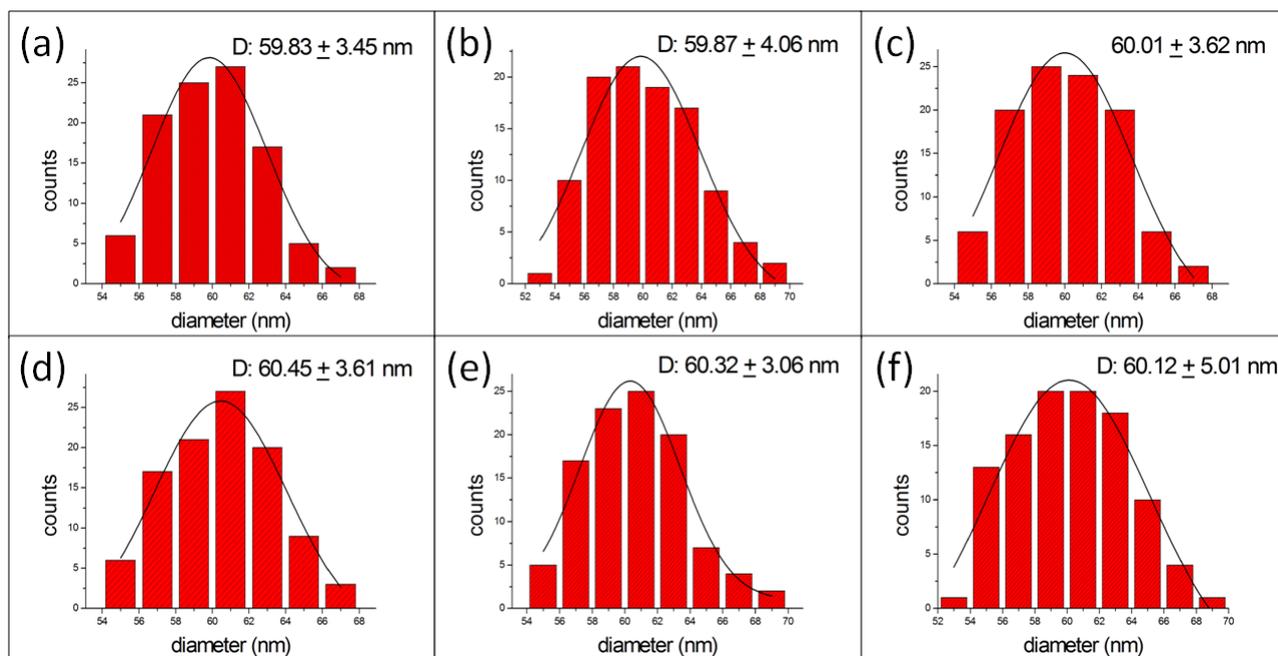


Figure S3. Size distribution analysis of 60 nm Au MBNPs synthesized at different HEPES concentration, namely 0 mM (a), 0.2 mM (b), 1 mM (c), 2.5 mM (d), 5 mM (e) and 25 mM (f). Resulting histograms were fitted using Gaussian distribution, mean diameter and half width coming from the Gaussian fits are reported. Statistical analysis of colloid diameter was evaluated from TEM imaging of more than one hundred nanoparticles.

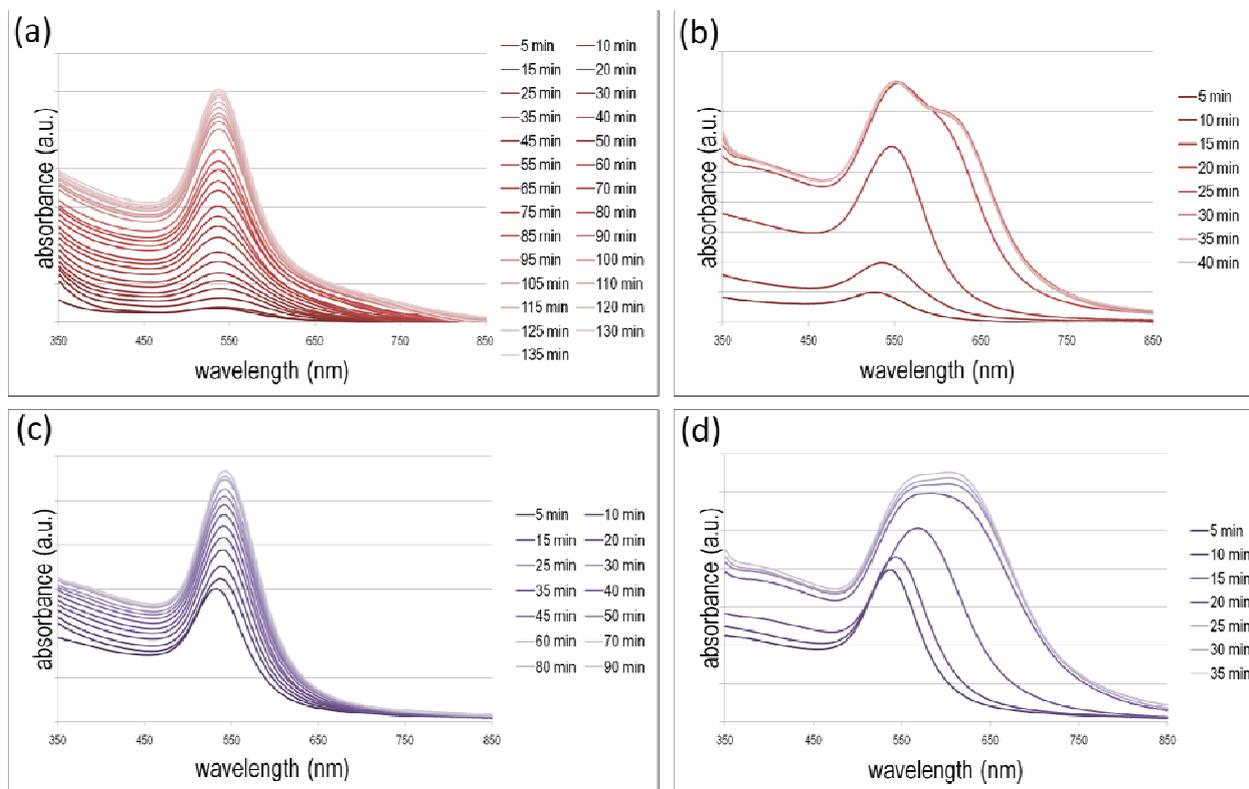


Figure S4. Time dependent evolution of synthesis carried out in absence of hydroxylamine in the reaction mixture (negative controls) by performing UV-Vis measurements every 5 minutes. (a,b) represent 18 nm Au seeds enlarged in 0.2 and 25 mM HEPES, respectively. (c,d) show 40 nm Au seeds growth in 0.2 and 25 mM HEPES.

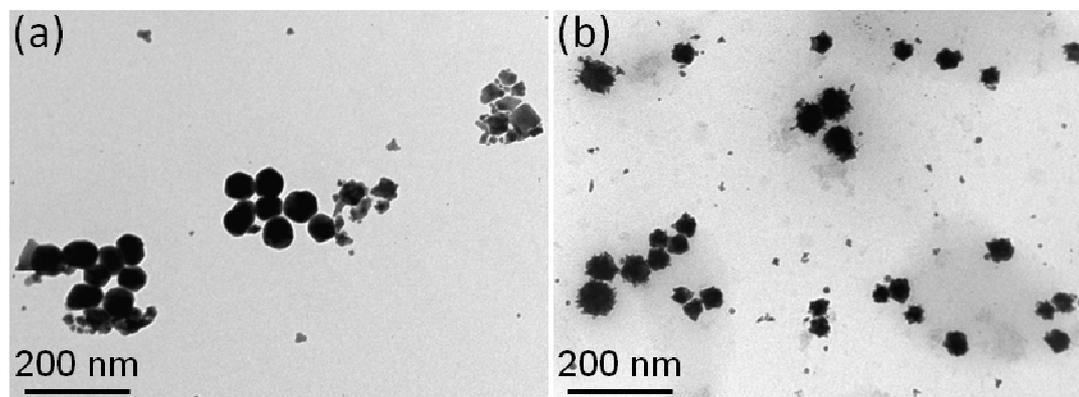


Figure S5. TEM images of 40 nm Au seeds growth without hydroxylamine in (a) 0.2 mM of HEPES and (b) 25 mM of HEPES (negative controls).

HEPES concentration	Molar extinction coefficient @633 nm $\times 10^9$ ($M^{-1}cm^{-1}$)
0	4.07
0.2	7.14
1	18.15
2.5	21.93
5	22.02
25	21.21

Table S1. Molar extinction coefficient values for 60 nm AuMBNPs measured at 633 nm, namely the wavelength of the laser source employed in SERS experiments.