Supporting Information

From silver plates to spherical nanoparticles: snapshots of microwave-assisted polyol synthesis

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Figure S1. Selected area electron diffraction (SAED) patterns confirming the face-centered cubic metallic silver as the sole crystalline phase. Representative SAED images for all the samples synthetized in this work. **a)** electron diffraction pattern of a single silver platelet. Diffraction spots indicate that the platelet is a single crystal with the $[\bar{1}\,11]$ zone axis. **b)** electron diffraction pattern of silver nanospheres. The rings corresponding to the random orientated NPs were used for the planes indexation. Notice that some rings can be observed in **a)**, coming from some Ag NPs surrounding the single silver platelet.

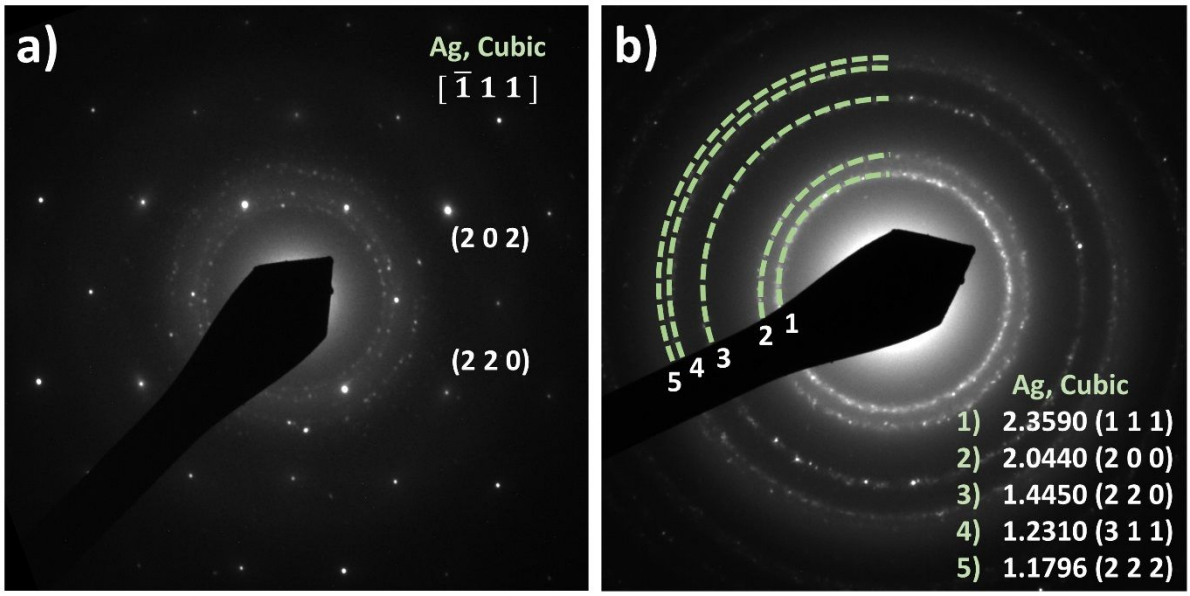

Figure S2. Controlling particle size and tuning Ag NPs on-demand using cross experiments. **a)** representative TEM image of a trial prepared with the synthetic conditions fixed to 20 min, 130 ^{o}C and 20 mM of AgNO3 to obtain larger monodispersed Ag NPs. Standard sample (10 min, 120 ^{o}C and 1 mM of $AgNO_3$) is also showed for comparison in **b)**. **c)** UV-Vis of the above samples.

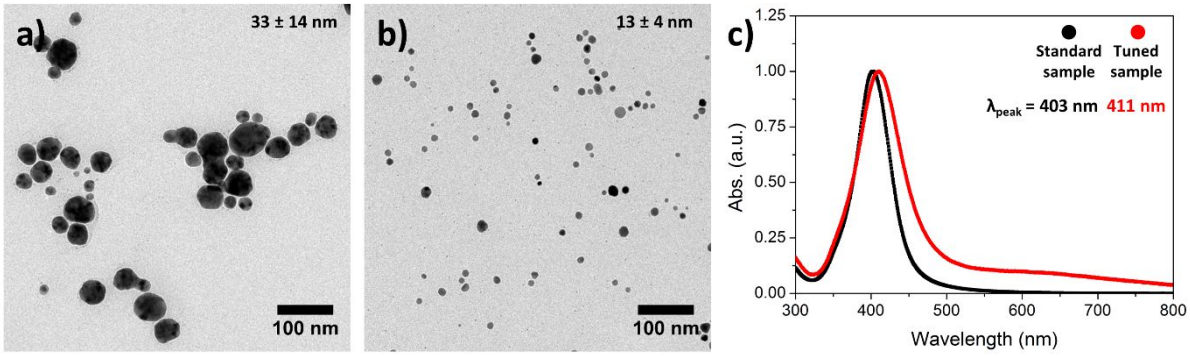

Figure S3. Scalability of the Ag NPs synthetic protocol. **a-b)** representative TEM images of a sample scaled-up four-fold prepared with the different MW-reactors (CEM Discover reactor –Explorer 12-Hybrid– at a frequency of 2.45 GHz and 300W of power [x4.CEM MW-reactor] and Microwave Advanced Flexible Synthesis Platform –flexiwave– from Milestone at a frequency of 2.45 GHz and 500W of power [x4.flexiwave MW-reactor]). Standard sample (10 min, 120 ^{o}C and 1 mM of $AgNO_3$ not scale-up and with CEM MW-reactor) is also showed for comparison **c)**. **d)** UV-Vis measurements of the above samples.

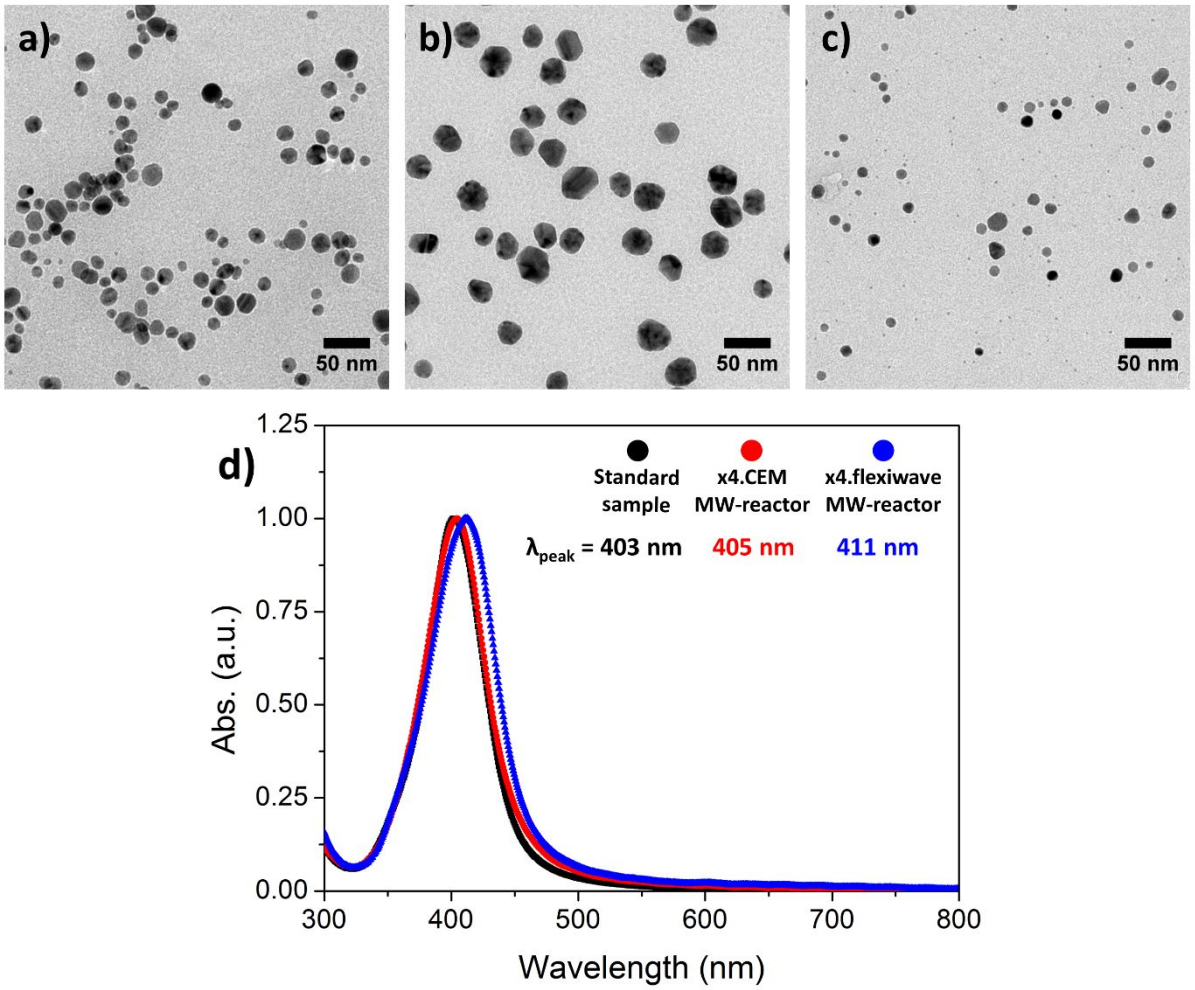

Figure S4. PVP-capped Ag NPs stability in water. **a)** digital images of the samples corresponding to their colloidal stability in solution along time (initial preparation, 2 weeks, 4 weeks and 9 months after). Aggregates or precipitates were not observed. **b-g)** TEM and HRTEM images corresponding to their shape time-stability in water. **b-d)** correspond to platelets obtained for t=10 s of reaction, while **e-g)** to nanoparticles obtained for t=10 min of reaction. The last sample is used as the standard sample referred along the text. **b,e)** were studied after the synthesis while images **c,f)** nine months after. **d,g)** HRTEM images corresponding to the white square insets of **c,f)**, respectively. Crystalline silver is clearly observed. Moreover, corresponding energy-dispersive X-ray spectroscopy (EDXS) only show silver without oxidation (data not included).

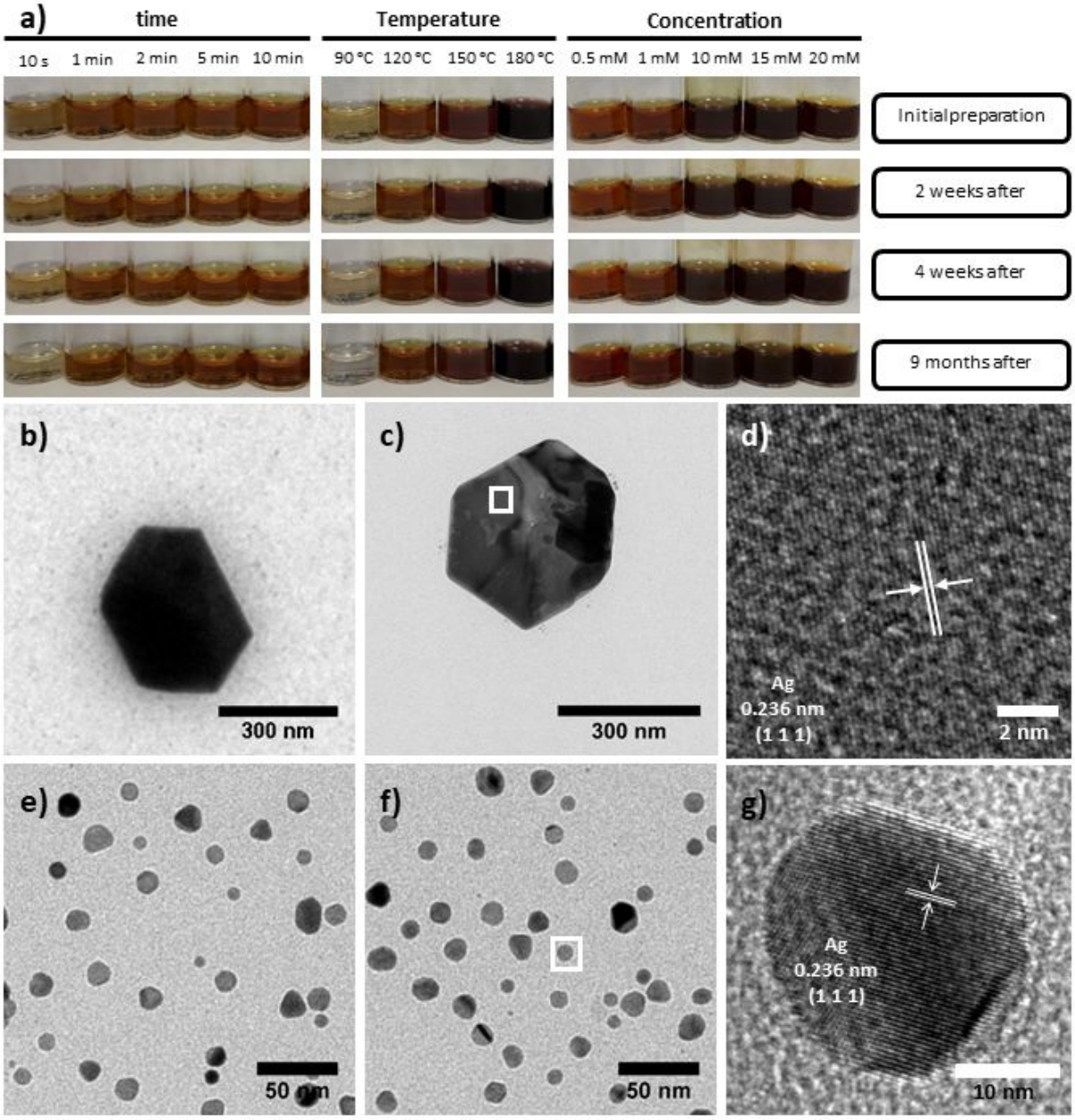

Figure S5. PVP aging effect on the Ag NPs synthesis. **a-c)** representative TEM images of different samples prepared with fresh PVP (i.e., used once it was received). **d-f)** representative TEM images of the same samples, but prepared with older PVP (i.e., used after 4 months of being opened and used for the first time). Images **a)** and **d)** correspond to the reaction time effect sample of 10 s, images **b)** and **e)** to the reaction temperature effect sample of 90 ºC, and images **c)** and **f)** to the standard sample (10 min, 120 ºC and 1 mM of $AgNO_3$).