

Electronic Supplementary Information

Synthesis of Ultrasmall Metal Nanoparticles and Continuous Shells at the Liquid/Liquid Interface in Ouzo Emulsions

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Table of Contents

Table of Contents	2
Experimental Procedures	3
Materials	3
One-pot <i>in situ</i> synthesis of metal nanoparticle-shells	3
<i>Ex situ</i> synthesis of metal NP-shells	3
X-ray diffraction (XRD)	3
Transmission electron microscopy (TEM)	3
Nanoparticle tracking analysis (NTA)	3
DLS and Zeta potential	3
Results and Discussion	4
References	12
Author Contributions	12

Experimental Procedures

Materials

Chloro(triphenylphosphine)gold(I) (Au(PPh₃)Cl) was purchased from Strem Chemicals (reference number 79-1000). Sodium borohydride (NaBH₄), bis(triphenylphosphine)palladium(II) (Pd(PPh₃)₂Cl₂), poly(vinylphosphonic acid) (PVPA) and poly(allylamine hydrochloride) (PAA HCl) were all purchased from Sigma-Aldrich (reference numbers 452882, 208671, 661740 and 733644). Tetrahydrofuran stabilized with ~320 ppm butylated hydroxytoluene (BHT) was purchased from VWR Chemicals (reference number 28552). All chemicals were of reagent grade and were used as received without further purification.

One-pot *in situ* synthesis of metal nanoparticle-shells

In a typical preparation, 0.75 mL of a 10 mM NaBH₄ aqueous solution was quickly added to 0.25 mL of 1.5 mM Au(PPh₃)Cl in THF solution to initiate nanoparticles (NPs) synthesis at the interface of the two immiscible liquids, as described by Rao et al.¹ After 1 min, 50 μ L of a 4.4 mg/mL PAA HCl (in water) was added to the system in order to stabilize the nanoparticle-shells (NP-shells). For the synthesis of hybrid Au-Pd shells, an equimolar ratio of Au(PPh₃)Cl and Pd(PPh₃)₂Cl₂ was used to prepare a 1.5 mM metallic precursors stock solution.

Ex situ synthesis of metal NP-shells

In a typical *ex situ* preparation, 0.75 mL of a 10 mM NaBH₄ in THF solution was rapidly added to 0.25 mL of a 1.5 mM Au(PPh₃)Cl in THF solution to form AuNPs in suspension in THF. Then, 0.75 mL of water was rapidly added to 0.25 mL of the NPs/THF suspension. Finally, after 1 min, 50 μ L of a 4.4 mg/mL PVPA aqueous solution was added.

X-ray diffraction (XRD)

XRD experiments were achieved with a Bruker D8 Advance diffractometer working with a monochromatized Cu K α 1 radiation (1.5406 Å) at 40 kV and 40 mA. Scans from 10° to 120° over 6 h with a rotation speed of 30 rpm were performed for samples dried on a monocrystalline silicon wafer. Crystallite size was obtained with the Scherrer formula (Equation S1), preferably by selecting a high intensity peak.

Transmission electron microscopy (TEM)

Copper grids coated with a carbon film were used to deposit a 5 μ L drop of the metal NP-shells suspension, sampled at specific times (typically 1 min or 30 min) after the beginning of the synthesis. Observations were performed with a JEOL JEM 2100 HR TEM operated at 200 kV with a sample holder composed of Cr, Fe and Au. Images were captured with a Gatan Orius SC200D and a Gatan Ultra Scan 1000XP for high resolution transmission electron microscopy (HRTEM). Energy-dispersive X-ray spectroscopy (EDX) spectra were acquired with an Oxford X-Max 80T detector using a 5 nm spot. Selected area electron diffraction (SAED) micrographs were obtained with the acquisition of 10 images.

Nanoparticle tracking analysis (NTA)

NTA was carried out with a Nanosight LM10 device system (Malvern Panalytical) equipped with a 40 mW laser working at a wavelength of 638 nm. Video sequences were recorded via a CCD camera operating at 30 frames per second and evaluated via the NANOSIGHT NTA 2.0 Analytical Software Suite. NTA is a technique monitoring the movement of a diffraction spot caused by the illumination of a dispersion of nano-objects with a laser. These spots are individually followed, making this technique well suited for highly polydispersed suspensions as compared to dynamic light scattering (DLS), and particulate size is then determined from the Brownian motion. However, this analysis is limited to a maximum size of 1 μ m for practical purposes: larger particles often exhibit asymmetrical scattering (increasing errors to detect movement) and motion of bigger particles is reduced (limited Brownian motion). Measurements were carried out in triplicate (standard deviation represented in the histogram in grey) at 25°C with samples diluted 10 times.

DLS and Zeta potential

Dynamic light scattering (DLS) was carried out on a Vasco Kin (Cordouan) with a laser working at a wavelength of 638 nm. Zeta potential characterization was carried out with a Zetasizer Nano ZS from Malvern Panalytical with a laser working at an excitation of 631 nm and a ZEN1002 dip cell thermostated at 25°C.

Results and Discussion

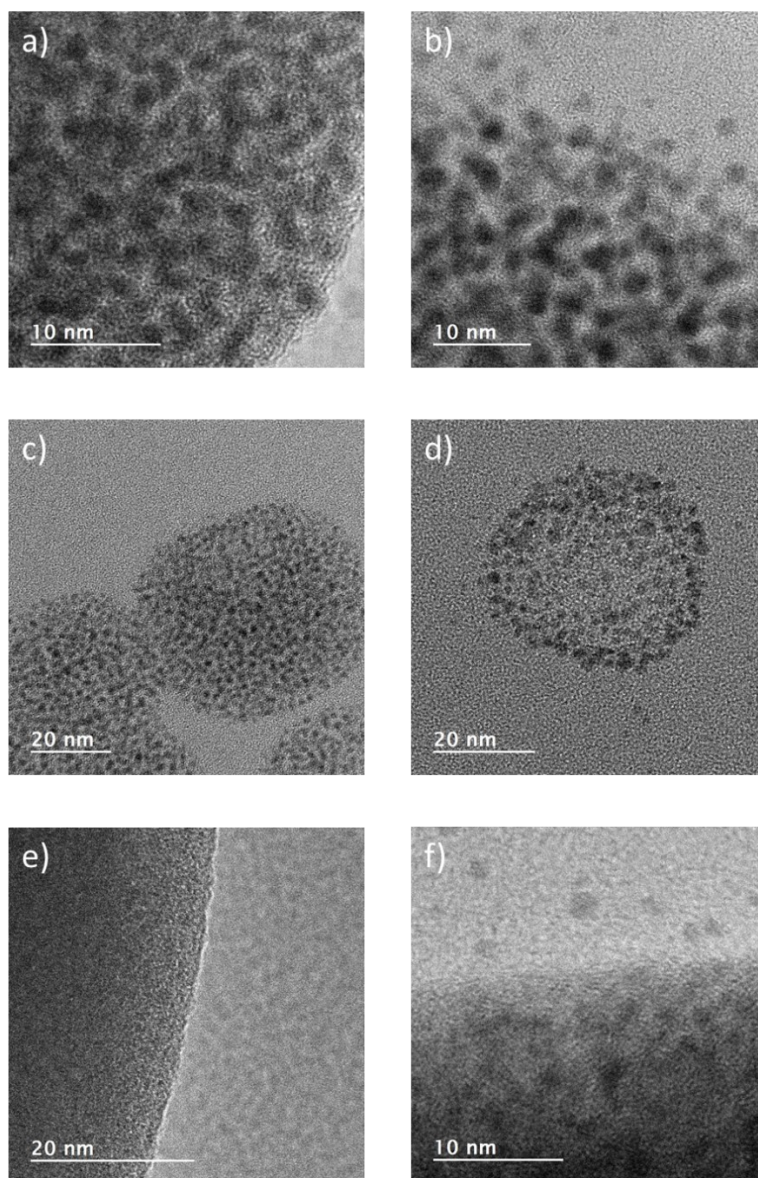


Figure S1. HRTEM micrographs of the following samples: typical *in situ* synthesis of AuNPs after a reaction time of a) 1 min and b) 30 min; c) with the addition of 50 μ L of 4.4 mg/mL PAA HCl. d) *ex situ* synthesized AuNPs at the surface of a droplet, combined with the addition of 50 μ L of 4.4 mg/mL PVPA; e) *in situ* synthesized Pd continuous shells and; f) Au-Pd (equimolar amounts) NP-shells.

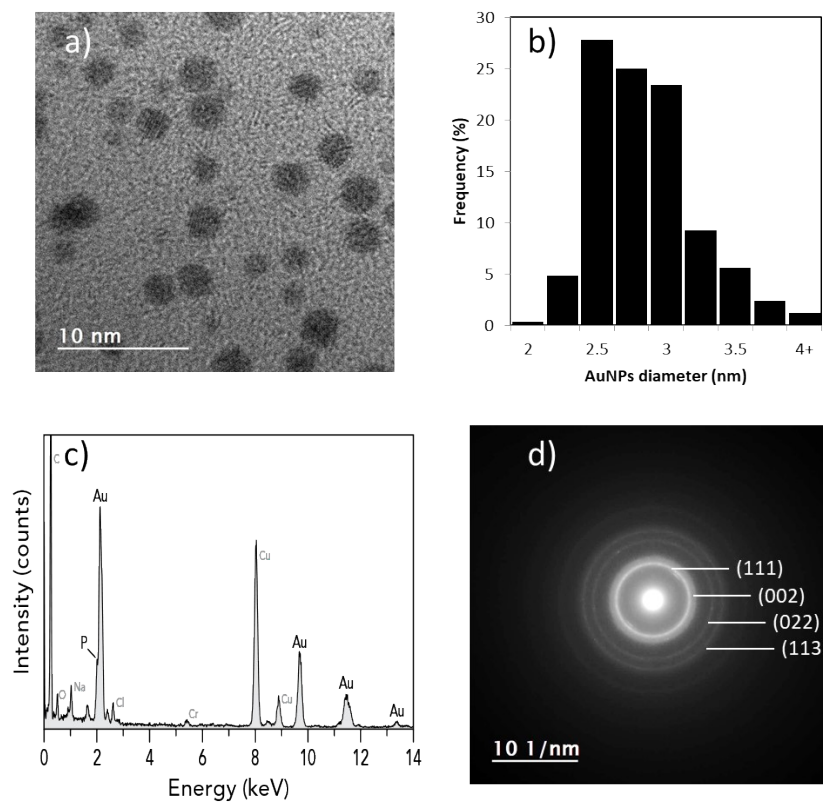


Figure S2. a) HRTEM micrograph of AuNPs synthesized *in situ* and sampled after 30 min; b) associated size distribution of AuNPs; c) EDX spectrum of AuNPs (peaks identified in black are associated to AuNPs); d) SAED characterization with the corresponding Au crystal planes. Note that the phosphorus (P) originating from the triphenylphosphine ligands is associated to gold (no phosphorous is detected when no gold is present – results not shown).

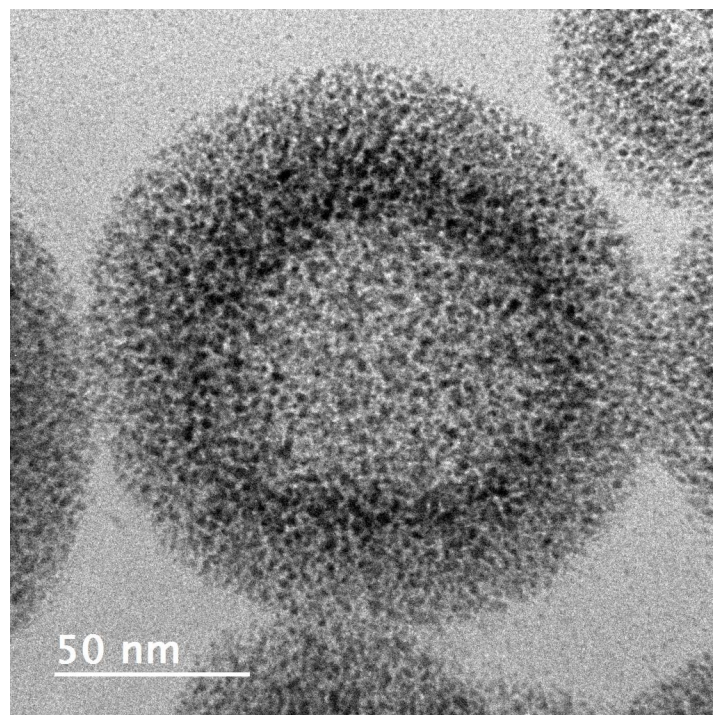


Figure S3. HRTEM micrograph of AuNPs-shell sampled 30 min after synthesis displaying the hollowness of the structure.

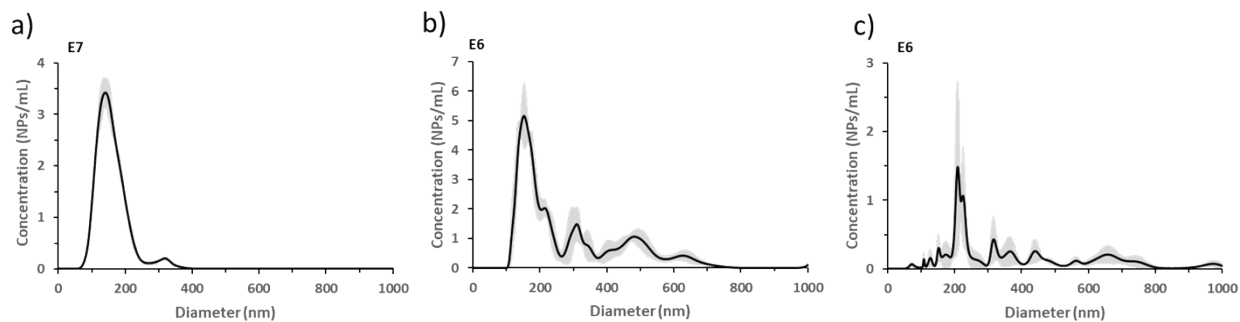


Figure S4. Evolution in time of the AuNP-shells size distribution for an *in situ* synthesis. Reaction times of: a) 1 min; b) 30 min; and c) 2 h. The black curve corresponds to the average of three samples, and the thickness of the grey area to the standard deviation.

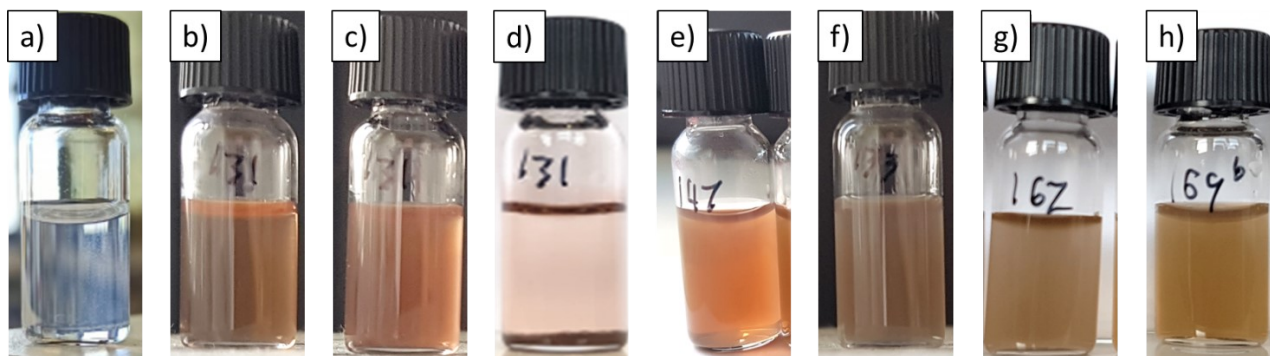


Figure S5. Ouzo emulsions with the following synthesis conditions: a) mixing of 0.75 mL water with 0.25 mL of THF after 1 day; b) mixing of 0.75 mL of a 10 mM NaBH_4 solution and 0.25 mL of 1.5 mM $\text{Au}(\text{PPh}_3)\text{Cl}$ in THF after a reaction time of 1 min; c) idem after a reaction time of 30 min; and d) after 1 day; e) with the addition of 50 μL of a 4.4 mg/mL PAA HCl aqueous solution at the beginning of the reaction; f) same synthesis conditions as in (c), with $\text{Pd}(\text{PPh}_3)_2\text{Cl}_2$ as the precursor; g) synthesis with 0.75 mL of a 10 mM NaBH_4 solution and 0.25 mL of 0.75 mM $\text{Au}(\text{PPh}_3)\text{Cl}$ and 0.75 mM $\text{Pd}(\text{PPh}_3)_2\text{Cl}_2$ in THF after 30 min; and h) with the addition of 50 μL of 4.4 mg/mL PAA HCl aqueous solution, 30 min after the beginning of the reaction.

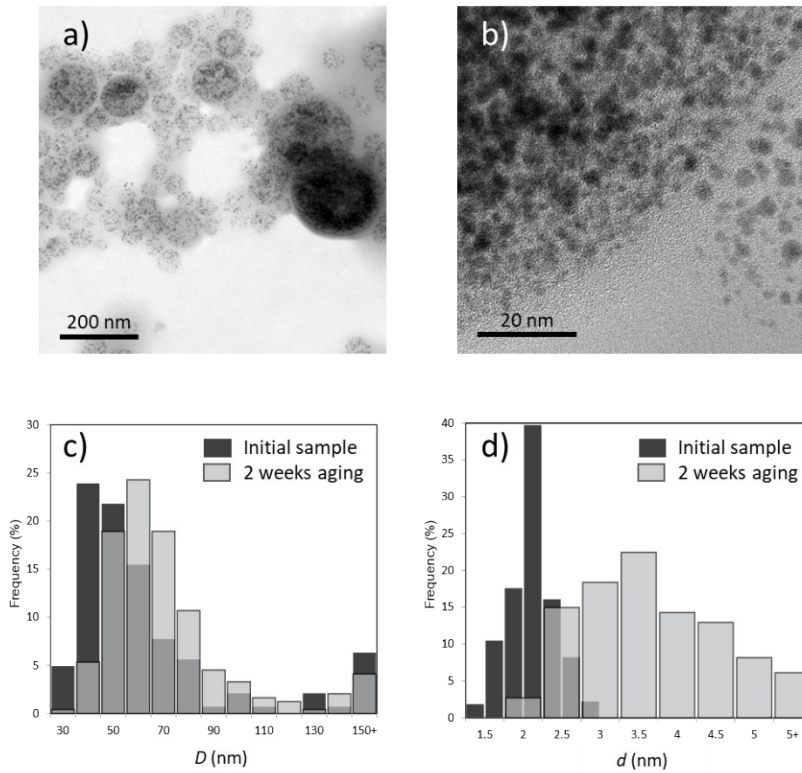


Figure S6. TEM micrographs of AuNPs shells after 2 weeks, stabilized with PAA HCl (sample after 1 min of reaction time is displayed in Figure 2a): a) NP-shells and b) high resolution micrographs showing the individual AuNPs forming a shell. Note that the individual nanoparticles form a less compact structure, while the shells are overall less homogeneous, compared to the freshly prepared sample (1 min reaction time). NP-shells size distributions obtained by statistical analysis of TEM micrographs with ImageJ, comparing the freshly prepared sample (1 min reaction time), and the same sample after 2 weeks of aging: c) diameter of the NP-shells (D) and d) diameter of the individual AuNPs (d).

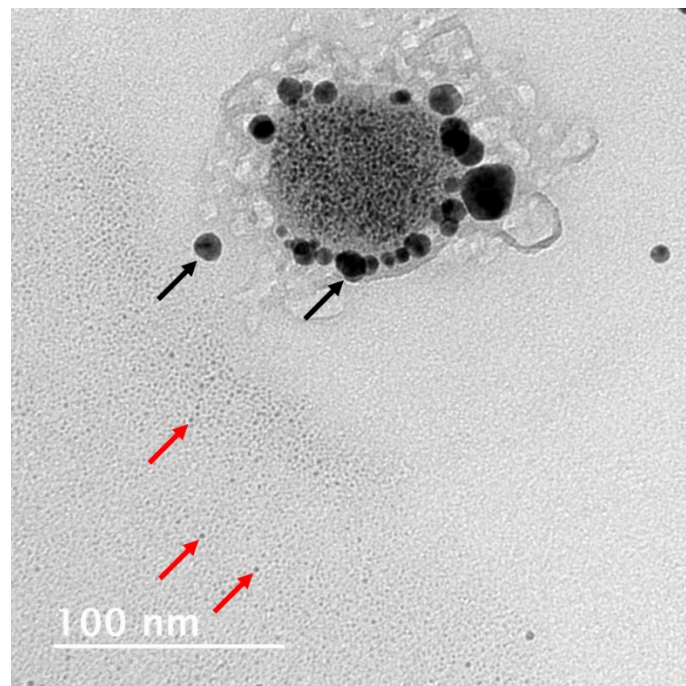


Figure S7. TEM micrograph of *ex situ* synthesized AuNPs combined with 50 μ L of 4.4 mg/mL PAA HCl solution. Note the presence of larger particles (black arrows) as compared to the pristine particles (red arrows), indicating that this polymer (PAA HCl) seems inadequate for this synthesis.

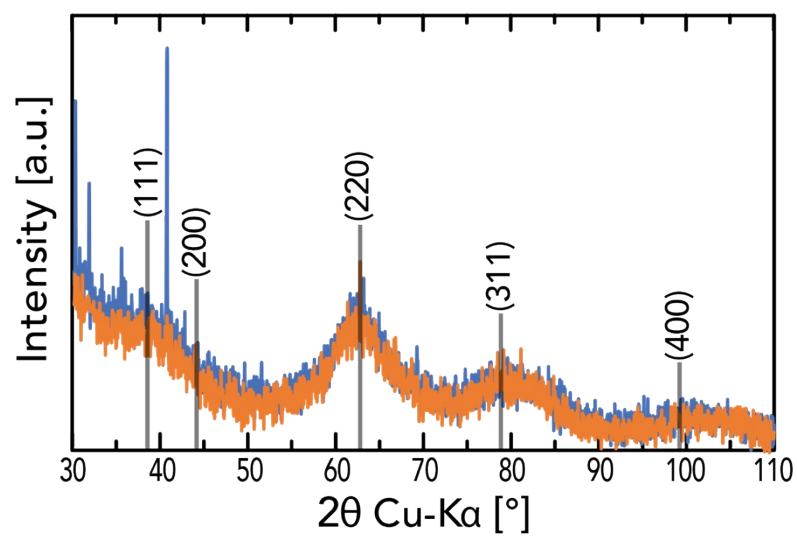


Figure S8. XRD characterization of AuNPs synthesized *in situ* (blue) and *ex situ* (orange) with highlighted peaks related to the crystalline structure of gold (face centered cubic).

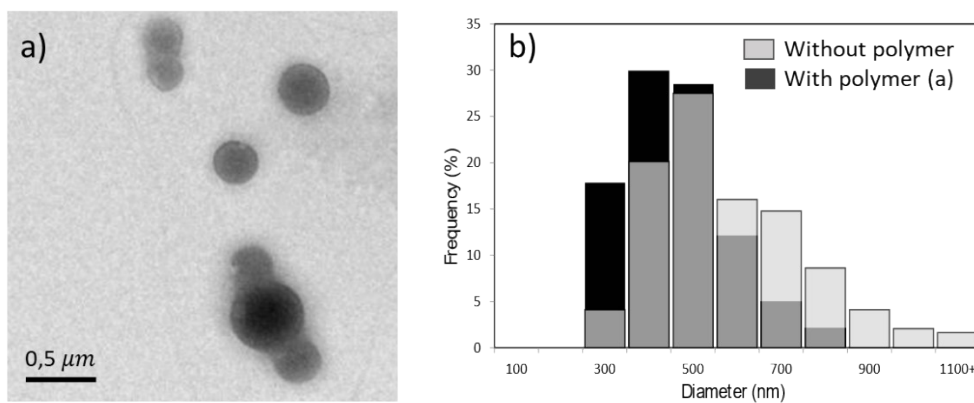


Figure S9. a) TEM micrograph of Pd shells synthesized *in situ* with the addition of 50 μL of 4.4 mg/mL PVPA. b) Histogram of Pd shells synthesized *in situ* with and without the addition of PVPA after 1 min reaction time. The stabilizing effect of the polymer on the distribution is noteworthy.

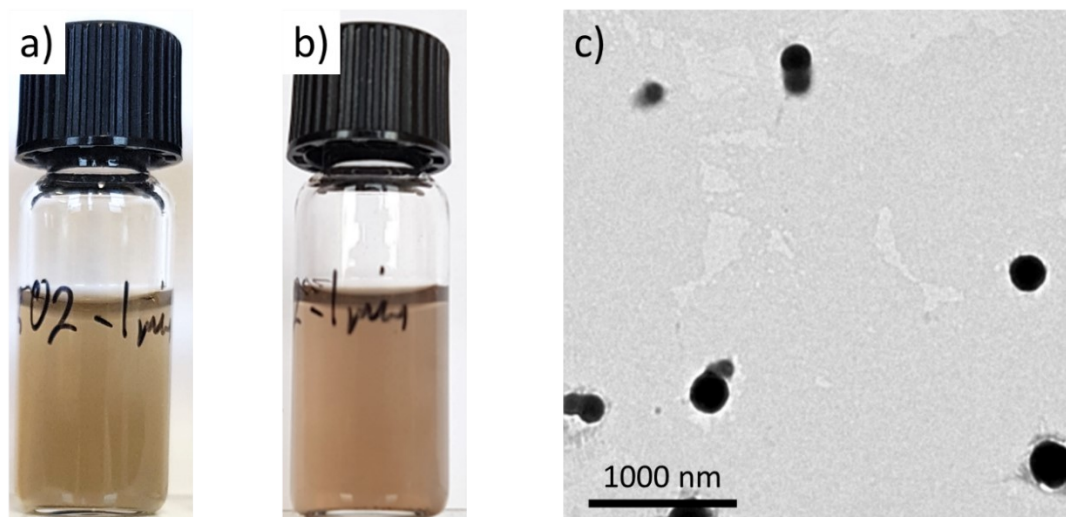


Figure S10. Ouzo emulsions with the following synthesis conditions: mixing of 0.75 mL of a 10 mM NaBH_4 solution and 0.25 mL of 0.5 mM $\text{Pd}(\text{PPh}_3)_2\text{Cl}_2$ in THF after a reaction time of after aging for 1 day (a) and 1 month (b), alongside TEM micrograph of 1 month (c). The objects display stability over time.

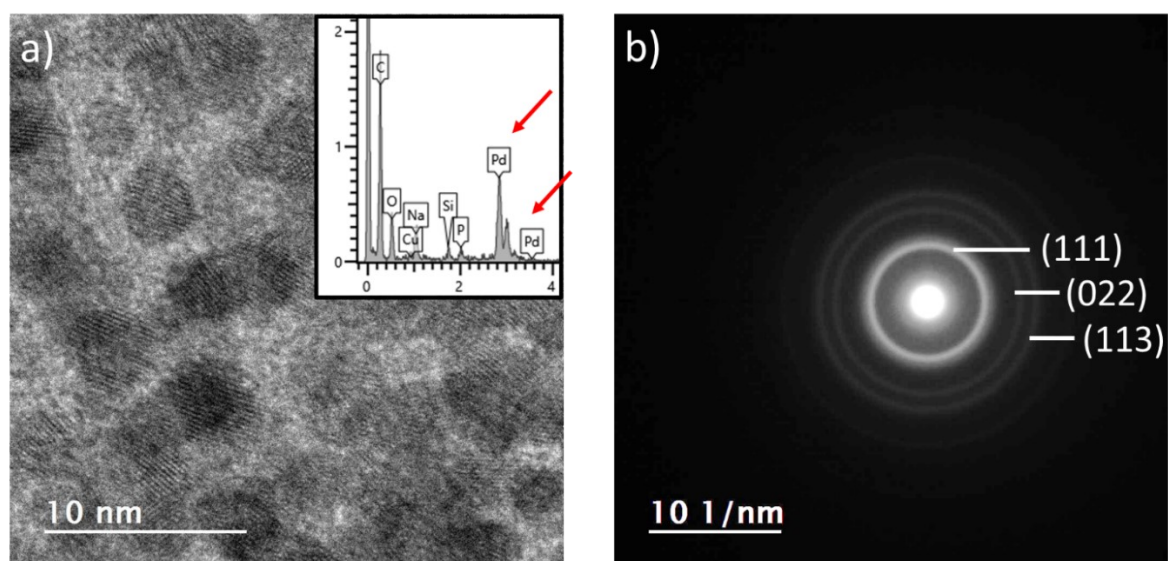


Figure S11. a) HRTEM micrograph of PdNPs synthesized *ex situ* alongside its EDX spectrum in inset, with Pd peaks indicated with red arrows. b) SAED characterization of PdNPs synthesized *ex situ* with the corresponding Pd crystal planes.

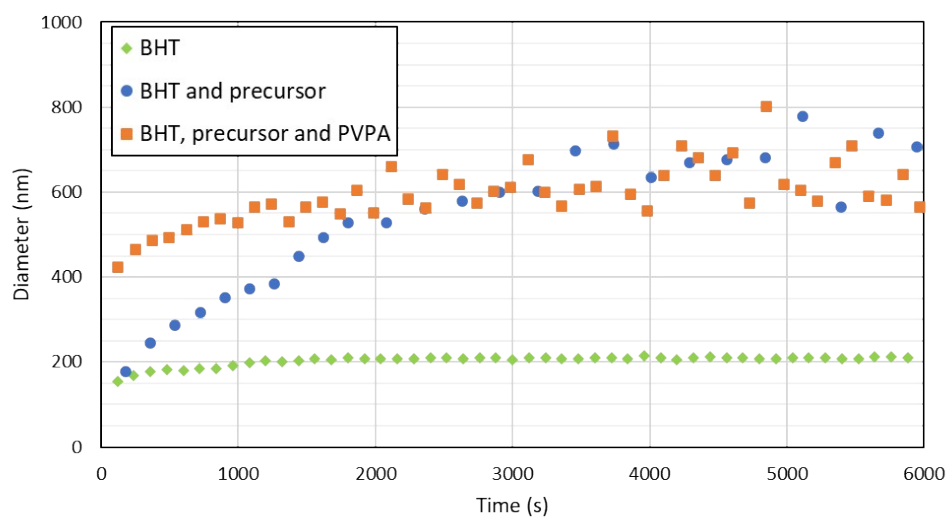


Figure S12. Evolution in time of the BHT rich droplets (average size) as measured by DLS, for an Ouzo emulsion composed of 0.25 mL of 320 ppm BHT in THF and 0.75 mL water, with further addition of 1.5 mM AuPPh₃Cl (precursor) and 50 μ L of 4.4 mg/mL PVPA (respectively in green diamonds, blue circles, and orange squares).

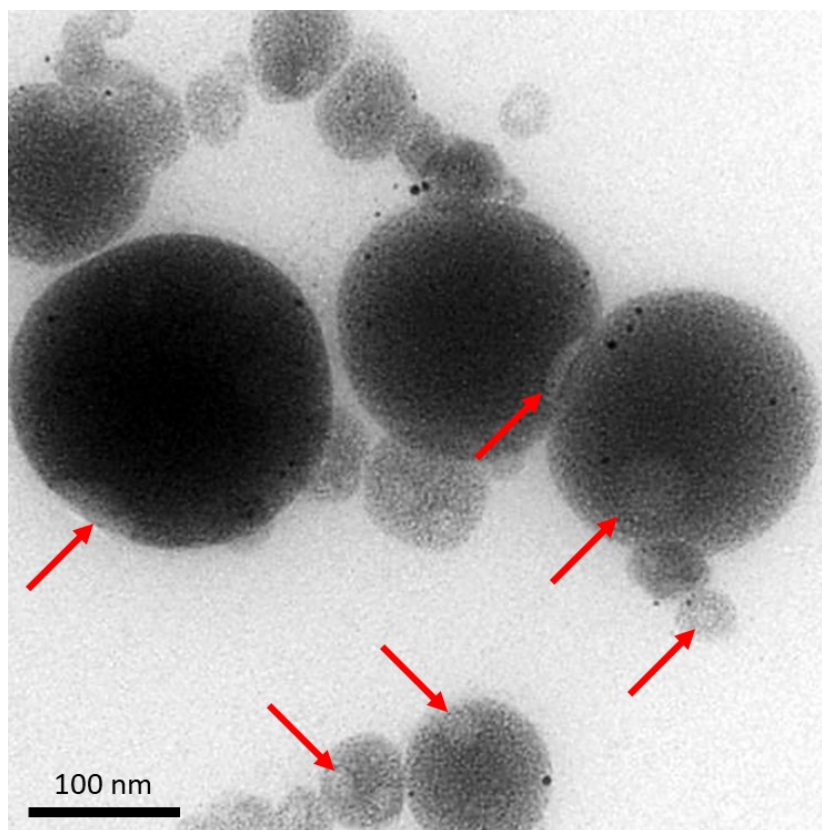


Figure S13. TEM micrograph of AuNPs synthesized *in situ* combined with 50 μ L of 4.4 mg/mL PAA HCl solution. Note the presence of a paler circular area on all NP-shells, some of which are indicated with red arrows.

Table S1. Average diameters measured from TEM, of NP-shells (D) and individual NPs (d) as functions of synthesis conditions.

Synthesis	Metal precursor	Concentration (mM)	Sampling time	Polymer	D (nm)	d (nm)
<i>in situ</i>	Au	1.5	1 min	-	160 ± 80	2.7 ± 0.3
	Au	1.5	30 min	-	800 ± 400	2.7 ± 0.6
	Au	1.5	30 min	PAA HCl	50 ± 20	2.8 ± 0.3
	Au	1.5	2 weeks	PAA HCl	70 ± 20	3.4 ± 0.8
	Pd	1.5	30 min	-	500 ± 200	-
	Pd	1.5	30 min	PVPA	410 ± 90	-
	Pd	0.5	30 min	-	180 ± 30	-
	Pd	0.5	1 month	-	200 ± 30	-
	Au + Pd	1.5	30 min	-	800 ± 200	-
	Au + Pd	1.5	30 min	PAA HCl	200 ± 40	-
<i>ex situ</i>	Au	1.5	30 min	-	-	2.9 ± 0.6
	Au	1.5	30 min	PVPA	100 ± 40	2.7 ± 0.4

Equation S1. Theoretical coverage of AuNP-shells.

$$coverage = \frac{m * PF}{\frac{4}{6} * \rho * d} / \sum \left[4\pi * \left(\frac{D}{2} \right)^2 \right]$$

where m is the absolute mass of gold for a chosen volume (μg), PF is the packing fraction, ρ is the density of gold ($\mu\text{g}/\text{nm}^3$), d is the average diameter of the AuNPs (nm), and D is the diameter of the droplets (nm). The coverage has a value of 1 if the sum of the surface area of all the droplets is equal to the cross-sections (including packing fraction) of all the nanoparticles. If the coverage is inferior to one, it means that the surface of the droplets is not entirely covered with NPs and vice-versa if it is superior to 1. The following hypotheses need to be taken into account: the mass corresponds to the starting precursor, as reaction is complete; the droplets size distribution corresponds to the hydrodynamic diameter; and packing is considered to be the most efficient 2D packing, which is hexagonal packing (~0.91). Results are shown in the table below.

Sample	m (μg)	ρ ($\mu\text{g}/\text{nm}^3$)	PF	d (nm)	$\sum \left[4\pi * \left(\frac{D}{2} \right)^2 \right]$	Coverage
<i>in situ</i> Au – 1 min	73.86	$1.93 * 10^{-14}$	0.9069	2.7	$2.74 * 10^{15}$	0.8
<i>in situ</i> Au – 30 min	73.86	$1.93 * 10^{-14}$	0.9069	2.7	$2.25 * 10^{15}$	1.0

Equation S2. Apparent density equation of droplets covered with a single layer of nanoparticles.

$$\rho_{app} = \frac{4D^2 / [PF * d^2] * d^3 * \rho_{Au} + D^3 * \rho_{drop}}{d^3 + D^3} * 10^{27}$$

where ρ_{app} is the apparent density of the droplet (g/mL), PF is the packing fraction (the most efficient packing being equals to ~0.91), d is the average diameter of the AuNPs (nm), D is the diameter of the droplets (nm), ρ_{Au} is the density of gold (g/mL), ρ_{drop} is the density of the droplet (g/mL).

Equation S3. Scherrer equation for the determination of crystallite size by X-ray diffraction.

$$\tau = \frac{K\lambda}{\beta \cos\theta}$$

where τ is the average crystal domain size (nm), K is the shape factor (with a typical value of 0.9 when considering spherical crystallites), λ is the X-ray wavelength (nm), θ is the Bragg angle (radian) and β is the full width at half maximum (FWHM), minus the peak broadening caused by the instrument (radian).

References

1 C. N. R. Rao, G. U. Kulkarni, P. J. Thomas, V. V. Agrawal and P. Saravanan, *The Journal of Physical Chemistry B*, 2003, **107**, 7391-7395.

Author Contributions

O.G. Data curation: Lead; Ideas and concepts: Equal; Writing – original draft: Lead; Writing – review and editing: Equal; Formal analysis: Equal; Investigation: Equal

N.V. Ideas and concepts: Equal; Funding: Lead; Project administration: Equal; Writing – review and editing: Equal; Formal analysis: Equal; Investigation: Equal

F.G. Ideas and concepts: Equal; Funding: Equal; Project administration: Lead; Writing – review and editing: Equal; Formal analysis: Equal; Investigation: Equal