

Supporting Information.

Scaled-up production of plasmonic nanoparticles using microfluidics: from metal precursors to functionalized and sterilized nanoparticles

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Supporting Information Figures

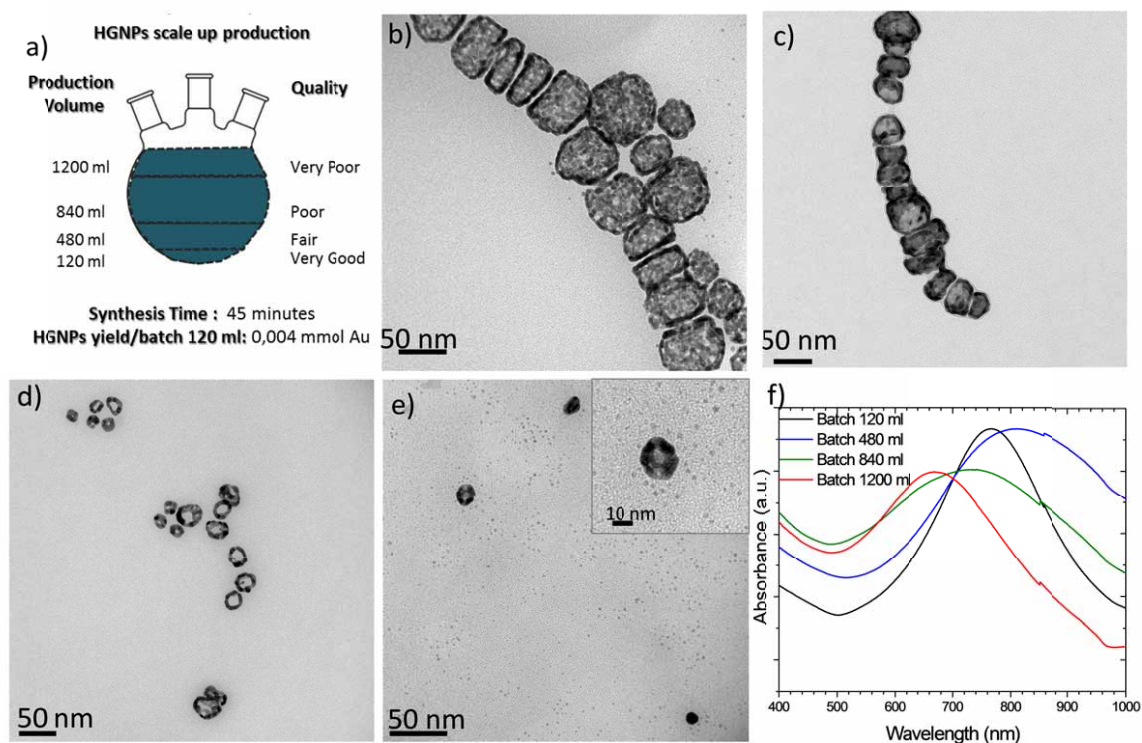


Fig S1. a) Schematic of the scaled-up production of HG NPs in a batch reactor, $[Au] = 0.03$ mM, Co/PVP = 621. b-e) TEM images of HG NPs obtained at a scale-up volume of: b) 120 mL, c) 480 mL, d) 840 mL and e) 1200 mL. f) UV-VIS spectra from the nanoparticles produced with different batch reactor volumes.

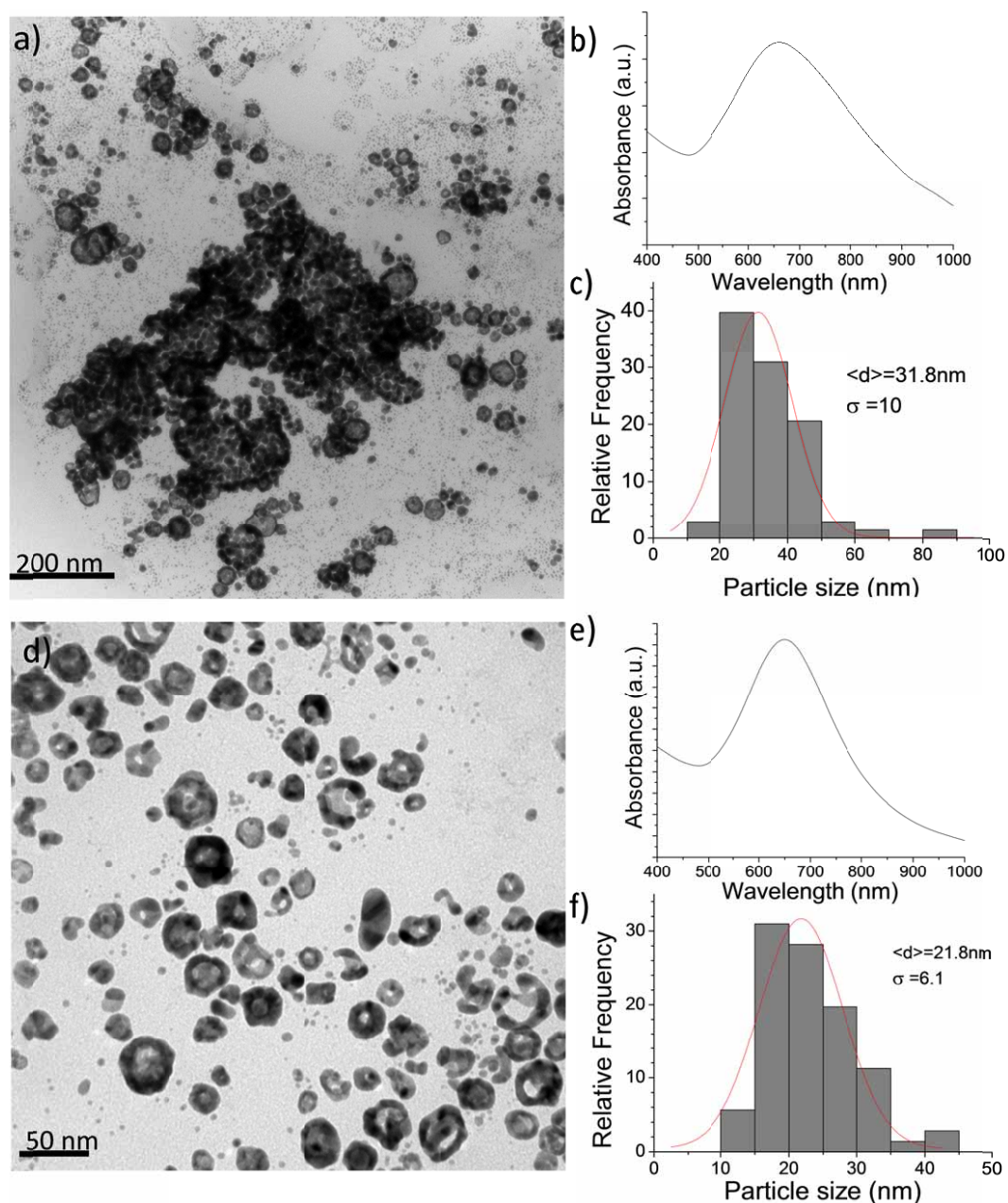


Fig S2. HG NPs obtained in the microfluidic reactor at different Co/PVP ratios, residence time = 6 min, Co/Au = 9.0, [Au] = 0.18 mM. Co/PVP = 62:10: a) TEM image, b) UV-VIS spectrum, c) Primary particle size distribution (n = 100 particles). Co/PVP = 62:10: d) TEM image, e) UV-VIS spectrum, f) Primary particle size distribution (n = 100 particles).

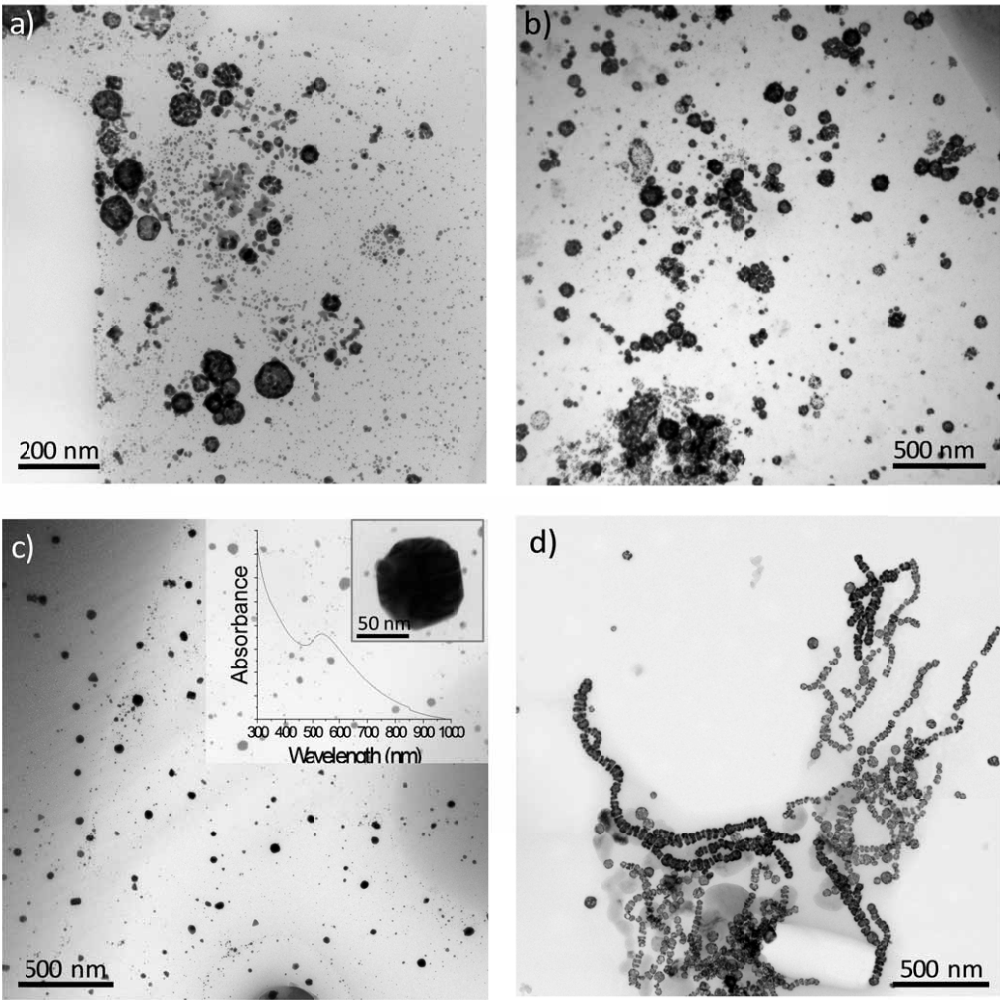


Fig S3. TEM images of HG NPs obtained at a different Co/Au flow ratios, residence time of 6 minutes (3 minutes synthesis of Co NPS + 3 minutes Au shell growth), [Au]= 0.18 mM, Co/PVP= 621. a) Co/Au= 24. b) Co/Au= 12. c) Co/Au= 6.5; inset: TEM image of a detail Au NP (not hollow structure) and UV-VIS spectrum. d) TEM image from HG NPs obtained in the batch reactor, they are assembled in a backbone structure; volume synthesis= 120 mL, Co/PVP= 621, [Au]= 0.03 mM.

External Diameter (mm)	Internal Diameter (mm)	Thickness (mm)	Length (cm)	Q O ₂ (mL/s)	Q _{product} (mL/s)	QO ₂ /Q _{product}
1.6	0.8	0.4	913	7.64·10 ⁻⁵	55	5.04·10 ⁻³
3.2	1.6	0.8	2238	1.89·10 ⁻⁴	550	1.23·10 ⁻³

$$P = \frac{(\text{amount of permeate}) \cdot (\text{film thickness})}{(\text{surface area}) \cdot (\text{pressure across film})}$$
$$P(25^{\circ}\text{C}, \text{O}_2 - \text{Teflon}) = 4.2 \cdot 10^{-10} \left[\frac{\text{cm}^3 \text{cm}}{\text{s cm}^2 \text{cmHg}} \right] \quad (\text{Bhadha, 1999})$$

Fig S4. Permeability of O₂ through the PTFE tubing and estimation of O₂ content at the reaction media. [Paul M. Bhadha, Welding Journal 1999, 78, 7, 35-40]

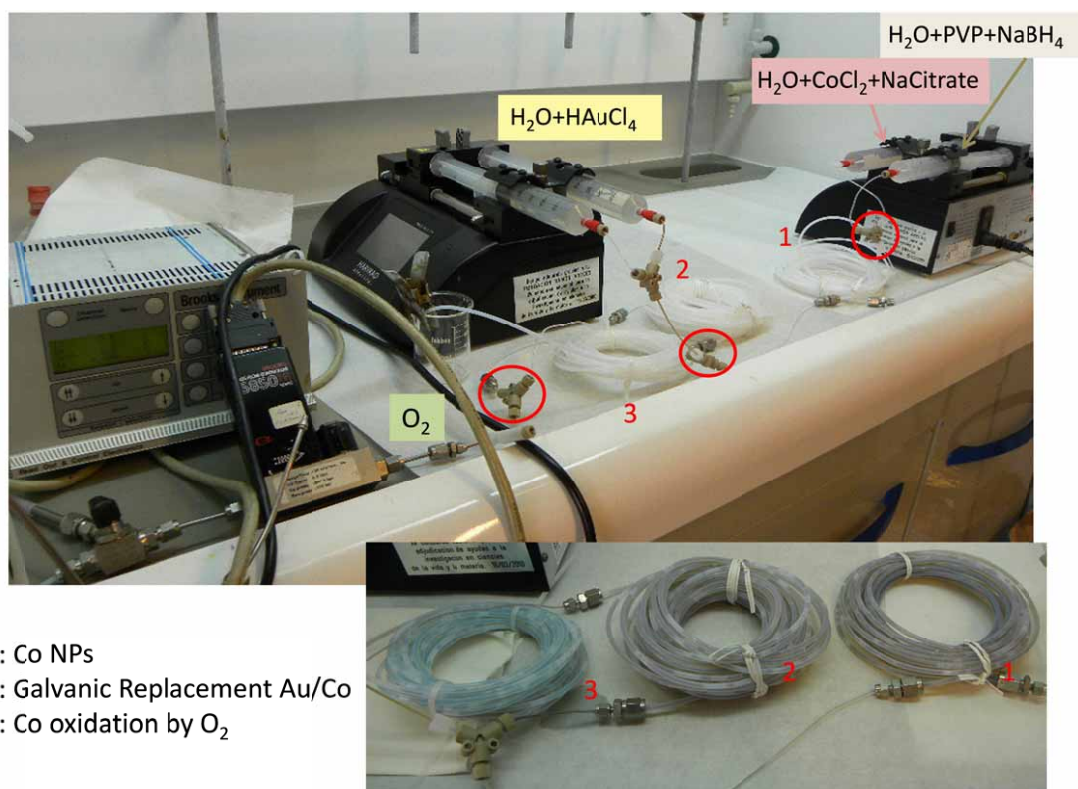


Fig S5. Scaled-up microfluidic reactor to produce HG NPs. Stage 1: Synthesis of Co NPs with segmented flow generation, $Q = 300 \text{ mL/h}$, $L_t = 7.46 \text{ m}$, $d_i = 1.6 \text{ mm}$. Stage 2: Au nanoshell formation by the galvanic replacement of cobalt, $Q = 550 \text{ mL/h}$, $L_t = 14.92 \text{ m}$, $d_i = 1.6 \text{ mm}$. Stage 3: O₂ segmented flow to oxidize the remaining Co core, $Q = 1030 \text{ mL/h}$, $L_t = 8.5 \text{ m}$, $d_i = 1.6 \text{ mm}$. The optical image below shows the HG NPs color at each stage.

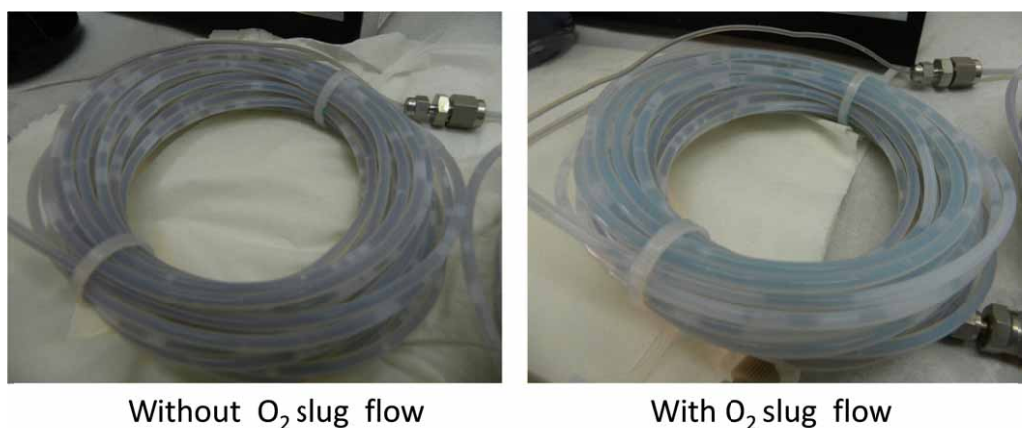


Fig S6. Appearance of the suspension of HG NPs obtained at the stage 3 coil without and with O₂ segmented flow.

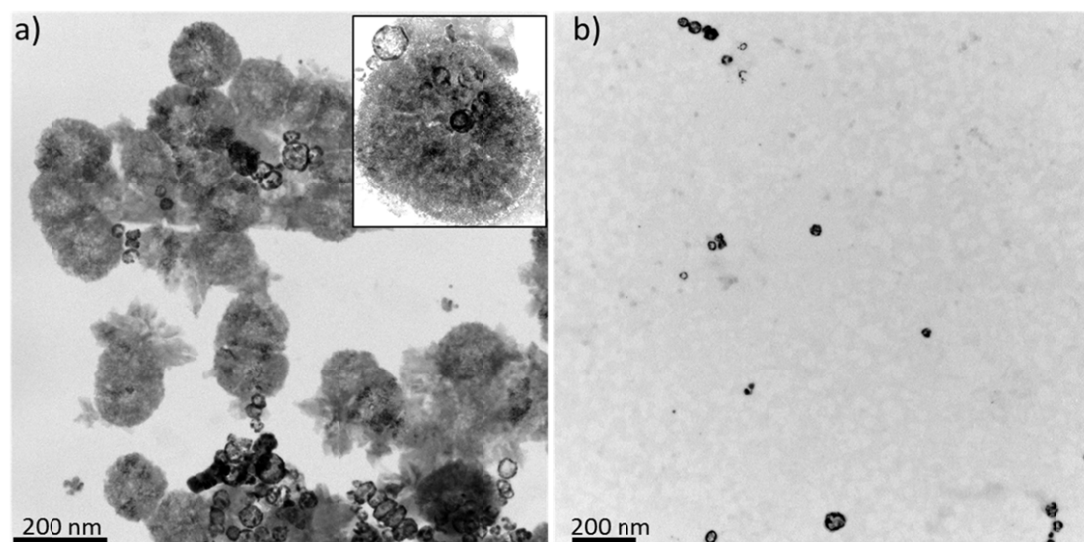


Fig S7. TEM photographs of SH-PEG grafted HGNPs after synthesis. A solution of a heavy-metal salt (phosphotungstic acid 1 wt%) was used as negative staining to allow electron observation of SH-PEG. a) Batch reactor. b) Microfluidic reactor. It is important to point out that before dialysis SH-PEG curled up in a ball engulfing the HGNPs when the batch reactor was used (Figure a). Those large agglomerates (inset) disappear after dialysis (results not shown). When using the microfluidic reactor the presence of those polymeric agglomerates is avoided (Figure b).

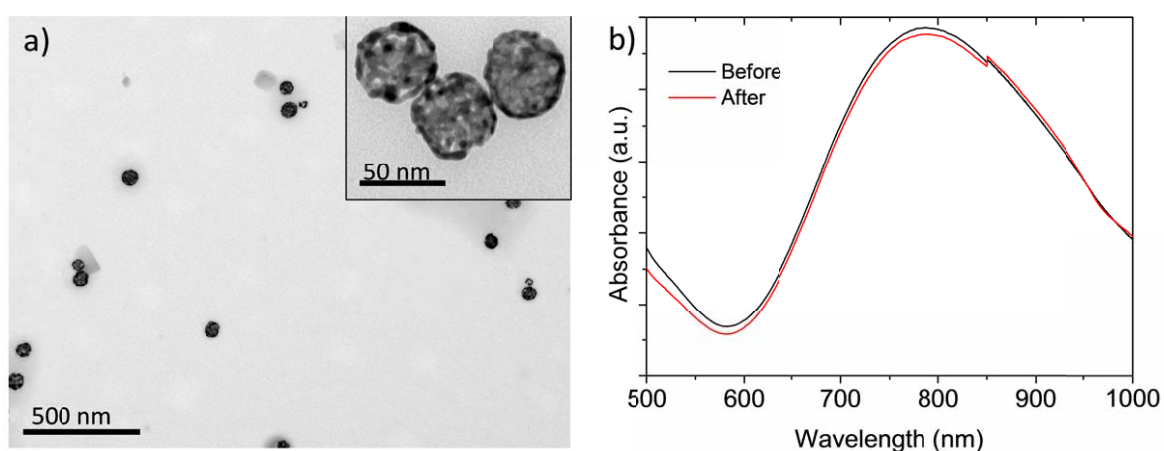


Fig S8. TEM images of HGNPs obtained after the UV-light sterilization process; inset image shows that the HGNPs morphology is stable after the UV-treatment. b) UV-VIS spectra from HGNPs measured before and after of the sterilization process.