Simple Control of Surface Topography of Gold Nanoshells by a Surfactant-less Seeded-Growth Method

Antonio Topete,[a] *Manuel Alatorre-Meda,*[a,#] *Eva M. Villar-Álvarez,*[a] *Adriana Cambón,*[a] *Silvia Barbosa,*[a,*] *Pablo Taboada,*[a,*] *Víctor Mosquera*[a]

Grupo de Física de Coloides y Polímeros, Departamento de Física de la Materia Condensada, Universidad de Santiago de Compostela, Santiago de Compostela, 15782, Spain.

Authors to whom correspondence should be addressed: silvia.barbosa@usc.es; pablo.taboada@usc.es

[#]Present address: 3B´s Research Group- Biomaterials, Biodegradables and Biomimetics, University of Minho, 4806-909, Guimarães, Portugal.

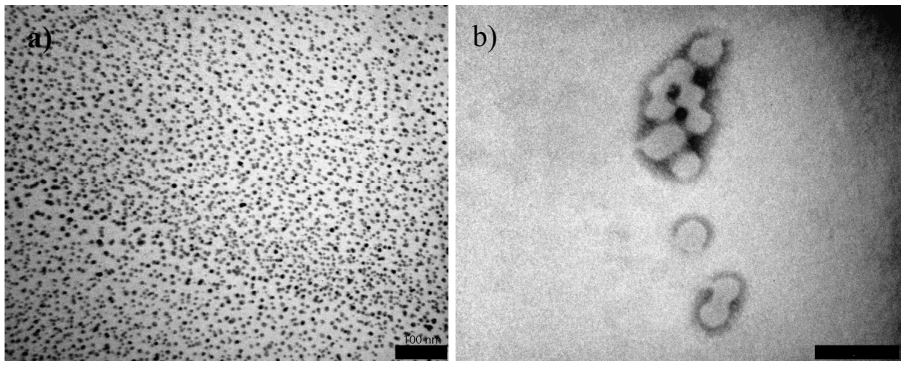

Figure S1: TEM images of a) citrate-capped Au seeds prepared by reduction with $NaBH_4$, and b) PLGA NPs stained with phosphotungstic acid. Scale bars are 200 nm.

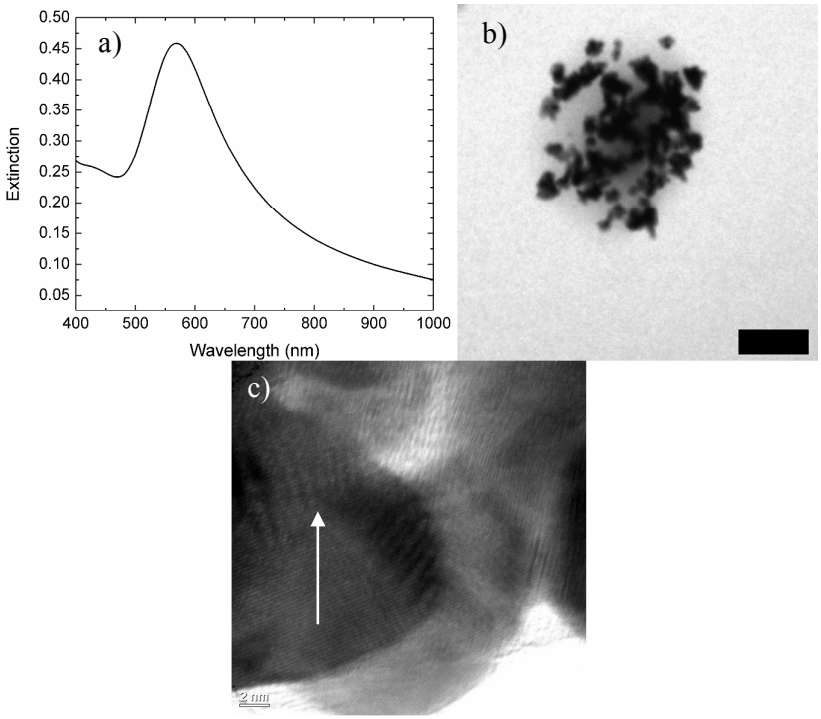

Figure S2: a) UV-vis extinction spectrum of NP-seed in the presence of Au growth solution and in the absence of AA after 1 day of reaction. Although chitosan by itself acts as reductant, its activity is not sufficient to generate fully-developed BGNS. b) TEM image of a NP-seed after 1 day under the aforementioned conditions (Scale bar is 50 nm). c) HR-TEM image showing the agglomeration of small flat crystals (as observed from the presence of Moiré patterns, see arrow) as precursors of branches.

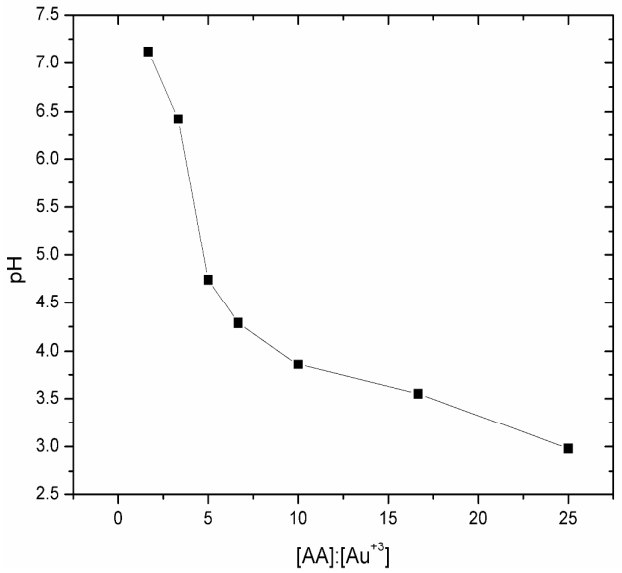

Figure S3. pH of the reaction solutions with different initial [AA]:[Au^{+3}] molar ratios of a 0.5 M AA solution. Initial pH of Au growth and AA solutions were 9.87 and 1.95, respectively.

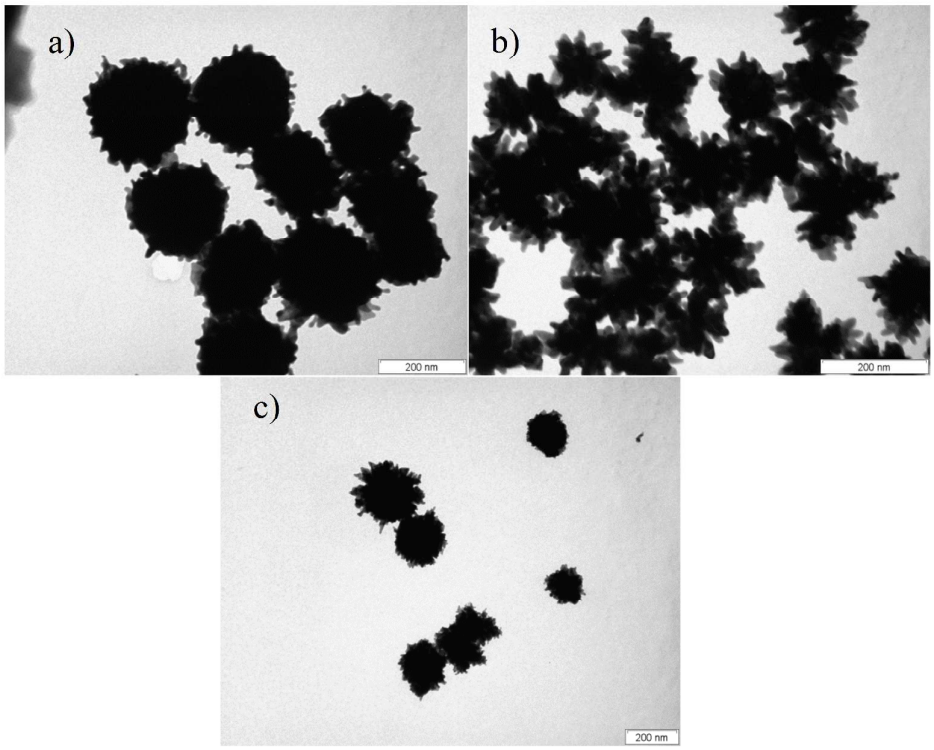

Figure S4: TEM images of Au nanoshells grown at different conditions: a) pH 4.0, 20 µl; b) pH 7.0, 50 µl; c) pH 7.0, 60 µl of a 0.5 M AA solution.

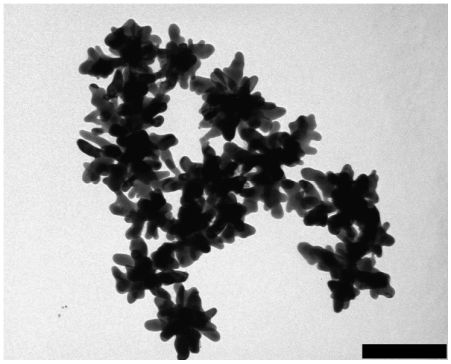

Figure S5: BGNS obtained after using 10 µL of 0.25 M AA with a more branched structure. Scale bar is 200 nm.

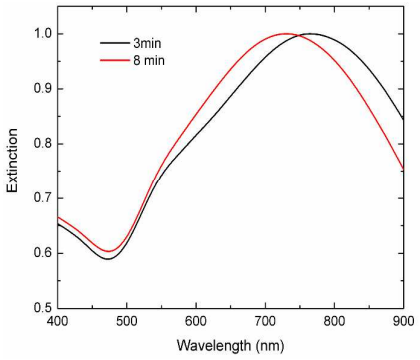

Figure S6: UV-vis extnction spectra of BGNs after 3 and 8 minutes of reaction. A slight blue shift of the plasmon peak is observed indicating that the structure undergoes a reshaping into a more thermodynamically stable geometry with a lower anisotropy degree. Reactants volumes were 2.5 mL of Au growth solution, 0.5 mL of NP-seed and 30 µL of AA (0.5 M), respectively.

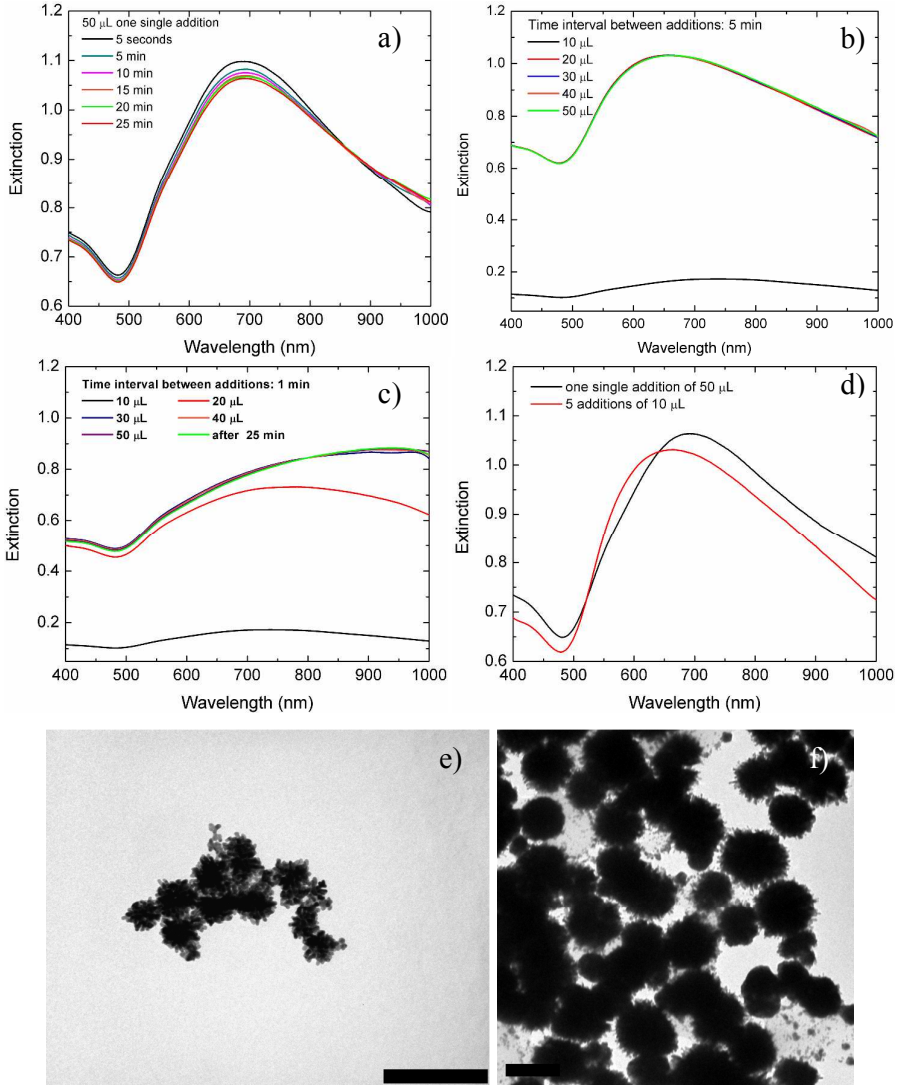

Figure S7: UV-vis spectra of BGNS: a) after one-off addition of 50 µL of 0.5 M AA solution (spectra were measured after 5 s, 5, 10, 15, 20 and 25 min); b) after stepwise addition of 10 µL each 5 min; c) after stepwise addition of 10 µL each 1 min. d) Comparison of the spectra obtained after a single 50 µL addition and 5 addition of 10 µL aliquots of AA added each 5 min. e) TEM images of BGNs obtained after multiple additions of 10 µL aliquots of AA and f) after a single addition of 50 µL. Scale bar is 200 nm in e) and f).

Estimation of SERS enhancement: The estimate for the calculation of the SERS enhancement factor (EF) of the nanoshells inside HeLa cells compared to the bulk Raman signal was made through the equation:[S1]

$$EF = \frac{Vol_{bulk} \cdot T_{bulk} \cdot I_{bulk} \cdot SN_{SERS}}{Vol_{SERS} \cdot T_{SERS} \cdot I_{SERS} \cdot SN_{bulk}}$$

where *EF* is the enhancement factor estimate, Vol_{bulk} the total cellular volume probed by bulk native Raman; Vol_{SERS} the cytoplasmatic volume probed by SERS; T_{bulk} and T_{SERS} the acqusition for bulk Raman and SERS measurements in cells, respectively; I_{bulk} and I_{SERS} the laser power used for unenhanced Raman and SERS measurements, respectively; and SN_{bulk} and SN_{SERS} the signal to noise ratio for unenhanced nad SERS spectra, respectively.

References

1. Ochsenkühn, M. A.; Jess, P. R. T.; Stoquert, H.; Dholakaia, K.; Campbell, C. J. Nanoshells for Surface-enhanced Raman Spectroscopy in Eukaryotic Cells: Cellular Response and Sensor Development. *ACS Nano* **2009**, *3*, 3613-3621.