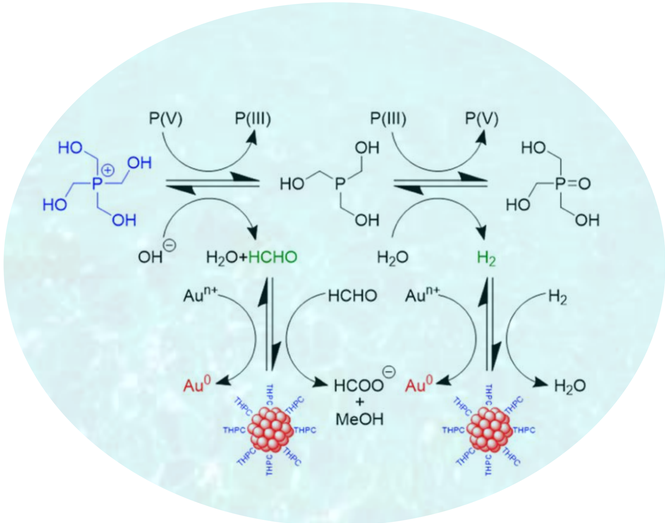
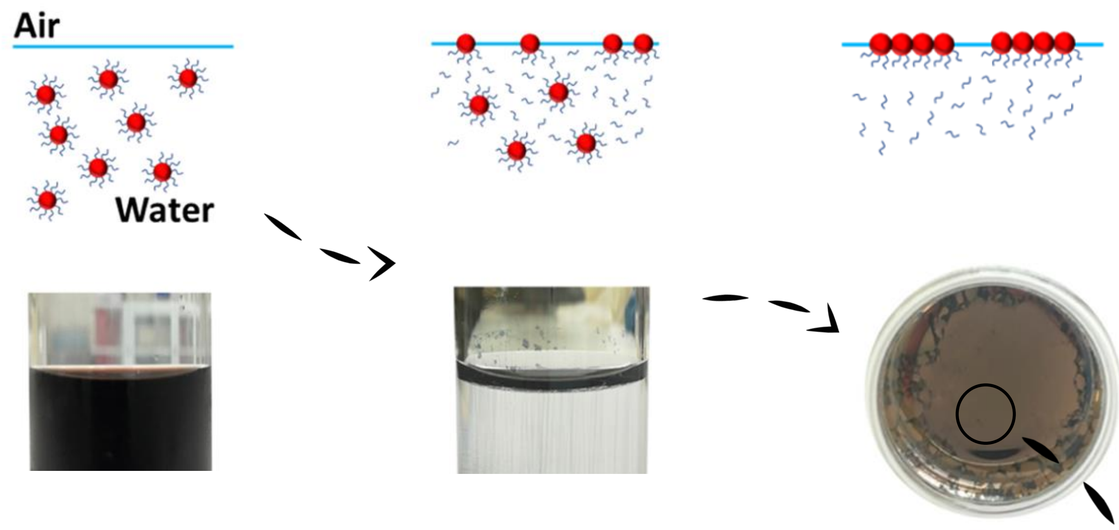
Spontaneous Formation of Cold-Welded Plasmonic Nanoassemblies with Refracted Shapes for Intense Raman Scattering

Andrea Mariño-López[1], María Blanco-Formoso,[1] Leonardo N. Furini,[1] Ana Sousa-Castillo,[1] Ecem Tiryaki,[1] Moisés Pérez-Lorenzo,[1] Martín Testa-Anta,[2] , Verónica Salgueiriño,[2] Nicholas A. Kotov,[3] Ramón A. Álvarez-Puebla,[4,5] and Miguel A. Correa-Duarte[1]

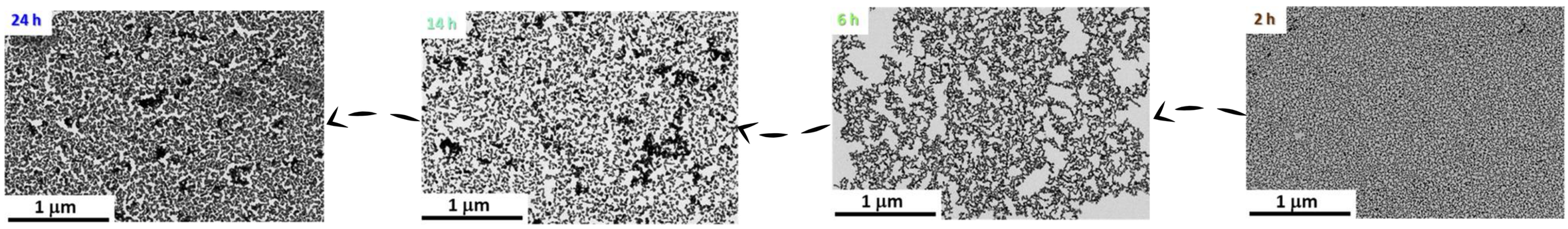
[1] Department of Physical Chemistry, Biomedical Research Center (CINBIO), Southern Galicia Institute of Health Research (IISGS) and Biomedical Research Networking Center for Mental Health (CIBERSAM), Universidade de Vigo, 36310 Vigo, Spain
[2] Department of Applied Physics, Universidade de Vigo, 36310 Vigo, Spain
[3] Department of Chemical Engineering, University of Michigan, Ann Arbor, Michigan 48109, United States
[4] Department of Physical Chemistry and EMaS, Universitat Rovira i Virgili, 43007 Tarragona, Spain
[5] ICREA, Passeig Lluís Companys 23, 08010 Barcelona, Spain



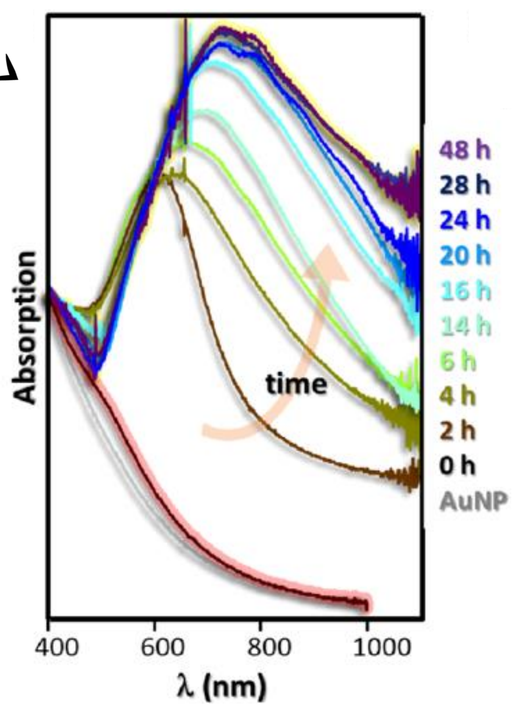
Mechanism of formation for THPC-stabilized 3 nm gold nanoparticles (AuNPs). *Phosphorus(V) from THPC is reduced to phosphorus(III) producing formaldehyde. This intermediate is able to reduce gold(III) to metallic gold. Furthermore, phosphorus(III) has sufficient reducing power to generate hydrogen from water, which can reduce more amount of gold(III) producing more metallic gold. Finally, AuNPs are weakly stabilized by THPC.*



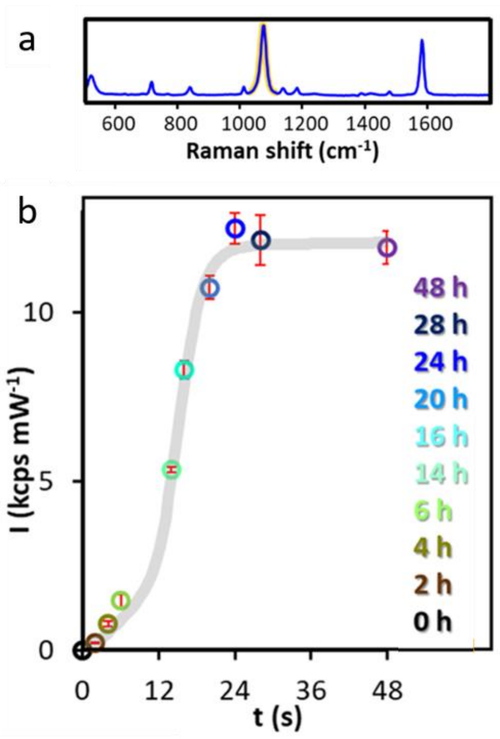
Formation of the gold film at the air-water interface. *When AuNPs solution is located in a closed container at 80 °C, the constitution of a monolayer of AuNPs at the air-water interface can be observed. This occurs through the migration of AuNPs from the bulk solution to the interface air-water, as depicted in the illustration.*



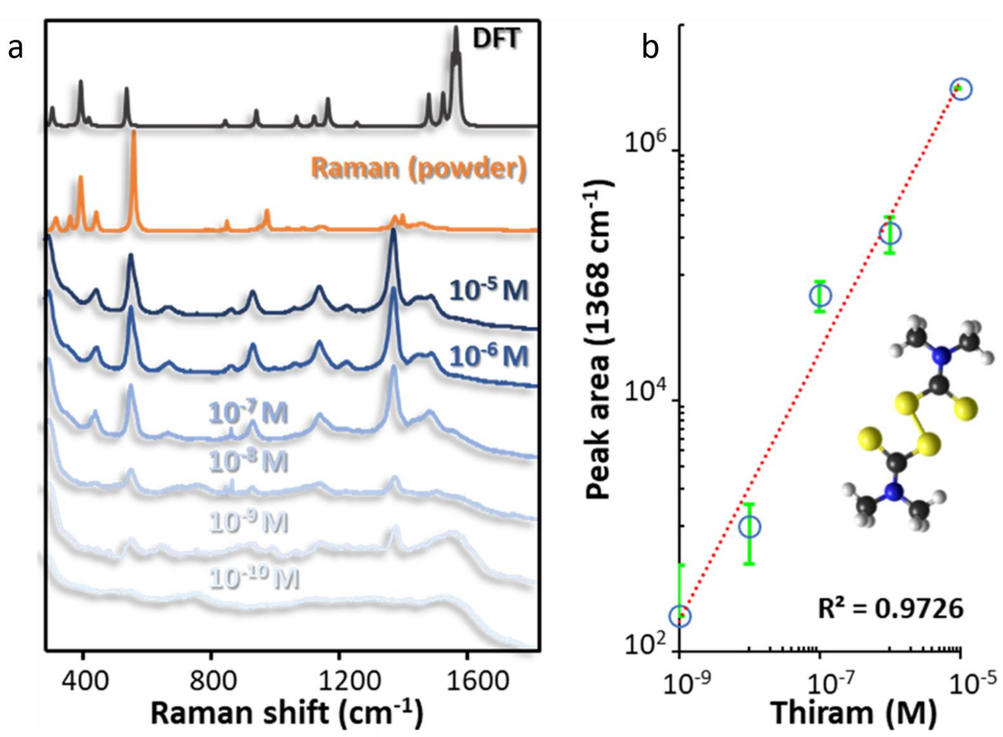
TEM images of the evolution of the film structure at the air-water interface at different assembly times. *The geometric evolvement of the film over time shows that these structures grow into curved complex geometries.*



LSPR variation of the film at different times of formation. *Plasmon resonance cannot be observed for the 3 nm AuNP prepared. As interfacial self-assembly progresses, the LSPR band redshifts and increases its intensity until it reaches a maximum at 740 nm after 24 h.*



(a) SERS spectrum of MBA. (b) Intensity of the ring breathing (1079 cm⁻¹) vs. the different times of the film formation, reaching the maximum at 24 h.



(a) Theoretical (unscaled) and experimental Raman spectra of thiram. SERS spectra of thiram in water, contaminated with different concentrations of the analyte after adding the AuNPs and waiting 24 h for the formation of a stable cold-welded film. (b) Correlation of the peak area of the CS stretching with the thiram concentration.

Concave-shaped nanostructures made of continuous segments of plasmonic metals are endowed with strong capabilities to enhance Raman scattering. Herein, we show that these plasmonic films can spontaneously form via accumulation and self-organization of gold nanoparticles (AuNPs) at the air-water interface by virtue of the weakly-bonded THPC ligand onto the particle surface. Upon heating to 80 °C, AuNPs are cold-welded to each other forming monoparticulate films with a homogeneous structure with a high density of hot spots.

Furthermore, nanoassemblies effectively adsorb molecular analytes during their migration from the bulk solution to the surface, reaching huge local concentrations of those analytes located on the favorable plasmonic shapes. This can be exploited by surface-enhanced Raman scattering for ultrasensitive quantification of aliphatic molecules in aqueous medium.

Reference: *Langmuir* **2019**, *35*, 4110–4116

ZEPTONIC ZEPTONIC GROUP
galicia
INSTITUTO DE INVESTIGACIÓN SANITARIA Galicia Sur
XUNTA DE GALICIA
GOBIERNO DE ESPAÑA MINISTERIO DE CIENCIA, INNOVACIÓN Y UNIVERSIDADES
UNIÓN EUROPEA
Universidade Vigo cinbio
team nano tech