Supporting information

Catalytic Effect of Gold Nanoparticles Self-Assembled in Multilayered Polyelectrolyte Films

Mariana Chirea, †* Carlos M. Pereira†, Fernando Silva†

[†] Departamento de Química da Faculdade de Ciências da Universidade do Porto,

Rua do Campo Alegre, 687, 4169-007 Porto (Portugal)

*E-mail: mariana.chirea@fc.up.pt

I.FT-IR spectra of Mercaptoundecanoic acid (MUA) and gold nanoparticles stabilized with MUA:

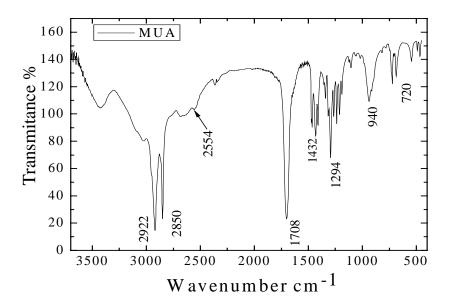


Figure S1. FT-IR spectrum of Mercaptoundecanoic acid.

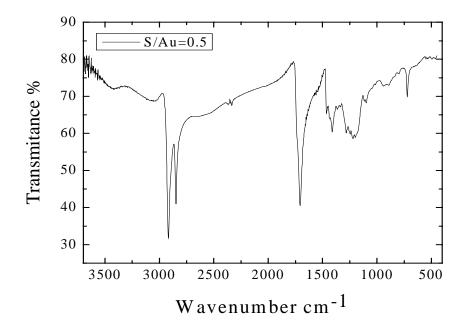


Figure S2. FT-IR spectrum of Au NPs stabilized with Mercaptoundecanoic acid. Thiol /gold molar ratio 0.5. Average diameters: 4.0 nm.

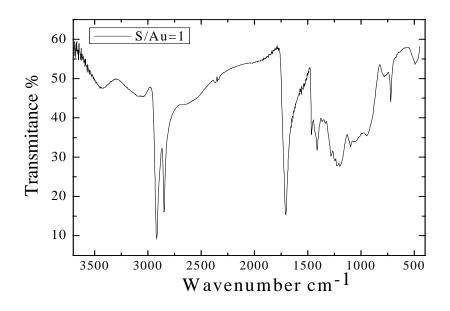


Figure S3. FT-IR spectrum of Au NPs stabilized with Mercaptoundecanoic acid. Thiol /gold molar ratio 1. Average diameters: 3.3 nm.

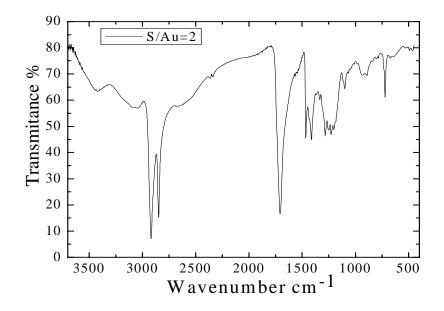


Figure S4. FT-IR spectrum of Au NPs stabilized with Mercaptoundecanoic acid. Thiol /gold molar ratio 2. Average diameters: 3.0 nm.

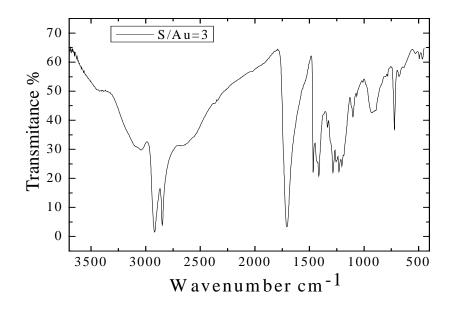


Figure S5. FT-IR spectrum of Au NPs stabilized with Mercaptoundecanoic acid. Thiol /gold molar ratio 3. Average diameters: 1.0 nm.

 $\nu_{\text{O-H}}$ broad stretching band superimposed on the aliphatic C-H stretch vibration around 3000cm $^{\text{-1}}$.

 v_{C-H} saturated vibration stretching at 2800-3100 cm⁻¹

 v_{S-H} stretching vibration at 2554 cm⁻¹ for the MUA (figure S1) disappears when the thiol is adsorbed on the Au-MUA NPs surface. This represents strong evidence that the thiol is bounded on the gold nanoparticles' surface trough the sulfur atom group.

 $v_{C=O}$ as strong peak at 1708cm⁻¹(in the range 1670-1710 cm⁻¹) in all the FT-IR spectra clearly indicates that the pure MUA molecules (figure S1) and the MUA molecules on the Au NPs surface exist as dimmers(figure S2,S3, S4, S5). This proves that the ligands on the Au Mua NPs surface exist mainly in the form of carboxylic acid.

The fingerprint region of the FT-IR spectra shows bands at 1432cm^{-1} and 1294cm^{-1} which correspond to the interacting $v_{\text{C-O}}$ stretch and in-plane $v_{\text{C-O-H}}$ deformation vibration. The peak at 940cm^{-1} (in the range $875-960 \text{ cm}^{-1}$) is characteristic of out-of-plane $v_{\text{O-H}}$ bending mode in intermolecular hydrogen bonding dimmer structure. These peaks are slightly diminished in the case of gold nanoparticles' spectra. These data confirms the presence of the thiol on the gold nanoparticles surfaces and proves that the thiol exists in the form of carboxylic acid.

II. Tapping mode AFM images of poly(L-Arginine) as 4th layer and Au-MUA NPs as 5th layer within multilayer composites:

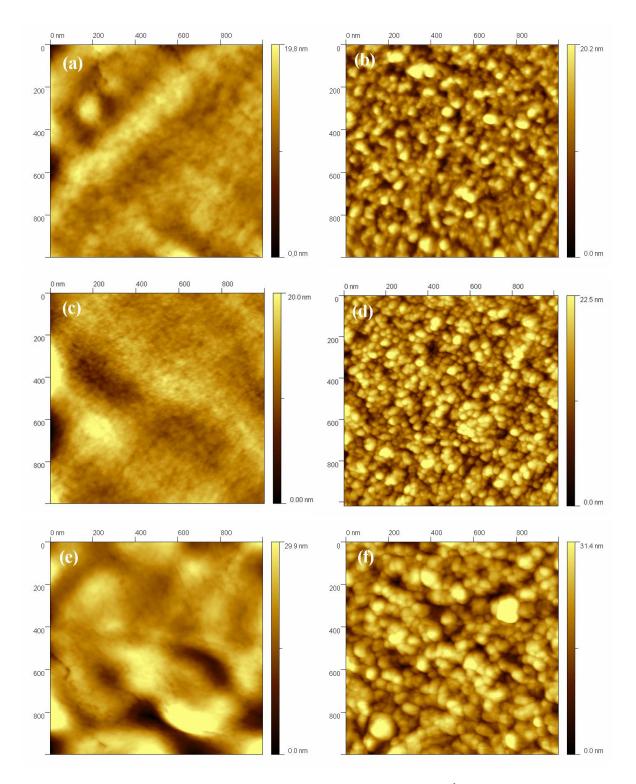


Figure S6. Topographic tapping mode AFM images of pArg as 4^{th} and Au-MUA NP as 5^{th} layers within the pArg/Au-MUA NPs multilayer composites. The Au-MUA NPs were 1.0 nm (a, b), 3.0 nm (c, d) and 4.0 nm average diameters (e, f).

In Figure S6 the root mean squared roughnesses were:

Cluster	RMS (nm)	Figure S6
diameter		
(nm)		
pArg as 4 th layer		
1.0	1.46	а
3.0	1.62	с
4.0	2.0	e
Au-MUA as 5 th layer		
1.0	2.60	b
3.0	4.10	d
4.0	5.82	f

Table S1.