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Layer-by-layer functionalization of gold nanorods by polyelectrolytes to control surface spacer and precisely tune the surface plasmon resonance position

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1 We present a layer-by-layer functionalization of gold 2 nanorods (GNRs) by polyelectrolytes in order to control 3 precisely the spacer surrounding the metallic nanoparticles 4 but also to modulate its plasmonic properties. Alternate 5 functionalization with negatively and positively charged 6 polyelectrolytes ensures a 2 nm step control of the spacer 7 from 0 nm up to 10 nm, depending on the number of layers. 8 Such process changes the local refractive index and thus 9 induces a red shift of the surface plasmon resonance. Both 10 solution and solid samples were studied.

11	Keywords:	golo	d nano	oparticles	function	alization,
12	polyelectroly	/tes	layers,	spacer	thickness	control,
13	plasmonic p	roper	ties mod	lulation		

14 The enhancement of the metallic nanoparticles synthesis protocols impacts since many years the field of materials science.¹⁻³ In fact, controlling precisely the size, 15 16 17 shape and the core metal gives access to specific plasmonic 18 properties. Numerous studies describe them and their 19 various applications in designing new meta-materials, 20 sensing and biomedicine⁴⁻⁸ each underlying that the control 21 of the direct environment of the metallic nanoparticle is 22 mandatory whatever we consider inter-particles coupling or 23 targeted organic compound functionalized on the metallic nanoparticles.⁹ Different methods experienced the change of 24 25 their initial surfactant coating by other appropriate spacer. 26 Two of the most commonly used are the DNA linker¹⁰ and the silica shell coating.¹¹ The first one shows the advantage 27 of having a precise length for the linker and allows 28 29 designing either hybrid organic / metallic system or dimer 30 nanoparticles. Despite it is quite easy to use; DNA linker is 31 still expensive and does not allow a good surface coverage 32 in case of organic functionalization. Moreover, the stability of the hybrid system is not optimized. On the other hand, 33 34 silica shell surrounding metallic nanoparticles increases the 35 stability of the system and exhibits a potentially high surface 36 coverage with further functionalization with organic 37 compound using click chemistry. However, it is hard to control the shell thickness for value bellow 10 nm; which is 38 39 a huge drawback because the value of the enhanced 40 electromagnetic field for plasmonic nanoparticles decreases 41 as the inverse of the cube distance from the surface, 42 enforcing a spacer thickness smaller than 10 nm.

43 Considering the different drawbacks of the previous 44 spacers, using polyelectrolytes could represent a new way in 45 the functionalization of metallic nanoparticles. In fact, as 46 polyelectrolytes are organic polymers where the initial 47 monomer is positively or negatively charged, specific 48 electrostatic interactions afford an easy control of the spacer 49 thickness and at the same time increase the colloidal stability of the system.¹³⁻¹⁶ Moreover, controlling the direct 50

51 environment of the metallic nanoparticles means controlling

52 the local refractive index and thus enables the modulation of

53 the localized surface plasmon resonance (LSPR).¹⁷⁻

54 In this paper, negative and positive polyelectrolytes are 55 sequentially used to functionalize GNRs. Using such layer-56 by-layer process ensures a perfect control of the spacer surrounding the metallic nanoparticles, an increase of its 57 58 colloidal stability and a higher density when deposited on 59 glass substrate. Zetametry measurements are performed to 60 characterize the layer-by-layer deposition and the evolution 61 of the colloidal stability over the process. Extinction spectroscopy is used to show the spectral shift observed 62 63 over the LSPR bands during the layer-by-layer process.

64 Gold nanorods with specific aspect ratio were prepared 65 by a modified "seed mediated growth method" using binary surfactant mixtures.²⁰ In this synthesis procedure, sodium 66 oleate (NaOL) is combined with CTAB and thus achieves a 67 68 greater tunability of GNRs dimensions. This anionic 69 surfactant has a double bond that allows the reduction of the 70 gold salt in the absence of other reducers, in this case 71 ascorbic acid (AA), so a lower molar ratio of gold:AA is 72 used compared to the original method. The mixture of 73 CTAB and NaOL also enables the use of lower 74 concentration of surfactant in the reaction.¹

75 The reaction has two steps. First, a small quantity of 76 gold salt is reduced using sodium borohydride as a strong 77 reducing agent in order to create small gold nanospheres 78 called "seeds", which will be used as cores of the gold 79 nanorods. Secondly, a growth solution provides the gold salt 80 and the other reactants for the growth of these seeds with the 81 desired size and shape. These reactions are prepared as 82 follows.

83 Seed Solution: 5 mL of 0.5 mM HAuCl₄ is mixed with 84 5 mL of 0.2 M CTAB solution in a beaker. 0.6 mL of fresh 85 NaBH₄ is diluted to 1 mL with water and then injected to the 86 Au(III)-CTAB solution under vigorous stirring. The solution 87 color changes from yellow to brownish yellow and the 88 stirring is stopped after 2 min. The seed solution is aged at 89 room temperature for (at least) 30 min before use.

90 Growth solution: 3.5 g of CTAB and 0.617 g of NaOL 91 are dissolved in 125 mL of water in a 0.5 L Erlenmeyer 92 flask. 12 mL of AgNO₃ solution (4 mM) is added. The 93 mixture is kept undisturbed at 30°C for 15 min after which 94 125 mL of 1 mM HAuCl₄ solution is added. The solution 95 becomes colorless after 90 min of stirring (700 rpm) and 2 96 mLof HCl (37 wt. % in water, 12.1 M) is then introduced to 97 adjust the pH. After another 15 min of slow stirring (400 98 rpm), 0.625 mL of 0.064 M AA is added and the solution is 99 vigorously stirred for 30 s. Finally, 0.2 mL of the seed 100 solution is injected into the growth solution. The resultant

1 mixture is stirred for 30 s and left undisturbed at 30°C for 2 12-15 h for GNRs growth.

3 The synthesized GNRs were characterized using 4 extinction spectroscopy and scanning electron microscopy 5 (SEM) (Figure 1). They show two different LSPR bands: 6 the transversal one is located at 525 nm and the longitudinal 7 one at 881 nm. The spectrum is related to the original 8 synthesized solution, within the GNRs are surrounding by a 9 double layer of surfactant (mainly CTAB) and the solvent 10 which contains an excess of surfactant. The size distribution of the GNRs was measured thanks to the SEM images over 11 12 one thousand nanoparticles. The average values are 97 nm 13 for the long axis and 21 nm for the short one, which gives 14 an aspect ratio around 4.6.

15 In order to use gold nanoparticles for enhanced 16 spectroscopies, the control of the distance between the 17 metallic surface and the molecules under interest is 18 mandatory. To achieve this goal, polyelectrolytes are under 19 great interest due to the layer-by-layer process which 20 ensures a precise control of the functionalization. Before deposition of the polyelectrolytes, surfactants surrounding 21 22 the GNRs (CTAB and NaOL) need to be removed. So 10



Figure 1. a) Extinction spectrum of synthesized gold nanorods. Insert shows the size distribution measured on 1034 nanoparticles; b) SEM image of the corresponding gold nanorods. Scale bar represents 100 nm.

mL of GNRs solution are centrifugated at 6 000 rpm during
20 min (relative centrifugal force RCF = 3 461 g) and then

25 the pellet is dispersed in 10 mL of milliQ water. This cycle 26 is done two more times.

27 Assuming that naked GNRs are slightly positively 28 charged, the first layer needs to be a negatively charged 29 polyelectrolyte; we choose sodium polystyrene sulfonate 30 (PSS, $M = 70\ 000\ g/mol$), purchased from Sigma-Aldrich 31 and used without further purification. So 10 mL of naked 32 GNRs solution is mixed with 3 mL of PSS solution (10 33 mg/mL in water) under 2 min of gentle stirring. The mixed 34 solution is kept undisturbed for 45 min to allow the 35 electrostatic interactions between the GNRs and the 36 polyelectrolytes thanks to the natural Brownian motion. To 37 remove the excess of polyelectrolytes, centrifugation is 38 performed at 12 000 rpm during 10 min (RCF = 15 455 g) 39 and the pellet is dispersed in 10 mL of NaCl solution (0.5 40 mM) to prevent the floculation of the hybrid nanoparticles 41 (gold nanorods with one layer, GNRs-1L). The addition of 42 NaCl increases the ionic strength of the solution which 43 stabilizes the polyelectrolyte layer in water. Without NaCl, the functionalized GNRs precipitate within few hours. 44

45 To set the second polyelectrolyte layer, we choose the 46 poly(diallyldimethylammonium chloride) (PDADMAC, M 47 < 100 000 g/mol) which is positively charged. The same 48 process is used for the second layer. Briefly, 10 mL of 49 GNRs-1L are mixed with 3 mL of PDADMAC solution 50 (purchased from Sigma-Aldrich and used without further 51 purification or dilution). After 2 min of gentle stirring and 52 45 min at rest, the same centrifugation parameters are used. 53 The final pellet is dispersed in 10 mL of NaCl solution. The 54 use of NaCl solution instead of milliQ water is very 55 important to prevent the flocculation of the gold nanorods 56 with two layers of polyelectrolytes (GNRs-2L).

57 We can continue the laver-by-laver process deposition 58 by alternating between PSS and **PDADMAC** 59 polyelectrolytes, depending on the main charged surface of 60 the hybrids. Because the centrifugation step is more and 61 more critical as the number of layer increases, the rotation 62 speed (or even the RCF) needs to be adjusted in



Figure 2. Evolution of the zeta potential of hybrid nanoparticles, starting from naked GNRs (0 layer) to three layers of polyelectrolytes.

consequence to prevent full aggregation of the pellet (which
 makes it very difficult to disperse in NaCl solution).
 Furthermore, the molecular weight of the different
 polyelectrolytes were chosen depending on the size (and
 aspect ratio) of the gold nanorods. If their size increases,
 longer polyelectrolyte chains are needed.

7 During the layer-by-layer process, each step was 8 controlled by zetametry. Measuring the GNRs zeta potential, 9 formerly the electrokinetic potential, is an easy way to 10 check if each layer is correctly deposited and at the same time to measure the stability of the hybrid system. Figure 2 11 shows the variation of the zeta potential when the GNRs are 12 functionalized with up to three layers of polyelectrolytes. 13 14 First of all, we clearly see the sign alternation of the zeta 15 potential as long as we increase the number of layers. It is 16 positive for the naked GNRs, then negative for the first layer 17 of PSS, positive again for the second layer of PDADMAC 18 and then negative again for the third layer of PSS which is 19 in accordance with the main charge of the last 20 polyelectrolyte deposited. Secondly, as the number of layer 21 increases, the absolute value of the zeta potential increases also, indicating that the stability behavior of the hybrid 22 23 nanoparticles in solution is more efficient. It starts from 20 24 mV for naked GNRs to increase to 60 mV for a three layers 25 system. Considering that each polyelectrolyte layer thickness is around 2 nm,²¹ this layer-by-layer process 26 27 allows to perfectly controlling the spacer between the 28 surface of the metallic nanoparticle and the future studied 29 organic compound to perform efficient enhanced spectroscopies. This layer-by-layer process is also a good 30 31 way to prevent aggregation of the gold nanoparticles in 32 solution.

Addition of polyelectrolytes layers around GNRs
would also affect their optical plasmonic properties. In fact,
LSPR bands are very sensitive to their direct environment,
meaning the local refractive index in solution. Thus, putting
more layers of polyelectrolytes surrounding the GNRs
would change the average value of the refractive index,



Figure 3. Extinction spectra of functionalized GNRs from 1 to 4 layers of polyelectrolytes. S0 is referred to the synthesized GNRs. Insert shows the evolution of the observed spectral shift with the estimated refractive index.

39 inducing LSPR bands spectral shifts. Figure 3 shows the 40 evolution of the extinction spectra of the GNRs as long as 41 we do the layer-by-layer process. We mainly observe a 42 spectral red-shift of the LSPR bands which is small in the 43 case of the transverse one but very important (up to 80 nm) 44 for the longitudinal one. The way we estimate the average 45 value of the local refractive index is based on the 46 assumption that the surface plasmon effect is mainly efficient in the first 10 nm closed to the surface of the 47 metallic nanoparticles.^{12, 22} Surfactants or polyelectrolytes 48 49 layers are localized within this small area and need to be 50 taken into account, in addition to the solvent, to estimate the 51 relative value of the refractive index directly surrounding 52 the GNRs. The complete calculation assumptions are 53 described in the supporting information but simply the 54 equation used is:

56
$$RI = 1,33 \times \frac{v_{tot} - \sum_{i} v_{layer}}{v_{tot}} + \sum_{i} RI_{layer} \times \frac{v_{layer}}{v_{tot}}$$
 (1)
57

55

58 where **RI** is the refractive index (1.33 is the value of the 59 water solvent), V_{tot} the total volume considered, V_{laver} the 60 volume of a considered layer and i the number of layers. 61 Considering equation 1, we clearly observe a linear 62 dependence between the optical shift of the LSPR bands and 63 the value of the refractive index (insert of Figure 3). This 64 allows at the same time a precise control of the layer-by-65 layer deposition process by spectroscopic measurements but 66 also a fine modulation tuning of the LSPR bands. So a quick 67 and simple prediction can be done on the modulation of the 68 LSPR bands' position when considering further layers of polyelectrolytes. Therefore, using polyelectrolytes is an 69 70 efficient way to both functionalize metallic nanoparticles 71 and tune the LSPR bands position, which could be 72 mandatory for enhanced spectroscopies when a good 73 spectral overlap with other absorption band is needed.



Figure 4. Left: AFM imaging of deposited GNRs-1L. Right: corresponding gap measurements between 2 GNRs-1L.

To go further than these results obtained in solution 1 2 we considered solid substrates to see how polyelectrolytes 3 can be used to ensure space between GNRs. So we prepared 4 GNRs-1L and deposited a diluted solution by the droplet 5 method on a silicon wafer to perform atomic force 6 microscopy (AFM). Keep in mind that a single PSS layer is 7 2 nm thickness. Figure 4 shows the distance measurement 8 between side-by-side and head-to-head dimers. The average gap value between two GNRs is 8 nm which clearly 9 indicates that the PSS layer induces repulsive forces 10 between the nanoparticles. It means that polyelectrolytes 11 functionalization prevents the aggregation in solution but 12 also modulates the gap between deposited nanoparticles 13 which is very important when dealing with inter-14 nanoparticles' coupling. AFM measurement with more than 15 16 one layer was not possible due to the quantity of polymer surrounding the GNRs which pollutes the AFM tip and 17 18 makes imaging complicated. Looking at the study of Möhwald and co-workers²¹, a single layer of polyelectrolyte 19 20 is 2 nm thick, two layers are 4 nm thick and three layers are 21 6 nm thick. Considering these layers thickness and the 22 repulsive forces, we can estimate the distance between two 23 GNRs-2L and two GNRs-3L to be over 8 and 12 nm 24 respectively, when deposited on substrate.

25 To go further, multi-layered GNRs were deposited on glass substrates to allow absorption measurements on solid 26 27 sample. Prior to the deposition, the glass slide was washed using first ethanol and secondly oxygen plasma cleaner. 28 29 Then we deposit 50 µL of high concentrated solution of layered GNRs by the droplet method and we waited until 30 31 the complete solvent evaporation. Figure 5 shows the 32 absorption spectra obtained on different glass slides where 33 GNRs from zero layer to four layers of polyelectrolytes 34 were deposited. There are two main observations. First of all, we observed the same behavior as the solution samples. The 35 36 longitudinal LSPR band is optically red-shifted as long as 37 we increase the number of polyelectrolytes layers 38 surrounding the GNRs, meaning as long as the local refractive index increases. In contrast with the solution 39



Figure 5. Extinction spectra of functionalized GNRs deposited on glass slides. Number of polyelectrolytes goes from 0 to 4 layers.

samples, it is rather difficult to estimate the value of the 40 41 local refractive index on deposited sample. In fact, in 42 solution you can consider each GNR individually so only 43 the solvent and the layers have to be considered. When 44 deposited on glass substrate, the direct environment of each 45 GNR is composed of air, glass and other GNRs. So 46 estimating an average value of the local refractive index 47 cannot be efficiently achieved. The second observation is 48 the broadening of both transverse and longitudinal LSPR 49 bands for samples with higher number of layers. This 50 observation is explained by the high density of GNRs that 51 are deposited on the glass substrate. To characterize the 52 GNRs' packing, SEM imaging was performed on GNRs-1L 53 deposited on silicon wafer. Due to vacuum and electron gun 54 source condition, an extra step of oxygen plasma cleaner 55 was done to remove organic compounds like 56 polyelectrolytes and possible rest of surfactant. The main 57 advantage of this extra step is to increase the SEM imaging 58 resolution. But the drawback is that destroying the 59 polyelectrolyte layers changes the distance between the 60 GNRs, especially for high number of layers or when GNRs are closely packed. That is why SEM measurements are 61 only used to characterize the close packing and not the inter-62 particle distances. SEM imaging, in supporting information, 63 clearly show wide areas of high density packing of GNRs. 64 Regarding absorption spectroscopy, these closed packed 65 66 nanorods induce the broadening of the LSPR bands but also a specific band that appears around 660 nm, due to 67 transverse coupling between GNRs allowed by the short 68 69 inter-particles distance.²³ Thus increasing the number of 70 polyelectrolytes layers allows to tune the LSPR bands 71 position but also to modulate the inter-particles coupling by 72 controlling the distance between GNRs.

73 In conclusion, control of the distance between metallic nanoparticles and targeted organic dye is mandatory for 74 75 enhanced spectroscopies. Different spacers can be used like 76 silica shell or DNA but polyelectrolytes show many 77 advantages. First of all, as it is a layer-by-layer process, you 78 can control precisely the thickness of the spacer with a 2 nm 79 single layer precision and also increase the colloidal 80 stability of the functionalized gold nanoparticles. Then, as any modification of the GNRs' surface, putting some 81 82 electrolytes modulates the position of the LSPR bands, but 83 its linear dependence makes it easily predictable. Finally, 84 for surface deposition, functionalized GNRs can grant 85 access to selection of the gap between nanoparticles which 86 govern the strength of inter-particles coupling and thus, the 87 local field enhancement. To summarize, polyelectrolytes 88 offer new possibilities in term of spacer control and further 89 metallic nanoparticle's functionalization, especially with 90 charged organic compounds. 91

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