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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:** gold nanoparticles functionalization,  
12 polyelectrolytes layers, spacer thickness control,  
13 plasmonic properties modulation

14 The enhancement of the metallic nanoparticles  
15 synthesis protocols impacts since many years the field of  
16 materials science.<sup>1-3</sup> In fact, controlling precisely the size,  
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 biomedicine<sup>4-8</sup> 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  
24 nanoparticles.<sup>9</sup> Different methods experienced the change of  
25 their initial surfactant coating by other appropriate spacer.  
26 Two of the most commonly used are the DNA linker<sup>10</sup> and  
27 the silica shell coating.<sup>11</sup> The first one shows the advantage  
28 of having a precise length for the linker and allows  
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  
33 of the hybrid system is not optimized. On the other hand,  
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  
38 control the shell thickness for value bellow 10 nm; which is  
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.<sup>12</sup>

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  
50 stability of the system.<sup>13-16</sup> Moreover, controlling the direct

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).<sup>17-19</sup>

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  
57 surrounding the metallic nanoparticles, an increase of its  
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  
62 spectroscopy is used to show the spectral shift observed  
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  
66 surfactant mixtures.<sup>20</sup> In this synthesis procedure, sodium  
67 oleate (NaOL) is combined with CTAB and thus achieves a  
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.<sup>15</sup>

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.

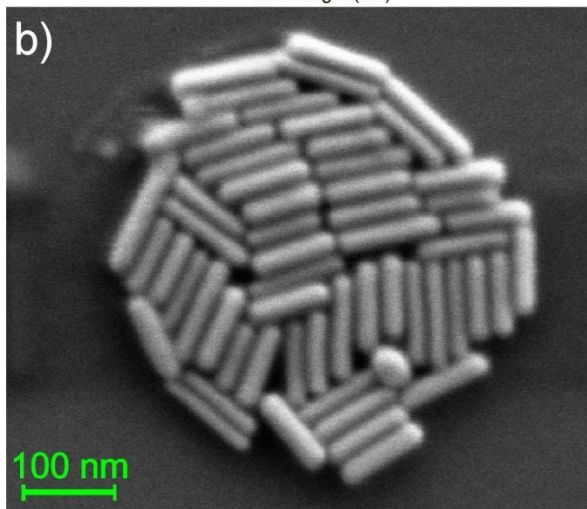
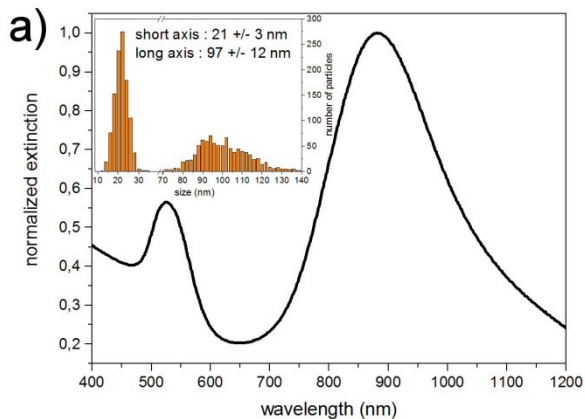
83 **Seed Solution:** 5 mL of 0.5 mM HAuCl<sub>4</sub> is mixed with  
84 5 mL of 0.2 M CTAB solution in a beaker. 0.6 mL of fresh  
85 NaBH<sub>4</sub> is diluted to 1 mL with water and then injected to the  
86 Au(III)-CTAB solution under vigorous stirring. The solution  
87 color changes from yellow 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 AgNO<sub>3</sub> 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 HAuCl<sub>4</sub> solution is added. The solution  
95 becomes colorless after 90 min of stirring (700 rpm) and 2  
96 mL of 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 surrounded by a  
9 double layer of surfactant (mainly CTAB) and the solvent  
10 which contains an excess of surfactant. The size distribution  
11 of the GNRs was measured thanks to the SEM images over  
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  
21 deposition of the polyelectrolytes, surfactants surrounding  
22 the GNRs (CTAB and NaOL) need to be removed. So 10



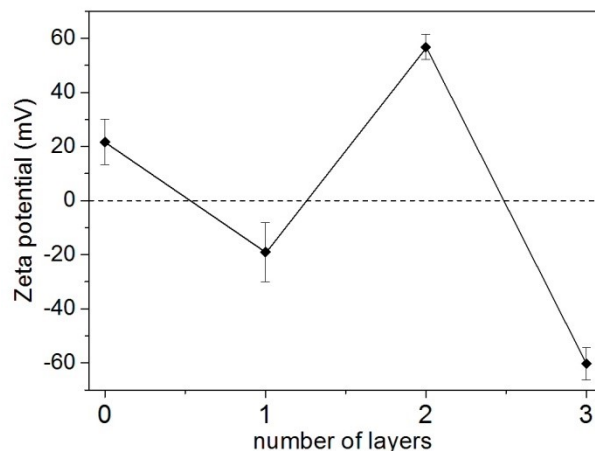
**Figure 1.** a) Extinction spectrum of synthesized gold nanorods. Insert shows the size distribution measured on 1034 nanoparticles; b) SEM image of the corresponding gold nanorods. Scale bar represents 100 nm.

23 mL of GNRs solution are centrifugated at 6 000 rpm during  
24 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 flocculation 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,  
44 the functionalized GNRs precipitate within few hours.

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 layer-by-layer 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

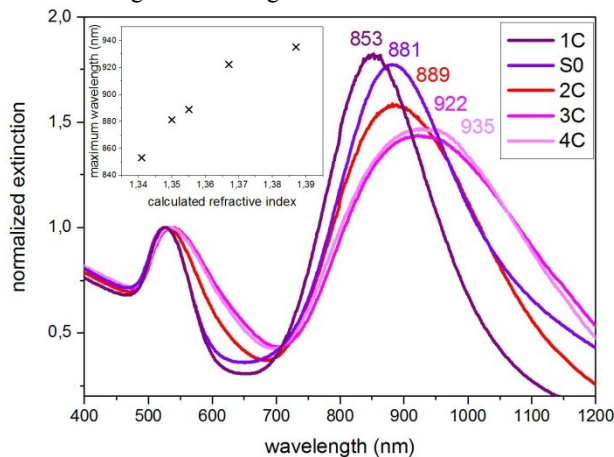


**Figure 2.** Evolution of the zeta potential of hybrid nanoparticles, starting from naked GNRs (0 layer) to three layers of polyelectrolytes.

1 consequence to prevent full aggregation of the pellet (which  
 2 makes it very difficult to disperse in NaCl solution).  
 3 Furthermore, the molecular weight of the different  
 4 polyelectrolytes were chosen depending on the size (and  
 5 aspect ratio) of the gold nanorods. If their size increases,  
 6 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  
 11 time to measure the stability of the hybrid system. Figure 2  
 12 shows the variation of the zeta potential when the GNRs are  
 13 functionalized with up to three layers of polyelectrolytes.  
 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  
 22 also, indicating that the stability behavior of the hybrid  
 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  
 26 thickness is around 2 nm,<sup>21</sup> this layer-by-layer process  
 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  
 30 spectroscopies. This layer-by-layer process is also a good  
 31 way to prevent aggregation of the gold nanoparticles in  
 32 solution.

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

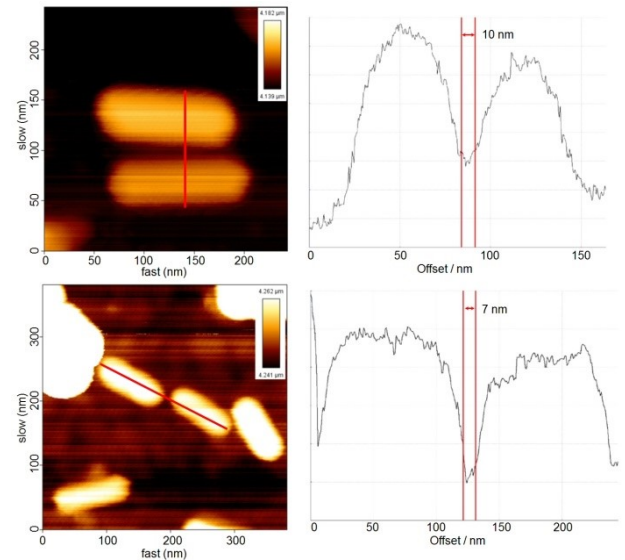


**Figure 3.** Extinction spectra of functionalized GNRs from 1 to 4 layers of polyelectrolytes. S0 is referred to the synthesized GNRs. Insert shows the evolution of the observed spectral shift with the estimated refractive index.

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  
 47 efficient in the first 10 nm closed to the surface of the  
 48 metallic nanoparticles.<sup>12, 22</sup> Surfactants or polyelectrolytes  
 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:

$$56 \quad RI = 1,33 \times \frac{V_{tot} - \sum_i V_{layer}}{V_{tot}} + \sum_i RI_{layer} \times \frac{V_{layer}}{V_{tot}} \quad (1)$$

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

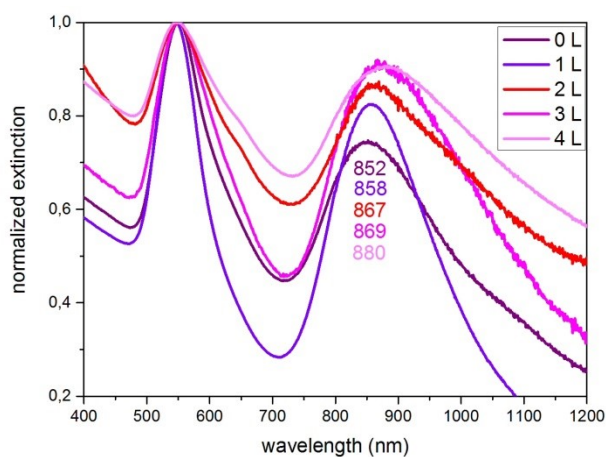


**Figure 4.** Left: AFM imaging of deposited GNRs-1L. Right: corresponding gap measurements between 2 GNRs-1L.



1 To go further than these results obtained in solution  
 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  
 9 gap value between two GNRs is 8 nm which clearly  
 10 indicates that the PSS layer induces repulsive forces  
 11 between the nanoparticles. It means that polyelectrolytes  
 12 functionalization prevents the aggregation in solution but  
 13 also modulates the gap between deposited nanoparticles  
 14 which is very important when dealing with inter-  
 15 nanoparticles' coupling. AFM measurement with more than  
 16 one layer was not possible due to the quantity of polymer  
 17 surrounding the GNRs which pollutes the AFM tip and  
 18 makes imaging complicated. Looking at the study of  
 19 Möhwald and co-workers<sup>21</sup>, a single layer of polyelectrolyte  
 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  
 26 glass substrates to allow absorption measurements on solid  
 27 sample. Prior to the deposition, the glass slide was washed  
 28 using first ethanol and secondly oxygen plasma cleaner.  
 29 Then we deposit 50  $\mu$ L of high concentrated solution of  
 30 layered GNRs by the droplet method and we waited until  
 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,  
 35 we observed the same behavior as the solution samples. The  
 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  
 39 refractive index increases. In contrast with the solution



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

40 samples, it is rather difficult to estimate the value of the  
 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  
 61 are closely packed. That is why SEM measurements are  
 62 only used to characterize the close packing and not the inter-  
 63 particle distances. SEM imaging, in supporting information,  
 64 clearly show wide areas of high density packing of GNRs.  
 65 Regarding absorption spectroscopy, these closed packed  
 66 nanorods induce the broadening of the LSPR bands but also  
 67 a specific band that appears around 660 nm, due to  
 68 transverse coupling between GNRs allowed by the short  
 69 inter-particles distance.<sup>23</sup> 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  
 74 nanoparticles and targeted organic dye is mandatory for  
 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  
 81 any modification of the GNRs' surface, putting some  
 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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95 Supporting Information is available on  
 96 [http://dx.doi.org/10.1246/cl.\\*\\*\\*\\*\\*](http://dx.doi.org/10.1246/cl.*****)  
 97

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