Response to Reviewer 1 Comments

Point 1: Introduction – Pag. 1 Lines 22-39: some references could be added, in particular the Authors should also highlight that NPMs, and in particular NPG, has a larger impact nowadays in plasmonics (see for instance Garoli et al. ACS Photonics 2018, 5, 3408-3414), which goes beyond SERS, for instance high bio-chemo-sensing performances have been recently demonstrated by Ruffato et al. (Opt. Express 2011, 19, 13164-13170) or by Garoli et al. (Nanoscale 2015, 9, 915-922), or extraordinary optical transmission (Garoli et al. Journal of Vacuum Science & Technology B 2013, 31, 012601).

Response 1: Thank you for the comment, and we read the additional references and added them at the proper positions.

Point 2: In addition to references 23-25, the Authors can also cite other techniques to synthetize nanoporous gold films, such as Garoli et al. Optical Materials Express 2015, 5, 2246-2256.

Response 2: We studied the techniques that recommended by the reviewer, and cited it in the revised manuscript for comparing.

Point 3: Pag. 2 Line 42: define quantitatively "ultrapure" water.

Response 3: We added the definition of ultrapure water in the revised manuscript.

Point 4: It is not clear to me if the SiO2 coating is obtained by oxidation of gold rather than for hydrolysis, at least for very small thickness of SiO2…how do the Authors know that the coating is due to the process they introduce in Figure 1 rather than for simple oxidation? A technique used to cover NPG with SiO2 was also recently proposed by Garoli et al. (see Nanoscale 2015, 9, 915-922), where they use ALD instead of chemical synthesis to have a more aware control of the SiO2 deposition. The Authors should make a comparison between their technique and the aforementioned one. I suggest them to highlight the advantages and drawbacks of both. This comparison would enrich a lot the discussion about the fabrication step reported in the article.

Response 4: Thank you for the comments. In our lab, we do not have the facility for depositing silica with ALD method, so we used a wet chemical method reported by Pastoriza-Santos et al. and Obare et al.. The formation of the mesoporous silica coating is due to base-catalyzed hydrolysis of TEOS and subsequent condensation of silica onto the surface of the CTAB molecules (Chem. Mat 2006, 18, 2465; Nano Lett. 2001, 1, 601). We have added a comparison of the two methods.

Point 5: Is the SPR a localized SPR? The red-shift should also indicate how much

sensitive is the NPG over a change of RI due to the change of SiO2 thickness. If after 5h the thickness of SiO2 is 5nm, and the spectral shift is about 60nm, the Authors could also extract the corresponding sensitivity of the material in terms of wavelength shift over a RI change. Roughly speaking the RI changes from 1 to 1.45 (average SiO2 RI in the visible), so 60nm/0.45 is about 135nm/RIU, which is pretty in line with the usual RI sensors based on LSPR.

Response 5: Thank you for the comments and suggestions. We revised SPR into LSPR.
In this work only one medium was used to tune the LSPR, so we didn't make any conclusion between the RI and the LSPR shift. In our future work we will change the shell outside the NPG into different materials with varied RI, and we would to provide more experiment results to support the relationship between RI and LSPR of NPG.

Point 6: Did the Authors evaluate the angular dependence of the extinction for particular cases (for instance the 0h and 5h cases) to check if also SPPs are present in their porous films? The peak at 490nm is due to interband transitions of the bulk gold or of the porous gold? I think that the latter is indeed the case, and the Authors should discuss this part also supported by numerical simulations (FDTD in 2D should work, just keeping a section of the nanoporous gold). An article recently appeared on ACS Photonics (2018, 5, 3408-3414) reports on the spectral tuning of the NPG films dispersion upon modification of the fractal-like pattern. This article can help the Authors to discuss better this part in their work.

Response 6: In this work, we didn't check SPPs. According to previous study, the band at 490 nm is related to the photoluminescence of the gold, resulting from electro transitions between the filled d-bands and the Fermi level in the conduction band [Phys. Rev. Lett. 22, 185(1969); Phys. Rev. B 33, 7923(1986).] . Additionally, we checked the recommended references, and further discussed in our manuscript.

Point 7: Pag. 4 Line 110: "as-prepared"?

Response 7: "as-prepared NPG" is bare NPG without silica coating, and we changed it to bare NPG in the revised manuscript.

Point 8: The spectra in Figure 4(b) are called "normalized spectra": normalized to what?

Response 8: The Raman intensities are normalized to with the Raman signal obtained from the bare NPG.

Point 9: Do the Authors have spectra with the same number of counts? This is to understand better what is the quality of the signal with the same number of counts for all three the cases analyzed by the Authors.

Response 9: Thank you for the comments, and we unified the counts number in the revised manuscript.

Point 10: What is the excitation wavelength for the case AuNPs and SiO2@AuNPs cases reported in Figure 4(e)-(f)?

Response 10: The Excitation wavelength is 633 nm, and we added it in the revised manuscript.

Point 11: Pag. 5 Line 115-117: the Authors write "It can be seen that the signal intensities decrease with the silica coating, indicating both the SPR and silica shell caused light bending contribute to the SERS activity of the core-shell 3D porous substrate." The Authors should be more clear about the term "light bending" and should also provide a clear and simple explanation to the observed decreasing of the SERS intensity. One reason can be simply that, being the excitation wavelength at 532nm, the LSPR is red-shifting for larger amount of SiO2 covering gold and so the enhancement due to plasmons is going far from the excitation wavelength, resulting then in a weakening of the SERS signal as now the molecules do not couple anymore efficiently with the LSPR of the NPG film.

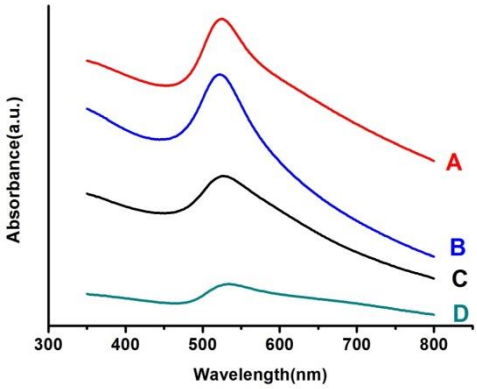
Response 11: Thank you for the reviewer's comment, and we have revised this part in the revised manuscript.

Point 12: Is the number of molecules used for all the experiments the same?

Response 12: To evaluate the SERS ability of silica coated NPG, 10^{-5}M CV aqueous solution was used; but for silica coated gold nanoparticles, 10^{-4}M CV aqueous solution was used.

Point 13: How does it look like the extinction spectra of the AuNPs? To make a fair comparison, such particles should resonate close to 633nm as the NPG film. Only in this way one can prove definitely the superior capability of NPG film with respect to AuNPs to enhance SERS.

Response 13: The resonance band of AuNPs that used in the experiment is around 520 nm(as shown in the following figures), which is identical with that of NPG films that used in the experiment.



Figre x1. Absorption spectra of AuNPs prepared with laser ablation. A) 25mins laser ablation, B) 20mins laser ablation, C) 15mins laser ablation, and D) 10mins laser ablation

Point 14: Pag. 5 Lines 125-128: The sentence does not make any sense to me. What are the Authors trying to say?

Response 14: Thanks, we revised this part in the revised manuscript.

Point 15: The Authors should also simulate core-shell nanoparticles. No images and no spectra for the AuNPs are reported, and this information should be added to the article to make the comparison between the two systems fair.

Response 15: Thank you for the referee's comments. We are carrying on the simulation, and the part for the isolated nanoparticle has been finished, but for the assembled nanoparticles, the simulation hasn't been finished yet.

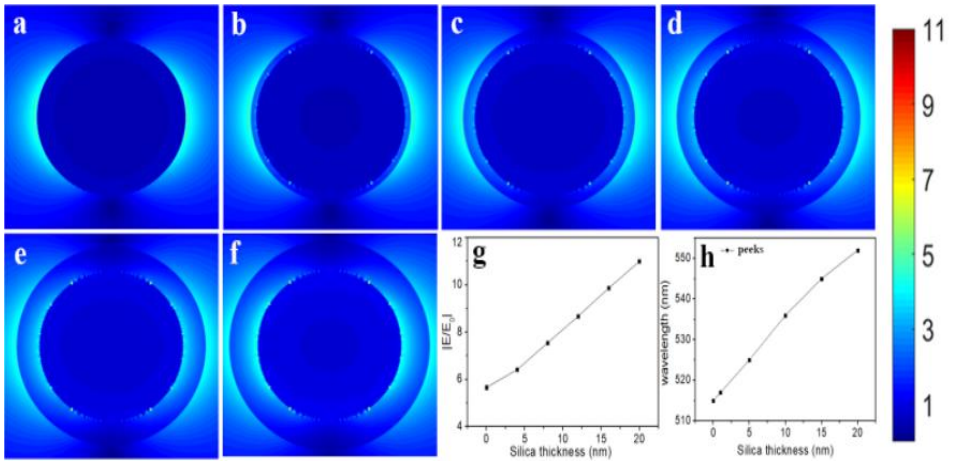


Figure x2. The local electromagnetic distributions on the top surface of AuNPs and SiO2 coated AuNPs. （a）0nm,（b）4nm,（c）8nm,（d）12nm,（e）16nm, and（f）20nm. (g) Variation of electric field intensity with silica thickness. (h) Variation of extinction wavelength with silica thickness.