pH effects on novel SERS active substrates

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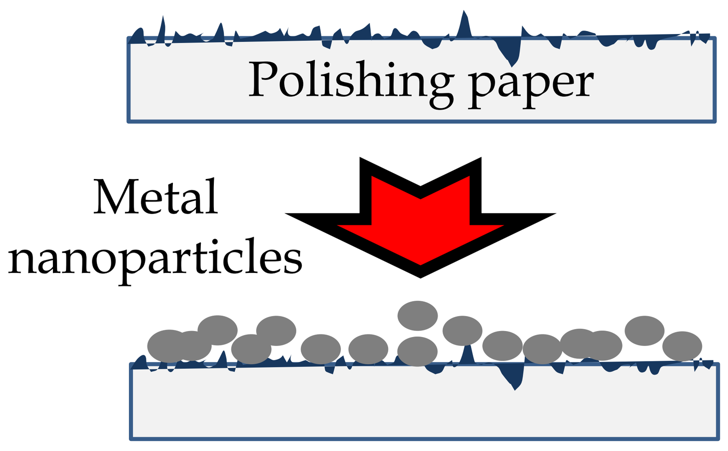
Gold and Silver Nanoparticles obtained from Pulsed Laser Deposition (PLD)[1-3] have been deposited on glass and a micrometric grit polishing paper (also called 'sandpaper'). It has been observed that pH values different from neutral can foster the SERS activity of some molecules. In this work we firstly tested the resistance of the substrates to different pH conditions from acid to basic. SERS measurements, then, were performed using an aqueous solution of Rhodamine 6G (R6G, weakly Raman-active) at different pH values between 3 and 11. No degradation of the SERS activity was observed in the pH investigated range for both glass and sandpaper substrates. For R6G differences of the SERS activity were observed depending on the acid or alkaline treatment.

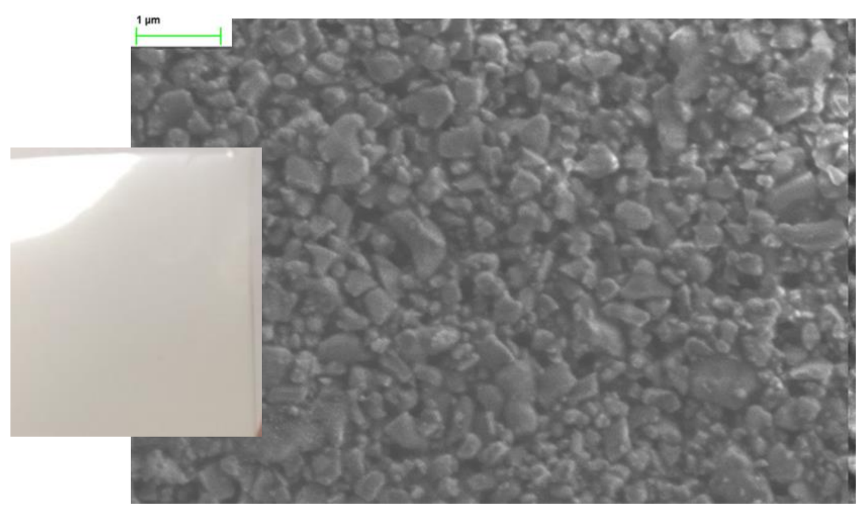
Pulsed Laser Deposition (PLD)

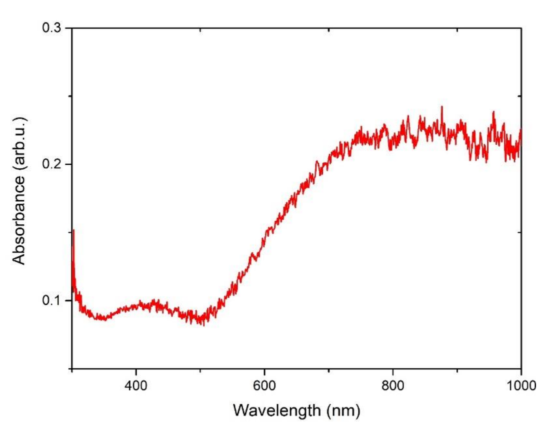


*Laser : **KrF** 248 nm*
E=200 mJ
*Fluence = **3.0 J/cm^{-2}***
***Ar pressure** inside the camera:*
Au : 100 Pa – Ag: 70 Pa

Substrate characterization

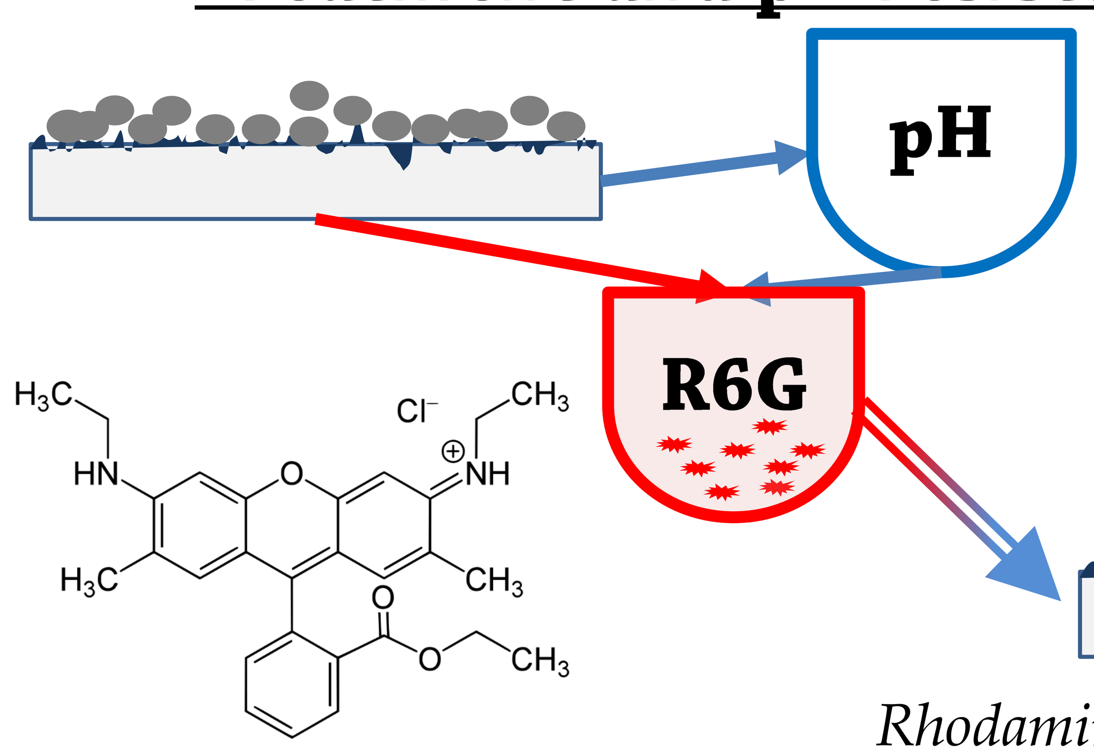
SEM images of silver coated white polishing film. The micrometric grit **allowed** a microstructured distribution.



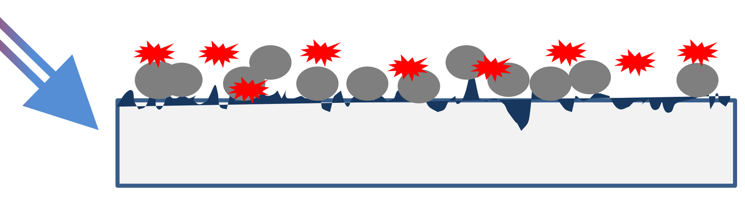


Absorbance spectra of Au-coated glass. The absorbance peak is **due to** the collective plasmonic vibration of the Au nanoparticles.

Treatment and pH resistance assessment



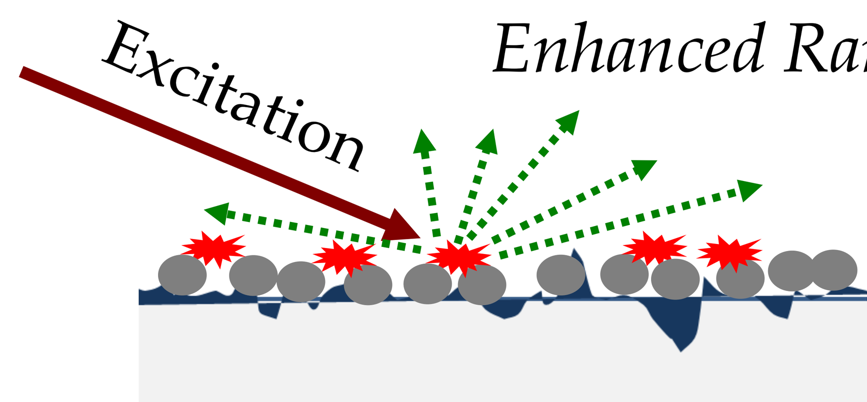
One series of samples **has been** immersed in controlled pH solutions (*pH 3, 7, 11*) for 1 hour, while another batch **has not**.

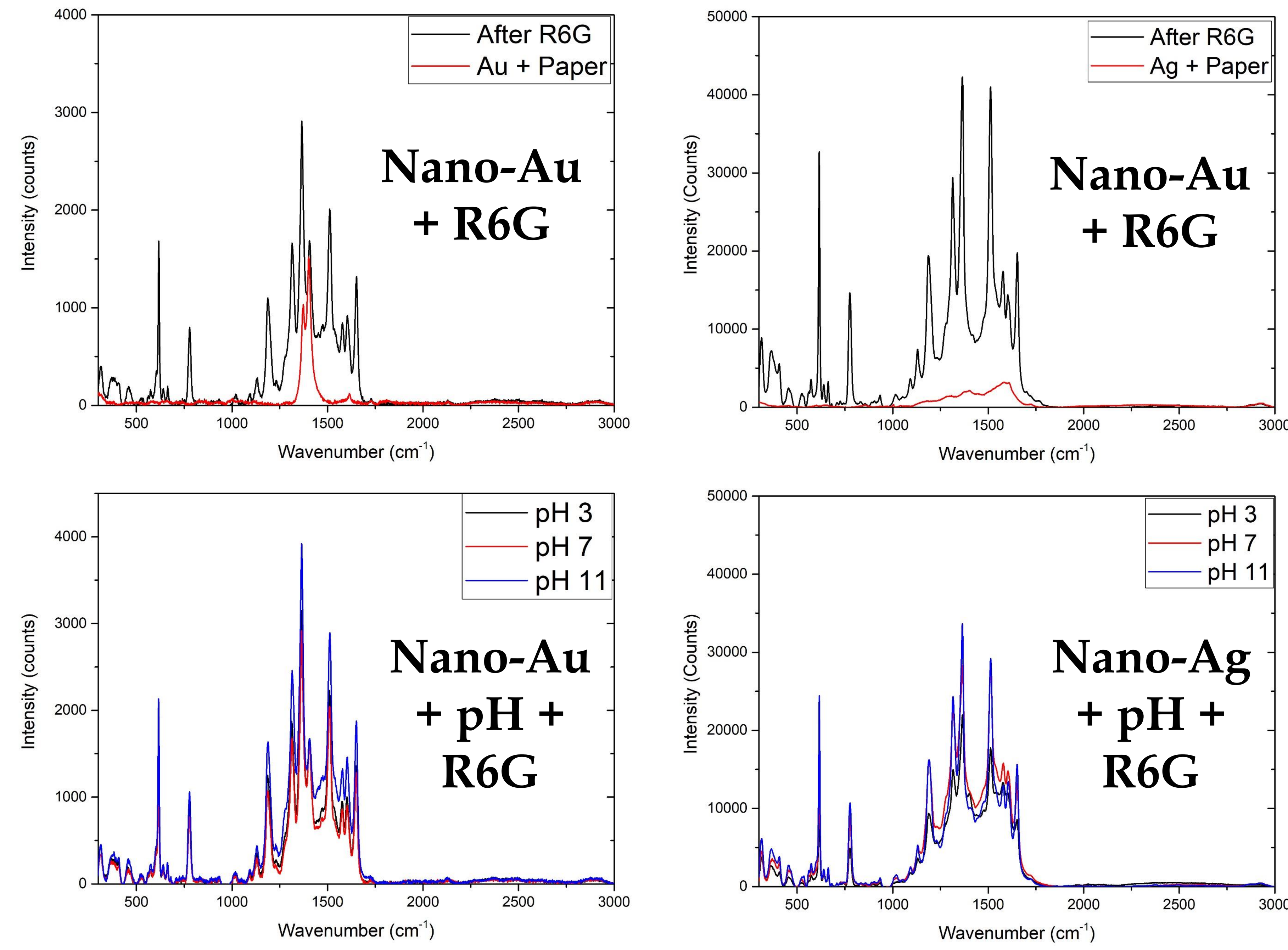


Rhodamine 6G is SERS active
***but** @[R6G] no Raman activity is observed.*

[R6G] = 2.5 · 10^{-5} M

Surface Enhanced Raman Spectroscopy

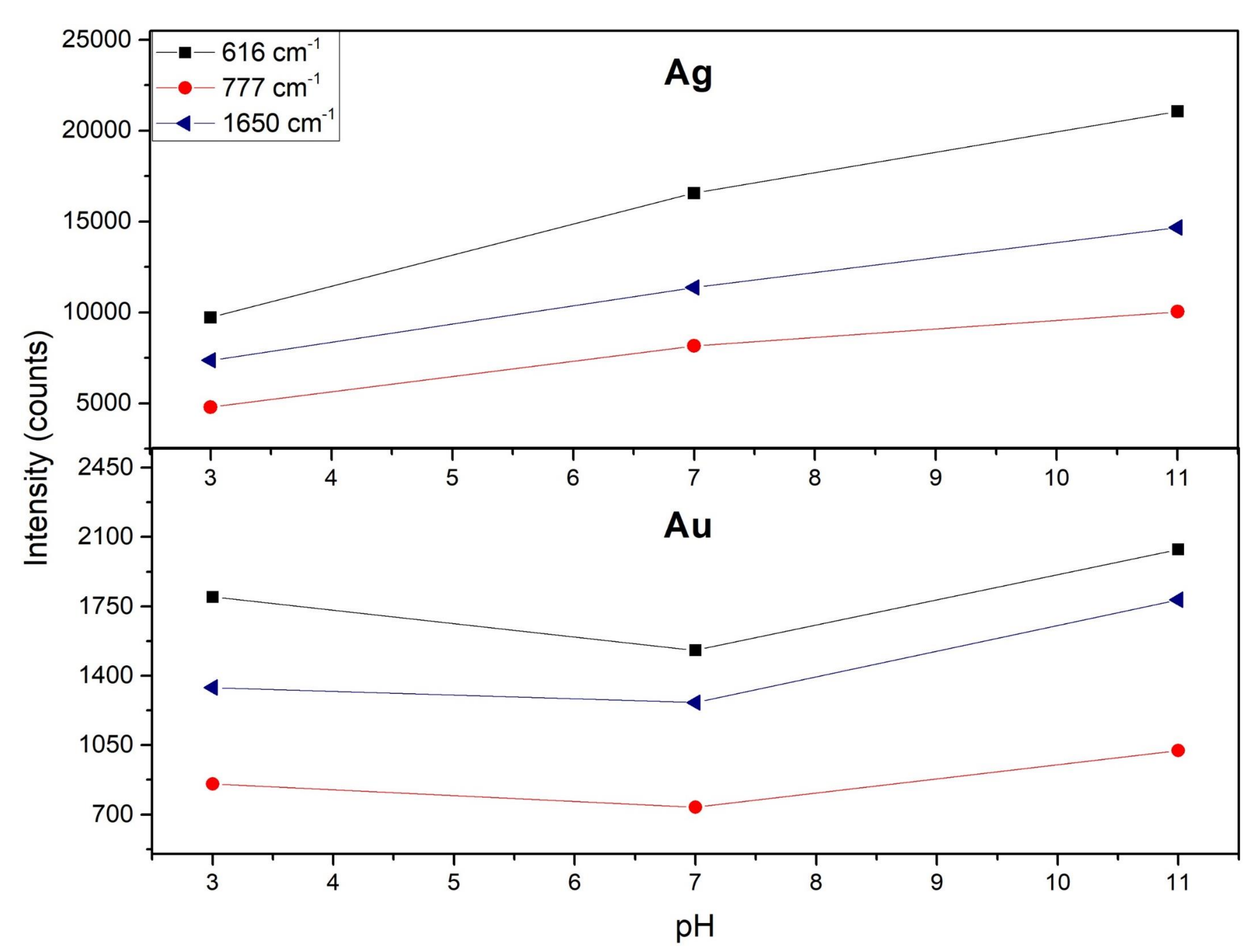




SERS amplification on Rhodamine 6G develops on all substrates, **even after** acid and alkaline treatment. Peaks due to paper substrate **are unchanged** by the treatment, indicating that the substrate **is not affected** by pH changes in the 3-11 pH range.

Conclusions

- Gold and silver nanoparticles deposited by PLD **are effective in** imparting SERS effect to paper and glass substrates.
- The enhancement effect is **OVER** 10 times higher for nano-Ag covered substrates compared to nano-Au covered substrates.
- Acid and alkaline treatments **DOES NOT** inhibit SERS activity.
- Alkaline treatment lead to a **higher enhancement** overall, both on glass and on paper, for both NP. Acid treatment improve the enhancement **only with Au NP**.
- The observed behavior points out for a difference in the adsorption of R6G on Ag and Au mediated by the pH (DFT studies are underway).



References:
[1] Agarwal, N. R., Tommasini, M., Fazio, E., Neri, F., Ponterio, R. C., Trusso, S., Ossi, P. M. (2014). Applied Physics A, 117(1), 347-351.
[2] Fazio, E., Trusso, S., Ponterio, R. C. (2013). Applied surface science, 272, 36-41.
[3] Fazio, E., Neri, F., Ponterio, R. C., Trusso, S., Tommasini, M., Ossi, P. M. (2014). Micromachines, 5(4), 1296-1309.