Peak position (cm <sup>-1</sup> )	SERS band assignment
937	$C_x$ - $C_x$ -H bending
1184	$C_x$ - $C_x$ stretching
1312	$C_x$ -H bending
1361	$C_x$ - $C_x$ stretching
1510	$C_x$ - $C_x$ stretching
1657	$C_x$ - $C_x$ stretching

Table 1: SERS band assignment for R6G

Peak position (cm <sup>-1</sup> )	SERS band assignment
843	Tyrosine
886	Tryptophan
956	Tyrosine
1000	Phenylalanine
1145	C-C stretching
1171	C-H in plane bending of Ty-
	rosine
1222	Amide III
1263	Amide III/C-N stretch
1297	$CH_2$ deformation
1339	Tryptophan
1380	Tryptophan
1417	$\delta(CH_2)$
1524	Amide II
1568	Tryptophan, Histidine
1650	Amide I

Table 2: SERS band assignment for bovine serum albumin

Peak fitting is carried out using Voigt function and a Levenberg Marquardt method is employed which gives convergence in 8 iterations. Only two peaks are fitted and the peak positions are 367.9 and 373.9 eV for Ag 3d5/2 and Ag 3d3/2 respectively. These values are in accordance with

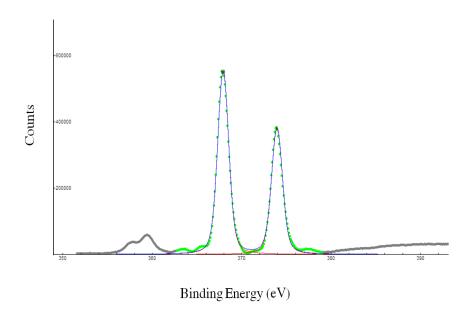


Figure 1: Peak fitting carried out for Ag 3d XPS peak showing no extra oxide component known literature values<sup>1</sup> for metallic Ag. Further, presence of oxide can also be determined by asymmetrical peak shape and peak fitting would show an extra peak on the higher energy side to the main Ag 3d peaks<sup>2</sup>. There is also a study which shows reduction in SERS intensity with oxidation of Ag<sup>3</sup> which does not match well with our data. The authors have shown a rapid decline in SERS activity with increasing thickness of oxide layer (EF reduces from 106 to 103) which we do not observe in our case.

## References

- [1] Weiping Cai, Huicai Zhong, and Lide Zhang. Optical measurements of oxidation behavior of silver nanometer particle within pores of silica host. *J. Appl. Phys.*, 83(3), 1998.
- [2] V. G. Pol, D. N. Srivastava, O. Palchik, V. Palchik, M. A. Slifkin, A. M. Weiss, and and A. Gedanken\*. Sonochemical Deposition of Silver Nanoparticles on Silica Spheres. *Langmuir*, 18(8):3352–3357, 2002.
- [3] Yun Han, Robert Lupitskyy, Tseng-Ming Chou, Christopher M Stafford, Henry Du, and Svetlana Sukhishvili. Effect of Oxidation on Surface-Enhanced Raman Scattering Activity of Silver Nanoparticles: A Quantitative Correlation. *Anal. Chem.*, 83(15):5873–5880, 2011.