

## Electronic Supplementary Information

### **Silver Nanoparticles, Nanoneedles and Nanorings: Impact of Electromagnetic Near-Field on Surface-Enhanced Raman Scattering**

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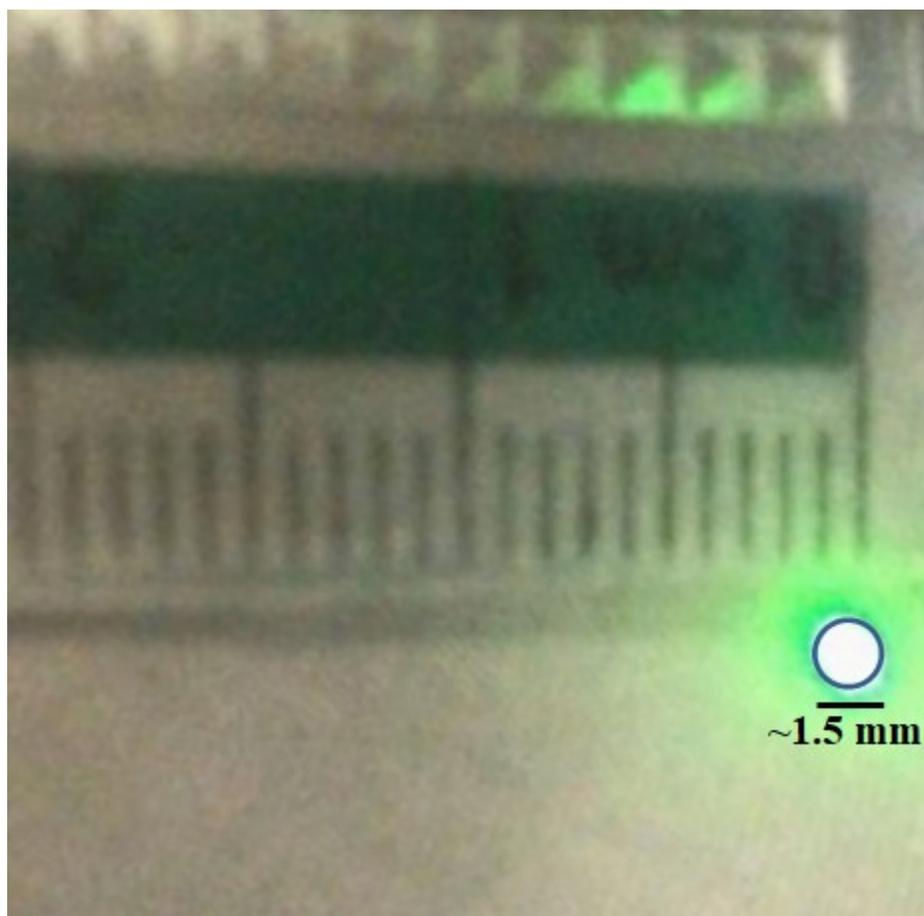
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## 1. Focus spot size of the laser

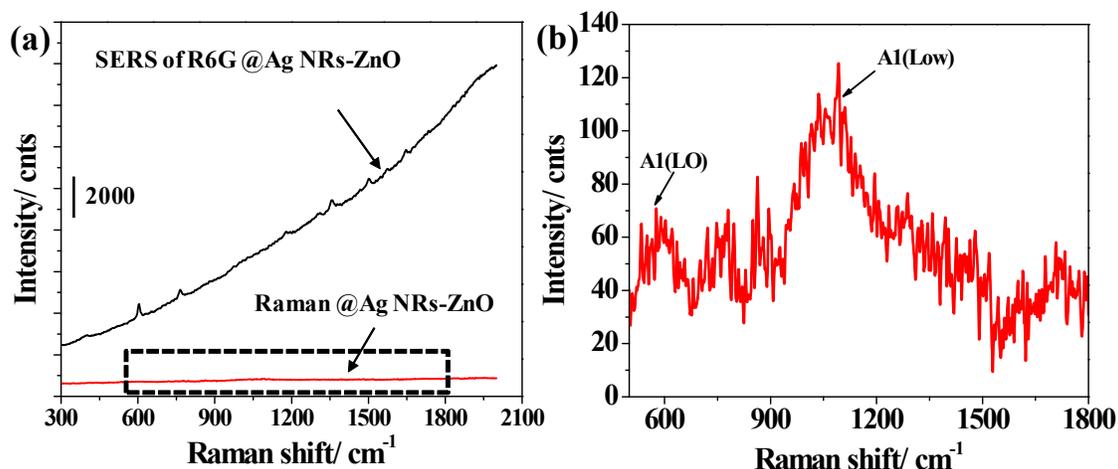
Under this investigation, an in-Situ Raman Spectrometer (Model # Horiba IHR-320) consisted of 10 m fiber optics and CCD was used in SERS measurements. An excitation laser of 532 nm of maximum power 300 mW was used. To avoid dissociation, the excitation was filtered to 40% and fed through an optical fiber. A long working distance lens (40x) was used to shine and collect the scattered signal in a backscattering configuration. The laser spot at the specimen was found quite large. We have re-examined the spot size and it was estimated to be 1-1.5 mm as shown in Fig. ESI1.



**Figure ESI1.** A snapshot of focused spot of laser at the same experimental conditions (excitation: 532 nm, power: 300 mW, filter: 40%, objective: 40X, grating: 600 g/mm and slit: 40  $\mu\text{m}$ ).

## 2. Raman spectrum of Ag NRs-ZnO:

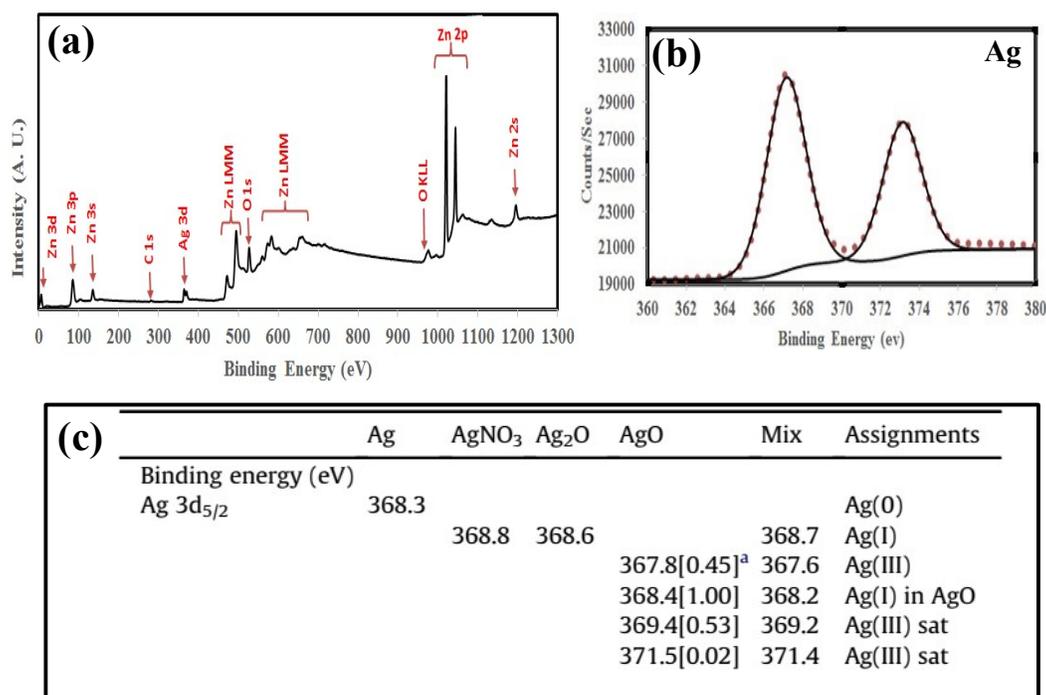
SERS spectrum of R6G adsorbed on Ag NRs-ZnO was recorded and shown in Fig. SI2a (black). As-fabricated Ag NRs were incubated with R6G of  $1 \times 10^{-6}$  M for 15 min. and washed copiously before SERS measurements. It was noted that the obvious strong fluorescence background did exist in the SERS spectrum. On the other hand, the Raman spectrum of Ag NRs-ZnO as shown in Fig. ESI2a (red) was observed to be quite different. A zoom-in view as marked by the black dashed rectangle in Fig. ESI2a was shown in Fig. ESI2b. It is noteworthy that two broadened Raman bands located at  $596 \text{ cm}^{-1}$  ( $A_1$ : longitudinal mode) and  $1098 \text{ cm}^{-1}$  ( $A_1E_2$ : Symmetry) were observed and coincided well with the work as reported by R. S. Zeferino [1].



**Figure ESI2.** (a) SERS spectrum of R6G @Ag NRs-ZnO (black) and Raman spectrum @Ag NRs-ZnO (red) and (b) Zoom-in view of the Raman spectrum @Ag NRs-ZnO as marked by the black dashed rectangle in Fig SI2a.

### 3. XPS measurement:

The purity of Ag nanoparticles was examined by XPS measurement and Ag(0) was distinguishable from Ag(I) or Ag(III) mainly through the Ag 3d<sub>5/2</sub> binding energies. Fig. ESI3a shows the wide survey spectrum in the range of 0-1300 eV and the Ag 3d XPS of the Ag NRs-ZnO sample (Fig. ESI3b). A. M. Ferraria et al. at the Technical University of Lisbon presented some excellent results and analysis of a variety of Ag species [2]. The main results of their work are summarized in Fig. ESI3c. As can be seen, the deconvolution of Ag 3d<sub>5/2</sub> showed only one peak, indicating the formation of only one oxidation state. Comparing the binding energy of the obtained peak (367.15 eV) with the work reported by A. M. Ferraria, one can easily conclude that the Ag produced in this work was pure metallic Ag [2].



**Figure ESI3.** XPS analysis of Ag NRs-ZnO. (a) Wide survey spectrum in the range of 0-1300 eV, (b) XPS spectrum of Ag3d core level and (c) reported XPS for Ag and AgO [2].

#### 4. SERS enhancements

Eight SERS bands of R6G were observed in presence of Ag NPs-ZnO, Ag NRs-ZnO and Ag NNs-ZnO. Considering the SERS band and Raman bands of R6G, enhancement factors (EF) were estimated using the following empirical formula [3-5],

$$EF = \left( \frac{I_{SERS}}{I_{bulk}} \right) \times \left( \frac{C_{bulk}}{C_{SERS}} \right)$$

whereas,  $I_{SERS}$  and  $I_{bulk}$ , represent intensities of SERS and Raman measurements at a specific vibrational mode respectively.  $C_{SERS}$  and  $C_{bulk}$  represent the molarities of molecules used in SERS and Raman measurements respectively

Table ESI: SERS bands of R6G, corresponding band assignments and EFs in presence of Ag NPs-ZnO, Ag NRs-ZnO and Ag NNs-ZnO.

SERS Band of R6G (cm <sup>-1</sup> )	Band Assignment	Band Intensity @Ag NPs-ZnO	EF	Band Intensity @Ag NNs-ZnO	EF	Band Intensity @Ag NRs-ZnO	EF
610	C-C ring bending mode (in-plane) in phenyl rings	Weak (645 cnts)	~2.16×10 <sup>4</sup>	Moderate (944 cnts)	~3.17×10 <sup>4</sup>	Strong (1262 cnts)	~4.24×10 <sup>4</sup>
769	C-H bending mode (out-of-plane)	Weak (222 cnts)	~0.81×10 <sup>4</sup>	Moderate (351 cnts)	~1.29×10 <sup>4</sup>	Strong (773 cnts)	~2.83×10 <sup>4</sup>
1182	C-H bending mode (in-plane) in xanthene ring	Weak (279 cnts)	~1.82×10 <sup>4</sup>	Moderate (330 cnts)	~2.16×10 <sup>4</sup>	Strong (405 cnts)	~2.65×10 <sup>4</sup>
1310	Hybrid mode in xanthene/phenyl rings and NHC <sub>2</sub> H <sub>5</sub> group	Weak (27 cnts)	~0.14×10 <sup>4</sup>	Moderate (163 cnts)	~0.85×10 <sup>4</sup>	Strong (321 cnts)	~1.67×10 <sup>4</sup>
1361	C-C stretching mode in xanthene ring	Weak (283 cnts)	~1.48×10 <sup>4</sup>	Moderate (438 cnts)	~2.29×10 <sup>4</sup>	Strong (1063 cnts)	~5.57×10 <sup>4</sup>
1508	C-C stretching mode in xanthene ring	Weak (102 cnts)	~0.81×10 <sup>4</sup>	Moderate (387 cnts)	~3.07×10 <sup>4</sup>	Strong (761 cnts)	~6.04×10 <sup>4</sup>
1579	C-C stretching mode in phenyl ring	Weak (122 cnts)	~0.86×10 <sup>4</sup>	Moderate (123 cnts)	~0.86×10 <sup>4</sup>	Strong (439 cnts)	~3.09×10 <sup>4</sup>
1652	C-C stretching mode in xanthene ring	Weak (178 cnts)	~0.82×10 <sup>4</sup>	Moderate (320 cnts)	~1.48×10 <sup>4</sup>	Strong (502 cnts)	~2.31×10 <sup>4</sup>

## Reference

1. Zeferino, R. Sánchez, M. Barboza Flores, and U. Pal. "Photoluminescence and Raman scattering in Ag-doped ZnO nanoparticles." *Journal of applied physics* 109, no. 1 (2011): 014308.
2. Ferraria, Ana Maria, Ana Patrícia Carapeto, and Ana Maria Botelho do Rego. "X-ray photoelectron spectroscopy: silver salts revisited." *Vacuum* 86, no. 12 (2012): 1988-1991.
3. Ozaki Y., Kneipp K., Aroca R. (2014). *Frontiers of surface-enhanced Raman scattering: single nanoparticles to single cells*. John Wiley & Sons Inc., New York, United States (ISBN10: 111835902X)
4. Hossain, Mohammad Kamal. "Surface-enhanced Raman scattering: a technique of choice for molecular detection." In *Materials Science Forum*, vol. 754, pp. 143-169. Trans Tech Publications Ltd, 2013.
5. Yamamoto, Yuko S., Mitsuru Ishikawa, Yukihiro Ozaki, and Tamitake Itoh. "Fundamental studies on enhancement and blinking mechanism of surface-enhanced Raman scattering (SERS) and basic applications of SERS biological sensing." *Frontiers of Physics* 9, no. 1 (2014): 31-46.