

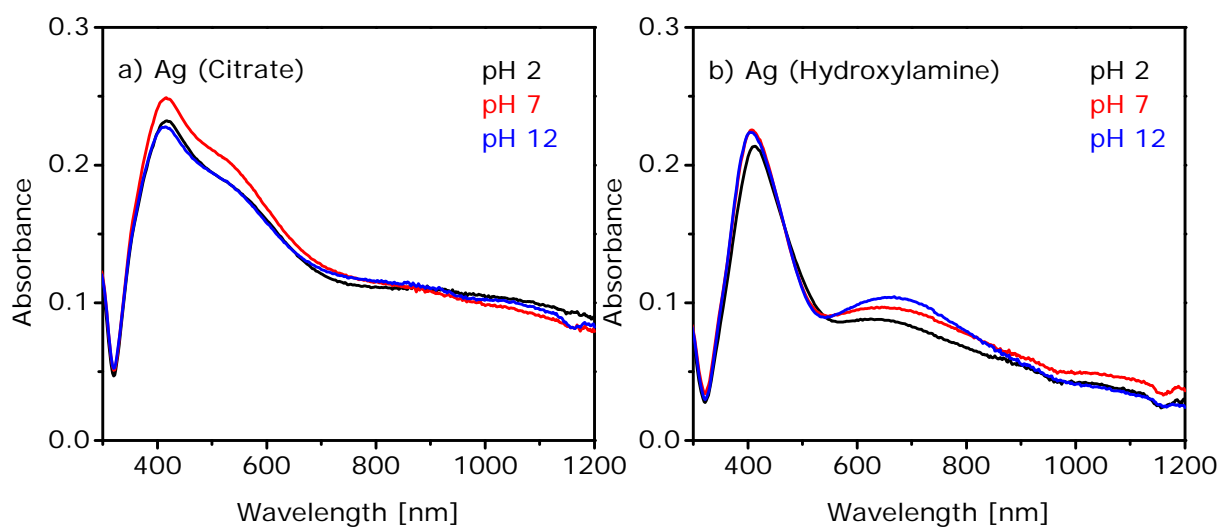
# Combined near-infrared excited SEHRS and SERS spectra for pH sensors using silver nanostructures

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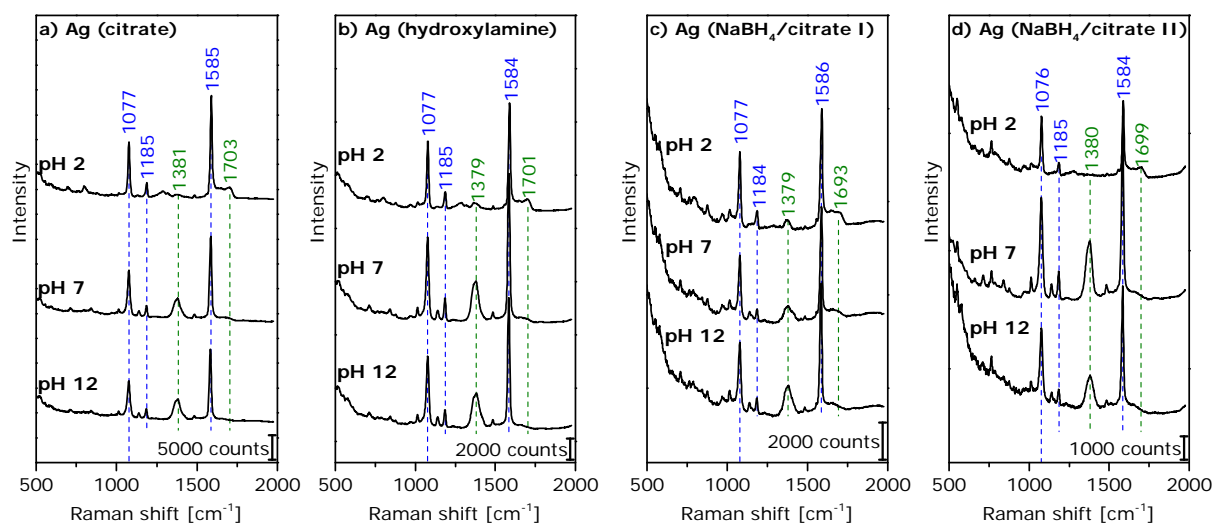
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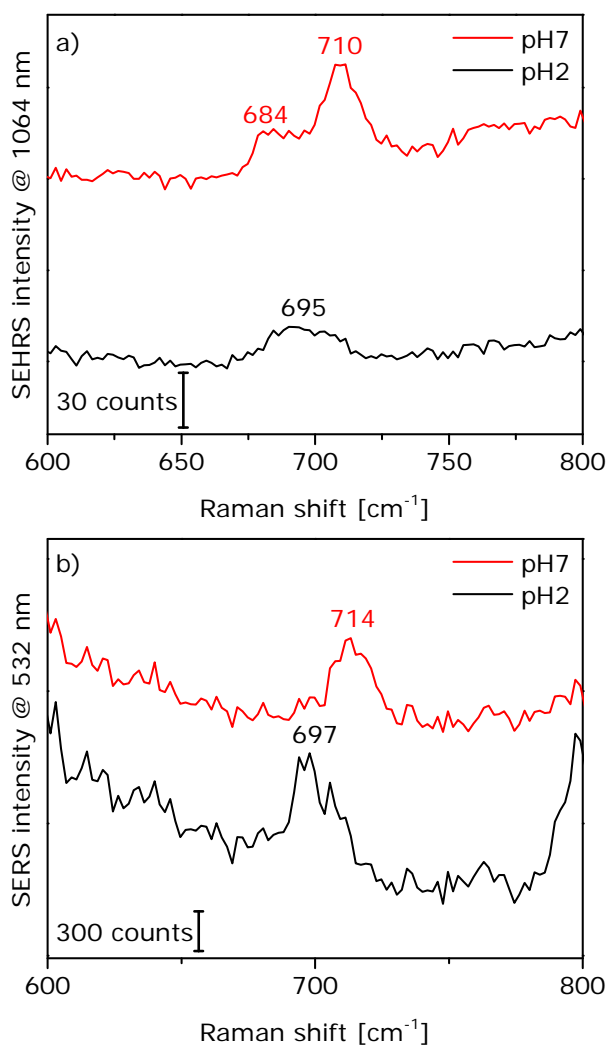
**Electronic Supplementary Information**



**Fig. S1.** Absorbance spectra of citrate reduced/stabilized (a) and hydroxylamine reduced (b) Ag nanoparticles with *p*MBA at different pH values.



**Fig. S2.** SERS spectra of *p*MBA excited at 532 nm with citrate reduced/stabilized (a), hydroxylamine reduced (b), NaBH<sub>4</sub> reduced, citrate stabilized I (c) and II (d) Ag nanoparticles. Excitation intensity:  $3 \times 10^5$  W/cm<sup>2</sup>, acquisition time: 1 s (a,b,d), 2 s (c), *p*MBA concentration:  $9 \times 10^{-7}$  M, averages of 30 spectra.



**Fig. S3.** Extracts of SEHRS (a) and SERS spectra (b) of *p*MBA with Ag (citrate) nanoparticles at an excitation wavelength of 1064 nm and 532 nm, respectively. Experimental conditions as described in Fig. 2 and S2, respectively.

**Table S1.** Band positions ( $\text{cm}^{-1}$ ) in SEHRS and SERS spectra of *p*MBA with Ag (citrate) at pH 7 and band assignments.

SEHRS (1064 nm)	SERS (1064 nm)	SERS (532 nm)	Assignment	References
	363		phenyl deformation + C-S-stretching	1, 2
520	523		in-plane ring deformation	2, 3
684			C-H out-of-plane deformation	4
695*		697*	C-H out-of-plane deformation + out-of-plane $\gamma(\text{CCC})$	
710	716	714	out-of-plane $\gamma(\text{CCC})$	1, 4, 5
		800*	out-of-plane C-COOH	6
836	839	842	COO <sup>-</sup> deformation	1, 5, 6
1009	1012	1013	ring deformation	7
1069	1075	1077	ring breathing	7
	1138	1139	C-COO <sup>-</sup> stretching	7
1178	1182	1185	C-H-in-plane-bending	7
1365		1368 (shoulder)	COO <sup>-</sup> stretching (COO <sup>-</sup> surface-bound)	5, 8
	1375	1381	COO <sup>-</sup> stretching (COO <sup>-</sup> non-surface-bound)	5
1479		1485	C-H in-plane-bending	7
1576	1583	1585	ring stretching	7
1685*		1703*	C=O stretching of protonated carboxyl group	5

\*band only observed at acidic pH

## References

- 1 S. B. Lee, K. Kim and M. S. Kim, *J. Raman Spectrosc.*, 1991, **22**, 811-817.
- 2 R. A. Alvarez-Puebla, D. S. Dos Santos and R. F. Aroca, *Analyst*, 2004, **129**, 1251-1256.
- 3 A. S. L. Lee and Y. S. Li, *Spectrochim. Acta, Part A*, 1996, **52**, 173-184.
- 4 Y. Wang, W. Ji, H. M. Sui, Y. Kitahama, W. D. Ruan, Y. Ozaki and B. Zhao, *J. Phys. Chem. C*, 2014, **118**, 10191-10197.

- 5 A. Michota and J. Bukowska, *J. Raman Spectrosc.*, 2003, **34**, 21-25.
- 6 C. X. Ma and J. M. Harris, *Langmuir*, 2011, **27**, 3527-3533.
- 7 Y. Liu, H. Yuan, A. M. Fales and T. Vo-Dinh, *J. Raman Spectrosc.*, 2013, **44**, 980-986.
- 8 H. K. Park, S. B. Lee, K. Kim and M. S. Kim, *J. Phys. Chem.*, 1990, **94**, 7576-7580.