ChemComm

COMMUNICATION

SERS from molecules bridging the gap of particle-in-cavity structures†‡

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We demonstrate that by combining silver nanoparticles and structured gold SSV surfaces the SERS for those molecules that bridge the nanoparticle–cavity gap is preferentially enhanced using 4-mercaptoaniline and 4-mercaptobenzoic acid as examples.

It is now well established that the electromagnetic 'hot spots,' such as those formed in the gap between nanoparticles[1–4] or between an atomically sharp metal tip and surface,[5,6] can be used to attain SERS (surface enhanced Raman spectra) of the molecules confined in such gaps. Controlling the surface plasmons resulting in SERS activity can also be achieved by defining the nanostructure using nanofabrication methods.[7–12] Recently we have reported a theoretical study of the plasmonic properties when a nanoparticle is confined in the cavity of a structured metal surface,[13] representing the combination of these two approaches. The calculations predict an additional enhancement of the electromagnetic field over that obtained on the sphere segment void (SSV) surface at the particle–cavity junction of two orders of magnitude, with the cavity acting to harvest the light, which is then focussed in the presence of the nanoparticle. Here we report an experimental study in which such particle-in-cavity structures are used to study the SERS of two of the more widely studied SERS probes, 4-mercaptoaniline (MA, also known as *p*-aminothiophenol) and 4-mercaptobenzoic acid (MBA).

The Au SSV substrates were prepared as described previously,[14,15] modified by immersion in an ethanolic solution of the adsorbate (MA or MBA), and rinsed in ethanol prior to collection of the reference SERS data. The modified substrates were then soaked in an aqueous suspension of polydisperse citrate stabilized Ag nanoparticles (average diameter 18 nm, pH 9.8, see ESI‡ for further details) for 2 hours and then rinsed with purified water before re-collecting the SERS. The MA and MBA modified surfaces were hydrophilic and readily wet by the aqueous solution. Similar data

were collected on the unstructured (flat) regions of the gold-coated glass slide, *i.e.* outside the templated area.

MA was selected as a probe molecule, as it bonds to the Au *via* cleavage of the SH bond, which should leave the amine group free to interact with the citrate protected Ag NPs. The SERS spectrum of MA has been extensively studied,[16–19] and shows both peaks attributed to charge transfer (CT) enhancement (9b, 3, 19b and 8b at 1140, 1386, 1425 and 1562 cm^{-1} respectively) and electromagnetic (EM) enhancement (7a and 8a at 1076 and 1590 cm^{-1}). As shown in Fig. 1(a), both types of peaks are observed for MA on the Au SSV substrate. After the addition of NPs (Fig. 1(b)), there is a very large increase in the SERS intensity (a factor of ×83 for the peak at 1076 cm^{-1}) and the spectrum is now dominated by the EM enhanced

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† This article is part of a ChemComm web-based themed issue on Surface Enhanced Raman Spectroscopy.
‡ Electronic supplementary information (ESI) available: Further experimental details and SEM images of the Au SSV substrate. See DOI: 10.1039/c0cc05325b
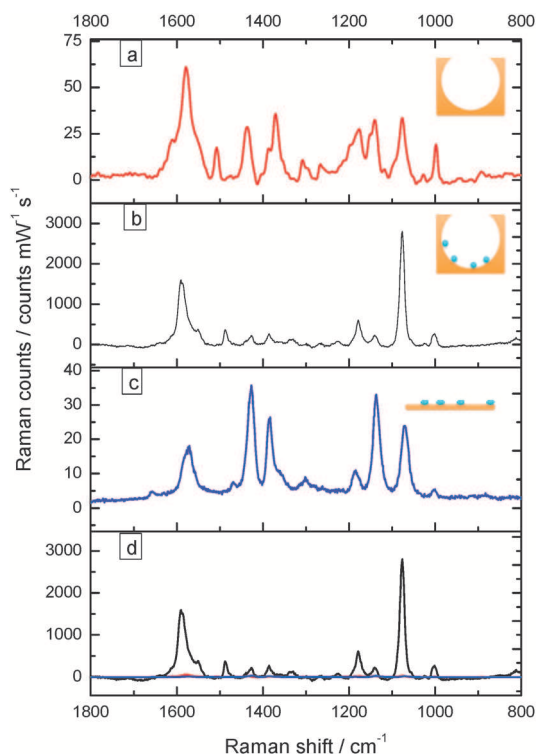

Fig. 1 SER spectra of (a) MA on a 600 nm 0.75*d* SSV substrate, (b) MA monolayer after soaking in Ag NP solution for 2 h, (c) MA monolayer on flat Au with NPs, and (d) all three spectra on the same scale to illustrate the differences in enhancement.
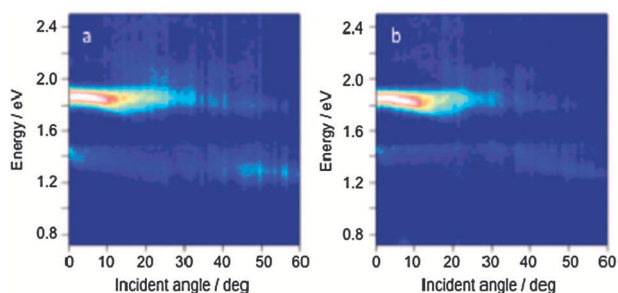
Fig. 2 Reflectance maps of (a) Au SSV with a monolayer of MA, (b) followed by modification with Ag NPs. Colour scale of absorbance from dark blue (0), yellow (1.1), white (1.6).

peaks at 1076 and 1588 cm^{-1}. No additional peaks attributable to the citrate stabilizer were observed.

The amount of Ag immobilized on the Au SSV substrate was quantitatively determined by electrochemical stripping voltammetry;[20] the value obtained, 0.46 mC cm^{-2}, corresponds to 5.4×10^{10} NPs cm^{-2} (assuming that the 18 nm average diameter of the particles was retained and the molar volume of Ag is 10.27 cm^3 mol^{-1}) or an average of 158 NPs per void.

In the presence of the nanoparticles the SERS signal was found to vary by 13% of the maximum signal using a 30 μm diameter spot (average over 19 voids), consistent with the reproducibility of the SERS on the SSV surface.[21] When the spot size was reduced to 0.5 μm diameter (1 void) the variability increased to 68%, with the minimum signal corresponding to 10× that of the SSV substrate without the nanoparticles, indicating that the number of nanoparticles per void and/or their position in the voids plays an important part in the magnitude of the enhancement.

The surface plasmons leading to EM enhancement for SSV substrates are well understood and are attributable to features of the structure.[14,15,22,23] As shown in Fig. 2, no discernable difference was observed in the reflectance spectra obtained for the MA modified Au SSV substrate upon adsorption of the Ag NPs (see the ESI‡), confirming that the increased SERS signal was not a result of Ag monolayer formation or a gross change in the SSV structure. This was further verified by examination of the SEM images, which also showed that the underlying SSV structure had been retained and that large aggregates of Ag nanoparticles were not present. The small size of the nanoparticles (average diameter 18 nm) meant that it was not possible to image individual nanoparticles or to determine the number of nanoparticles within each void of the SSV structure using the conventional SEM. In contrast large aggregates were seen in FEG-SEM images. As these would have been visible in the conventional SEM, their presence was attributed to beam damage.

The role of the SSV structure in the observed enhancement was examined experimentally by comparison of the enhanced spectrum with a spectrum obtained on a flat region of the gold-coated glass slide. As shown in Fig. 1(c), adsorption of the Ag NPs on the MA modified flat Au did yield weak SERS. In contrast to the SSV structured region, both the CT and EM bands were observed, with the CT modes being more strongly enhanced, in agreement with previous reports that SERS on flat surfaces is largely attributable to CT enhancement (Fig. 1(d)).[18,24]

The attribution of the peaks in the MA spectrum to CT and EM enhancements has recently been called into question by Wu *et al.*[25,26] They have shown that even low laser powers can cause photo-induced dimerisation of MA to form 4,4'-dimercaptobenzene (DMAB) on roughened Ag substrates and attribute the CT modes to the formation of such dimers. The presence of the peaks at 1425, 1386 and 1140 cm^{-1} in the spectra obtained for the unmodified SSV and flat Au-NP substrate may therefore indicate DMAB formation. The spectra obtained for the SSV substrate modified with NPs, however, show only evidence of MA and not DMAB. The absence of modes attributable to DMAB cannot be simply interpreted as an absence of the dimers. Instead we suggest that it provides evidence that the additional electromagnetic enhancement resulting from the cavity–particle interaction is much larger for those molecules bridging this gap. Our calculations show that the field enhancement at the particle–cavity junction follows a power law dependence on the distance between the particle and the cavity surface with the field enhancement exponent varying between 1.5 and 2.[13] The field enhancement for the MA monomer should, therefore, be 2.8 to 4 times that for the DMAB dimer (assuming that the gap distance doubles), corresponding to a relative increase in the SERS intensities of ×64 to ×256, given its dependence on the fourth power of the optical field.[27] Thus, the spectra from the particle-in-cavity structure should be dominated by the monomer peaks as observed here.

The SERS of MBA (Fig. 3(a)) on the Au SSV substrate shows two large peaks at 1080 and 1580 cm^{-1} which are
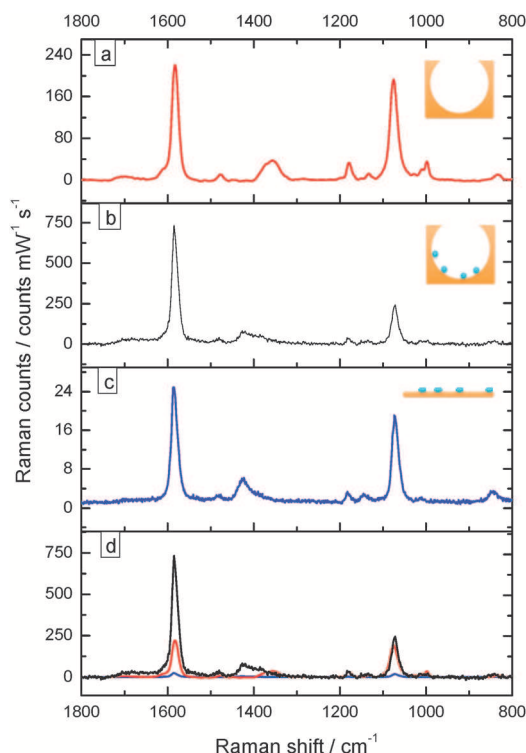

Fig. 3 SER spectra of (a) MBA on a 600 nm 0.75d SSV substrate, (b) MBA monolayer after soaking in Ag NP solution for 2 h, (c) MBA monolayer on flat Au with NPs and (d) all three spectra on the same scale to show enhancement.

attributed to the 12 (CT enhanced) and 8a (EM enhanced) ring modes.[18] The broad band at 1360 cm^{-1} is assigned to the v_s(COO$^-$) mode.[24] After formation of the MBA–NP adduct (Fig. 3(b)), the intensity of the EM enhanced mode is preferentially increased, and there is a shift in the position of the v_s(COO$^-$) mode to 1422 cm^{-1}. The SERS obtained for the Ag NP on a flat region of the MBA modified Au surface is shown in Fig. 3(c) and a similar shift in the v_s(COO$^-$) confirms interaction with the Ag NPs (Fig. 3(d)).

The additional SERS enhancement upon modification with Ag NPs observed for MBA in comparison to that observed for MA is notably smaller (only ×3 for the peak at 1580 cm^{-1}). The weaker interaction between the carboxylate group and the NP results in a lower coverage of Ag NP, as confirmed by the stripping voltammetry, which yielded a charge density of 0.12 mC cm^{-2}, corresponding to approximately 40 NPs per void.

In summary, we have shown that the modification of an adsorbate modified Au SSV substrate by Ag NPs results in a considerable increase in the SERS enhancement for adsorbates trapped between the SSV substrate and the NP. In contrast, SERS following adsorption of the Ag NPs on the adsorbate modified flat Au is far weaker. Whilst it is possible that some of the additional enhancement observed is due to a charge transfer interaction from the Au SSV–Ag NP SERS coupling, our theoretical calculations suggest that the significant contributor to the observed enhancement is an EM hot spot created at the junction of the Au SSV and Ag NP. The nanoparticle in the void further focuses the optical fields and concentrates light near the surface of the nano-voids.

Notes and references

1 F. Hubenthal, D. Blázquez Sánchez, N. Borg, H. Schmidt, H. D. Kronfeldt and F. Träger, *Appl. Phys. B: Lasers Opt.*, 2009, **95**, 351.
2 A. M. Schwartzberg, C. D. Grant, A. Wolcott, C. E. Talley, T. R. Huser, R. Bogomolni and J. Z. Zhang, *J. Phys. Chem. B*, 2004, **108**, 19191.
3 R. C. Maher, S. A. Maier, L. F. Cohen, L. Koh, A. Laromaine, J. A. G. Dick and M. M. Stevens, *J. Phys. Chem. C*, 2010, **114**, 7231.
4 J. J. Mock, M. Barbic, D. R. Smith, D. A. Schultz and S. Schultz, *J. Chem. Phys.*, 2002, **116**, 6755.
5 B.-S. Yeo, J. Stadler, T. Schmid, R. Zenobi and W. Zhang, *Chem. Phys. Lett.*, 2009, **472**, 1.
6 E. Bailo and V. Deckert, *Chem. Soc. Rev.*, 2008, **37**, 921.
7 M. E. Abdelsalam, S. Mahajan, P. N. Bartlett, J. J. Baumberg and A. E. Russell, *J. Am. Chem. Soc.*, 2007, **129**, 7399.
8 S. Cintra, M. E. Abdelsalam, P. N. Bartlett, J. J. Baumberg, T. A. Kelf, Y. Sugawara and A. E. Russell, *Faraday Discuss.*, 2006, **132**, 191.
9 L. A. Dick, A. D. McFarland, C. L. Haynes and R. P. Van Duyne, *J. Phys. Chem. B*, 2002, **106**, 853.
10 J. Henzie, J. Lee, M. H. Lee, W. Hasan and T. W. Odom, *Annu. Rev. Phys. Chem.*, 2009, **60**, 147.
11 X.-M. Lin, Y. Cui, Y.-H. Xu, B. Ren and Z.-Q. Tian, *Anal. Bioanal. Chem.*, 2009, **394**, 1729.
12 R. P. Van Duyne, J. C. Hulteen and D. A. Treichel, *J. Chem. Phys.*, 1993, **99**, 2101.
13 F. M. Huang, D. Wilding, J. D. Speed, A. E. Russell, P. N. Bartlett and J. J. Baumberg, *Nano Lett.*, 2011, **11**, 1221.
14 S. Cintra, M. E. Abdelsalam, P. N. Bartlett, J. J. Baumberg, T. A. Kelf, Y. Sugawara and A. E. Russell, *Faraday Discuss.*, 2006, **132**, 191.
15 R. M. Cole, J. J. Baumberg, F. J. Garcia de Abajo, S. Mahajan, M. E. Abdelsalam and P. N. Bartlett, *Nano Lett.*, 2007, **7**, 2094.
16 C. Chenal, R. L. Birke and J. R. Lombardi, *ChemPhysChem*, 2008, **9**, 1617.
17 D. P. Fromm, A. Sundaramurthy, A. Kinkhabwala, J. Schuck, G. S. Kino and W. E. Moerner, *J. Chem. Phys.*, 2006, **124**, 061101.
18 M. Osawa, N. Matruda, K. Yoshii and I. Uchida, *J. Phys. Chem.*, 1994, **98**, 12702.
19 T. Shegai, A. Vaskevich, I. Rubinstein and G. Haran, *J. Am. Chem. Soc.*, 2009, **131**, 14390.
20 W. R. Vandaveer and I. Fritsch, *Anal. Chem.*, 2002, **74**, 3575–3578.
21 S. Mahajan, J. J. Baumberg, A. E. Russell and P. N. Bartlett, *Phys. Chem. Chem. Phys.*, 2007, **9**, 6016.
22 T. A. Kelf, Y. Sugawara, R. M. Cole, J. J. Baumberg, M. E. Abdelsalam, S. Cintra, S. Mahajan, A. E. Russell and P. N. Bartlett, *Phys. Rev. B: Condens. Matter Mater. Phys.*, 2006, **74**, 1.
23 S. Mahajan, R. M. Cole, B. F. Soares, S. H. Pelfrey, A. E. Russell, J. J. Baumberg and P. N. Bartlett, *J. Phys. Chem. C*, 2009, **113**, 9284.
24 A. Michota and J. Bukowska, *J. Raman Spectrosc.*, 2003, **34**, 21.
25 Y.-F. Huang, H.-P. Zhu, G.-K. Liu, D.-Y. Wu, B. Ren and Z.-Q. Tian, *J. Am. Chem. Soc.*, 2010, **132**, 9244.
26 D.-Y. Wu, L.-B. Zhao, X.-M. Liu, R. Huang, Y.-F. Huang, B. Ren and Z.-Q. Tian, *Chem. Commun.*, 2011, **47**, 2520.
27 E. C. Le Ru and P. G. Etchegoin, *Chem. Phys. Lett.*, 2006, **423**, 63.