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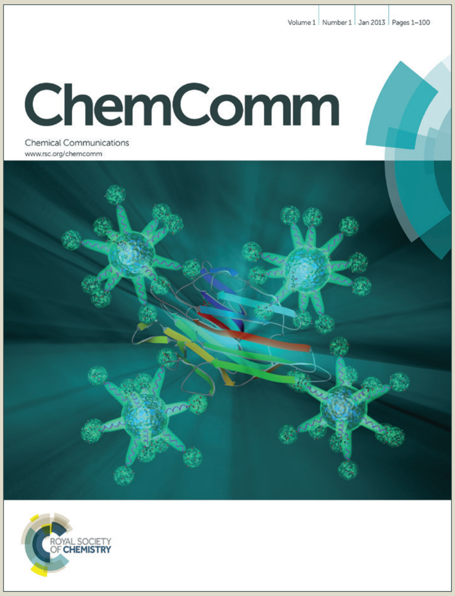

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COMMUNICATION

Electrochemical modulation of SERS at the liquid/liquid interface†

Cite this: DOI: 10.1039/x0xx00000x

Samuel G. Booth,[a] David P. Cowcher,[a,b] Roy Goodacre[a,b] and Robert A. W. Dryfe[a*]

Received 00th January 2012,
Accepted 00th January 2012

DOI: 10.1039/x0xx00000x

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A surface enhanced Raman scattering system to detect silver nanoparticle adsorption at the water|1,2-dichlorobenzene interface is reported. The Raman response as a function of distance on either side of the interface reveals a reproducible spatial variation, which is potential dependent for a number of adsorption and desorption cycles.

Surface enhanced Raman scattering (SERS) is a process by which the surface plasmon – the coherent oscillations of the delocalised electrons present at a metallic surface – may be excited by incident photons of suitable wavelength. This excitation provides a large increase in the intensity of the signal of any Raman active molecule adsorbed or microscopically close to the surface of the metal.[1-5] Aggregated nanoparticles are often used to act as the enhancement site. In the field of electrochemistry it has been shown that dye molecules may be selectively adsorbed to silver electrodes, through applied potential, to produce a SERS effect related to the analyte surface coverage.[6] An alternative medium for SERS, which has attracted some interest of late, employs particles adsorbed at a liquid|liquid interface (LLI) as a way of verifying nanoparticle thin film formation. Nanoparticle films have been shown to retain a surface plasmon,[7] which may be used as a point of detection for trace analytes in solution. The LLI has been utilized for nanoparticle thin film formation with subsequent attachment to a solid substrate for use in SERS detection.[8-11] Different methods have been utilised in order to produce a SERS response at the LLI using gold nanoparticles, silver nanoparticles and "metal like" liquid films, and mixtures of gold and silver nanostructures with varying shape.[12-14] As more becomes understood about the electrical and optical properties of the nanostructures formed at the LLI, greater signal enhancements may be achieved.[15]

The LLI may be polarised externally with a 4-electrode potentiostat where the potential is applied via two counter and two reference electrodes,[16] the resultant Galvani potential difference refers to the aqueous phase potential relative to the organic phase. To date there are no reports on SERS used in conjunction with electrochemical techniques at the interface between two immiscible electrolyte solutions (ITIES); although one report has had success in using it in the case of a three-phase system,[17] involving flowing an organic and aqueous phase above a solid electrode.

Due to the difficulty of detecting a SERS enhancement at the LLI compared with traditional nanoparticle aggregation, most research has relied on the use of dye molecules to provide a resonant enhancement to aid detection. These reporters are able to adhere to the nanoparticle surface and resonate at the frequency of the incident light source giving an intense resonance enhancement of the order of 10^6 compared with a standard signal. The aim of this study was to detect the presence of the silver nanoparticles at the LLI by examining their interaction with the electrolyte in the organic phase. The cation bis(triphenylphosphoranylidene)ammonium ($BTPPA^+$) should be able to bond directly to the nanoparticles (which are capped with citrate ions) through the protonated nitrogen group giving a chemical enhancement of the signal. This molecule was also used in the SERS experiment conducted by Cecchini *et al*.[12]

The experimental system shown in Figure 1 was employed with the laser initially focused on the organic bulk phase. From this position the height of the stage, z, was altered in 5 µm increments in order to observe changes in the Raman spectra at the LLI.

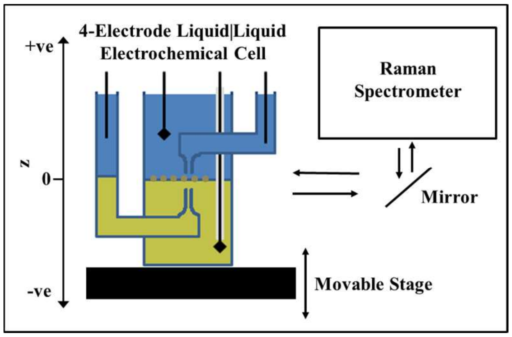

Figure 1. Experimental set up showing the electrochemical cell on the movable stage. The Galvani potential across the water|1,2-DCB interface was controlled through a 4-electrode potentiostat.

Figure 2 shows the difference in response for the bulk phase and the LLI region following nanoparticle adsorption. The peaks at 1038 cm^{-1} of the organic solvent, 1,2-dichlorobenzene (1,2-DCB), and 999 cm^{-1} from BTPPA$^+$ were chosen for analysis because of their high intensity, sharpness and lower signal overlap than the broad SERS peaks near 200 cm^{-1}.

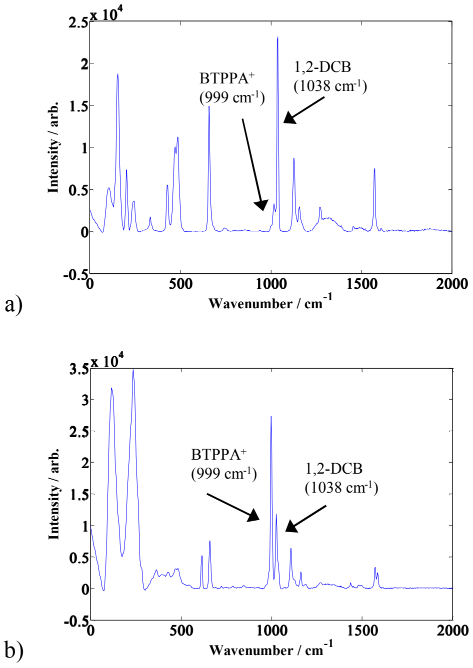

Figure 2. Raman spectra showing the change in response of the solvent signal at 1038.0 cm^{-1} and the analyte signal at 999.4 cm^{-1} seen when sampling: (a) the bulk organic phase; and (b) the LLI in the presence of silver nanoparticles.

The change in peak area as a function of depth was examined (Figure 3) showing an enhancement, which increased over time, showing spontaneous particle adsorption from the aqueous phase. A minor enhancement was seen in the same time period for the solvent peak at 1038.0 cm^{-1} due to the proximity to the nanoparticle layer. The variation in interfacial position points to a rearrangement of the LLI as the silver nanoparticles adsorb. Following this preliminary experiment, the SERS technique was used in combination with potential control. The nanoparticles have been shown to have an overall negative surface charge due to the coverage of citrate,[18] therefore a negative potential may be applied to the aqueous phase, relative to the organic phase, in order to drive particle adsorption. Adsorption is caused by the weak surface charge on the particles interacting with the strongly polarisable liquid/liquid interfacial region.[19] Desorption back into the bulk aqueous solution is also possible by reversing the polarity. Abid *et al.*[20] have previously demonstrated that nanoparticles can undergo a number of adsorption and desorption cycles using potential control. The nanoparticles were then seen to aggregate. In Abid's work, the behaviour was monitored by optical second-harmonic generation (SHG): when plasmon coupling causes a red-shift, the initial signal can no longer be resolved, therefore indicating aggregation.

A potentiostat was used to examine the potential dependence of the Raman signal intensity on the presence of silver nanoparticles at the LLI. Following an initial depth scan (100 spectra collected at 5 µm intervals proceeding from the organic bulk phase to the aqueous bulk phase), 100 µL of silver sol was added to the aqueous phase. Preparation and characterization of the particles are described in the Supporting Information. Initially there was no signal enhancement as the silver nanoparticles were predominantly dispersed in the bulk aqueous solution, however a fixed potential of 0.0 V was subsequently applied for 20 min to induce particle adsorption at the LLI.

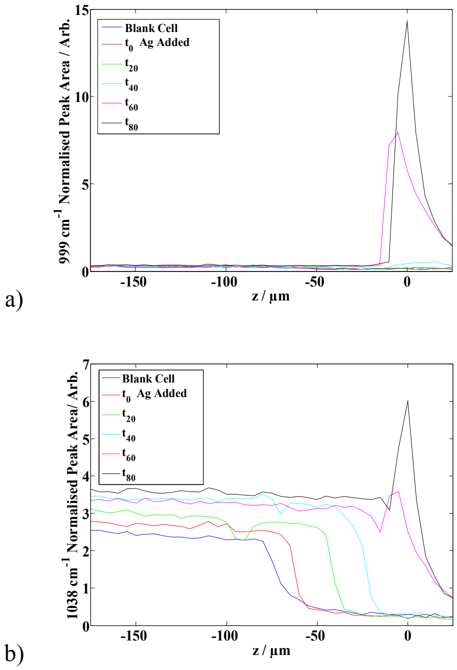

Figure 3. Raman depth profile through the LLI recording the spontaneous adsorption of silver nanoparticles with time, recorded in minutes after silver injection, the dependence of the intensities of: (a) the BTPPA$^+$ peak at 999 cm^{-1}; and (b) the 1,2-DCB peak at 1038 cm^{-1}.

Preliminary experiments at a number of intermediate potentials indicated that 0.0 V was below the potential of zero charge (PZC) for the LLI in the presence of nanoparticles. As noted above, this equates to a negative potential on the aqueous phase/relative to the organic, causing electrostatic repulsion of the nanoparticles in the bulk aqueous phase, in turn driving nanoparticle adsorption at the LLI, and simultaneously increasing the concentration of BTPPA$^+$ cation on the organic side of the interface therefore causing an enhancement of the organic cation signal (Figure 4). The potential was then changed to 1.0 V, which caused a reduction of the SERS enhancement presumably by driving the particles and BTPPA$^+$ back into their respective bulk phases. The Raman beam spot size is of the order of 1-2 µm therefore it is possible to detect silver adsorbed at different positions on the meniscus of the LLI leading to the additional enhancement peaks seen in Figure 4a. The noisy response for the solvent peak is believed to be due to the increased motion of the interface (LLI) under potential, rather than any partition of the silver particles to the organic phase, as a similar change in solvent signal was seen at positive potentials in the absence of the silver particles (see Supporting information). Following detection of the enhancement, the polarity of the cell was reversed to cause desorption of the particles. As can be seen from Figure 4, some enhancement relative to the initial cell remains. However there is a clear distinction between the two potentials. The adsorption/desorption cycle could be repeated for a number of cycles as shown in Figure 5. As found previously by Younan *et al.*[7] the initial long range adsorption of the nanoparticles is more dependent on time than interfacial potential. However, within the range of the electric double layer either side of the LLI, the potential appears to provide control over the adsorption and desorption of the nanoparticles.

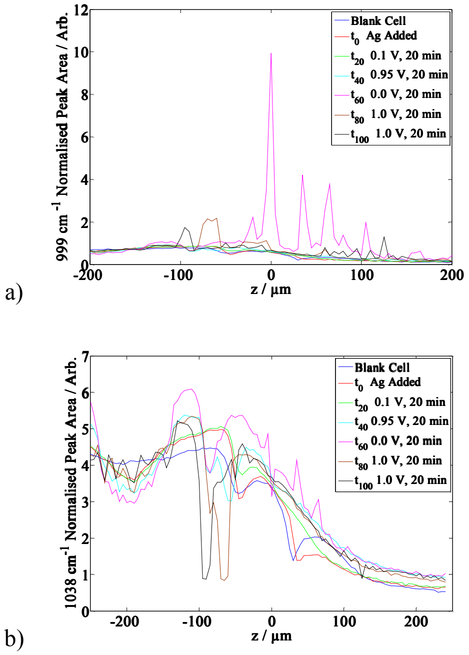

Figure 4. Raman depth profile through the LLI recording the potential controlled adsorption and desorption of the silver nanoparticles; time shown in minutes: (a) the BTPPA$^+$ peak at 999 cm^{-1}; (b) the 1,2-DCB peak at 1038 cm^{-1}.

There are two contributions towards the signal enhancement to consider. First, the adsorption of the silver nanoparticles is controlled by the potential due to their surface charge; therefore they should be driven to the LLI when the potential is 0.0 V and driven away from the LLI at 1.0 V.

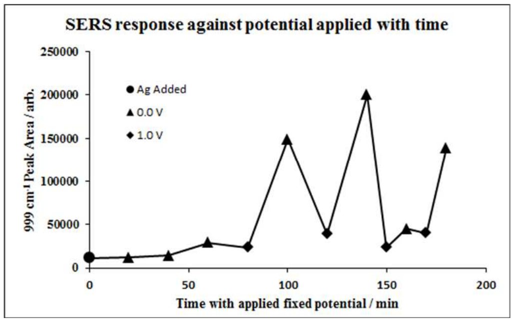

Figure 5. Variation in SERS signal intensity with applied potential as a function of time, based on the BTPPA$^+$ peak area at 999 cm^{-1}.

Second, the same dependence of concentration on potential should apply to the BTPPA$^+$ cation in the organic phase. It is not trivial to resolve the contribution from each factor. As there are a finite number of cycles which may be performed before the signal is lost, it appears that the initial aim of controlling the position of the nanoparticles is achieved. The variation in SERS response may be related to the extent of aggregation of the particle assembly. The loss of signal probably indicates that nanoparticle rafts form, which can be desorbed from the LLI under potential: some of the particles were subsequently seen to adsorb at the liquid/air interface, from where the signal cannot be recovered (See supporting information).

Conclusions

It has been shown that citrate stabilised silver particles are reversibly attached to a LLI of water|1,2-dichlorobenzene, as it was possible to remove the particles through a fixed potential bias of the interfacial region. This confirms the use of SERS, in combination with electrochemical techniques, to control nanoparticle adsorption and therefore offers a novel approach to the selective detection of analytes using liquid|liquid systems.

Acknowledgements We thank EPSRC for support (EP/H047786/1).

Notes and references

[a] Department of Chemistry, University of Manchester, Oxford Road, Manchester M13 9PL, UK, e-mail: robert.dryfe@manchester.ac.uk

[b] Manchester Institute of Biotechnology, University of Manchester, Princess Street, M1 7DN, UK

† w Electronic supplementary information (ESI) available: Experimental set up and particle characterisation. See DOI: 10.1039/c000000x/

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