Supplementary Information

Chemicals

Lithium chloride (LiCl, ≥ 99.99%), hydrochloric acid (HCl, ≥ 99.999%) and bis(triphenylphosphoranylidene)ammonium chloride (BTPPA.Cl, ≥ 98%) were purchased, from Sigma-Aldrich (Sigma-Aldrich, Gillingham, UK). Sodium tetrakis[3,5-bis(trifluoromethyl)phenyl]borate, (NaTFPB, ≥ 97%) was supplied by Alfa Aesar (Ward Hill, MA, United States) and 1,2-dichlorobenzene (1,2-DCB, ≥ 99%) came from Fluka. All of the chemicals required for this project were used without further purification. Ultrapure Millipore filtered water (Milli-Q, 18.2 MΩ cm resistivity) was used for all solution preparations. All glassware was cleaned and treated in Piranha solution (30% hydrogen peroxide, H_2O_2 and concentrated sulfuric acid, H_2SO_4, Fischer Scientific, 1:4 by volume) then boiled in ultrapure water and dried before use.

Silver Colloid

Silver nanoparticles were prepared using a modified Lee-Meisel[1] procedure as specified by Shadi *et al*.[2] To ensure that the particles were the desired size with a narrow size distribution, the wavelength of the surface plasmon resonance peak in the visible region was examined by UV-visible absorption spectroscopy. This was conducted on an Ocean Optics USB4000-UV-VIS spectrometer using a DH-2000-BAL balanced deuterium, tungsten, halogen light source. The silver nanoparticles had an absorption peak around 420 nm with a full width half height (FWHH) of 116 nm, typical of colloid prepared in our laboratory.[2] The particles were added to the aqueous phase (0.1 M LiCl, 1.0 mM HCl) of the electrochemical cell.

Electrochemical Control

Measurements were performed in a glass liquid|liquid cell (diameter 9 mm) using a 4-electrode system. Platinum flag electrodes were used for the aqueous working and organic counter electrodes. The organic electrode was coated in glass to avoid contact with the aqueous phase. Silver/silver chloride (Ag/AgCl) electrodes were used as the organic and aqueous reference electrodes. These were contained in different compartments and connected by Luggin capillaries. The organic reference is placed in an aqueous solution containing BTPPACl to act as a common ion across the liquid interface with the bulk organic phase. The potential was applied using a "Compactstat" potentiostat (Ivium Technologies, Eindhoven, NL).

Cell Composition

Ag (s)	AgCl (s)	10 mM LiCl 1.0 mM BTPPA.Cl (aqueous)	15.0 mM BTPPATFPB (1,2-DCB)	0.1 M LiCl 1.0 mM HCl (aqueous)	AgCl (s)	Ag (s)

Raman Spectroscopy

Raman spectra were recorded using a Renishaw inVia Raman microscope (Reinshaw plc., Wooton-Under-Edge, UK), with excitation from a 64 mW 785 nm 'Type R' diode laser (IPS, Monmouth Junction, NJ, USA). A 90° adapter was used to attach the 20x objective to the microscope, enabling Raman measurements – with a horizontal angle of incidence relative to the high-precision mapping stage. Use of this, longer working distance objective allowed focusing within the solution. Scattered light was collected using the same objective. This allowed 'side-on' depth scans (typically 1 μm) of the electrochemical cell. Spectra were collected in static scan mode using a 600 lines/mm grating which was calibrated using a silicon standard. All data analysis was performed using MatLab version R2012a (The Mathworks, Natick, MA, USA).

Figure S1: Photograph looking down on the liquid/liquid electrochemical cell following loss of the SERS signal, showing the presence of a silver nanoparticle raft formed, on prolonged potential cycling, at the liquid/air interface

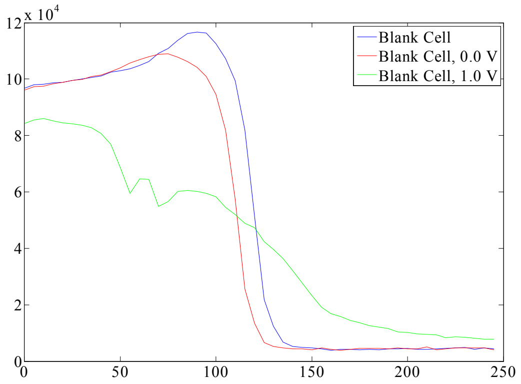

Figure S2: The effect of applied potential on the solvent peak (1038 cm^{-1}) with no Ag particles present. The application of a potential difference of 1.0 V causes the interface to expand, which produces a distortion of the interface akin to that in seen in Figure 4b.

1 P. C. Lee and D. Meisel, *Journal of Physical Chemistry*, 1982, **86**, 3391.

2 I. T. Shadi, W. Cheung and R. Goodacre, *Analytical and Bioanalytical Chemistry*, 2009, **394**, 1833.