

Silver Nanoparticles for the Simultaneous Raman Detection of Anions, Cations and Neutral Molecules.

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Abstract

Here we describe the possibility of using metal nanoparticles for the simultaneous detection of cations, anions and neutral molecules by means of surface-enhanced Raman spectroscopy (SERS) and surface-enhanced resonance Raman spectroscopy (SERRS). Silver nanoparticles were prepared by chemical reduction and their surfaces were modified either by treatment with positively or negatively charged coatings or by simply changing the aggregation agents. Non adsorbing SO_4^{2-} was used as an aggregating agent for the detection of anions. Each of the differently modified colloid/polymer mixtures can be deposited as a part of an array on planar silica substrates. In use, a small (<μl) drop is applied to the array and the Raman spectra from each of the different clusters recorded simultaneously. Since the individual signals from each cluster are spatially resolved, the spectra from each class of analyte can be detected separately. Using this approach it was possible to design an array which allowed anions and cations to be detected simultaneously on different tracks of the CCD detector.

Key words, Raman, analysis, SERS

Introduction

Surface-enhanced Raman spectroscopy (SERS) and surface-enhanced resonance Raman spectroscopy (SERRS) are very sensitive tools which are already widely used for trace analysis¹⁻⁴, indeed single molecule detection has been reported⁵. Citrate-reduced silver colloids (CRSCs) are used extensively for SER(R)S studies of cations but are typically found to be ineffective for detection of anions since the metal surface bears a negatively charged citrate layer. This problem can be solved to some extent by using surface modifying agents which create a positive metal surface⁶. However, the analyte molecules may react with the modifying layer or the analytes may not be attracted to the modifier even if it bears the correct charge. Alternatively, we have concentrated on finding materials which aggregate the colloids but also allow negatively-charged molecules to access the surface directly, without the use of charged modifiers^{1,2}.

Experimental and Instrumentation

Silver colloids were prepared using the standard Lee and Meisel citrate reduction method⁷. The uv/vis absorption spectra of the colloids typically had $\lambda_{\text{max}} = 406$ nm with a full width half maximum (FWHM) of 80 nm but colloids

with λ_{max} as long as 412 nm gave equally acceptable Raman spectra. The transmission electron microscopic analysis showed the colloid particles are far from monodisperse (Figure 2). Most of the spectra were recorded on a compact Raman system of in-house design and construction which used a Brimrose Corporation (BWL-20) frequency-doubled, diode-pumped Nd: YVO4 laser operating at 532 nm and a thermoelectrically-cooled CCD detector (Andor Technology, Model DV401) operating at $\approx 50^\circ$ C, coupled to a 125 mm spectrograph.⁸ The spectrometer was calibrated using the standard Raman band positions of a 50/50 v/v toluene/acetonitrile mixture.

Simultaneous detection experiments were carried out on a conventional macro Raman system based on a Spectra-Physics 2020 Ar⁺ laser pumping a Spectra Physics 3900 Ti/Sapphire laser (785 nm). The Raman scattering was collected using a 180° backscattering geometry and passed through a Jobin-Yvon HR640 spectrometer to a Andor Technology DV430 CCD. The line focus was achieved by inserting a cylindrical lens into the path of the excitation beam while the Raman scattering signals were collected from two different tracks on the CCD detector. Transmission electron microscopic analysis was carried out on a Philip Tecnai F-20 high resolution transmission electron microscope.

Results and discussion

Here we report the extension of our previous work on small anions¹ to simultaneous detection of even oppositely-charged analytes. The main problem to overcome is that, even after finding methods for detecting anions by SERS, universal detection of anions and the normally easier cations would still be expected to be very difficult, since the experimental conditions required for detection of positively and negatively charged analytes are very different.³ Here we show a method of preparing arrays of polymer modified nanoparticles clusters, in which each of several $<100 \mu\text{m}$ diameter clusters (Figure 1) is modified so that it is sensitive to a different class of analyte (e.g. anions or cations).

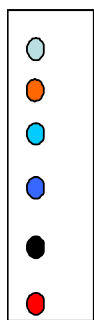


Figure.1: Single dipstick with a series of selective modified colloids which detect anions, cations and neutral molecules.

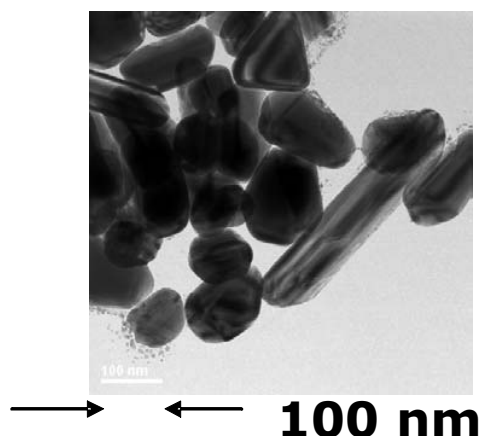


Figure 2: TEM image of the citrate-reduced Ag colloid used in this work. This section was chosen to emphasize the variety of morphologies found in such samples and the fact that monodisperse colloids are not essential for observation of SER(R)S.

We have previously reported³ the use of polycarbophil (PC) polymer to stabilize the Ag colloid. In that work it was found that the negative charge of the PC which covers the Ag particles prevents negative analytes accessing to the enhancing medium but it allows positive and neutral molecules to adsorb. Therefore PC-stabilized colloids can be used to identify cationic analytes such as crystal violet. These systems select against neutral analytes, such as nicotine, because detectable SERS signal are only obtained for these molecules if the colloid is aggregated with a salt (the positively-charged CV does not need a supplementary aggregating agent or any further treatment since the colloid particles already contain a negative charge). However, salt addition makes them sensitive to neutral molecules, this means that it is possible to prepare PC/colloid spots which are sensitive to different analytes, as shown in Figure 3. In a similar manner it is possible to coat the silver nano-particles with surface modifying agents (such as cysteamine hydrochloride) that attract negatively charged analytes.

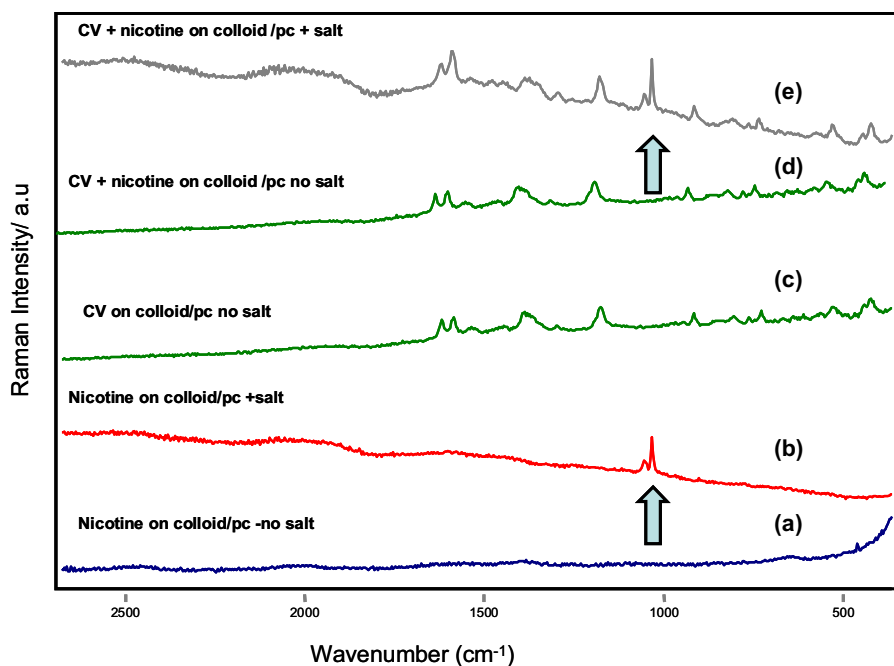


Figure 3: SERS spectra ($\lambda_{\text{ex}} = 785 \text{ nm}$, 20 s accumulation) of nicotine, CV and nicotine/ CV obtained with PC treated Ag colloids on TLC plates. In the case of spectrum (e) 200 μl of 50 ppm nicotine and 200 μl of 10^{-6} M CV were mixed together and then 10 μl of the mixture was added to modified Ag spot.

Each of the differently modified colloid/polymer mixtures can be deposited as a part of an planar array. When a complex mixture of compounds must be analysed, a small (μl) drop is applied to the array and the Raman spectra from each of the different clusters recorded simultaneously (as shown in Figure 4). Since the individual signals from each cluster are spatially resolved, the spectra from each class of analyte can be detected separately. Moreover, the signals from different analytes of the same

general type can still be resolved from the Raman spectra from each cluster, giving a dual multiplexing effect.

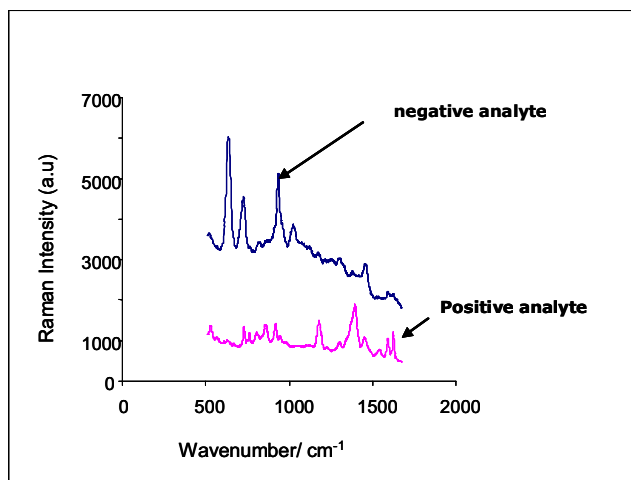


Figure 4: SERS spectra of ppm (parts per million) concentrations of perchlorate (anion) and a cationic dye in the same aqueous sample. Both spectra were recorded simultaneously from two different <math>< \text{mm}</math> silver particle clusters whose surfaces had been modified to make them sensitive to these particular analytes. For simplicity, data from samples with only one analyte of each class are shown.

Conclusion

A method of preparing arrays of SERS active materials each of which is selective for a different analyte has been developed. The use of a line focused laser to read these arrays allows simultaneous multianalyte detection. Here this method was used to demonstrate for the first time that it is possible to detect SERS signal of trace anions and cations simultaneously but of course the approach can readily be extended to allow multianalyte detection of many different sample types.

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