

Title

SERS-Active Silver Nanoparticle Arrays on Track Etch Membrane Support as Flow-through Water Quality Sensors

Authors

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Introduction

Timely detection of water supply contamination, accurate assessment of related risks, and development of appropriate remediation strategies depend on the availability of reliable water quality monitoring technologies (Bartram and Ballance, 1996). At the core of these technologies are deployable environmental sensors subject to such criteria as fingerprinting capability, low fouling characteristics, reproducibility, and low detection limits. The lack of sensing devices that meet these demands is the main limitation of pollution detection methods in use today.

The detection process can be viewed as consisting of two consecutive stages: (1) selective *preconcentration*/separation of pollutants and (2) *measurement* of pollutant concentration. To reliably determine the occurrence of molecular contaminants or microbial pathogens in natural and treated waters, large volumes of source water have to be sampled and preconcentrated to much smaller volumes. In addition to separating pollutants from the system matrix, preconcentration enhances detection sensitivity, which is especially important for the detection of water pollutants in very low concentrations. The practical worth of preconcentration is exemplified by the use of membranes for the detection of microbial pathogens in aqueous systems (Juliano and Sobsey, 1997; Sobsey, 1999; Wiesner and Chellam, 1999; Quintero-Betancourt, et al., 2002; Morales-Morales, et al., 2003; Straub and Chandler, 2003).

At the measurement stage, the employed detection methods have to be sensitive and selective. The remarkable sensitivity and molecular specificity afforded by surface enhanced Raman scattering (SERS) (Albrecht and Creighton, 1977; Jeanmaire and Vanduyne, 1977); (Chang and Furtak, 1982; Moscovits, 1985; Campion and Kambhampati, 1998) makes this spectroscopic technique especially attractive for those sensing applications, where both low detection limits and fingerprinting capability are needed (Mullen, et al., 1992; Hill, et al., 1994; Vo-Dinh, 1995; Weissenbacher, et al., 1997; Vo-Dinh, 1998; Weissenbacher, et al., 1998; Sanchez-Cortes, et al., 2001; Mosier-Boss and Lieberman, 2003). What all SERS-active systems have in common, however, is that the morphology of substrates has a profound effect on their optical properties. In the case of nanoparticle suspensions, the relatively poor stability of sols and the dependence of nanoparticle aggregate morphology on the nature and concentration of the analyte partly offsets the advantage of high enhancements typical of such substrates. The difficulty in fabricating SERS-active substrates that reproducibly yield high enhancements is the single most significant factor that hampers further applications of the SERS method for sensing. Development of highly enhancing, but also stable, reproducible, and robust SERS-active substrates is, therefore, very important for SERS to mature into an “off-the-shelf” detection method.

Experimental Details

The objective of this work was to develop flow-through SERS-active substrates by assembling arrays of silver nanoparticles on the surface of track etch polycarbonate membranes (Apel, 2001; Smuleac, et al., 2004; Burban, et al., 2005; Sportsman, et al., 2005; Won, et al., 2005). Our approach was to employ 3-aminopropyltrimethoxysilane as the chemical linker between polycarbonate surface and silver nanoparticles.

SERS enhancing properties of the resulting membrane-supported arrays were tested and compared with those of source nanoparticle suspensions using methylene blue (MB) as an analyte relevant for pathogen detection and inactivation techniques (Murinda, et al., 2002; Garwood, et al., 2003; Mohr, et al., 2004; Wagner, et al., 2004; Pelletier, et al., 2006). Finally, we considered sensitivity in a broader context that included membrane-enabled preconcentration as the factor that augments the inherently high sensitivity of nanoparticle-based SERS substrates and studied the effect of preconcentration on the sensitivity of the developed sensors.

Aqueous suspensions of silver nanoparticles (Ag hydrosols) were prepared using the procedure described by Lee and Meisel and used both as the source enhancing substrate for control measurements and for membrane coating. Substrates were 25 mm diameter, 5 μm nominal pore size hydrophobic polyvinylpyrrolidone(PVP)-free polycarbonate track etch membranes.

For surface modification, the membranes were immersed in a 25 % by weight solution of APTMS in methanol for 5 minutes. After incubation in APTMS, membranes were rinsed in pure methanol for 45 minutes with three changes of the solvent. After the final rinse, membranes were immersed in silver hydrosol for 24 hours.

Under the hydraulic conditions tested in our experiments, particles were not removed from the membrane surface. However, under mechanical stress, such as tapping or scratching, the particles could be easily removed; the modified membranes, therefore, were handled using tweezers and were stored immersed in ultrapure water in a Petri dish.

The distribution of nanoparticles on the membrane surface was evaluated using SEM imaging. Figure 1A illustrates the flat surface and narrow pore size distribution of a bare PCTE membrane. Figure 1B shows the membrane surface after modification by APTMS and silver. Homogeneous sub-monolayer coverage of the membrane surface by silver nanoparticles, as well as some internal pore coverage can be observed. The membrane surface coverage by silver particles was determined using image processing of SEM micrographs of modified membranes. The surface coverage was calculated to be 56.6%.

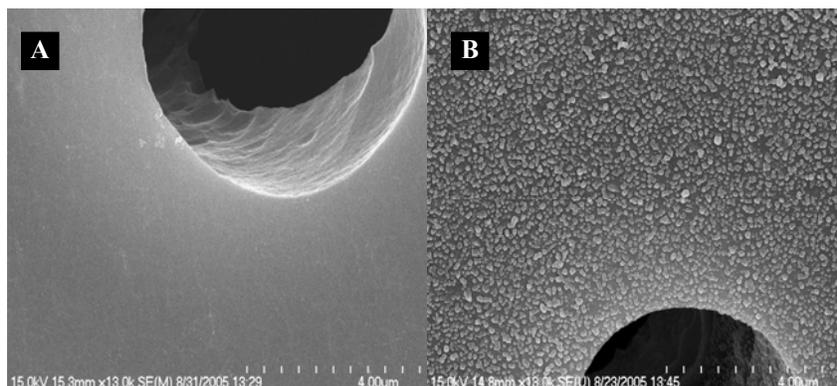


Figure 1: SEM micrographs of PCTE membrane filter that is non-modified (A), modified using APTMS linker (B). Images recorded at 13,000x.

To evaluate Raman enhancing properties of modified membranes and compare them with those of source hydrosols, MB was chosen as the test compound. Figure 2 shows UV and Raman spectra of MB with relevant band assignments (Naujok, et al., 1993), as well as the chemical structure of this compound.

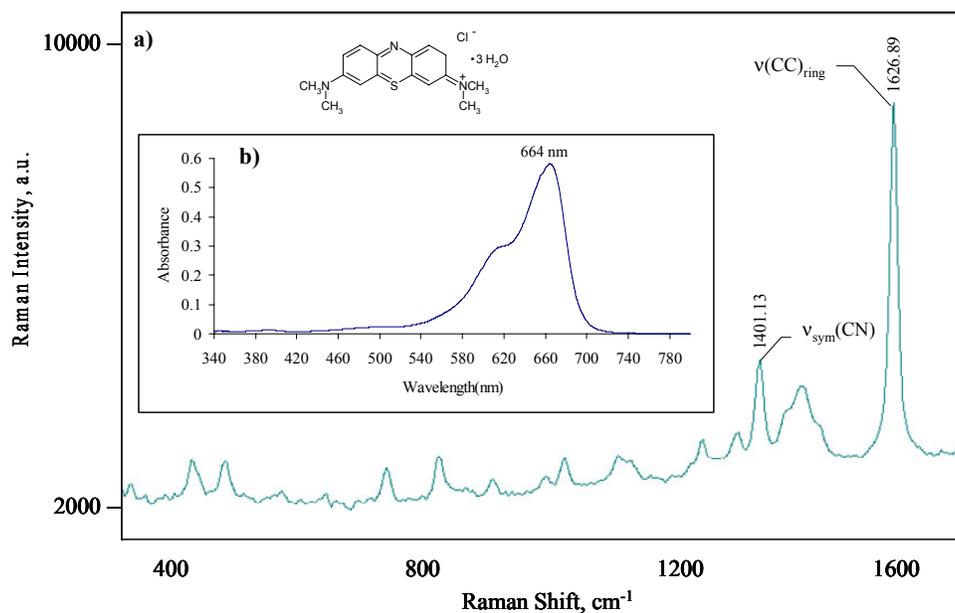


Figure 2: Absorption and Raman spectra of methylene blue.

The excitation wavelength used in this work was 532 nm that is far from the resonance frequency of MB. Much lower detection limits, and perhaps higher enhancements factors, could have been observed had the resonant excitation been chosen. Nonetheless, this laser line is suitable for the comparison of modified membranes and silver hydrosol with respect to their Raman enhancing properties, which was one of the goals of this study.

First, Raman spectra of bare and modified membranes were recorded. In contrast to the spectrum of the bare membrane, the spectrum of the modified membrane was found to be relatively featureless. Raman spectra of aqueous solutions of MB with concentrations ranging from 10^{-7} mol/L to 10^{-2} mol/L were then measured. The two most intense peaks on the Raman spectrum, 1401 cm^{-1} and 1626 cm^{-1} corresponding to the symmetric CN stretch and CC ring stretch, respectively (Fig 2). A linear increase in Raman intensity for both these peaks was observed for solutions in the 10^{-5} mol/L to 10^{-3} mol/L range. To avoid saturation effects, Raman intensity recorded for 10^{-4} mol/L solutions was used in the computation of enhancement SERS enhancement factors.

To evaluate the Raman enhancement of assembled nanoparticle arrays, Raman spectra from solutions of known concentrations of MB on the membrane surface were recorded and compared to those obtained from the same solution concentrations on the precoagulated silver hydrosol. Figure 3 shows the Raman spectra recorded for a 1 mmol/L solution of MB, and the enhanced peaks from silver sol and a modified membrane at 1626 cm^{-1} .

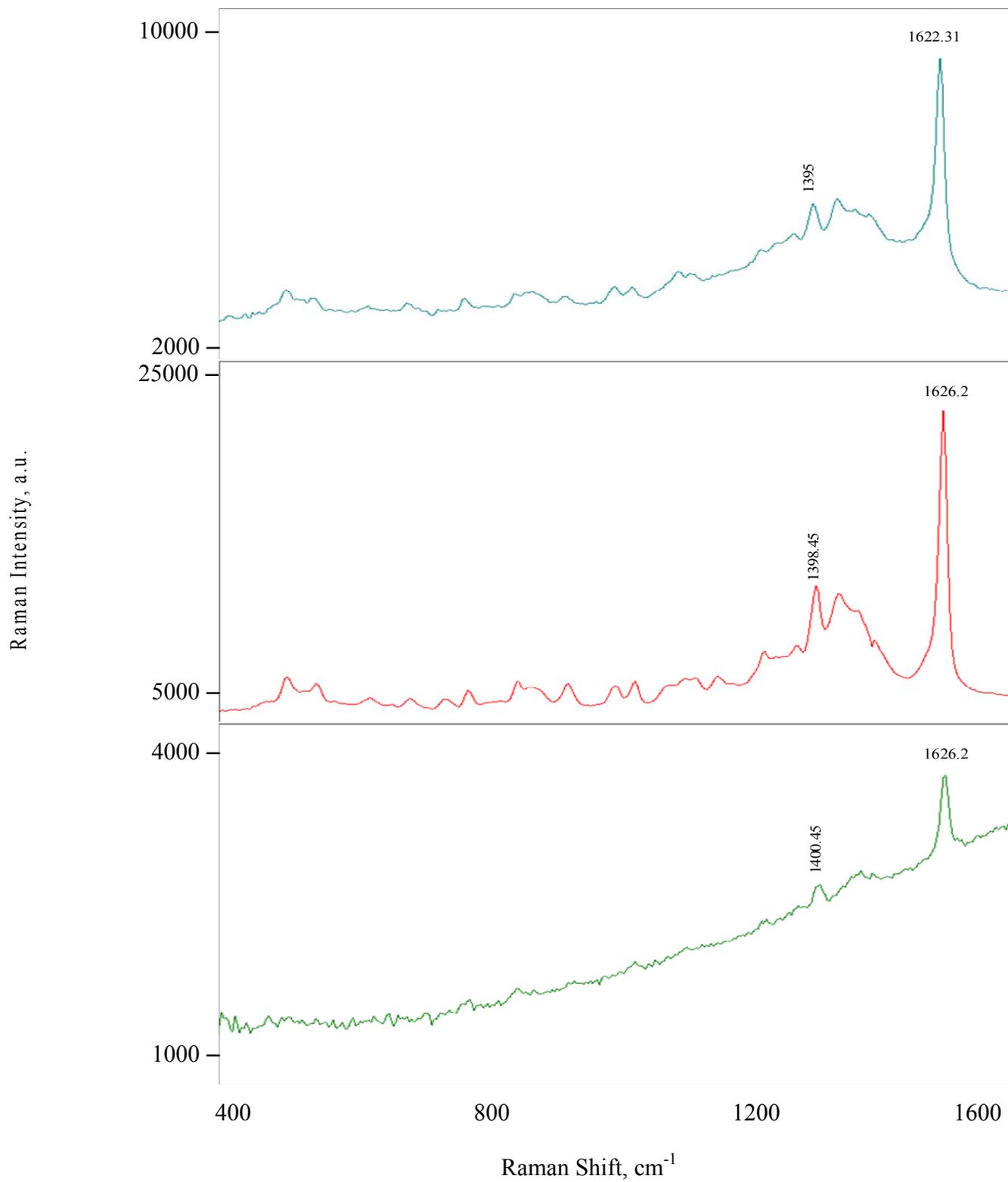


Figure 3: Raman spectrum of a 1 mmol/L aqueous solution of methylene blue (bottom), a 10^{-5} mol/L aqueous solution of MB in pre-coagulated silver sol (middle), and a 10^{-5} mol/L aqueous solution of methylene blue after “drop and dry” on a modified membrane

A slight shift of the peaks can be observed, pointing to varying MB/silver nanoparticles interactions for the different enhancing substrates. To calculate the enhancement factors of the silver sol and the modified membranes, the following equation was used:

$$EF = \frac{I_a C_b}{I_b C_a}, \quad (4)$$

where I_a and I_b indicate the normalized Raman intensities for a given peak, I_a being the enhanced intensity (from the Ag hydrosol or the modified membranes) and I_b the comparative basis, at MB concentrations C_a and C_b . By comparing intensities of the 1626 cm^{-1} peak in the SERS spectrum of a) 0.01 mmol/L solution of MB at the modified membrane surface and b) 10^{-6} mol/L solution of MB enhanced by precoagulated sol with Raman signal from 10^{-4} mol/L aqueous MB solution, average enhancement factors of 157.9 ($t95\%=141.3$) and 111.7 ($t95\%=11.8$) were obtained for silver sol and modified membrane, respectively, considering all possible intensity combinations between enhanced peaks and source MB peaks. While the EF of the sol is slightly higher than that of the modified membrane, so is the standardized error, indicating that the modified membranes have better SERS reproducibility than the sols.

To study possible changes in the filtration performance of membranes after modification, clean water flux tests were conducted both for untreated membranes and nanoparticle-modified membranes. Membrane resistance was calculated to be $(1.09 \cdot 10^7 \pm 0.01) \text{ m}^{-1}$ and $(1.15 \cdot 10^7 \pm 0.02) \text{ m}^{-1}$ for bare and modified membranes, respectively. The above measurements clearly indicate that the particle attachment to membrane surface did not result in any significant changes in the membrane resistance.

To evaluate the effect of preconcentration on the sensitivity of the developed sensors, an aqueous solution of known concentration (10^{-7} mol/L) of MB was filtered through the membrane at a constant volume flow of 4 mL/sec for 2 hours. The membrane was let to dry and the SERS spectrum of MB at the membrane surface was then recorded. To ensure that any increased enhancement was solely due to preconcentration, parallel measurements were conducted both for modified membranes immersed in a 10^{-7} mol/L MB(aq) solution for 2 hours, and modified membranes inoculated with a 10^{-7} mol/L MB (aq) solution using “drop and dry” method. While no MB peaks were observed in the SERS spectrum from the modified membranes after “drop and dry” or 2 hours immersion, preconcentration resulted in the appearance of the 1390 cm^{-1} peak. For all tested membranes, the preconcentration experiments have reproducibly resulted in an improved detection limit. Interestingly, the MB peak at 1627 cm^{-1} did not appear after preconcentration, instead, the 1401 cm^{-1} peak was shifted 10 cm^{-1} with respect to its original position. Shifts could also be noticed at the precoagulated sol and modified membranes; the shifts in SERS are indicative of the disturbance of the electronic configuration of an analyte due to chemisorption. We attribute the difference in SERS spectra from MB chemisorbed by the “drop and dry” method and chemisorbed during preconcentration experiments to the different molecule-surface interactions. Convective forces present during preconcentration together with the natural hydrophobicity of the membrane substrates might favor MB chemisorption to the silver nanoparticles through the CN bond, rather than through the less polar CC bond, which could explain the predominance of the CN peak.

Based on the intensity of the 1401 cm^{-1} band in the Raman spectrum of a 10^{-2} mol/L MB aqueous solution, the enhancement factor (EF) was calculated using (4) to be $1.17 \cdot 10^5$ ($t_{95\%} = 1.92 \cdot 10^4$). This result shows that preconcentration is effective in increasing the enhancement provided by the membrane substrate and that the detection limit can be significantly lowered (since by “drop and dry” or prolonged immersion no detection of MB 10^{-7} mol/L was possible). Additionally, the spread in the measurements (with respect to the EF value) is one order of magnitude lower than the averaged EF; for precoagulated silver sols.

Conclusions

Silver nanoparticle arrays were assembled on track etch membrane supports and established to be SERS-active with reproducible Raman enhancements. The improved reproducibility was attributed to the well defined geometry of track etch membranes. The hydrodynamic control of analyte transport to the permeable SERS-active surface was demonstrated to allow for a dramatic improvement of the detection limit of the sensor. Better insight into processes that govern analyte partitioning from dissolved phase onto the surface of the permeable substrate is needed; boundary layer structure, membrane morphology, and surface chemistry of membrane and SERS-active sites are likely to determine the extent of preconcentration. The reported findings indicate the potential benefit of combining high specification SERS-active systems and the flow-through design for the development of analytical sensors for the trace detection of pollutants in water.

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