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Use of sol-gel techniques in the development of surface-enhanced Raman scattering (SERS) substrates suitable for in situ detection of chemicals in sea-water

T. Murphy, H. Schmidt, H.-D. Kronfeldt

Optisches Institut der Technischen Universität Berlin, Sekretariat PN 0-1, Hardenbergstr. 36, 10623 Berlin, Germany
(Fax +49-30/3142-2742, E-mail: kf@mail.physik.tu-berlin.de)

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Abstract. The development of surface-enhanced Raman scattering substrates suitable for in situ environmental analysis in sea-water is presented. Substrates consist of metal colloids encapsulated in a sol-gel-derived xerogel layer. Control of the gel parameters, such as porosity, pore size, and polarity, enables tailoring of sensitivity to different analyte groups. Gold and silver colloids were used along with tetraethoxysilane (TEOS) and methyltriethoxysilane (MTEOS) precursors. Substrates are characterised by measurement of optical spectra and use of scanning electron microscopy (SEM). Activity is discussed in terms of the choice of precursor and choice of metal colloid. Spectra were obtained for a range of substituted benzene derivatives with limits of detection (LODs) of 100 ppb and 10 ppb for chlorobenzene and phenylacetylene, respectively. Substrate selectivity is shown by the contrasting response of a single substrate type to similar molecules, in particular phenylacetylene and benzonitrile. Details of mechanical and chemical stability tests on the substrates are also included.

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The discovery in the 1970s by Fleischman and co-workers of a large enhancement of the Raman signal of pyridine molecules adsorbed to electrochemically roughened silver electrodes [1] sparked a renewed interest in Raman spectroscopy as an analytical tool. Raman spectroscopy is a non-intrusive method allowing substance identification and quantification. The normal Raman signal is weak limiting its application in the field. However, reported enhancement factors of this signal of the order of 10^7 [2] bring the effect into the region of trace analysis in the environment.

Two theories exist explaining the origins of this enhancement; the short-range chemical model and the long-range electromagnetic model [3]. Both require a metal surface exhibiting a characteristic roughness. A vast array of surface-enhanced Raman scattering (SERS) active surfaces have been documented; for example roughened metal electrodes, chemically etched foils, metal island films [3], and coated microparticles [4] etc. The largest enhancement factors have been demonstrated with suspended metal colloids [5]. However, no single “best method” has emerged from the various active surface types. There is generally a trade-off between attainable activity and required robustness for the particular application. In the context of in situ measurements in the marine, a solid SERS substrate is required which exhibits a high selectivity towards the target analyte and is capable of withstanding the chemically and mechanically harsh marine environment.

In this work, the high activity of suspended colloids is combined with sol-gel techniques to embed the metal. SERS activity has been shown from photochemically reduced dimethyl hexafluoroacetylacetonate gold(III), $(CH_3)_2Au(tfac)$, in sol-gel-derived monoliths [6]. However, response times were large due to the bulk of the monolith. Spectra of *trans*-1,2-bis (4-pyridyl)-ethylene (BPE) and benzoic acid have been obtained using ‘spotting’ techniques from substrates containing silver in sol-gel-derived films [7, 8]. A sol and then a gel are produced through the subsequent hydrolysis and condensation of the alkoxy silane precursor. Further drying of the gel forms a porous silica structure, i.e. a xerogel. Thin xerogel films and monoliths have the advantage that they are mechanically and chemically stable and that porosity, pore size distribution, and surface polarity can be controlled by judicious selection of pH and type of catalyst, water precursor ratio, choice of precursor, and preparation procedure [9]. With the precursor tetraethoxysilane, the silanol groups on the silica surface result in a hydrophilic film. When using an organically modified precursor, where one or more of the alkoxy groups are replaced by an organic group, these groups replace the majority of silanol groups at the surface giving an *Or*ganically *Mo*dified *Sil*icate, ORMOSIL [10]. For example, the non-polar CH_3 group of methyltriethoxysilane renders the film hydrophobic. Previous work from our group showed that sol-gel techniques can be used to improve the stability of a gold-coated aluminium oxide sub-micron particle substrate. It was also demonstrated that a gold colloid encapsulated in a tetraethoxysilane (TEOS)-based xerogel is suitable for application in sea-water [11]. On the other hand, silver has a 10–100 times larger SERS activity than gold [12], which should result in a higher sensitivity of a silver substrate. However, bare silver metal was shown to be chemically unstable in sea-water with SERS activity falling to zero within a few minutes due to the adsorption of chloride ions or the formation of AgCl on the silver surface [11]. In this work we demonstrate that silver colloids, when encapsulated in certain xerogel films, operate effectively in sea-water.

1 Experimental

Gold chloride and silver nitrate salts were thermally reduced in thin xerogel films prepared from tetraethoxysilane (TEOS) and methyltriethoxysilane (MTEOS). In the following these substrates will be named depending on metal and precursor type used, for example, an Ag:MTEOS substrate refers to a silver colloid in a MTEOS-derived xerogel substrate. All SERS measurements are conducted in artificial sea-water. Analytes tested include pyridine, chlorobenzene, toluene, phenylacetylene, and benzonitrile.

The procedure to determine the concentration response was as follows. A fresh substrate piece was used for each measurement set. The cuvette was filled with the sample solution, working smallest to largest concentration, the substrate was placed in the cuvette and after 15 min a spectrum was recorded. Using the same substrate section the next concentration was tested and so on.

All chemicals used were purchased from Fluka and used as provided. Where applicable, analytical-grade chemicals were used.

Artificial sea-water was prepared by mixing 265 g NaCl, 32 g $MgSO_4 \cdot 7H_2O$, 22 g $MgCl_2 \cdot 6H_2O$, 15 g $CaCl_2 \cdot 2H_2O$, 7 g KCl, 2 g $NaHCO_3$, 1 g $NaNO_3$, and 0.2 g $Na_2HPO_4 \cdot 2H_2O$ to a volume of $10\,\ell$ with de-ionised water.

Microscope slides and polished silicon wafers (Wacker Siltronic AG) were cut into 10×26 mm sections, washed in detergent, rinsed in de-ionised water, soaked in 2 M HNO_3 acid for 2 h, rinsed again and stored until use in methanol. The preparation of the substrates was as follows: working at room temperature, 52 mg ($HAuCl_4 \cdot 3H_2O$) was dissolved in 0.84 M K_2CO_3, or, 84 mg $AgNO_3$ in pH 1 HNO_3. To this, ethanol and either MTEOS or TEOS were added so that the molar ratio of H_2O to precursor, R, was 4 and ethanol to precursor 3.1. This implies a 3% weight ratio of metal to starting solution. The mixture was stirred and after 2 min ageing time a glass or silicon section was spin-coated with the solution at 2000 rpm for 10 seconds. The substrates were baked for 17 h at 70 °C, after which the metal salt was thermally reduced by heating to 230 °C for 2 h. Before measurement, substrates were cut into further 5×10 mm sections, inserted into a holder and placed in a cuvette containing the sample solution.

2 Instrumentation

A 90° geometry was used for all SERS measurements. Spectra were recorded with a Jobin Yvon double monochromator, model U1000. All measurements were made with a resolution of $4\,\text{cm}^{-1}$. The detector was a thermoelectrically cooled Hamamatsu photomultiplier, model 928, operating in photon counting mode. The excitation source was the 647.1 nm line of a Kr^+ ion laser, Spectra Physics, model 2020. SERS measurements were made with 100 mW of laser power. Optical absorption spectra were recorded on a Perkin-Elmer spectrometer, model Lamda 19.

3 Results and discussions

3.1 Characterisation of substrates

The thin-film substrates were characterised using UV-VIS absorption spectra and scanning electron microscopy, SEM. Figure 1 depicts the optical extinction spectra of Au:MTEOS and Ag:MTEOS films. According to Mie's theory, the spectra are a superposition of absorption and scattering of the colloid particles. The peak position is related to the diameter and shape of the colloid particles. The gold substrate has two characteristic peaks at 535 nm and 620 nm, whereas the silver substrate has its maximum at 420 nm. SEM images of the substrates demonstrate that the colloid particles are not uniform in size, rather that they range from 30 to 120 nm with a maximum frequency of occurrence of 50-nm particles for the silver and gold colloids. Figure 2 shows the SEM image of a Ag:MTEOS substrate. The absorption spectra are in agreement with this finding. No significant cracks or blemishes were visible on the substrate surface. The average film thickness was determined to be 600 nm by measuring at various points along a cleaved face.

3.2 Effect of the sol-gel precursor

The choice of the sol-gel precursor determines the surface polarity of the resulting xerogel. A TEOS-based xerogel has a hydrophilic surface due to silanol groups. Hence, a Au:TEOS substrate is sensitive to polar molecules but shows a poor response to non-polar or weakly polar substances such as toluene and chlorobenzene. Shown in Fig. 3 is the Raman spectrum from 1 mM (80 ppm) pyridine obtained using such a substrate. The peaks at 1014 and $1039\,\text{cm}^{-1}$ are in keeping with the literature for pyridine adsorbed to gold metal surfaces [13]. They are attributed to the A_1 ring stretching vibration and A_1 triangular ring deformation of the six-membered ring [14]. In contrast to this, the use of MTEOS as a precursor increases sensitivity to non-polar analytes because of the enriching properties of the hydrophobic surface.

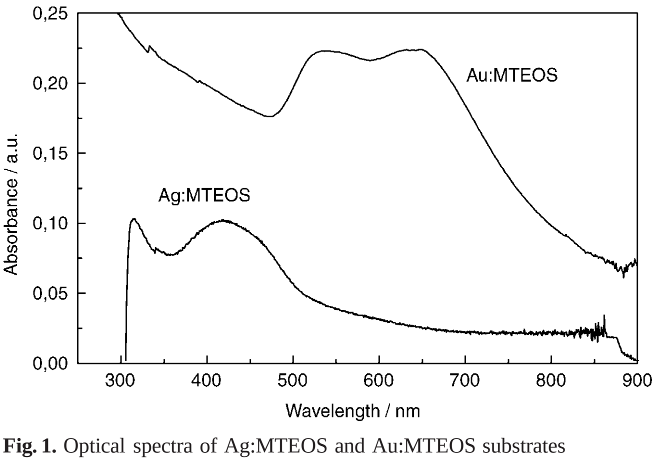

Fig. 1. Optical spectra of Ag:MTEOS and Au:MTEOS substrates

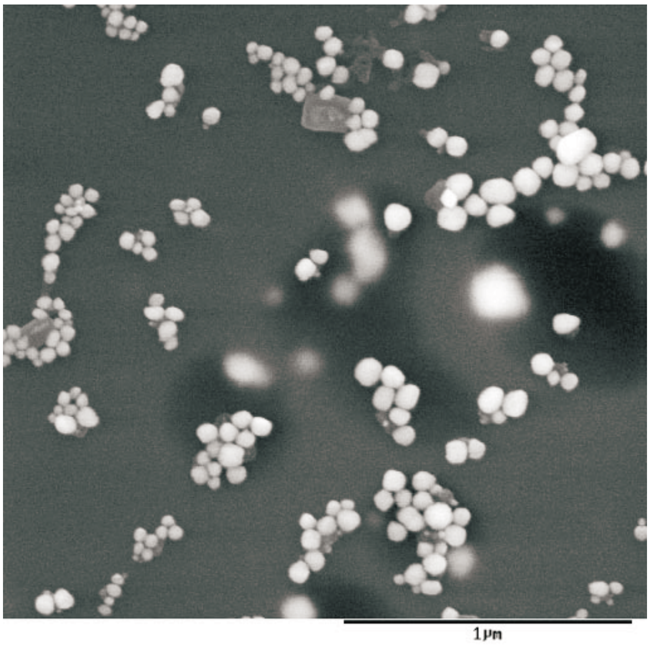

Fig. 2. Scanning electron microscope investigation of a Ag:MTEOS substrate

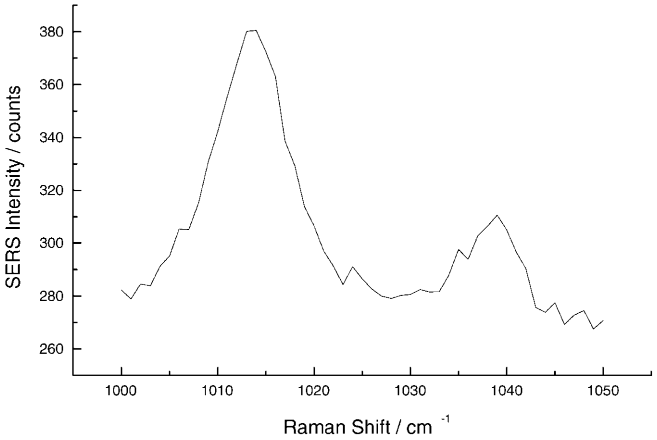

Fig. 3. SERS spectrum of 1 mM pyridine in sea-water using an Au:TEOS substrate

This principle was shown for a fluorescence-quenching sensor for dissolved oxygen in water [15]: the hydrophobic film causes a partitioning of oxygen out of solution into the gas phase within the sensing film, hence improving the sensitivity to the analyte. The weakly polar analytes chlorobenzene and toluene were detectable in 1 mM concentrations using a Au:MTEOS substrate. As expected, this substrate type showed a poor sensitivity to the polar pyridine molecule.

3.3 Effect of the metal

Gold and silver colloids in a MTEOS-based ORMOSIL film were compared using a 1 mM chlorobenzene solution as a test analyte. The silver colloid demonstrated a 30 times higher sensitivity than gold. In the case of these substrates, the hydrophobic film plays a double role. As well as enriching the analyte, the water-repelling film protects the silver metal from sea-water. A comparison with a TEOS substrate was not possible as silver colloids in TEOS-based films became inactive within a matter of hours when measuring in sea-water.

3.4 Selectivity of substrates

Figure 4 demonstrates the response of a Ag:MTEOS substrate to phenylacetylene. No benzonitrile signal was seen when using this substrate type. These two molecules are almost identical in size, structure, and Raman spectra. They are differentiated by substitution of the acetylene's CH group with a nitrogen atom. This leads to a higher dipole moment of the nitrile compared with the acetylene (3.9 *D* and 0.72 *D*, respectively). This is a deciding factor in terms of the selectivity observed: the nitrile does not enter the surface. Furthermore, in the SERS spectra the peak attributed to the $\mathrm{C} \equiv \mathrm{C}$ stretching vibration, which is at $2111\,\mathrm{cm}^{-1}$ in the liquid phase [16], has been shifted to $1988\,\mathrm{cm}^{-1}$ and the peak has been broadened considerably. This implies a large interaction between the acetylene group and the silver metal thus showing that the analyte strongly adsorbs to the metal surface. No such strong adsorption was observed with benzonitrile.

3.5 Concentration response

Shown in Fig. 5 is the response of a Ag:MTEOS substrate to varying concentrations of chlorobenzene in sea-water. The graph on the right shows a Langmuir fit to the measured data using the height of the peak at $1000\,\mathrm{cm}^{-1}$. The Langmuir adsorption isotherm describes a chemisorption process and is usually applied to adsorption of gases to solid surfaces. Limits of detection as low as 100 ppb and 10 ppb have been obtained for chlorobenzene and phenylacetylene, respectively, using the 3σ criterion. Signals were seen within 1 min upon insertion into solution with steady state achieved after 15 min. This is assumed to arise through the time required for the analyte to diffuse into the gel. The substrates showed a reversible concentration response. Chlorobenzene is readily removed by flushing with blank sea-water, whereas phenylacetylene adsorbs much more strongly. The substrates had to be exposed to a vacuum to completely remove phenylacetylene.

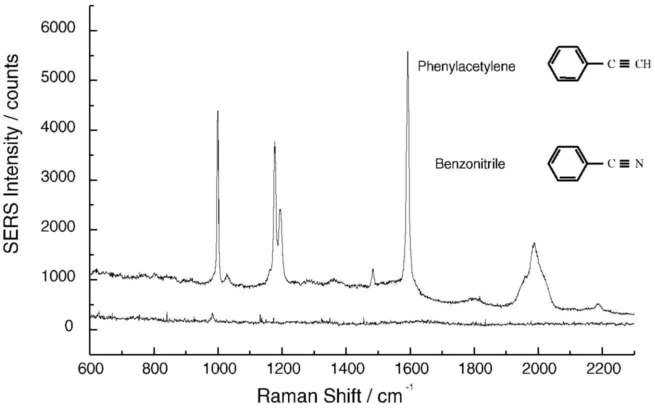

Fig. 4. SERS spectra of 1 mM phenylacetylene (*upper*) and benzonitrile (*lower*) in sea-water using a Ag:MTEOS substrate

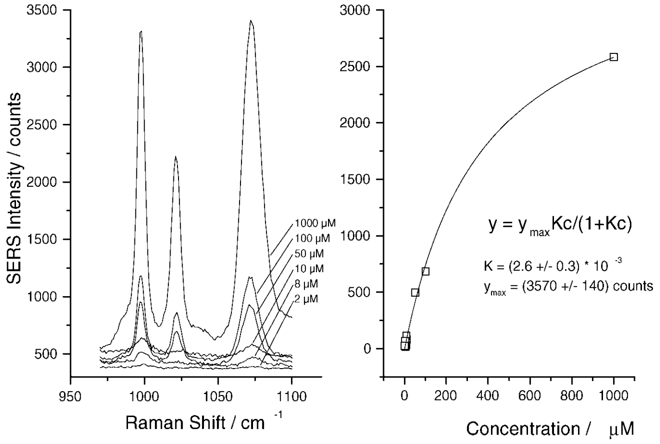

Fig. 5. *Left*: SERS spectra of chlorobenzene in sea-water in concentration range 2 to 1000 μM using a Ag:MTEOS substrate. *Right*: Langmuir fit to peak intensity at 1000 cm^{-1}

3.6 Stability of substrates

The substrates were submitted to a series of tests to ascertain mechanical and chemical stability. A 1-mM phenylacetylene or pyridine sea-water sample was used as a reference, depending on the substrate type. The surface of the substrates was vigorously wiped with a cotton swab soaked in ethanol, methanol, or 0.1 M HNO_3. The activity of the substrates remained unaltered after the tests providing evidence that the enhancement does not result from an accumulation of metal clusters on the porous film surface as wiping and etching would remove surface metal. Repeated immersion of a Ag:MTEOS substrate in 2 M HNO_3 followed by measurement with 1 mM phenylacetylene showed that the activity first rose by 30% after 5 min immersion, then fell by 40% after an additional 20 min of etching. SEM studies after the nitric acid treatment showed that the substrate surface remained mostly unaltered. To test the durability, Ag:MTEOS substrates were stored in blank sea-water for one week. Again within an experimental error of 20%, the measured activity remained the same.

To be suitable for on-line analysis in water, substrates used must withstand flowing streams. Few SERS active substrate types are suited for these conditions [17]. Tests have been made with the ORMOSIL substrates in a standard 1-cm rectangular flow-through cell with a maximum pump speed of 36 ml/min. No loss of performance was observed indicating that the substrates used here are suited for their intended application.

4 Conclusion

Sol-gel techniques have been used to develop a SERS substrate type consisting of silver or gold colloids encapsulated in thin sol-gel-based xerogel films. By selection of the precursor type, the film may be rendered hydrophobic or hydrophilic. The hydrophobic nature was used to increase the sensitivity to weakly polar analytes such as toluene, chlorobenzene, and phenylacetylene, and also to allow the use of a silver colloid in sea-water. The substrates have an inherent selectivity to target substances based on polarity and interaction strengths between the molecule and colloid metal. Mechanical and chemical stability tests demonstrate that they are suitable for operation in sea-water under flow conditions. This work shows that a silver colloid may be used for extended periods in sea-water.

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