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Surface-enhanced Raman spectroscopy of trans-stilbene adsorbed on platinum- or self-assembled monolayer-modified silver film over nanosphere surfaces

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Abstract

With trans-stilbene chosen as an example it is shown that a major problem in applying surface-enhanced Raman (SER) spectroscopy, namely the low tendency of nonpolar solutes to adsorb on SER active surfaces, can be overcome by modifying silver films over nanospheres (AgFON) with platinum or alkane thiols. The advantage of these surfaces is their stability in air and the possibility of applying atomic force microscopy for studies of the correlation between the surface structure and the enhancement factor. © 1997 Elsevier Science B.V.

1. Introduction

Surface-enhanced (resonance) Raman (SE(R)R) spectroscopy is a widely used technique for obtaining vibrational spectra at some roughened metal surfaces, most notably Ag, Cu and Au. Recent review articles provide a comprehensive picture of the extensive literature in this burgeoning field concerning both fundamental studies into the enhancement mechanism(s) of SERS as well as its applications in electrochemical surface science, ultrahigh vacuum (UHV) surface science, materials science, analytical chemistry, biochemistry, and medicine [1–12]. Consequently SERS has attracted much attention because of its ability to provide vibrational spectra of minute amounts of samples, even if these show a high fluorescence yield in normal solution. The application of SERS, however, as an analytical tool is seriously hampered by two requirements: (i) the

compound under investigation should readily adsorb on the SER active surface and (ii) the SER active surface should be prepared in a most reproducible procedure.

The second requirement is difficult to fulfill in studies applying solid metal electrodes roughened by oxidation reduction cycles. Newly developed procedures allow reproducible production of hydrosols with uniform particle sizes, the SER enhancement factor still being dependent on the nature of the anion used to stabilize the colloid [13,14]. Alternatives for making SER active surfaces in contact with a vacuum are the deposition of silver island films over planar substrates [15,16] or over nanospheres [17]. In the latter case, silver is recommended because of the high electromagnetic enhancement factor with radiation around 500 nm.

Silver films over nanospheres (AgFON) can be used as SER active surfaces both in contact with a

vacuum, air or aqueous solution. They suffer, like silver surfaces in general, from their low tendency to adsorb nonpolar molecules. Nevertheless, in order to make use of the phenomenon of surface enhancement, different recipes have been developed in the past to promote adsorption on SER active surfaces.

(i) Functional groups were added to the compound to provide an anchor like an SH group [18–20].

(ii) Binding mediators are attached to the surfaces, which in turn hold the molecule under study (e.g. thiols) [21–25].

(iii) The SER active surface is coated with a thin layer of a second metal which does not disturb the electromagnetic enhancement mechanism, but provides sites of high affinity (e. g. rhodium on electrochemically roughened electrodes [26–28]).

The main disadvantages of method (i) are the limitations introduced by the necessity of derivatizing the compound under investigation. Binding mediators can contribute specific bands to the observed SER spectrum. As long as these bands do not obscure spectral regions which are important for the investigation of the sample, they can provide convenient internal intensity standards. The deposition of metals like Rh or Pt often enhances the amount of sample adsorption, but can also exert a catalytic function and lead to product formation as shown by Feilchenfeld and Weaver in case of adsorbed acetylene [27].

Trans-stilbene is one of the best studied among all hydrocarbon molecules because of its intriguing photophysical and photochemical properties and the challenge it therefore provides to theory. One of the questions still open refers to the interpretation of the Raman spectra of the neutral species in the excited states (S_1 and T_n) and especially the (transient) Raman spectra of the radical ions [29–32]. Therefore, it was tempting to explore the possibilities of applying SERS on modified surfaces to the case of *trans*-stilbene. This is even more so since SERS and intensive theoretical studies had already been performed for the isoelectronic system *trans*-1,2-bis(4-pyridyl)ethylene (BPE) [33].

In this Letter we report on the use of AgFON SER active surfaces, which were modified to improve adsorption for *trans*-stilbene as prototype of a nonpolar molecule by deposition of platinum or incubation with alkane thiols of various chain lengths.

These surfaces are stable on air and their topology can be characterized by atomic force microscopy (AFM). Thereby it is possible to aim at the relationship between the surface structure and the SER enhancement factor.

2. Experimental techniques

2.1. Surface preparation

The preparation of AgFONs is described in detail in Ref. [18]. In this study we used polystyrene spheres with a diameter of 542 nm, spin coated as methanolic solution onto a mica substrate. This was achieved by dropping 5 μ l of solution onto 1 cm² of cleaved mica and then rotating the sample with ca. 1000 rpm for 2 min. Then, by vapor deposition a 200 nm silver film was created as the SER active surface. Self assembled monolayers (SAM) of alkane thiols ($\text{CH}_3-(\text{CH}_2)_n\text{-SH}$) with $n = 2, 7, 10, 15$) were put on these surfaces by exposing the AgFON to a 1% solution of the appropriate thiol in ethanol for 48 hours [25]. Pulsed laser deposition (PLD) was used to coat the AgFON with platinum. In a vacuum deposition chamber (pressure $< 10^{-6}$ Torr) a platinum target was exposed to the laser radiation (repetition rate 10 Hz, 40 mJ per pulse) from a Quanta Ray DCR-1 Nd-YAG laser at 532 nm, for several minutes. Thus the AgFON in the chamber was covered with a platinum layer, whose thickness was related to the time of exposure.

2.2. Atomic force microscopy

The AFM pictures were recorded with an atomic force microscope from Digital Instruments, model Nanoscope II. Etched Si nanoprobe tips (Digital Instruments) were used with spring constants of approximately 0.15 N m⁻¹. The tips are conical in shape with a cone angle of 20° and an effective radius of curvature at the tip of 10 nm.

2.3. Raman spectroscopy

A Spectra Physics (model 2060) Ar⁺ laser operating at 514 nm (100 mW) was used for Raman excitation. SER spectra were obtained with an AC-

TON VM-505 single grating monochromator equipped with a photometrics PM-512 CCD camera. The samples were AgFONs, treated as described above, which had been dipped into a 10^{-3} M solution of trans-stilbene in methanol and then were rinsed with pure methanol to remove traces of non-adsorbed trans-stilbene. All experiments were performed in air at room temperature, the presented spectra represent the average of 6–8 measurements at different spots on the modified surface.

3. Results and discussion

3.1. Self assembled monolayers on AgFONs

In Fig. 1, we present the SER spectra recorded of trans-stilbene on SAMs over AgFONs. The SAM is made up from alkane thiols with a chain length varying between 2 and 15 methylene groups. The sulfur is covalently bonded to the silver surface and

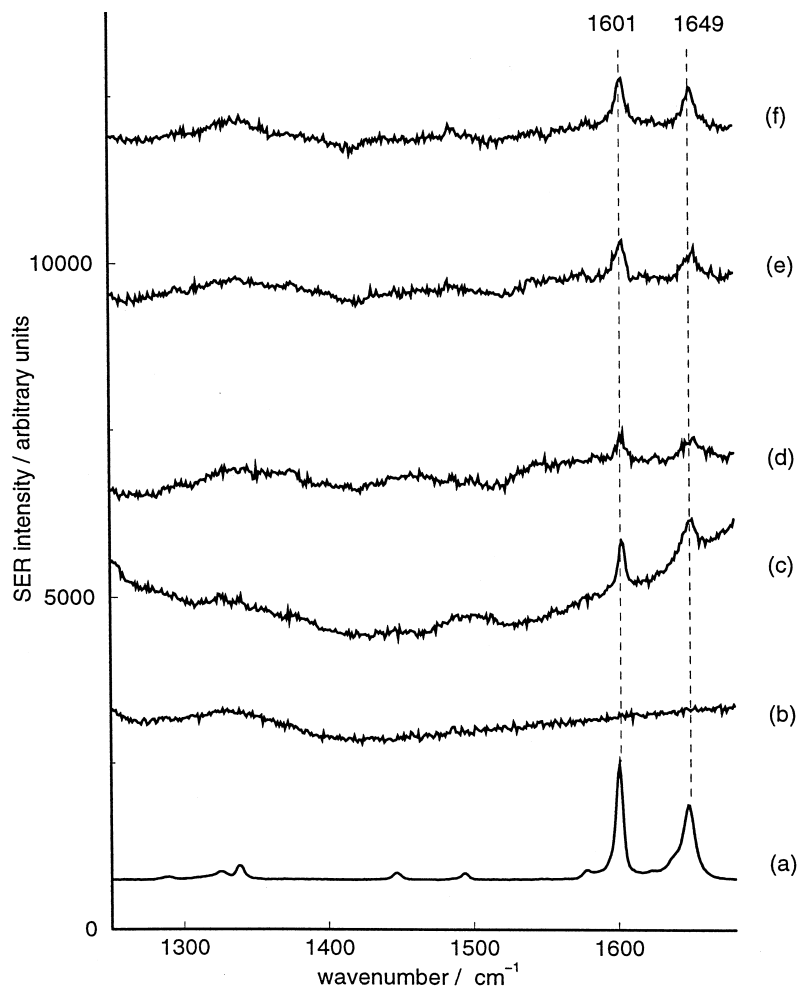


Fig. 1. Comparison of (a) Raman spectrum of solid trans-stilbene and Raman spectra recorded after contact with 10^{-4} M solution of trans-stilbene in methanol on (b) AgFON, (c) AgFON with SAM of propane thiol, (d) AgFON with SAM of octane thiol, (e) AgFON with SAM of undecane thiol, (f) AgFON with SAM of hexadecane thiol.

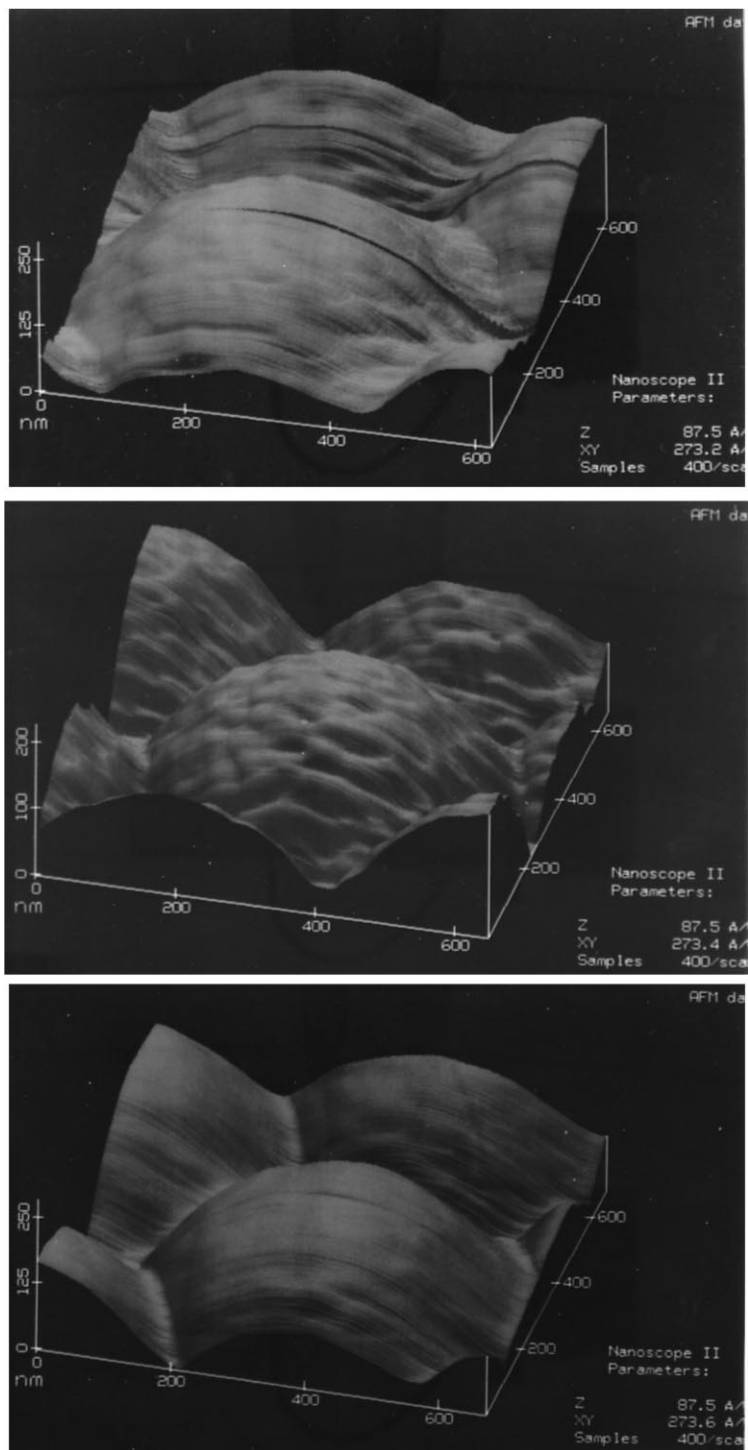


Fig. 2. AFM images of platinum coated AgFON with a platinum deposition time of (a) 1 min, (b) 2 min, (c) 8 min.

the aliphatic chain is oriented at approximately 30° to the surface normal [34]. The results presented in Fig. 1 prove that it is possible to record a SER spectrum of trans-stilbene in this way, which has not been achieved in an other way in air at room temperature. Within experimental accuracy, the peak positions are identical to those observed in the Raman spectra of the solid material. This can be taken as evidence that no specific interactions occur which would give rise to frequency shifts. An interesting question is, how the trans-stilbene is actually adsorbed in close proximity to the surface? The two

possibilities are (i) an adsorption on top of the monolayer, or (ii) an intercalation of the trans-stilbene between the aliphatic chains. The former possibility would lead to a steady decrease of signal intensity with increasing chain length and concomitantly an increasing distance from the surface. The second possibility would most likely demand the existence of a maximum in signal intensity at medium chain length, because of the action of the two factors with opposite chain length dependence. The average distance of trans-stilbene to the surface should increase with chain length and cause a reduction in

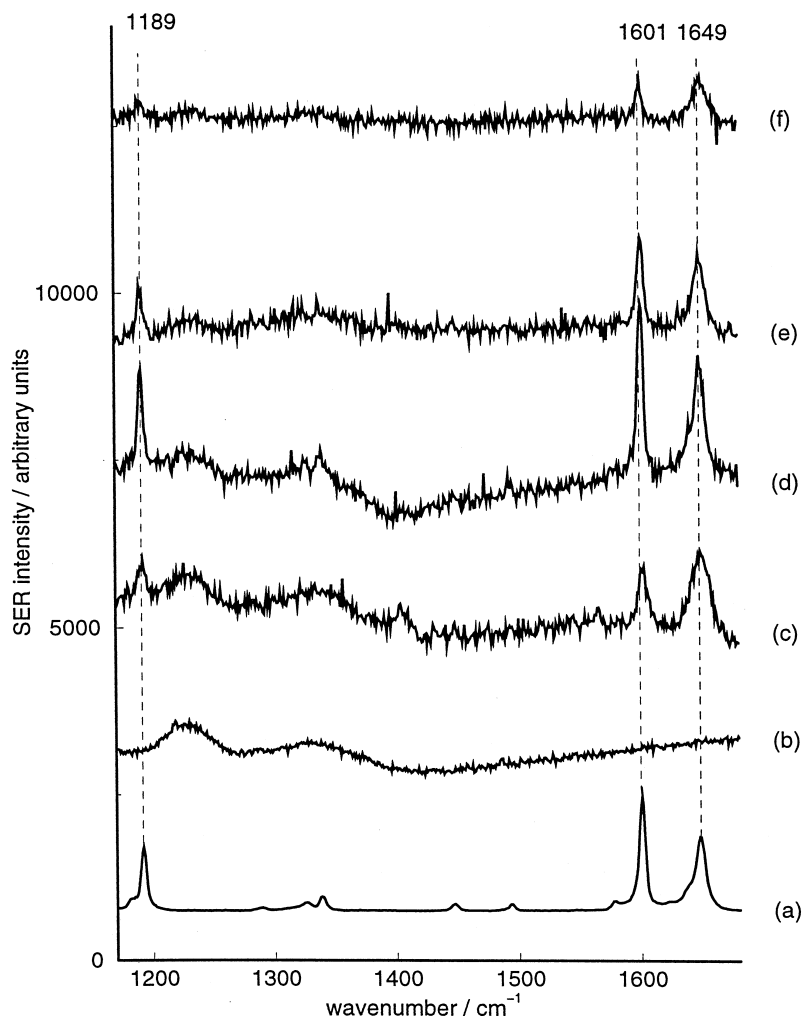


Fig. 3. Comparison of (a) Raman spectrum of solid trans-stilbene and Raman spectra recorded after contact with 10^{-4} M solution of trans-stilbene in methanol on (b) AgFON, (c) AgFON after 1 min of Pt deposition (d) AgFON after 2 min of Pt deposition, (e) AgFON after 4 min of Pt deposition, (f) AgFON after 8 min of Pt deposition.

SER enhancement. However, efficient intercalation should require a minimum chain length, that is the number of adsorbed molecules should increase with chain length. Our current data are not yet sufficient to answer the above raised question. Usually the discussion of adsorption geometry makes use of the changes of relative band intensity between the bulk and SER spectra. The fact that the relative intensities of the vinylic double bond and the phenylic ring-breathing mode are similar to those in the bulk may be taken as evidence that the *trans*-stilbene molecule does not lie flat on the surface formed by the alkane chains. We therefore think that intercalation with the long molecular axis oriented at small angle to the surface normal is more likely. This conclusion is supported by the spectra and calculations for BPE which is assumed to be oriented approximately normal to the unmodified silver surface [33].

3.2. Platinum coated AgFONs

The AFM pictures of platinum coated AgFONs (Fig. 2) demonstrate clearly the difference in surface morphology depending on the amount of platinum deposited. With a deposition time of 1 min the surface is still quite smooth – there is not much platinum on the silver surface. With a 2 min deposition time one can see a bumpy surface (which could be indicative of the formation of platinum islands). Finally with a deposition time of 8 min the surface is smooth again, as it is completely and evenly covered with platinum. The correlation between the surface morphology and the SER spectra shown in Fig. 3 is obvious: the signal intensity reaches a maximum for the sample with a deposition time of 2 min. This can be interpreted as follows: the *trans*-stilbene is readily adsorbed on the platinum islands readily and the underlying silver provides SER enhancement in the way described by the electromagnetic theory of SERS [35]. The signal intensity is increased as more platinum is put down and therefore more adsorbing surface is offered to the *trans*-stilbene molecules. If, however, a thick enough platinum layer is formed, then the efficiency of SER enhancement decreases. This observation parallels that of Feilchenfeld and Weaver [27] for the acetylene reaction product on Pt- and Rh-modified silver electrodes in that these au-

thors found a maximum of the SER signal at a coverage of about two monolayers. There are no evident changes in relative band intensities or position to those observed for the solid material. The relative intensities of the ethylenic and ring stretching modes are consequently similar to those observed for *trans*-stilbene on thiol-modified surfaces and may be taken as evidence against an adsorption geometry with the molecular plane being parallel to the surface. Furthermore we found no evidence for photoinduced or (photo-)catalytic reactions of the adsorbed species.

4. Conclusions

It has been shown that modification of silver films over nanospheres by coating them with either platinum or self assembled monolayers of alkane thiols enables one to obtain surface-enhanced Raman spectra of non polar substances like *trans*-stilbene. The enhancement is most probably purely electromagnetic, because in both cases there should be no contact between the silver surface and the scattering molecule. In contrast to analogous work with thiol-modified colloids, the modified AgFONs allow the use of an applied potential as an additional experimental parameter when used in contact with an electrolyte.

Acknowledgements

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