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Facile SERS substrates from Ag nanostructures chemically synthesized on glass surfaces

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A quick one-step fabrication of efficient SERS substrates by a modified approach based on a silver-mirror reaction (using Tollens' reagent) is reported. Commercially available microscope slides or cover glass (coverslips) were used as-received, without special surface treatment. In contrast to the commonly used two-step process, the composition of the Tollens reagent was modified to use a single-step process. The obtained rather homogeneous films of densely packed nanoislands are promising for application as substrates for Surface-Enhanced Raman Scattering (SERS), as demonstrated by several different kinds of molecules as analytes. In particular, the achieved level of detection of a standard dye analyte, down to 10^{-14} M of Rhodamine 6G, is in the range of best values reported in the literature. Low concentrations of some biomolecules are also detected, such as lysozyme (10^{-4} M), adenine (10^{-4} M), and salicylic acid (10^{-5} M). For some analytes, stronger SERS was observed in the drop, and for others after the solvent was dried. The possible reasons for this effect are described. By applying thermal annealing in the inert gas atmosphere, the Ag film morphology can be partially converted into a coral-like 3D structure that may be advantageous for the localization of the analyte in the "hot spots" and allow additional spectral tunability of the plasmon resonance.

Keywords: SERS substrate; LSPR; Tollens' reaction; Raman scattering.

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Introduction

Surface-enhanced Raman spectroscopy (SERS) is a very promising method of ultrasensitive chemical analysis of both organic [1–7] and inorganic [3,8,9] substances (analytes), approaching the level of real-life application [1,2,4,10–14]. The noble metal nanostructures that can support localized surface plasmon resonance (LSPR) and enable enhancement of the Raman scattering from the analyte molecule are referred to as "SERS substrate". An efficient SERS-substrate should not only have a large effective surface area but contain numerous "hot spots" – places of close contact between plasmonic nanoparticles (NP) [15–17]. Various approaches have been proposed to obtain SERS substrates with the highest possible density of the hot spots and their uniform distribution over the substrate surface. Although the best control over the uniformity of the metal nanostructures on the surface and the magnitude of the interparticle distance can be achieved with electron beam lithography [9], this method is not viable for real-life applications because of the relatively high price. More affordable are methods based on pre-patterning [3,18,19] or controlled nucleation of the metallic nanostructures on the surface [19] or methods based on self-assembling [5,20]. In the case of self-assembling, the desired morphology can be formed by an oxide or other non-expensive material and then covered with noble metal [21–24]. Alternatively, the hybrid nanostructures with predefined morphology and plasmonic properties can be first prepared in the solutions and then self-assembled on the substrate to form the hot spots between them [20,25,26]. In most approaches, the preparation of efficient and rigid SERS substrates requires sophisticated and skilled preparation (in the case of nanosphere lithography, for instance) or costly equipment and materials (as in the case of lithographic methods) [19,27]. Therefore, affordable fabrication of efficient SERS substrates is still an area of intense research [6,7,22,27–33].

The method of silver mirror reaction has been known for a long time as a simple and efficient method of obtaining smooth silver coating on flat surfaces. In recent years it has been often employed for various surfaces and 3D structures with Ag NPs for SERS application [34–41]. In Ref. [35] $AgNO_3$ - ascorbic acid solution was applied to flexible glass fiber filter paper. In Ref. [34], the optical properties and morphology of the nanostructured silver films were studied systematically as a function of the silver mirror reaction parameters, but no SERS study was reported for the obtained SERS substrates. In Ref. [36], leaflike fractal silver microstructures and perpendicularly aligned silver nanosheets were produced on commercially available copper foil and sandpaper-rubbed copper foil, respectively. Amino-modified polystyrene microspheres were used as a substrate for nanostructured Ag layer deposition in Ref. [41], resulting in a rather sensitive platform for the detection of various biomolecules and bacteria. Three-dimensional SERS substrates were obtained in Ref. [40] by deposition of Ag by silver mirror reaction on the surface of vertically aligned ZnO/TiO_2 nanotubes which provided the property of self-cleaning from the analyte. Filter paper is a substrate often used to fabricate cheap and flexible SERS substrates by wet chemistry routes, particularly using Tollens' reaction [39].

In the present work, we propose a simple way of obtaining the SERS substrates on silicon oxide surfaces. The one-step synthesis based on the modified silver mirror reaction deposits a layer of Ag nanoislands without any special cleaning or other treatment of the oxide surface. Good enhancement properties of the as-obtained SERS substrates are demonstrated for several different types of analytes. The substrates can be optionally subject to moderate thermal annealing to tune their morphology and spectral properties of the plasmon resonance.

I. Experimental

1.1. Materials.

All the chemical reagents used in our experiments were of analytical grade and used as received without further purification. H_2O was distilled and deionized. $AgNO_3$, NH_4OH, and glucose were purchased from Sigma-Aldrich and used as received.

1.2. Preparation of Tollens' reagent.

Preparation of Tollens' reagent Fresh Tollens' reagent was prepared as described by Fieser and Williamson [42] with some modifications.

1g $AgNO_3$ is dissolved in 100 mL of DI water. In order to prepare Tollens' reagent, NaOH solution is added to a solution of silver nitrate dropwise until a light brown precipitate is obtained. To this, concentrated ammonia solution is added dropwise until the brown precipitate of Ag_2O dissolves completely. The amount of ammonia should be sufficient enough to dissolve the precipitate completely until a clear solution is obtained. The complex obtained at the end is $(Ag(NH_3)_2)^+$ in which silver is in the oxidation state +1, i.e. Ag^+ acts as the main component of the Tollens' reagent. In this work, instead of following a two-step process, a single-step process is taken in order to obtain the freshly prepared reagent. For this, firstly, a small amount of aqueous ammonia is directly added to a solution of silver nitrate taken in a flask, and then in order to dissolve the precipitate formed, a sufficient amount of ammonia solution is poured dropwise in order to obtain a clear solution.

1.3. Synthesis of substrates.

To 5 % glucose solution, freshly prepared Tollens' reagent (1 ml) is added and the solution is warmed in a hot water bath. By changing the duration of the reaction between glucose and Tollens' reagent, the size and loading density of Ag nanoparticles can be adjusted, which allows tuning of the spectral parameters of the surface plasmon resonance. A series of SERS substrates (#1- #5) was obtained by immersing glass substrates into the prepared solution for a certain time:

#1 – 1 mL of Tollens reagent mixed with 2 mL of glucose solution, cover glass is covered with solution and left on a water bath for 2-3 minutes until evaporation of the solvent.

#2 – 1 mL of Tollens reagent mixed with 2 mL of glucose solution, microscope slide is covered with solution and left on water bath for 2-3 minutes until evaporation of the solvent.

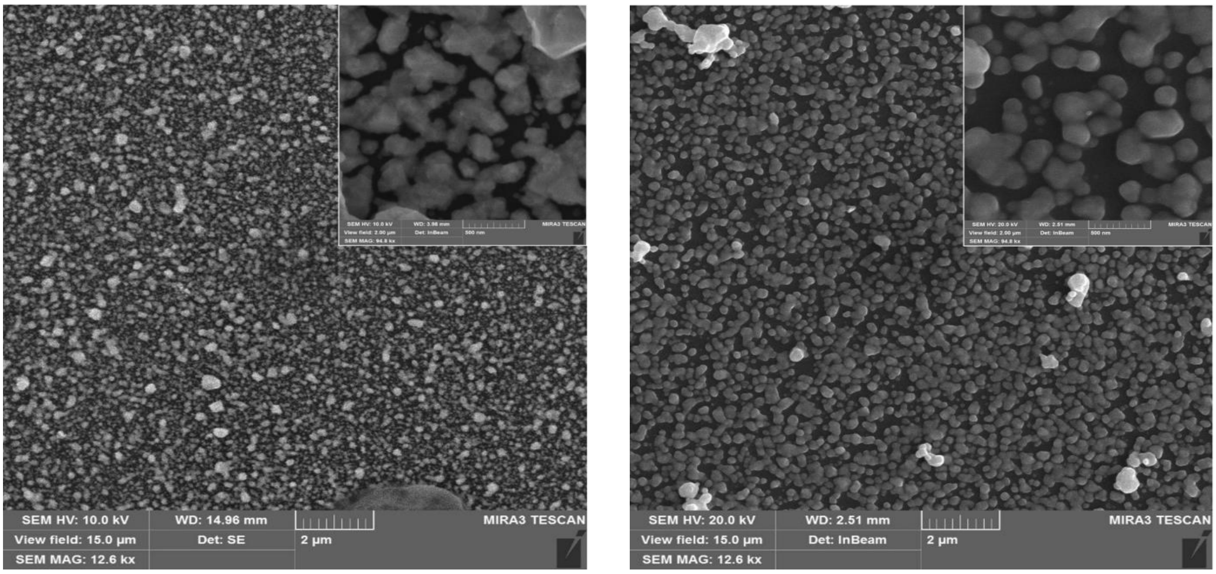
#3 – 5 mL of Tollens reagent mixed with 5 mL of glucose solution, cover glass with the SiO_2 spheres (0-50 μm) is covered with solution and left in a water bath for 2-3 minutes until evaporation of the solvent.

#4 – 2 mL of Tollens reagent mixed with 2 mL of glucose solution, the cover glass is covered with solution and left in a water bath for 2-3 minutes until evaporation of the solvent.

#5 – 100 μL of Tollens reagent mixed with 100 μL of glucose solution, cover glass is covered with solution, sample is left for drying in a Petri dish.

1.4. Characterization.

The morphology of the films was studied using scanning electron microscopy (SEM, Tescan Mira 3 MLU). Optical absorption spectra were obtained using a StellarNet Silver Nova 25 BWI6 spectrometer. Raman spectra were excited with 457 nm or 532 nm solid-state lasers and acquired using a single-stage spectrometer MDR-23 (LOMO) equipped with a cooled CCD detector (Andor iDus 420, UK). The laser power density on the samples was less than 10^3 W/cm^2, to preclude any thermal or photo-induced modification of the samples. A spectral resolution of 4 cm^{-1} was determined from the Si phonon peak width of a single crystal Si substrate. The Si phonon peak position of 520.5 cm^{-1} was used as a reference for determining the position of the peaks in the Raman/SERS spectra of the analyte.



(a) (b)

Fig.1. Representative SEM images of the Ag films (sample #4) deposited on the surface of microscopic slides (a) and after annealing for 10 min at 400 °C in the inert atmosphere (b). The insets show the images of the corresponding samples with higher magnification (the scale bar is 500 nm).

II. Results and discussion

2.1. Morphology study.

Figure 1a shows representative SEM images of the Ag films deposited on the surface of microscopic slides, using sample #4 as an example, a similar morphology was obtained for the rest of the samples. Annealing of the films in the inert atmosphere at 200 or 400 °C results in the rounding up of the nanostructures (Fig. 1,b). Although the size dispersion is rather large, from tens to hundreds of nanometers, the homogeneity of their distribution over the large areas (hundreds of μm or even some mm) of the substrate is very high. Despite the large size dispersion, the efficiency of SERS provided by this sort of Ag nanostructures is comparable to that of much more uniform nanostructures of a more sophisticated design [1,36,43]. In earlier SERS studies based on colloidal Ag NPs [22,33], we have already made a similar observation that the very polydisperse Ag NPs synthesized from bio-extract demonstrated SERS efficiency comparable to that of rather monodisperse Ag NPs synthesized by common chemical routes.

By using our modified silver mirror reaction for deposition on Silicon wafers a similar morphology of the nanostructured Ag films was obtained (images are not shown). This similarity in the growth mode on the SiO_2 and silicon surface can be due to the fact that the silicon wafers are known to be covered by a few nanometers of native oxide. However, annealing of such films at the same conditions as the films on glass results in very different morphology (Fig. 2). Along with the expected rounding up of the individual nanoparticles and their partial merging (Fig. 2,b), they tend to form a 3D structure with a high degree of porosity (Fig. 2,a). Such a porous noble metal film is supposed to be advantageous not only for SERS-based sensing applications, focused in this work but also for sensors or catalysis and was tried to be produced by different methods [31].

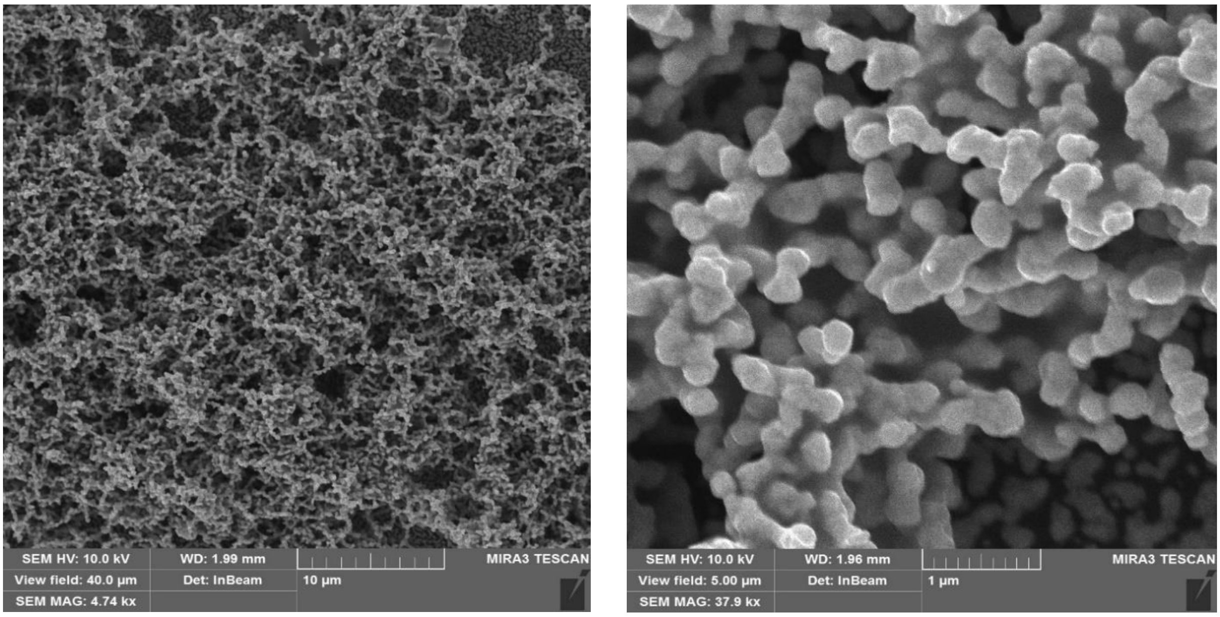
An important advantage of the silver mirror reaction method is that it allows easy deposition of a homogeneous layer of silver nanostructures on the surface with high curvature which are not accessible for deposition by other facile methods, such as thermal evaporation of metal, for instance [3,18,21]. Figure 3 shows SEM images of SiO_2 spheres (on Si substrate) covered with nanostructured Ag film using the silver mirror reaction method. One can see that the morphology of the obtained silver film is very similar to that obtained on the flat glass substrate (Fig. 1,a). In the image with large magnification (Fig. 3,b) one can see that the nanostructured silver film contains numerous gaps between the edges of the particles, which is an advantageous morphology for the formation of plasmonic “hot spots” in which the prevailing enhancement of the Raman is supposed to occur [44,45].

2.2. Raman/SERS study.

Figure 4 shows Raman spectra of rhodamine 6G of different concentration, 10^{-5} M (a) and 10^{-8} M (b), on SERS-substrates fabricated by silver mirror reaction. The general trend that is observed for this type of substrates is the higher SERS intensity from the solution (drop) than from the dried analyte. This trend qualitatively correlates with the results we observed earlier on Ag SERS substrates produced from colloidal NPs [33] or on ZnO nanoflowers coated with Ag by thermal evaporation [22]. In the latter works this difference was suggested to be due to different adsorption geometry of the analyte molecule in the solution and in the dry state. This assumption is confirmed by a slightly different relative intensity of the Raman peaks, both in the latter works and in the present study. A comparable SERS intensity is observed for different flat glass substrates, while on average an order of magnitude larger intensity is produced by the substrates covered with SiO_2 spheres (Fig. 4,a). The additional enhancement in the latter structures can be due to the self-localization of the analyte molecules in the gaps between the spheres (Fig. 3,a), which are more efficient places for the occurrence of the hot spots, as compared to the surface away from the gaps.

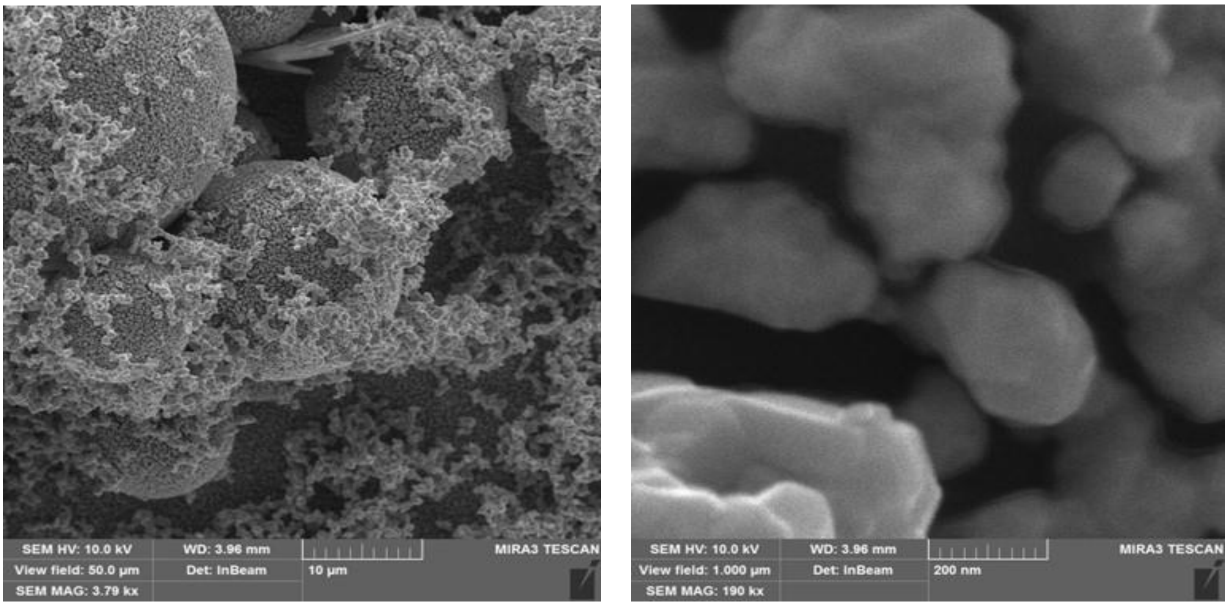
Besides the expected lower intensity of the Raman peaks for lower analyte concentration, a difference that can be noticed between the spectra of concentration, 10^{-5} M (Fig.4,a) and 10^{-8} M (Fig.4,b), are the strong Raman features centered around 1450 and 1550 cm^{-1} in Fig.4,b. These peaks are known to be related with the Raman scattering of the silver oxide [46] and can originate from a thin oxide layer that is formed on the surface of the silver nanostructures. The Raman scattering from this thin oxide is significantly enhanced via the same mechanism as the scattering from the analyte molecules situated on this surface. Although the reports on the SERS of inorganic materials are extremely rare compared to the number of SERS papers on organic molecules (about 10-20 papers vs tens of thousands, respectively), SERS of ZnO [8], TiO_2 [47], CdSe [3], MoS_2 [9] have been reported.

Stronger intensity of the silver oxide peaks in Fig.4,b than in Fig.4,a can be due to the fact that the three orders of magnitude higher concentration of the analyte in (a) may lead to a stronger absorption of the exciting laser light in the analyte layer, with correspondingly weak exciting intensity reaching the oxide layer. Moreover, these oxide peaks are partially “hidden” in (a) due to the strong intensity of the R6G modes, although related with them background is around the same order of magnitude, ~10^4, as the bands in Fig.4,b.



(b) (b)

Fig. 2. Representative SEM images of the Ag films deposited on the surface of a Si wafer and subject to annealing at 200 °C in the inert atmosphere. The two images are acquired with different magnifications: about 5000 in (a) and about 40 000 in (b).



(a) (b)

Fig. 3. Representative SEM images of the Ag films deposited on the surface of SiO_2 spheres. The two images are acquired with different magnifications: about 4 000× in (a) and 190 000× in (b).

It should be noted that the λ_{exc} = 457 nm used in this work was chosen because it is in the range of excitation of the LSPR of Ag nanostructures [22,33], as confirmed by observing a characteristic absorption band in the reflection and transmission optical spectra of the SERS substrates developed in this work (Fig. 5,a).

For R6G, which was used as a standard SERS analyte in our study, this excitation in not resonant, because the strongest absorption peak of this molecule is centered near 530 nm. Therefore, the detection limit of 10^{-8} M obtained under non-resonant excitation of the analyte proves good enhancing efficiency of the SERS substrates developed in the present work. At the λ_{exc} = 532 nm that is resonant with the analyte absorption, a much lower concentration could be detected – down to 10^{-14} M of R6G (Fig. 5,b), although this λ_{exc} is aside from the plasmon absorption band (Fig. 5,a). The latter observation may be an indication that at ultrasmall analyte concentrations the prevailing SERS intensity stems from the hot spots, where the local plasmon resonance may be strongly shifted into the green range due to coupling between the neighboring plasmonic particles forming the hot spots. The effect of a strong red shift of LSPR due to interparticle coupling has been systematically observed at aggregation of the colloidal plasmonic NPs in the solution [48].

Besides the detection of the low concentrations of the fluorescent dye that are common reference samples enabling comparison of the efficiency of SERS substrates developed in different works, we have employed the nanostructured silver films obtained in this work for the detection of several sorts of biomolecules. Figure 6 shows spectra of adenine in different concentrations. For comparison are shown the spectra of adenine sulfate powder, its aqueous 1M solution, and the molecular precipitate formed by drying of the latter solution on a Si substrate. One can see that without enhancement the Raman spectra of this important biomolecule are hardly detectable – only a weak peak can be registered from the bulk powder and no signal isdetectable from 1M solution (Fig. 6,b). On the contrary, the adenine solution deposited on the SERS substrate developed in this work results in a much stronger intensity of the characteristic Raman band, even at a concentration as low as 10^{-4} M (Fig. 6). However, we should note the non-monotonous and anomalous change of the Raman peaks intensity, as well as the shift of the peak position with the variation of the adenine concentration. In particular, the peak intensity increases when the concentration is decreased from 10^{-2} M to 10^{-4} M, but drops to zero at further dilution to 10^{-5} M. The position of the peak shifts from 732 cm^{-1} for 10^{-2} M to

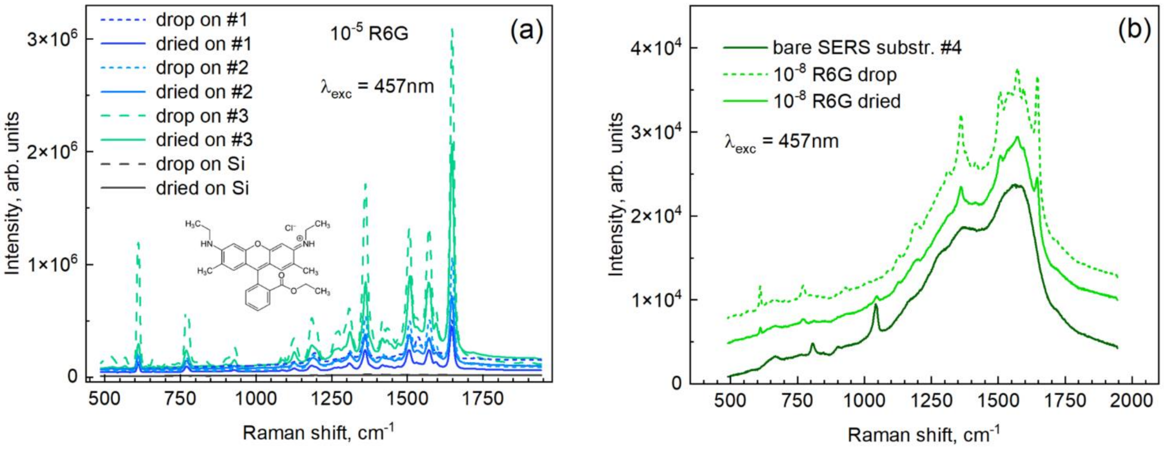


Fig. 4. Raman spectra of rhodamine 6G of different concentrations, 10^{-5} M (a) and 10^{-8} M (b), on SERS substrates fabricated by silver mirror reaction. The inset in (a) shows a structural formula of R6G molecule.

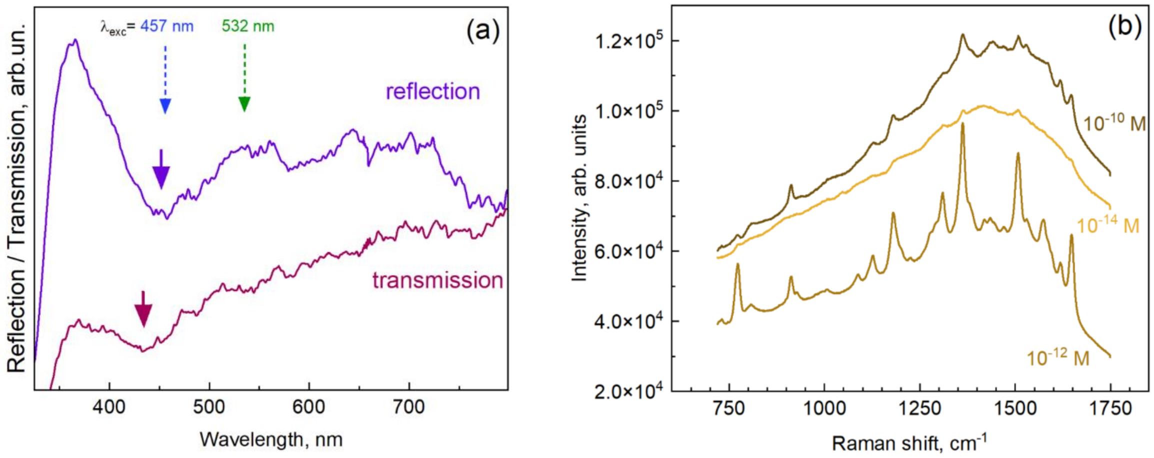


Fig. 5. (a) Representative optical reflection and transmission spectra of SERS substrates. The absorption feature related with LSPR in silver nanostructures is marked by solid arrows, the λ_{exc}'s used for the excitation of SERS spectra are shown by dashed arrows. (b) Representative SERS spectra of different concentrations of R6G (drop) at λ_{exc} = 532 nm that is resonant with R6G absorption.

729 cm^{-1} for 10^{-4} M, while it is centered at 722 cm^{-1} in the bulk powder. Both the absolute value of these peaks frequencies in the bulk form and its higher value in the SERS correlate with the literature [49]. The peak shift and anomalous non-monotonous behavior of the peak intensity in the SERS spectra can be related to a different orientation of these sorts of molecules at different concentrations, and perhaps different interaction with the substrate [49]. It should be noted that the discussed adenine peak is one of the key Raman fingerprints used in SERS detection DNA and other large biomolecules [2,7], where it can be subject to intramolecular interaction. Therefore, understanding the behaviour of this peak in the SERS spectra of pure adenine molecules is of crucial importance.

Another biomolecule used in this study was lysozyme, which is an important biomolecule to be detected [50] but has been relatively seldom studied by SERS [51–53]. From the spectra presented in Fig. 7a one can notice that the SERS spectrum of this molecule differs significantly from the Raman spectrum measured at the same λ_{exc} from the bulk powder sample, with only a few bands found at the same position, as indicated by vertical dotted lines in Fig. 7a. In general, the different appearance of the SERS and Raman spectra is a common phenomenon. This can be just a minor difference in the relative peak intensity, but a completely different set of peak frequencies can manifest itself if the modes not very efficient or even forbidden in normal Raman process start to dominate in SERS. The reason for that can be preferential enhancement of certain bond vibrations due to their close position in the area with higher magnitude of the electric field of LSPR, or weakening of the selection rules for Raman scattering due to electronic interaction of the molecule with plasmon or band electrons of the metal. Particularly for lysozyme, a pronounced discrepancy between the Raman and SERS spectra has been noticed by other authors as well [54,55].

Even more pronounced difference between the Raman and SERS spectra was observed for salicylic acid (Fig. 7,b). Although we were able to record very intense SERS bands (signal-tonoise ratio ~10^4) from a concentration as low as 10^{-5} M, the spectrum differs

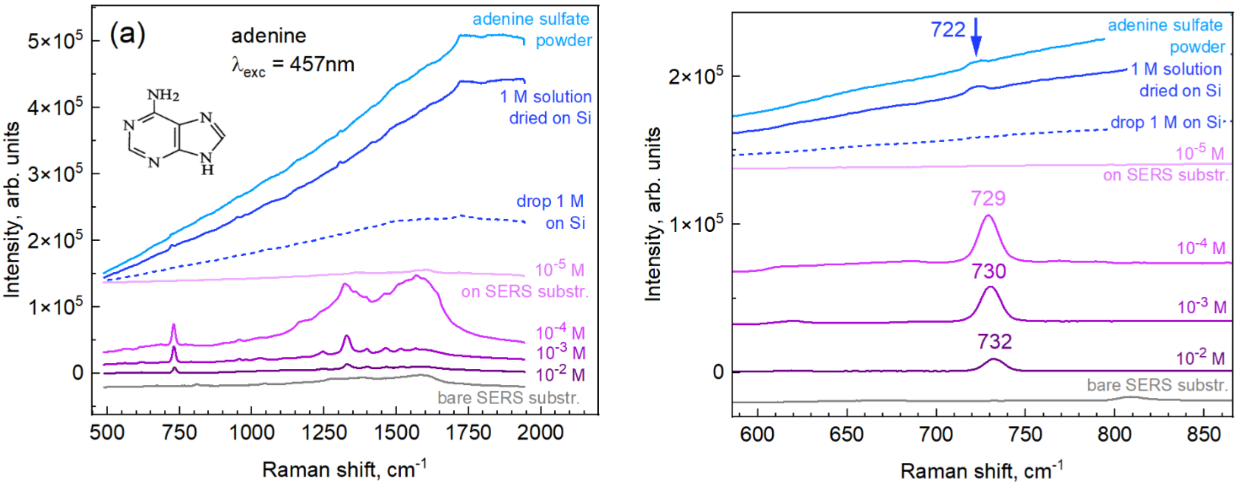


Fig. 6. Raman spectra of adenine of different concentrations on SERS substrates fabricated by silver mirror reaction. The adenine bulk spectra as well as the spectrum of the base SERS substrate are shown for comparison. The spectra in (a) show the full range of molecular vibrations, while the narrow spectral range of the strongest vibrational band of adenine (at 720-730 cm^{-1}) is shown in (b). The inset in (a) shows the structural formula of adenine molecule.

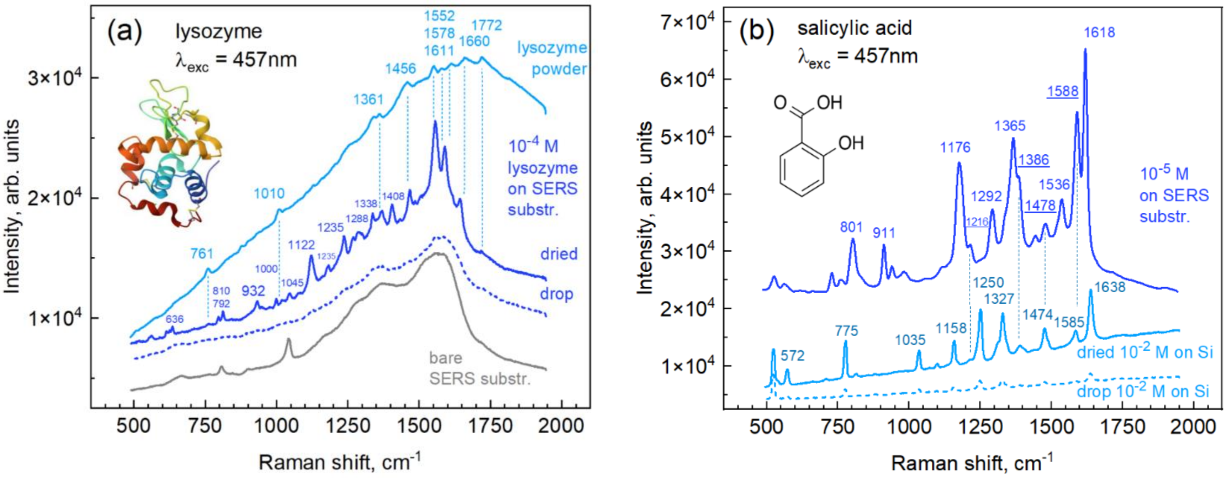


Fig. 7. (a) Raman spectra of 10^{-4} M lysozyme on SERS substrates fabricated by silver mirror reaction. The lysozyme bulk spectra as well as the spectrum of the base SERS substrate are shown for comparison. The inset shows the lysozyme structure [56]. (b) Raman spectra of 10^{-5} M salicylic acid on SERS substrates fabricated by silver mirror reaction. The inset in (b) shows the structural formula of salicylic acid.

significantly from the spectrum of concentrated (10^{-2}) salicylic acid on Si substrate. Only several bands (marked by dotted lines in Fig. 7,b) can be identified, whose positions coincide in the Raman and SERS spectra. The Raman spectrum in the present work coincides with the spectra reported by others [57]. In the latter work, the SERS spectrum of the 10^{-5} M solution in chloroform, mixed with colloidal Ag NPs solution, differs a lot from the Raman spectrum of the solid salicylic acid, but also is very different from the SERS spectrum in our work. We may assume that the Raman spectrum of this molecule is extremely sensitive to the adsorption geometry on each particular type of SERS substrate. Besides, the molecule itself may undergo some structural or electronic transformations as a result of interaction with plasmonic nanostructures [43], or as a result of pH change [58]. Experimental confirmations of the combined action of the latter two factors have been demonstrated for a similar molecule, para-hydroxybenzoic acid, in Ref. [59]. Therefore, understanding the reasons of the transformations of the SERS spectra of salicylic acid requires further investigations.

Conclusions

We have investigated the possibility of fabricating efficient SERS substrates based on the modification of the wet chemistry protocol known as a silver-mirror reaction or using Tollens' reagent. As a part of simplifying the fabrication process, commercially available microscope slides or cover glass (coverslips) were used as-received, without special surface treatment. In contrast to the commonly used two-step process, the composition of the Tollens reagent was modified to use a single-step process, which resulted in homogeneous films of densely packed nanoislands being obtained. The same morphology was obtained also on the very curved surface formed by commercially available glass spheres (beads) deposited on the glass slide. The efficiency of the produced SERS-substrates is demonstrated for several different kinds of molecules used as analytes. In particular, the achieved level of detection of a standard dye analyte, down to 10^{-14} M of Rhodamine 6G, is in the range of best values reported in the literature. Low concentrations of some biomolecules are also detected, such as lysozyme (10^{-4} M), adenine (10^{-4} M), and salicylic acid (10^{-5} M). For some analytes, stronger SERS was observed in the drop, for others after the solvent was dried. As possible reasons for this effect, we suggest different adsorption geometry and probably also different contributions of the chemical enhancement in the solution and in the dry form. By applying thermal annealing in the inert gas atmosphere, the Ag film morphology can be partially converted into a coral-like 3D structure that may be advantageous for the localization of the analyte in the hot spots and allow additional spectral tunability of the plasmon resonance.

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Доступні SERS- підкладки на основі срібних наноструктур, хімічно синтезованих на скляних поверхнях

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Повідомляється про швидке одноетапне виготовлення ефективних SERS-підкладок за допомогою модифікованого підходу на основі реакції срібного дзеркала (з використанням реактиву Толленса). Комерційно доступні мікроскопічні предметні скельця або покривні скельця використовували в готовому стані без спеціальної обробки поверхні. На відміну від зазвичай використовуваного двоетапного процесу, склад реактиву Толленса був модифікований для реалізації одноетапного процесу. Отримані гомогенні плівки щільно упакованих нанострівців є перспективними для застосування в якості підкладок для поверхнево-посиленої Раманівської спектроскопії (SERS), що продемонстровано на кількох різних типах молекул як аналітів. Зокрема, досягнутий рівень виявлення стандартного аналіта-барвника, аж до 10^{-14} М родаміну 6G, знаходиться в діапазоні найкращих значень, про які повідомляється в літературі. Також показане детектування низьких концентрації деяких біомолекул, таких як лізоцим (10^{-4} М), аденін (10^{-4} М), саліцилова кислота (10^{-5} М). Для деяких аналітів сильніший SERS спостерігався в краплі, для інших після висушування розчинника. Описано можливі причини такого ефекту. Застосовуючи термічний відпал в атмосфері інертного газу, морфологію плівки Ag можна частково перетворити на коралоподібну 3D-структуру, що може бути вигідним для локалізації аналіту в гарячих точках і забезпечити додаткову спектральну настроюваність плазмонного резонансу.

Ключові слова: підкладка SERS; LSPR; реакція Толленса; Раманівське розсіювання.