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Polymer-coated substrates for surface enhanced Raman spectroscopy

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New types of polymer-coated substrates for surface enhanced Raman spectroscopy (SERS) are suggested to protect superficial silver nanostructures and concentrate analytes for superior enhancement of spectral data.

The SERS-active materials are of great interest for creating principally new analytical tools for ecology and biomedical diagnostics.[1–4] Despite those already proved perspective applications, we face with new challenges of SERS prospective implementation in advanced monitoring of oil quality and gasoline pollutants at a low level of target analyte concentrations not exceeding 10^{-5} M.[5–9] From a chemical point of view, such an approach requires a 'smart' surface combining several features. First, noble metal nanostructures, mostly of silver and gold,[4] are often used to enhance Raman scattering by many orders of magnitude. The greatest enhancement is achieved if a plasmonic band position, a laser excitation wavelength and an absorption range of analyzing molecules belong to the same region.[8] In this case, a resonance Raman effect occurs since the excitation laser frequency is close to frequencies of electronic excited states and resonates with them [the surface-enhanced resonance Raman spectroscopy (SERRS)]. This can be achieved if a special layer exists immobilizing a compound catching a target analyte as a part of a stable complex with a shifted absorption region. The layer would better protect the noble metal nanostructure from chemical or mechanical damage and, at the same time, the layer should be permeable to allow analytes to form complexes nearby the silver nanostructure, otherwise the huge expected enhancement of spectral signals becomes impossible. Thus, thin polymer films (Figure 1) would play an important role in improving the application potential of SERS substrates.

The electron-rich structure of some analytes allows them to form stable intermolecular complexes with the appearance of new absorption Benesi–Hildebrand bands.[10] The formation of a new band in the visible light range solves, at least partly, a problem of 'invisibility' of such analytes by SERS. It means that a new opportunity appears to agitate the electronic system by means of plasmons of silver nanostructured materials and record bright SERS spectra if the complex is immobilized onto nanostructured metallic substrates.

SERS-active ultrasonic silver rain (USSR) substrates were prepared in two simple steps based on our previous works.[11–14,†]

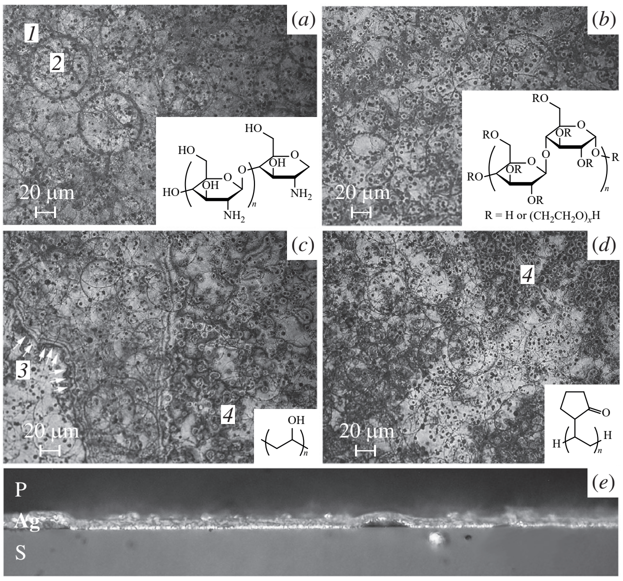

Figure 1 Microstructure of silver ring (USSR) SERS substrates (optical images) coated with various wide-spread polymer systems: (*a*) chitosan coating, (*1*) silver ring, (*2*) silver clusters; (*b*) HEC coating; (*c*) PVA coating, (*3*) dewetting and polymer film disruption, (*4*) perforation of polymer film on rough areas; (*d*) PVP coating; (*e*) cross-section of the coated substrates, P – 1–3 µm thick upper polymer layer, Ag – nanostructured silver (brighter color), S – substrate.

Note that polymer coatings applied here preserve untouched the unique silver-ring morphology of the prepared USSR nanostructured substrates (Figure 1). At the same time, only chitosan and hydroxyethylcellulose (HEC) coatings form continuous

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[†] First, the spray pyrolysis deposition of aqueous diaminsilver hydroxide was used, in which 0.1 M aqueous sodium hydroxide (Aldrich NaOH, high purity water, Milli-Q, Millipore) was added dropwise to a freshly prepared 0.01 M aqueous silver nitrate solution until complete precipitation of black-brown silver(I) oxide. This as-prepared oxide was thoroughly washed with deionized water and dissolved in a twofold molar excess of a 10% aqueous ammonia solution (prepared from 30% ammonium hydroxide, Aldrich) to have 0.01 M solution of a silver(I) complex; a higher concentration deteriorates the silver ring structure formation while superstoichiometric ammonia is needed to prevent Ag_2O precipitation at the aerosol production stage. The obtained transparent silver complex solution was filtered through Millex-LCR syringe driven filter units (Millipore, 0.45 mm pores). In the USSR deposition process, this initial ammonia solution of silver(I) oxide was nebulized into mist and 1–5 µm droplets were streamed onto 'warm' (200–270 °C) glasses.[11] Polymeric layers on the metal surface were prepared using 0.5 wt% polymer (chitosan, hydroxyethylcellulose, polyvinyl alcohol and polyvinylpyrrolidone) solutions in water. The spectra were measured from different points and different substrate series to optimize laser power density for providing non-damaging analysis and better signal reproducibility, in particular, the most of data presented below demonstrated 10–15% deviations only in the intensity of main characteristic peaks.

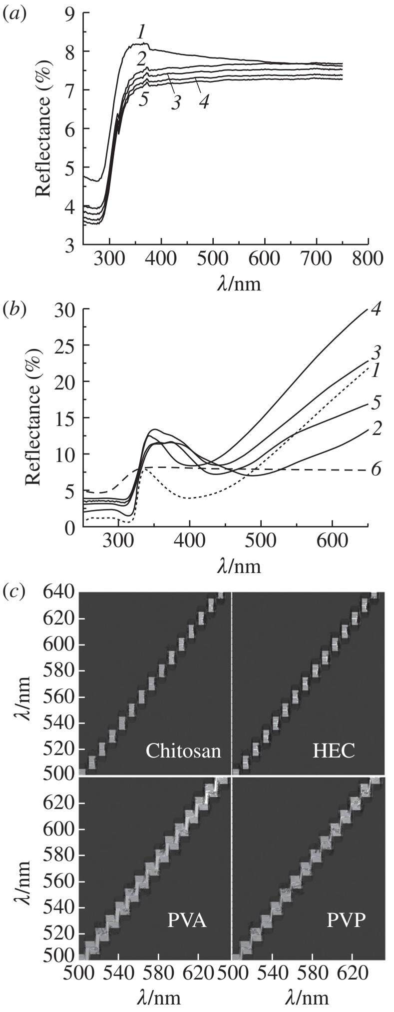

Figure 2 Reflectivity (incidence angle, 8°) and luminescence data of (*a*) polymer coatings and (*b*) polymer-coated SERS substrates with silver ring morphology. (*a*) Polymer coatings transparency: (*1*) a glass substrate, (*2*) PVP, (*3*) chitosan, (*4*) PVA, (*5*) HEC; (*b*) plasmon band position for the substrates with pure silver rings obtained by the ultrasonic silver rain method[11–14] and coated with polymer layers: (*1*) no polymer coating, (*2*) HEC (ε = 3.2–7.5), (*3*) PVA (ε = 1.9–2.1), (*4*) PVP (ε = 1.8–2.2), (*5*) chitosan (ε = 3.3–3.7), (*6*) pure glass; (*c*) luminescence scans of the same polymer coatings.

layers [Figure 1(*a*),(*b*)], while polyvinyl alcohol (PVA) and polyvynilpyrrolidone (PVP) demonstrate dewetting and polymer film disruption forming discontinuous layers [Figure 1(*c*),(*d*)]. Otherwise all the polymers are transparent [Figure 2(*a*)], demonstrate no luminescence in the working region [Figure 2(*c*), inset] and do not suppress or shift much the plasmonic band position typical of naked USSR substrates [Figure 2(*b*)]. The observed broadening of the plasmonic peaks correlates well with the increase in dielectric constants of the polymers applied as upper layers of the coated substrates (Figure 2).

No pronounced Raman scattering was observed from the pristine layers of the polymers placed onto the silver layer of the substrates [Figure 3(*a*), spectra *1*–*5*] even if the polymer layer thickness is essentially increased compared to the routine procedure used for substrate coating [Figure 3(*a*), spectrum *6*]. Thus, all the polymer coatings used are roughly similar and seem to be equally applied as coating due to their high transparency and the absence of noisy signals in Raman scattering. However, Figure 3 proves that it is not the case since different polymer coatings demonstrate remarkably surprising diversity in terms of the enhancement of SERS signals of the complexes used to detect dibenzothiophene (DBT) and other analytes. The intensity of conventional Raman scattering of all the compounds at the concentration used does not exceed essentially the background signal. At the same time, the DBT charge transfer complex with 2,3-dichloro-5,6-dicyano-1,4-benzoquinone (DDQ) demonstrates bright SERS/SERRS spectra with sharp characteristic peaks [Figure 3(*a*)]. Evidently, such remarkable growth of spectral intensities and new peak appearance for the analyzed DBT sample is a direct consequence of DBT–DDQ complex immobilization onto the nanostructured silver substrates since no characteristic signal in either RSS or SERS spectra is observed without the complex.

The characteristic signals of DBT appear at 770, 1027, 1072, 1137, 1236, 1321, 1480, 1558, 1601 (A_1 symmetry), 768, 938 (A_2 symmetry), 740, 770, 859, 940, 973 (B_1 symmetry), 704, 868, 1027, 1078, 1171, 1268, 1353, 1442, 1462, 1514, 1566 and 1590 cm^{-1} (B_2 symmetry). The peak at 1134 cm^{-1} corresponds to a breathing mode of the thiophene ring, the 1350 cm^{-1} vibration is a mixed mode corresponding to stretching vibrations of the thiophene ring and the stretching bands of the benzene rings, the 1650–1670 cm^{-1} mode is a sign of the C–C bonds of aromatic rings. Most of these peaks are different from DDQ vibration modes; therefore, the SERS spectrum of the DDQ–DBT charge transfer complex manifests unambiguously the presence of the DBT target compound [(Figure 3(*a*)].

At the same time, only polysaccharides like hydroxyethylcellulose or similar structures (chitosan coating) demonstrate such a behavior, while the signal almost disappears in the case of other polymers. It is known that even fully protonated chitosan tends to associate with nonpolar molecules as a result of hydrophobic interactions.[15] This behavior is based on the presence of the main polysaccharide backbones and *N*-acetyl groups at the C-2 position.[16] This type of interaction is non-inherent to the studied synthetic polymers (PVA, PVP). On the basis of this assumption, it should be proposed that the signal successfully forms due to hydrophobic interactions between biopolymer macromolecules with the DDQ–DBT charge transfer complex in nonpolar solvents such as oil components. Within the complex, DBT bands[17,18] become enhanced greatly [Figure 3(*a*)].

Meantime, the above example does not limit the possibilities that micrometer-thick [Figure 1(*e*)] polymer coating would give for extending the application abilities of SERS substrates. Figure 3 contains some pair of analytes demonstrating that polymers can enhance Raman signal due to analyte preconcentration or, *vice versa*, quench it when acting as barrier layers in some cases. Figure 3(*a*),(*d*) shows that the principle of better SERS enhancement works for various system since in addition to the DBT–DDQ complex, another one, tetracyanoquinodimethane $(NC)_2CC_6H_4$-$C(CN)_2$ (TCNQ)–PhOH complex, demonstrates the same behavior due to the chitosan coating on the nanostructured substrate. Figure 3(*b*),(*e*) shows that the application of a 633 nm laser is possible for the developed substrates due to a long absorption tail of the silver ring substrates [Figure 2(*b*)]. At the same time, it seems that the penetration of analytes in the polymer layer depends strongly on the chemical origin and molecular weights of the analyzed compounds. The substances of Figure 3(*a*),(*d*) (DBT and PhOH) are readily concentrated in the polymer layer due to the presence of counterpart molecules of the complexes (DBT–DDQ or TCNQ–PhOH), which gives strong SERS signals. However, low-weight analytes like methylene blue (MB) dye or PhOH reveal same or partly lower enhancement if a polymer layer is present as compared to bare silver ring substrates. For high molecular weight compounds like proteins (Hb), the 2–3 μm thickness of a polymer layer [Figure 1(*e*)] blocks almost completely such analytes from reaching the layer of nanostructured silver. As a result, SERS signal is absent [Figure 3(*c*)], while a similar compound (bilirubin) containing no large biopolymer

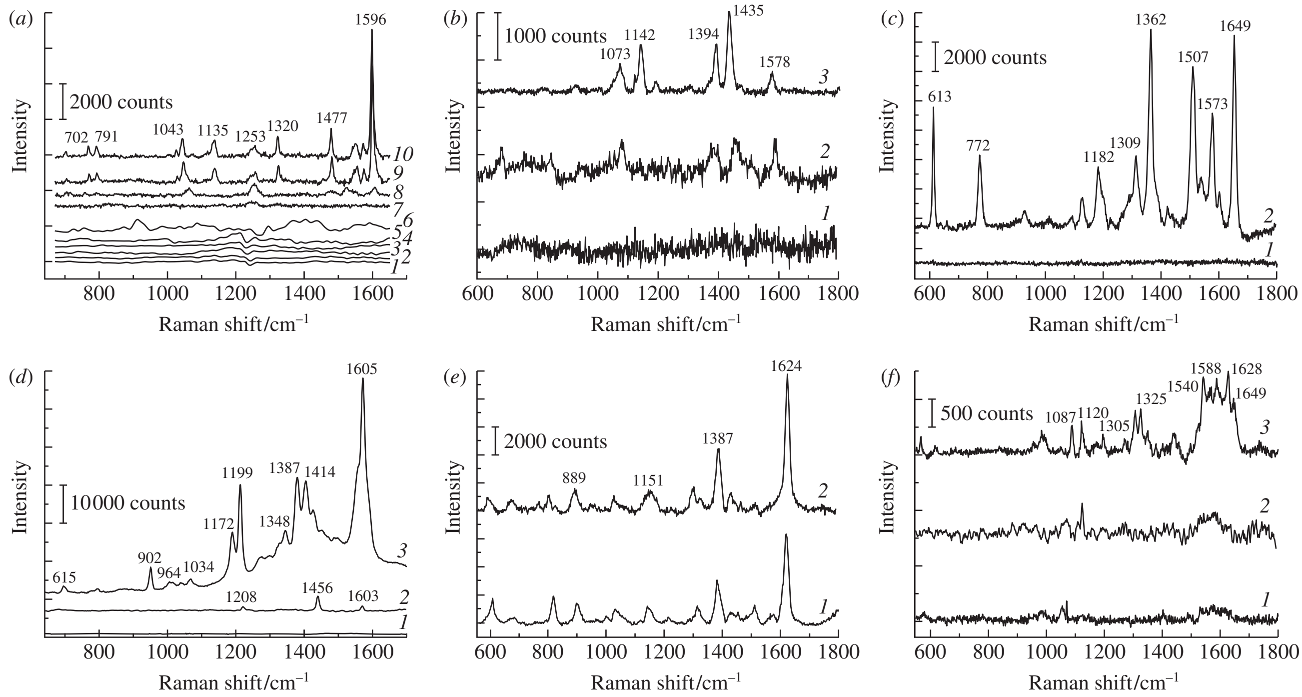

Figure 3 Vibration spectra of the samples. (*a*) Raman and SERS spectra of polymeric layers on a nanostructured silver ring layer: (*1*) pure glass; (*2*) HEC coating; (*3*) PVP; (*4*) PVA, (*5*) a chitosan layer itself and the same with 5-fold increased thickness (*6*). All the RSS spectra are measured using a 20 mW 633 nm argon laser and power neutral density filter (50%), 20× objective lens and 10 s of acquisition time. SERS spectra of the DBT–DDQ complex on glass coated with nanostructured silver rings and the following polymer layers: (*7*) PVP; (*8*) PVA; (*9*) chitosan; (*10*) HEC. All the spectra were measured for identical analyte concentrations of 10^{-4} M of DBT using a 20 mW 633 nm argon laser and power neutral density filter (10%), 20× objective lens and 10 s of acquisition time. (*b*) SERS spectra of 10^{-7} M aqueous solution of aminothiophenol, (*1*) chitosan coating, 514 nm laser, (*2*) same at the 633 nm excitation wavelength; (*3*) naked silver nanostructured substrate with no chitosan, 514 nm laser. (*c*) SERS spectra of hemoglobin (Hb) solution, (*1*) 10^{-5} M Hb concentration on a chitosan-coated silver ring substrate, 514 nm laser, (*2*) same with 10^{-7} M Hb concentration with no chitosan. (*d*) SERS spectra of the complex of TCNQ and phenol on a silver ring substrate coated with chitosan, (*1*) PhOH, 10^{-4} M, (*2*) TCNQ, 5×10^{-4} M, (*3*) consequential addition of TCNQ and PhOH of the same concentrations forming the complex. (*e*) SERS spectra of MB dye 10^{-7} M aqueous solution on silver ring substrates, 633 nm laser, (*1*) naked surface, (*2*) chitosan coating. (*f*) SERS spectra of 10^{-7} M toluene solution of bilirubin using silver ring substrates, 514 nm laser, (*1*) bare nanostructured substrate, (*2*) chitosan coating, (*3*) HEC coating.

compartment gives SERS enhancement even in a hydrophobic environment [Figure 3(*f*)].

From the whole set of selected polymers, polysaccharides (like cellulose derivatives) or aminosaccharides seem to be the most promising. Particularly, in a solid state, chitosan is characterized by an ordered fibrillar structure with a high degree of crystallinity, and polymorphism;[15] it demonstrates an extended twofold helix in a zigzag structure stabilized by intrachain hydrogen bonds across the glycosidic linkages. The chitosan biopolymer has some benefits since it can be cross-linked by simple chemical procedures; it can also preconcentrate or block some analytes due to unique chemical properties, polymer chain arrangement, gel structure and swelling properties.[15,19] The approach of molecular imprinting[15] makes it possible to build specific sites inside a polymer matrix that selectively recognises and binds a ligand used as a template during the polymer treatment[9] advancing further application abilities of the suggested polymer coated SERS substrates.

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