

SERS INVESTIGATION ON THE POLYMERIZATION OF CARBAZOLYL-DIACETYLENE MONOLAYERS ON GOLD AND SILVER SURFACES

E. Giorgetti^{1*}, M. Muniz-Miranda², G. Margheri³, G. Dellepiane⁴, A. Giusti⁴,
M. Alloisio⁴, C. Cuniberti⁴

^{1*}*INSTM and Istituto dei Sistemi Complessi - CNR, Via Madonna del Piano 10, 50019, Sesto Fiorentino, Italy. emilia.giorgetti@fi.isc.cnr.it*

²*INSTM and Dipartimento di Chimica, Università di Firenze, Via della Lastruccia 3, 50019, Sesto Fiorentino, Italy*

³*Istituto dei Sistemi Complessi - CNR, Via Madonna del Piano 10, 50019, Sesto Fiorentino, Italy*

⁴*INSTM and Dipartimento di Chimica e Chimica Industriale, Università di Genova, Via Dodecaneso 31, I-16146 Genova, Italy.*

Abstract – Surface Enhanced Raman Scattering (SERS) experiments were performed on different interfaces consisting of nanostructured surfaces of noble metals and adsorbed monomolecular layers of the novel carbazoyl diacetylene CDS9. The Raman electromagnetic enhancement ensured by the surface roughness or curvature of the metal permitted the monitoring of the spectroscopic properties of the organic layers. In particular, in the case of CDS9 films deposited by self assembling on gold and silver coated glass slides or used as a capping agent for gold nanoparticles and subsequently polymerized by UV radiation, SERS experiments permitted detection of two polymer phases, characterized by a different degree of order in the polymer backbone: the highly-conjugated blue phase and the less-extended red conformation.

Introduction

Organized assemblies of thiol or disulfide compounds obtained by chemisorption on noble metals can find important applications, ranging from materials to medical science. It has been demonstrated that introduction of conjugated diacetylene groups within the alkyl chains and subsequent polymerization by photoirradiation or thermal treatment permits fabrication of robust polymer monolayers with peculiar optoelectronic properties [1]. They can find interesting applications in high resolution lithography, nanosensing or nanophotonics. Moreover, the addition of carbazoyl units as terminal functional groups is expected to enhance both the non-linear behavior of these polymers and the electrical conductivity, due to the hole-transporting properties of carbazole.

The present work reports on the characterization of self-assembled monolayers (SAMs) of the carbazoyl diacetylene 14-*N*-carbazoyl-tetradeca-10,12-diyne disulfide (CDS9), obtained by S-S bond breakdown and subsequent chemisorption onto gold or silver surfaces *via* sulfur atoms. In particular, we studied the polymerization process of the monomeric units promoted by UV irradiation and monitored by SERS (Surface Enhanced Raman Scattering) with different exciting lines. The CDS9 SAMs were adsorbed on both gold and silver coated microscope slides or, as capping agents, on chemically prepared gold nanoparticles. Although the expected Raman signals were very weak, due to the extremely small thickness of the organic layers, we took advantage of the properties of metal-dielectric interfaces that can induce a huge enhancement of the Raman effect, thanks to the giant localization of the e.m. fields produced by roughness or nanostructuring.

CDS9 monolayers on silver surfaces

Silver coatings were prepared by high vacuum evaporation onto commercial microscope slides. Smooth and uniform coatings (type P) were obtained by electron gun assisted evaporation at a rate of 14.5 Å/sec. In this case the silver/air interface had a typical surface roughness of 1.8 nm

and a peak-to-valley value of 16 nm, measured by atomic force microscope. Nanostructured coatings were prepared by thermal evaporation at a slow rate, typically 0.25 Å/sec, and for different time durations. In particular, the evaporation time was: i) 8 min. for type S substrates, characterized by a smooth but nanostructured surface consisting of metal islands and voids and having a roughness of 1.7 nm and a peak-to-valley value of 13 nm; ii) 33 min. for type R coatings, characterized by surface RMS roughness of 4.2 nm and a peak-to-valley value of 30 nm. In the case of sample S, the mean diameter of metal islands was 43 nm. Fig. 1a shows the reflectance of type P, S and R samples (curves P, S_r and R) and the absorption of an S-type sample (curve S_a). Both R and S-type samples are good candidates for SERS experiments. In particular, the UV dip exhibited by curve R is the spectroscopic confirmation of the roughness of the silver layer. S-type samples look coloured and exhibit a broad absorption peak around 500 nm that is associated with the plasma resonance of metal islands and suggests a strong SERS activity of these substrates by laser excitation in the blue-green region.

CDS9 SAMs were grown on Ag surfaces by self-assembling from 1 mM chloroform solutions. After rinsing in pure chloroform, in order to remove excess CDS9, the samples were exposed for 45 min. to an UV lamp (model UVG-11, Ultraviolet Products Inc.) emitting at 254 nm. Fig. 1b shows the Raman spectra of CDS9 SAMs on different silver coatings: type-R coating and 488 nm exciting wavelength (A); type-S coating and 488 nm exciting wavelength (B); type-P coating and 514.5 nm exciting wavelength (C). The straight line in the figure indicates the position of the C=C stretching band at 1450 cm⁻¹, pertaining to the blue phase of the polymer [2].

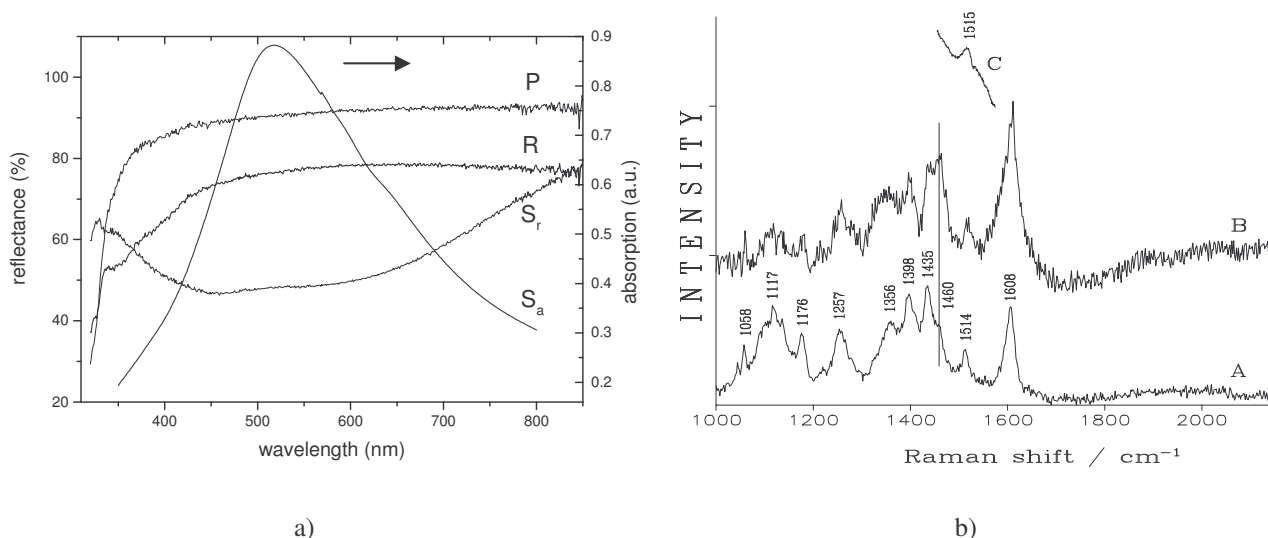


Fig. 1 a) UV-Vis spectra of different Ag coatings. b) Raman spectra of CDS9 SAMs on Ag.

Curve C of Fig.1b represents the best result obtained with P-type substrates. The spectrum is very noisy and only by long spectral accumulation we could detect a weak band at 1515 cm⁻¹. This band was absent before UV irradiation and is associated with the C=C stretching of the red form of the polymer, that is in Raman resonance with the exciting wavelength. In the case of S-type substrates (curve B in Fig. 1b), in spite of the small thickness of the organic layer and of the limited number of monomer units adsorbed on a surface consisting of metal islands separated by voids, we could observe a more intense and resolved Raman signal, due to the SERS effect provided by the nanostructuring of the metal/organic interface. A further improvement of the spectrum was obtained with metal coatings of type R (curve A in Fig. 1b). In fact, in this case, the SERS enhancement provided by the metal/organic interface and the higher surface coverage due to the absence of voids increased the spectral intensity and resolution. The most significant features of spectra A and B of Fig. 1b are the band at 1608 cm⁻¹ (aromatic C=C stretching), the band at 1514 cm⁻¹ (C=C stretching of red polymer phase) and the band at 1460 cm⁻¹ (C=C stretching of blue polymer phase) that appears as a small shoulder in curve A, while is well

resolved in curve B. In both cases, the absence of any signal in the region around 2100 cm^{-1} (not shown in the figure) corresponding to the $\text{C}\equiv\text{C}$ stretching indicates that, in agreement with SERS selection rules, these bonds are nearly parallel to the metal surface. The presence of the band at 1608 cm^{-1} , that is not visible in the spectra of CDS9 powders, indicates that, on silver surfaces, carbazolyl groups are nearly perpendicular to the plane of the metal. The previous results indicate that the arrangement of the polymer layer on silver can be represented as in Fig. 2 and that the red form of the polymer prevails on the blue one, particularly on rough coatings.

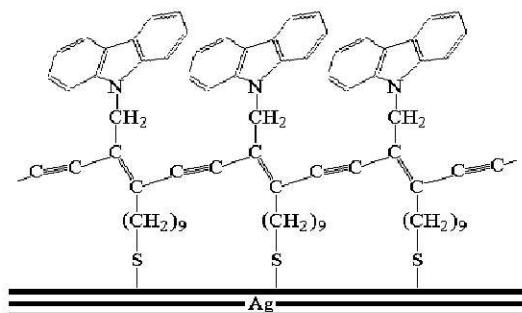


Fig. 2 Polymerization scheme of CDS9 SAMs on Ag surfaces.

CDS9 monolayers on gold surfaces

Gold coatings were obtained by sputtering onto thiol-functionalized silica substrates, using an electrical discharge deposition system. Au films of about 20 nm thickness were obtained and immediately immersed in a 1 mM chloroform solution of CDS9 to prepare the SAMs. The CDS9 SAMs were subsequently rinsed and polymerized by UV irradiation as described in the previous paragraph. The AFM images (Fig. 3a) indicated that these gold coatings are nearly flat, with a surface roughness around 1.9 nm and, consequently, unable to give rise to SERS enhancement. However, in the case of gold, it is not an easy task to tailor the surface roughness by tuning the deposition parameters, because this would require a very strict control on the deposition rate and extremely long sputtering times. As a consequence, we increased the surface roughness and the SERS activity of the samples by covering the CDS9 SAMs adsorbed on gold with Ag colloidal particles. In this way, we achieved a surface roughness of the order of 148 nm (Fig.3b) and an efficient SERS enhancement of the Raman spectra [3].

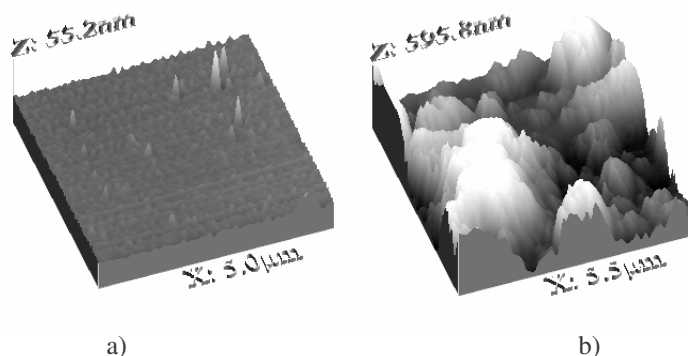


Fig. 3 AFM images of Au/polymer surfaces, with (a) and without (b) Ag particles.

As expected, no Raman signal was detected from the polymer monolayers deposited on a smooth gold surface while, after deposition of Ag colloidal particles, intense SERS spectra were observed, indicating the formation of the polymer in the two different forms. Fig. 4 shows the

SERS spectrum of an Au/CDS9/Ag colloids sample and the Raman spectrum of a powder CDS9 sample, both after UV polymerization. The exciting line (647.1 nm) is in resonance with the blue form of the polymer. In the case of the CDS9 SAM, the C=C stretching band of the red phase at about 1500 cm^{-1} is stronger than that of the blue one at about 1450 cm^{-1} , indicating, also in this case, the predominance of the less-conjugated form. In contrast, in the Raman spectrum of powders, only the band pertaining to the blue form appears. Moreover, in the triple bond region (not shown in Fig.4), the red and blue phases are both present in the spectrum of powders, as shown by the signals at 2100 and 2085 cm^{-1} , respectively. In the SERS, instead, the C=C bond stretching band is again absent, suggesting that these bonds are nearly parallel to the surface. The SERS analysis indicates that, also in the case of gold substrates, the polymerization of CDS9 SAMs follows the scheme of Fig. 2. A comparison between Fig. 1b and Fig.4 shows that, in the latter case, the band corresponding to the C=C stretching of the aromatic rings is missing. This suggests an increased disorder of the SAMs, probably induced by the deposition of Ag grains.

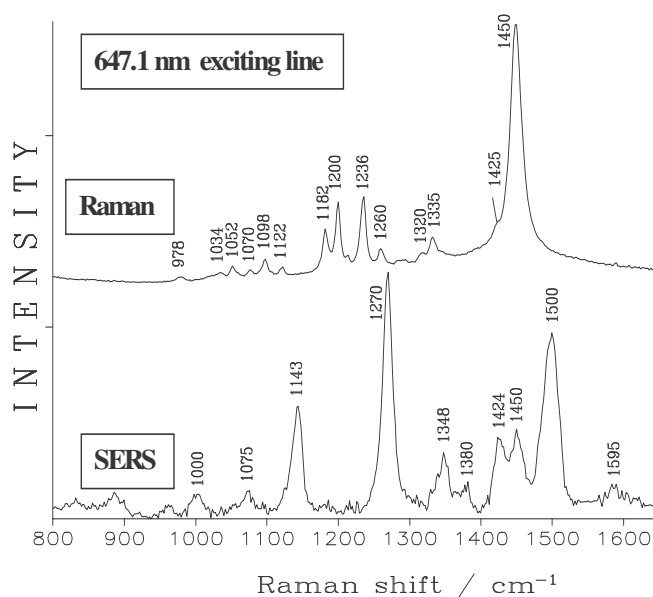


Fig. 4 SERS spectrum of a CDS9 SAM on gold and of a powder sample, after UV irradiation.

CDS9-capped gold nanoparticles

CDS9 stabilized gold nanoparticles in chloroform (AuNPs) were prepared by a modified version of the Burst method [4]. A typical TEM micrograph of an AuNP/CDS9 in chloroform is presented in Fig. 5a [5]. The particles are small, nearly spherical, with a diameter of about 4.5 nm and form a 2D structure, in which the closest core-core spacing is approximately equal to the estimated length of the half-moiety of CDS9 disulfide (2.2 nm) [2]. Fig. 5b illustrates the adsorption scheme of CDS9 molecules on AuNP.

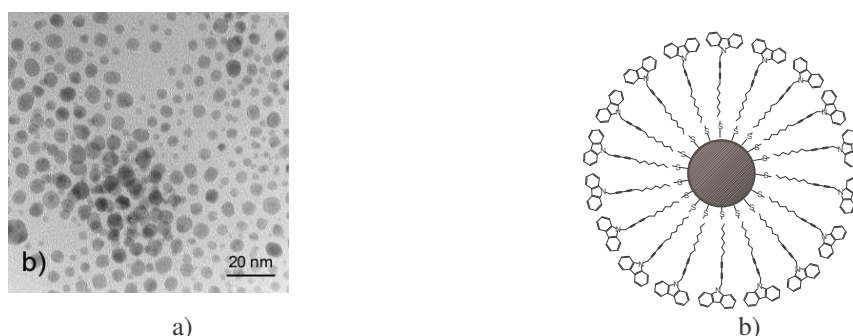


Fig 5 a) TEM image of AuNP/CDS9 particles. b) Schematic representation of gold nanoparticles (AuNPs) capped with CDS9.

Films of CDS9-capped AuNPs were fabricated by simple casting of the nanoparticle suspension in chloroform onto thiol-functionalized silica slides. As prepared, the samples were rinsed with spectroscopic grade solvent, dried in air and then photopolymerized in a Rayonet Photochemical Chamber Reactor, operating at 254 nm. The samples were then investigated by means of SERS spectroscopy with the 633 nm laser excitation line. Fig. 6 shows the SERS spectrum of a film of CDS9-coated AuNPs after 7 minutes of UV irradiation. In the high frequency region, only the very weak signal at 2070 cm^{-1} is observed, typical of the $\text{C}\equiv\text{C}$ stretching of blue polydiacetylenes [5]. The low frequency region gives further confirmation of the polymerization of CDS9 in its blue form, represented by the band at 1445 cm^{-1} , that is associated with the $\text{C}=\text{C}$ stretching of the polymer chain. No evidence of the red form, that was predominant in the case of CDS9 adsorption on gold and silver planar surfaces, is present in Fig. 6.

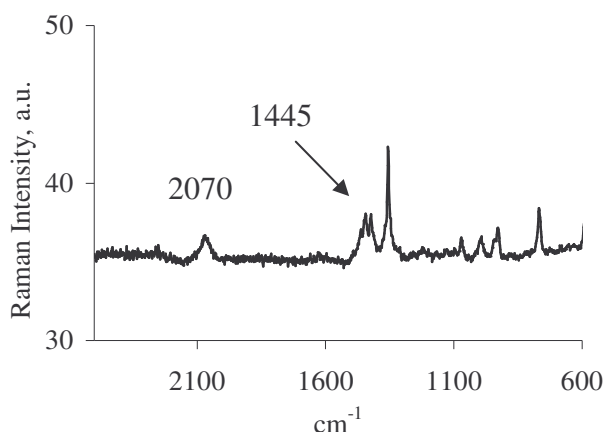


Fig. 6 SERS spectra of Au/polyCDS9 films after 7 minutes UV irradiation (Au absorption background subtracted). The sharp and intense signal at 1356 cm^{-1} can be attributed to the double bond stretchings of the carbazole rings.

Conclusions

The photopolymerization of monolayers of the diacetylene CDS9 on metal surfaces was studied by SERS technique. While the less conjugated red form was predominant either on gold or silver surfaces with different morphology, the blue form was found to prevail when CDS9 was used as capping agent on AuNPs. These results show that the topological characteristics of the metal substrate are a key factor in the diacetylene polymerization process.

Acknowledgments

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References

1. M.D. Mowery; A. Cook Smith; C.E. Evans; *Langmuir* 2000, *16*, 5998 and refs. therein.
2. E. Giorgetti et alii; *Langmuir*, 2006, *22*, 1129.
3. M. Muniz.Miranda et alii; *Macromol. Symp.*, 2005, *230*, 67.
4. M. Hoestetler et alii; *Langmuir*, 1998, *14*, 17 and refs. therein.
5. M. Alloisio et alii; *Journal of Phys. Chem. B* (submitted).