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SERS Investigation on the Polymerization of Carbazolyl-diacetylene Monolayers on Gold Surfaces

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Summary: Surface Enhanced Raman Scattering experiments were performed on self-assembled carbazolyl-diacetylene monolayers chemisorbed on smooth gold substrates and UV irradiated. The Raman enhancement was ensured by depositing silver colloidal nanoparticles, which strongly increase the surface roughness. The co-existence of two polymer phases, characterized by different degree of order in the polymeric backbone, was detected by SERS results, which suggest a polymerization scheme with conjugated triple bonds nearly parallel to the plane of the metal surface.

Keywords: AFM; gold; nanoparticles; polymerization; SERS

Introduction

Self-assembled monolayers (SAMs), obtained through chemisorption of molecules containing thiol or disulfide groups on metal surfaces, provide, after topochemical polymerization, robust monolayers with peculiar optoelectronic properties, which find applications in high resolution lithography or nanosensing. This paper shows a combined SERS (surface-enhanced Raman scattering) and AFM (atomic force microscopy) study of the SAMs of the novel carbazolyl-diacetylene 14-(9*H*-9-carbazolyl)-tetradeca-10,12-diyne-1-yl disulfide (CDS9), deposited on Au-coated glass substrates, for monitoring the polymerization process and obtaining information on the type and the structural arrangement of the polymer frame.

Experimental

Gold coatings of glass microscope slides were obtained by thermal deposition; self-assembled monolayers of CDS9 were grown by dipping the Au-coated substrates in a diluted chloroform soluton of CDS9. Polymerization of the SAMs was performed by exposure to UV lamp (model UVG-11, Ultraviolet Products Inc.), with peak emission at 254 nm. Colloidal silver, obtained in aqueous suspension according to Creighton[1] and activated by adding 10^{-3} M NaCl, was deposited on the samples after UV irradiation.

AFM images were obtained with a Nanosurf EasyScanDFM; the surface roughness was calculated as RMS (root mean square) parameter over images of $\sim 5\ \mu m \times 5\ \mu m$.

Raman spectra were recorded by using the 514.5 nm line of an Ar^+ laser or the 647.1 nm line of a Kr^+ laser and a Jobin-Yvon HG2S monochromator equipped with a cooled RCA-C31034A photomultiplier.

Absorption Spectra

The absorption spectra of CDS9 in solutions did not show bands in the visible region. By UV-irradiation of solid samples of CDS9, instead, the absorbance in the visibile region progressively increased by

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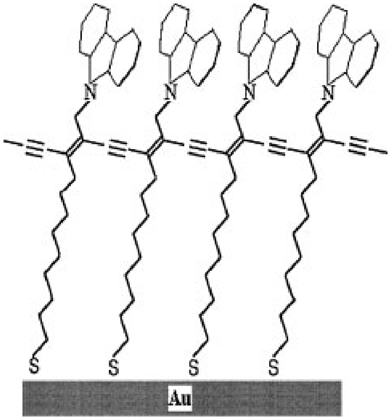

Figure 1.
Polymer layer on Au surfaces.

polymeric arrangement between diacetylenic groups (Figure 1), showing the formation of two different polymer forms: a red phase, related to an intense broad band between 500 and 550 nm, and a blue phase, characterized by higher structural order in the polymer chain, related to the shoulder ranging from 600 e 640 nm (Figure 2).

SERS-Activation of Smooth Gold Surfaces

In order to detect a satisfactory SERS signal from polymers of CDS9 adsorbed on smooth gold surfaces, dry Ag layers were deposited from Ag hydrosols after UV polymerization of CDS9. The AFM images (Figure 3) indicated the gold surface is nearly flat ($RMS = 1.92$ nm) and, consequently,

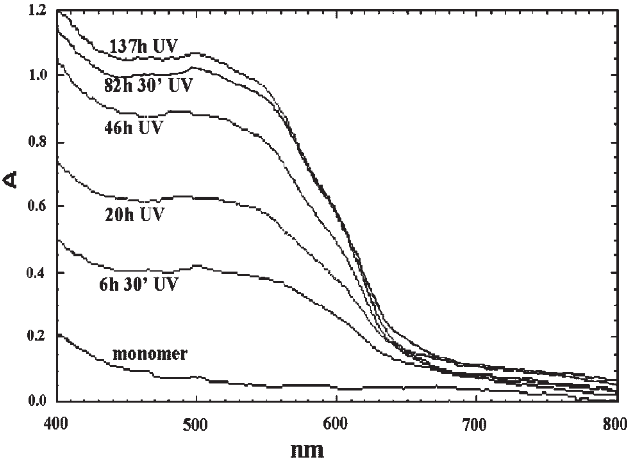

Figure 2.
Visible absorption spectra of CDS9 in KBr pellet under UV irradiation.

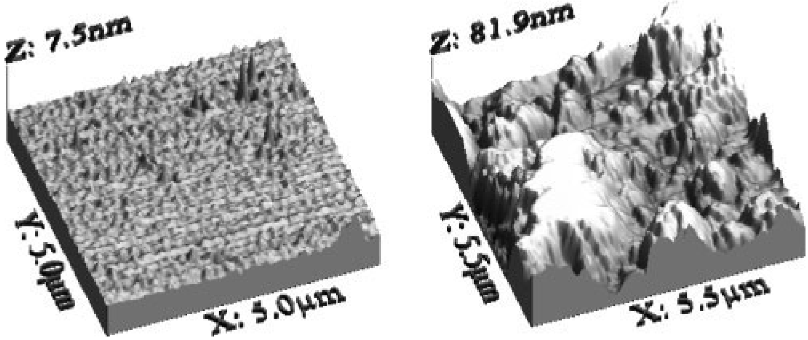

Figure 3.
AFM images of Au/polymer surfaces, with (right) and without (left) Ag particles.

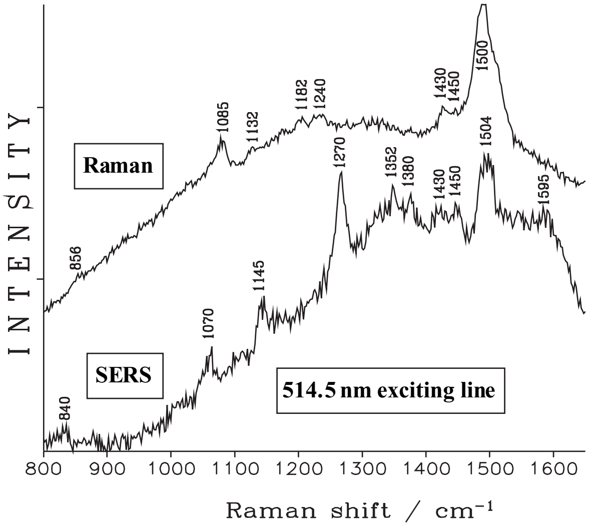

Figure 4.
SERS spectra of the polymer on Au surfaces.

unable to give rise to SERS enhancement. On the contrary, the surface roughness hugely increased by deposition of Ag colloidal particles (RMS = 148 nm) and an efficient electromagnetic SERS effect was expected from the Ag-covered samples.[2]

Raman and SERS Spectra

No Raman signal was detected from the polymer monolayers deposited on smooth gold surfaces. Instead, after deposition of Ag colloidal particles, intense SERS spectra were observed (Figures 4 and 5), indicating the formation of the polymer in the two different forms. The C=C stretching band of the red phase at about 1500 cm^{-1} was stronger than that of the blue one at about 1450 cm^{-1}, with both 514.5 nm and 647.1 nm exciting lines, indicating the predominance of this form.

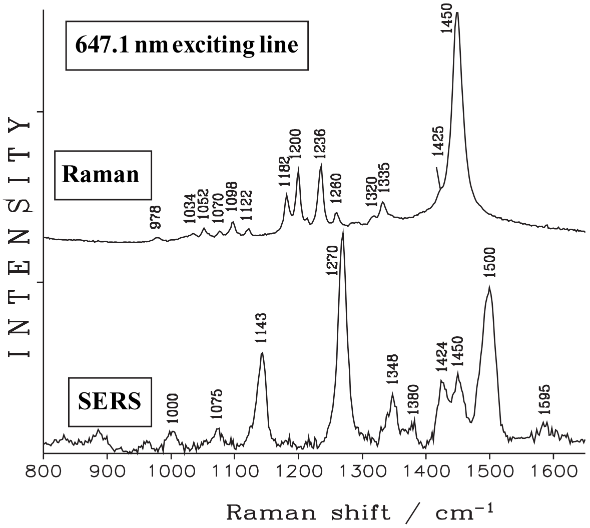

Figure 5.
Raman spectra of solid CDS9 after UV irradiation.

In the normal Raman spectra of powders the C≡C bond stretchings of the red and blue phases were observed at 2100 and 2085 cm^{-1}, respectively. In the SERS, instead, the C≡C bond stretchings were absent, suggesting that these bonds are nearly parallel to the surface, as less affected by the SERS effect with respect to the other vibrational modes.

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