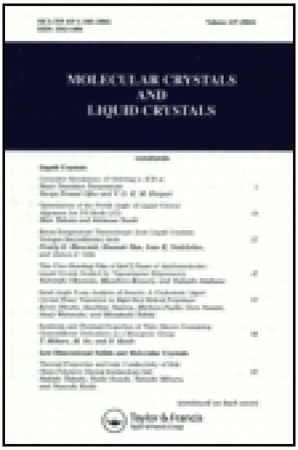

Molecular Crystals and Liquid Crystals Science and Technology. Section A. Molecular Crystals and Liquid Crystals

Publication details, including instructions for authors and subscription information:
http://www.tandfonline.com/loi/gmcl19

Fabrication and Structural Characterization of Azobenzene Monolayer on Silver Island Films By LB and SA Techniques

Jiang Zhao [a b], Jin Zhang [a], Huixin He [a], Haoli Zhang [a], Fusae Nakanishi [b] & Zhongfan Liu [a]

[a] Center for Intelligent Material Research (CIMR), College of Chemistry and Molecular Engineering, Peking University, Beijing, 100871, China

[b] National Institute of Materials and Chemical Research (NIMC), 1-1 Higashi, Tsukuba, Ibaraki, 305, Japan

To cite this article: Jiang Zhao, Jin Zhang, Huixin He, Haoli Zhang, Fusae Nakanishi & Zhongfan Liu (1998): Fabrication and Structural Characterization of Azobenzene Monolayer on Silver Island Films By LB and SA Techniques, Molecular Crystals and Liquid Crystals Science and Technology. Section A. Molecular Crystals and Liquid Crystals, 314:1, 297-302

To link to this article: http://dx.doi.org/10.1080/10587259808042491

Mol. Cryst. Liq. Cryst., 1998, Vol. 314, pp. 297–302
Reprints available directly from the publisher
Photocopying permitted by license only

Fabrication and Structural Characterization of Azobenzene Monolayer on Silver Island Films By LB and SA Techniques

JIANG ZHAO[a,b], JIN ZHANG[a], HUIXIN HE[a], HAOLI ZHANG[a], FUSAE NAKANISHI[b], and ZHONGFAN LIU[a]
[a]Center for Intelligent Material Research (CIMR), College of Chemistry and Molecular Engineering, Peking University, Beijing 100871, China; [b]National Institute of Materials and Chemical Research (NIMC), 1-1 Higashi, Tsukuba, Ibaraki 305, Japan

Langmuir-Blodgett monolayer and self-assembled monolayer of C_8H_{17}-Azo-O-$(CH_2)_3$-COOH (referred as ABD) molecules have been fabricated on sliver island film, which are found to have rigid structures. The enhanced infrared spectra of LB monolayer reveal the distribution of the electromagnetic field in the silver island film.

Keywords: Langmuir-Blodgett film, self-assembled monolayer, silver island film, surface enhanced infrared spectroscopy

INTRODUCTION

Surface enhanced spectroscopy, including surface enhanced Raman, luminescence, and infrared spectroscopy, has been attracting a great deal of research interest because of their prospective applications[1-6]. Generally speaking, these kinds of surface enhanced phenomena involve a strong and localized surface electromagnetic (EM) field, which is generated by surface plasmon oscillation excited on rough or island metal film by external radiation. When this intense surface EM field interacts with the molecules, an enhanced effect appears, such as enhanced Raman scattering, luminescence emitting, and infrared absorption. This is related to the electromagnetic (EM) mechanism of the surface enhanced spectroscopy[2-6]. Naturally, it is essentially important to study and to have a clear picture of the spatial distribution of the surface EM field generated by surface plasmon oscillation. As mentioned above, the surface EM field is highly localized, and the enhanced effect is short-ranged. Therefore, to probe this localized EM field, the modeled molecular system should be very small in dimension, and to be located very close to the metal surface. For this purpose, molecular assembling technique, such as Langmuir-Blodgett (LB) and self-assembling (SA) techniques are believed to be very efficient[7]. In this paper, we report our fabrication of monolayers of 4-Octyl-4'-(3-carboxytrimethyleneoxy)azobenzene (refereed as ABD) on silver island films by SA and LB techniques, and our studies on the enhanced infrared spectra of the monolayer, which gives us some insights into the EM field distribution and its effect in the surface enhanced infrared spectroscopy.

EXPERIMENT

Silver island films on CaF_2 (for infrared spectroscopy) and on mica (for atomic force microscopy (AFM)) are prepared by thermal evaporation in a vacuum chamber. The film's thickness is monitored and controlled by a quartz thickness gauge. In experiment, silver films of 10-60 nm in thickness are prepared. The morphology of these silver films are studied by a Nanoscope III Atomic Force Microscope (Digital Instruments, USA).

Langmuir-Blodgett monolayers of ABD are vertically transferred onto solid substrates from air/water interface using a commercial LB instrument (FACE, Japan). The monolayers are transferred at a constant surface pressure of 20 mN/m, and the temperature of the subphase is kept as 20°C. Self-assembled monolayer (SAM) of ABD molecules were fabricated by immersing the silver substrates in ABD/ethanol solution (1×10^{-3} M) for over 24 h. The molecules physically adsorbed on the substrates are washed off by pure ethanol. After the monolayers of ABD were fabricated, their transmission infrared spectra were measured by a Perkin-Elmer System 2000 Spectrometer, equipped with a liquid nitrogen cooled MCT detector. The resolution of the system was set to be 4 cm^{-1}.

RESULTS AND DISCUSSIONS

The AFM images of the silver film on mica surface clearly show the 'island' nature of the silver film, i.e., the silver film consists of well-separated silver islands with an average lateral diameter of 18-23 nm and a height of 2-3 nm. The size and shape of silver particles are remarkably small compared with the wavelength of the infrared radiation (μm), and thus-prepared silver substrates are believed to be active for surface enhanced infrared spectroscopy (SEIRS).

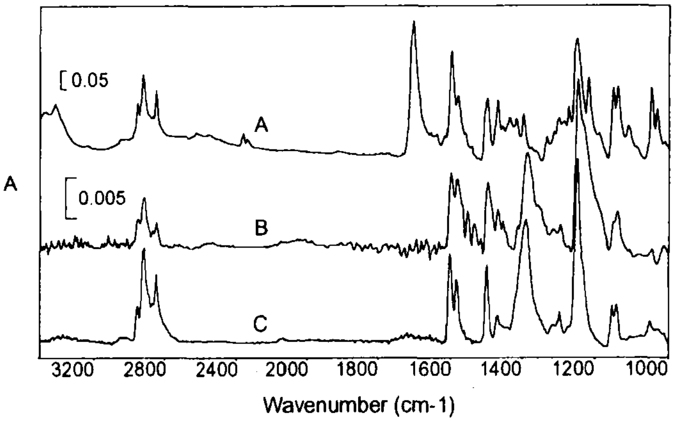

FIGURE 1 Infrared spectra of ABD sample in KBr pellet (A), ABD SAM (B), and ABD LB monolayer (C) on silver island films coated CaF2 substrates.

Figure 1 shows the transmission infrared spectra of ABD sample in KBr pellet (A), SAM of ABD molecules (B), and LB monolayer of ABD (C) on silver island film coated CaF_2 substrates. It is seen that the IR spectra of the monolayers are considerably enhanced due to the presence of silver island films. The major absorption peak positions and their band assignment are in good agreement with previous studies[8].

Comparing the spectra of ABD molecule in KBr pellet with those of LB monolayers and SAMs, it can be found that: 1) a new strong and broad band appears at 1390 cm^{-1} in the spectra of LB films or SAMs, which is assigned to the symmetric stretching of carboxylate group, $\nu_s(COO^-)$[9]; 2) the absorption band of stretching vibration mode of hydroxyl group and carbonyl group, $\nu(OH)$ and $\nu(C{=}O)$ (expected around 3340 and 1710 cm^{-1} respectively), is absent in spectra of LB monolayer and SAM. These data reveal that the ABD molecules adsorb on the silver island films surface through the COOH group by releasing its proton, i.e., ABD monolayer on silver island film shows the interfacial COO^- Ag^+ linkage[9]. (The absorption of $\nu_{as}(COO^-)$ does not appear for LB monolayer and SAM because of the selection rule of surface enhanced infrared spectroscopy)[5].

The frequency of the C-H stretching vibration bands of methylene groups are believed to reflect the molecular packing status in the monolayer[7,9]. In the spectra, the frequency of $\nu_{as}(CH_2)$ and $\nu_s(CH_2)$ are 2921 and 2851 cm^{-1} for LB monolayer, and for SAM, they are 2920 and 2851 cm^{-1}, respectively, which are about 1 cm^{-1} higher than the case when the alkyl chain takes all-trans conformation, where the frequency of $\nu_{as}(CH_2)$ and $\nu_s(CH_2)$ are 2920 and 2850 cm^{-1}, respectively. These results indicate that, in the LB monolayer and SAM on the silver island film, there exist some guage conformation of the alkyl chains. However, the frequecies of $\nu_{as}(CH_2)$ and $\nu_s(CH_2)$ are lower than those in the solid state, which implies that the molecules are closely packed in some sense in the monolayers. We suggest that this is attributed to the strong π-π interaction between the aromatic rings in the azobenzene chromophore, which helps to organize the molecules together, leading to a rigid structure of the monolayer. Therefore, it is seen that both LB and SA techniques are efficient to fabricate rigid monolayer of ABD molecules.

However, there exist some difference in the spectra of the LB monolayer and SAM. One major feature is that the relative absorption intensity of some modes differs from the spectra of LB monolayer to those of SAM. For example, the relative intensity of $\nu_{as}(CH_2)$ and $\nu_s(CH_2)$, and that of the in-plane stretching vibration of the aromtic ring around 1600 and 1880 cm^{-1}, which may be attributed to the differnce in the molecular orientation of the LB monlayer and SAM. Therefore, it is implies that, although the LB monolayer and SAM of ABD have similiar structure on silver island film, remarkable difference of film structure still exists. This could be understood as following: By LB technique, a formerly formed rigid monolayer of ABD is transferred onto the silver film, and is chemisorbed by $COO^- Ag^+$ linkage. In the LB monolayer, the strong π-π interaction will keep the rigid structure of the monolayer at some sense. However, by SA technique, the monolayer is grown on the silver surface molecule by molecule. In this case, the morphology of the silver film will have greater effect on the film's structure than the case of LB technique.

From the difference between the LB and SA monolayer on the silver island film, it could imaged that, when a rigid Langmuir monolayer is transferrred onto a silver island film with very large corrugation ratio, the rigidness of the monolayer will keep some of the molecules out of contact with the silver island, especially in the region of deep voids. Specifically, in the case of ABD molecule, the carboxyl group (COOH) and the carboxylate group (COO^-) will co-exist on the silver film. Most importantly, the absorption frequency of these two groups are remarkably different in their infrared spectra, which makes it possible to compare the enhanced effect at different location in the silver film, and consequently, reveal the diatribution of the EM field in these films.

For this purpose, a very thin silver film is prepared, whose thickness is about 10 nm. From the morphological study on this silver film, it is discontinous in nature, i.e., most of the areas are covered by silver, while there are some tiny holes or gaps uncovered. The dimension of these uncovered areas are in the range of 80 nm × 120 nm, and they occupy about 2% of the whole area. Naturally, when the Langmuir monolayer of ABD is transferred onto this kind of silver film, the COOH group will be converted to COO^- when it is in contact with silver island, and will remain in its original form when out of contact wih silver, i.e., the COOH and COO^- groups will co-exist on this kind of discontinous silver film. This is clearly evidenced by the transmission infrared spectra of the ABD monolayer on it (shown in Figure 2). It is seen that the strong absorption band at 1703 cm^{-1} of $\nu(C{=}O)$ and the band at 1398 cm^{-1} of $\nu_s(COO^-)$ demonstrate the existence of COOH and COO^- group, respectively[9]. From the spectra, it is obviously seen that the absorption intensity of $\nu(C{=}O)$ is much higher than that of $\nu_s(COO^-)$, which indicates that the COOH groups residing between the silver islands experience much greater enhancement than the COO^- groups on the silver island, and also indicates that the amplitude of the EM field is much higher in the gaps between the silver island than on the top of the silver islands.

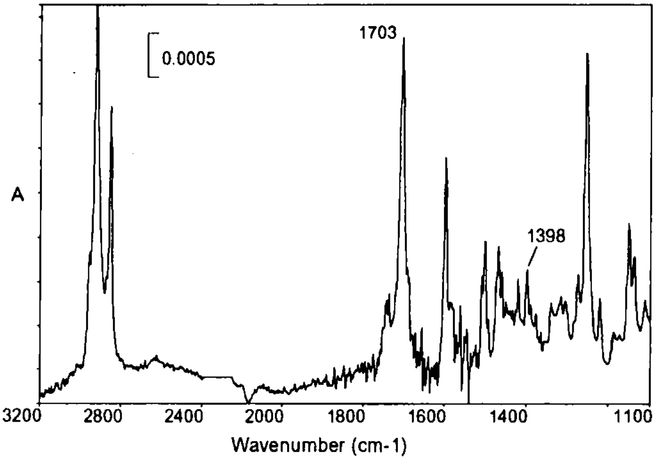

FIGURE 2 Enhanced infrared spectra of LB monolayer of ABD molecules on discontinuous silver film.

As described above, excitation of the surface plasmon oscillation on rough silver surface is essential to the surface enhanced spectroscopy. The surface plasmon on each silver particle (or island) will generate an intense surface EM field around the island. When the silver island are very close to each other, the EM field on different island will interact with each other, which will result in a much more intense EM field in the regions between the silver islands. This is the reason why the COOH group suffers much greater enhancement than the COO^- group in the infrared spectra, and it is also a direct evidence of the collective electron resonance mechanism of the surface enhanced infrared specrroscopy.

CONCLUSION

By LB and SA technique, rigid monolayers of 4-Octyl-4'-(3-carboxytrimethyleneoxy)azobenzene have been fabricated on silver island films. The infrared spectra of the LB monolayer on discontinuous silver island film reveal the different chemical forms of carboxyl group on the silver island and between the islands, and successfully reveal the distribution of the EM field in the silver island film.

Acknowledgments

This work is supported by the State Science & Technology Committee, the State Education Committee and the national Natural Science Foundation of China (NSFC).

References:

[1] R. K. Chang, T. E.Furtak, *Surface Enhanced Raman Scattering*, (Plenum, New York, 1982).
[2] A. Hartstein, J. R. Kirtley, and J. C. Tsang, Phys. Rev. Lett., **45** (1980) 201.
[3] T. Kamata, and A. Kato, J. Umemura and T. Takenaka, Langmuir, **3** (1987) 1150.
[4] M. Osawa, and M. Ikeda, J. Phys. Chem., **95** (1991) 9914.
[5] M. Osawa, K. Ataka, K. Yoshii, and Y. Nishikawa, Appl. Spectrosc. **47** (1993) 1497.
[6] E. Johnson, and R. Aroca, J. Phys. Chem., **99** (1995) 9325.
[7] A. Ulman, *An Introduction to Ultrathin Organic Films: from Langmuir-Blodgett to Self-assembly*, (Academic Press, Boston, 1991).
[8] Z. F. Liu, C. X. Zhao, M. Tang, and S. M. Cai, J. Phys. Chem., **100** (1996) 17337.
[9] L. J. Bellamy, *The Infrared Spectra of Complex Molecules*, (Wiley: New York, 1975).