Raman scattering in conducting metal-organic films deposited on nanoporous anodic alumina

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Abstract. Raman scattering in dielectric nanostructures on the base of aluminum oxide was studied. A method of high dielectric nanocomposite fabrication was proposed. Metal-containing conducting Langmuir – Blodgett films were shown to shield the anodic nanoporous alumina from the action of strong electrical fields.

1. Introduction
A functional area of perspective electronic devices is a layered nanostructure exhibited quantum effects in charge and energy transfer. So, although aluminum oxide possesses an ionic conductivity, anodic aluminum oxide (AOA) film may become a p-type semiconductor at high electrode potentials in electrolytes with the oxygen-contained anions [1]. To utilize, for example, in biomedical applications, an interdigital aluminum electrode structure with AOA coating is placed in the electrolytic environment under the influence of intense electric fields of near-electrode Helmholtz layer. The described instability of AOA band structure prevents its using as an insulating layer of capacity sensors. In this paper a method for improvement of AOA operating characteristics via strong electric fields shielding by iron-containing Langmuir – Blodgett (LB) films of aromatic compounds will be proposed. In such films, energy of electrically charged quasiparticles transported along the π-conjugated double bonds chain (long-range transfer) may be spent to excite dipole-active states (exciton associated with an electromagnetic field) of iron atoms.

The polymeric LB-films belong to strongly correlated many-electron systems with linear electron spectrum (narrow-gap semiconductors). Electric charge carriers in these systems are negatively charged excitons $X^-$ [2]. A valence band of these materials represents itself electronic states similar to p-electron orbitals with total angular momentum $j = 3/2$ and its projection $j_z = ± 3/2$, and their conduction band is s-electron orbitals with $j = 1/2$ and projection $j_z = ± 1/2$. According to current ideas [3], negatively charged excitons are formed under the action of a resonant electromagnetic field when the hole transits from the valence band to the conduction one and joins to two electrons in the conduction band. An arising three-particle excited state has zero orbital angular momentum ($L = 0$) and a spin $S$, equal to unity: $S = 1$ because of an absorbed photon holds unity spin and the hole adds spin $1/2$. Then, one can assume that transitions from the lower Zeeman sublevel with spin "up" ($s = +1/2$) in the valent band for the state $j = 3/2, j_z = +3/2$ to upper Zeeman sublevel $j = 3/2, j_z = −3/2$ with spin "down" ($s = −1/2$) in the valent band occur via a three-particle excited state with $L = 0, S = 1$.

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But, the total angular momentum $J$ of the excited system having a nonequilibrium spin $S = 1$ is equal to $J = 1$. Therefore, such transitions are double forbidden. First, the law of angular momentum conservation is violated for the system, as the change of total angular momentum value from $J = 1$ to $j = 3/2$ at the decay of exciton with electromagnetic quantum emission is accompanied by the increment $\Delta = 1/2$ of the system angular momentum with respect to its initial value before excitation. Secondly, if one assumes that $\Delta$ is a spin of additional electron with spin "down" at the upper Zeeman level of the valent band, then the probability to find the electron at this level is extremely low owing to the Pauli exclusion principle. Raman spectroscopy allows investigation of forbidden transitions. However, studies, which would reveal the type of electronic states and mechanisms of charged exciton transport in LB-structures being suitable for AOA shielding, has not been performed.

The goal of this paper is to carry out Raman spectroscopy of the organometallic LB-coating deposited on AOA and to propose a mechanism of shielding coherent exciton transport for such structures under the influence of strong electromagnetic fields.

2. Materials and methods
Two-stage anodic treatment of A99 grade aluminum foil in electrolyte with sulfuric acid was carried out by the method described in [1] to fabricate nanoporous AOA with pore diameter ~10 nm.

Langmuir monolayers from conductive polymer oligomer molecules 3-hexadecyl-2,5-di(thiophen-2-yl)-1H-pyrrrole (thiophene-pyrrole) with chemically bounded hydrophobic 16-link carbon chain were formed on an automated home-built Langmuir trough with controlled deposition on a substrate. Aqueous solution of ferric nitrate Fe(NO$_3$)$_3$ or ferric chloride FeCl$_3$ with pH adjusted by addition of hydrochloric acid HCl was used as a subphase for monolayer formation. Five or seven Langmuir monolayers in a highly ordered solid state were deposited on the AOA surface at a constant compression pressure to obtain a suspended LB-film.

Spectral studies in visible range were carried out using confocal micro-Raman spectrometer Nanofinder HE («LOTIS-TII», Tokyo, Japan) at laser excitation wavelength of 532 nm. Figures 1a and 1b demonstrate confocal microscopy images of the 5-monolayer thiophene-pyrrole LB-film deposited on nanoporous alumina and the nanoporous AOA surface, respectively.

![Figure 1](image.png)

Figure 1. A confocal microscopy image of 5-monolayer thiophene-pyrrole LB-film (a) deposited on nanoporous alumina (b).

3. Model
Fe atoms in aromatic compounds of pyrrole derivatives may be in a high- or low-spin state. In the metal-center low-spin state these pyrrole rings lie in the same plane. In the high-spin state the supramolecular complex becomes dome-shaped. Therefore, we can judge about the spin state of metal center by the vibration spectra of polymer matrix. Electrochemical and thermodynamic studies of Fe-
containing thiophene-pyrrole series oligomer films show that the valence of high-spin metal center is Fe\textsuperscript{II} [4].

It is assumed that the multiparticle excitation of the supramolecular complex consists of an electron in conduction band of the film, a hole in electron density of high-spin Fe\textsuperscript{II} and a negatively charged quasiparticle excitation of polymer matrix electron density that is caused by electron leaving from the valence band. Reverse electron transfer from d-electron orbitals of donor chain with π-conjugation occurs in several stages: first, there is an electron transfer to acceptor nitrogen atom of complex [Fe(pyrrole)\textsubscript{3}], and then – excitation energy transfer from the nitrogen atom of negatively charged complex [Fe(pyrrole)\textsubscript{3}]\textsuperscript{−} to the electron-hole excitation of metal center [5]. As a result, the exciton X\textsuperscript{−} consisting of an electron and an electron-hole pair is formed.

For ultrathin metal-containing polymeric 5-monolayer LB-films synthesized from thiophene-pyrrole oligomer derivative and having a thickness of monolayer conducting hydrophilic part \(d \sim 0.3\) nm the estimation of the exciton radius by the formula \(r_\text{exc} = \frac{1}{2} \sqrt{\pi ad}\) [6] gives a value of about 1.68 nm, where \(a\) is a radius of exciton in a bulk sample (in our calculations \(a\) was chosen as large as a value of film thickness: 12 nm).

**4. Raman scattering**

Raman spectra of AOA excited surface states are shown in figure 2a. The surface states have Raman peak at 1058 cm\(^{-1}\). They cause the ionic structure destruction of nanoporous AOA samples (pore diameter ~ 10 nm) with appearance of gap and are excited at high laser power \(P (P \geq 3.0 \text{ mW})\). These changes of quasi two-dimensional AOA band structure caused by intensive electromagnetic radiation correlate with changes of AOA electrical conductivity type from ionic to semiconducting one.

![Figure 2. Raman spectra of nanoporous alumina without (a) and with LB-film coating (b).](image)

The intensity of LB film Raman bands also depends on the power of laser radiation, as shown in figures 2b and 3. At low intensity \(P \sim 0.3 \text{ mW}\) the bands with maxima at 893, 1063, 1432, 1472 and 1515 cm\(^{-1}\) are resolved in the Raman spectrum of LB film deposited on AOA. The Raman peaks at 1432 cm\(^{-1}\) and 1472 cm\(^{-1}\) are close to semi-circle stretch of pyrrole rings and quadrant stretch of 3-substituted pyrrole rings, respectively. The Raman peaks at 893, 1063, and 1138 cm\(^{-1}\) are close to hexadecyl-link tail carbon trans chain C-C-C out-of-phase stretches, when wide band with maximum
of 1310 cm\(^{-1}\) is inter-ring C-C vibrations. All characteristic molecular vibrations, observed in the Raman spectrum of 5, 7 – monolayers LB film using 532 laser line are represented in Table 1.

Table 1. Characteristic molecular vibrations, observed in the Raman spectrum of 5, 7 – monolayers LB film using 532 laser line.

| Band center for LB film (cm\(^{-1}\)) | Region for vibration of similar molecular group (cm\(^{-1}\)) | Assignment | Reference |
|--------------------------------------|-------------------------------------------------|------------|-----------|
| 556                                 | 525                                             | ring in-plane deformation | [7]       |
| 653                                 | 586                                             | ring in-plane deformation | [7]       |
| 686                                 | 686                                             | thiophene-pyrrole molecule ring in-plane deformation | [4]       |
| 741                                 |                                                 | ring in-plane deformation |           |
| 811                                 | 808                                             | ring in-plane deformation | [7]       |
| 843                                 | 844                                             | thiophene-pyrrole molecule ring in-plane deformation | [4]       |
| 893                                 | 893                                             | trans hexadecyl-chain vibration | [8, p.118] |
| 1063                                | 1063                                            | hexadecyl-chain trans C–C–C out-of-phase stretches | [8, p.154] |
| 1138                                | 1138                                            | hexadecyl-chain trans C–C–C out-of-phase stretches | [8, p.140] |
| 1165                                | 1148                                            | Cl–O vibration | [4; 8, p.170] |
| 1231                                | 1236                                            | CH bending | [7]       |
| 1310                                | 1310                                            | inter-ring C–C vibration | [9]       |
| 1342                                | 1357                                            | semi-circle stretch of thiophene ring | [8, p.109] |
| 1410                                | 1408                                            | quadrant stretch + CH rock vibration of thiophene ring | [8, p.109] |
| 1432                                | 1420–1430                                       | semi-circle stretch of pyrrole rings | [8, p.109] |
| 1472                                | 1480–1490                                       | quadrant stretch + CH rock vibration of pyrrole rings | [8, p.109] |
| 1515                                | 1518                                            | NH bend + C–N stretch | [8, p.151] |
| 1581                                | 1585–1607                                       | C=C stretching in pyrrole rings | [9]       |

Increase of \( P \) from 0.3 to 3.0 mW leads to redistribution of electron density to another orbital being close but higher placed, therefore, instead of a line at 1472 cm\(^{-1}\) another one of 1460 cm\(^{-1}\) appears. Intensity of the last one is comparable with intensity of the line at 1310 cm\(^{-1}\) and 3.5 times lower than intensity of the line at 1472 cm\(^{-1}\). Spectral changes dependency on laser beam power can be explained in the following way: quadrant stretch of 3-substituted pyrrole ring occurs at low intensities in the plane of the ring, but at high intensities out-of-plane vibrations take place. In the last case, the probability of inter-ring C–C vibrations increases, that reveals as 1310 cm\(^{-1}\) line intensity increase. Out-of-plane quadrant stretch vibrations bend the pyrrole ring plane that leads to dome-shaped form of complex. The dome-shaped complex testifies the high-spin state Fe\(^{II}\).

5. Shielding effect
At high level of laser pumping a shielding of AOA by LB-film also takes place. For example, at \( P \approx 14.4 \) mW AOA spectral band with maximum at 1058 cm\(^{-1}\) is reduced 15 times, and the Raman peaks
at 463, 632 and 2934 cm\(^{-1}\) disappear in the presence of LB film deposited on the AOA surface. The shielding is due to the presence of free charge carriers.

Electromagnetic radiation scattered by AOA diffracts on spin-polarized dipole-active states of metal centers due to the precession of the nonequilibrium spin \(S\). The change in Raman spectrum intensity in figures 2b and 3, curves 2 has a period of 3.8 ± 0.4 nm that is close to calculated diameter of \(X^-\). Therefore, the LB-films under consideration are 2D photon crystals whose free charge carriers are the excitons \(X^-\).

At \(P \sim 14.4\) mW the line at 1460 cm\(^{-1}\) shifts to 1450 cm\(^{-1}\). This testifies a decrease of dipole polarization in the LB-structure due to the electric field shielding by the excitons.

6. Conclusion

Thus, the long-lived exciton states transfer in LB-film of metal-organic compound was established. As a result, the conducting LB-films shield the AOA layer from strong electromagnetic fields and preserve high-insulating properties of this layer.

7. References

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Figure 3. Raman spectra of 7-monolayer thiophene-pyrrole LB-film deposited on AOA at laser beam intensity \(P = 0.03\) mW (curve 1), 0.6 mW (curve 2).