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Porous Al and Cu structures as infrared signal enhancers

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Optical properties of porous aluminum and copper layers with adsorbed *p*-nitrobenzoic acid molecules (*p*-NBA) have been studied. There was observed the enhancement of certain molecular groups in the IR spectrum of *p*-NBA. The porous Cu substrates are similar to rough gold ones in the enhancement factor of COO^- groups in multilayered *p*-NBA films.

Исследованы оптические свойства пористых слоев алюминия и меди с адсорбированными молекулами *п*-нитробензойной кислоты (*п*-НБК). Наблюдалось усиление поглощения отдельных молекулярных групп в ИК спектре поглощения *п*-НБК. Пористые медные подложки по фактору усиления поглощения групп COO^- в многослойных пленках *п*-НБК аналогичны шероховатым золотым подложкам.

1. Introduction

The effects of metal surface enhanced IR absorption (SEIRA) [1–3] and surface enhanced Raman scattering (SERS) [4, 5] are well known to form a basis for some most sensitive analytical techniques in IR spectroscopy and Raman scattering. The key problem of successful use of these effects is the choice of metal surfaces and the processing technology thereof. Traditionally, the surfaces used in SEIRA are prepared by two main methods: chemical or electrochemical deposition [6–8] and thermal deposition [9–14] of the metals onto substrates. In order to realize SEIRA effect not only island films or rough thermally deposited surface of gold or silver, but volume-modified particles [15–17] have been applied. In particular, the chemical deposition of copper onto traditional in IR spectroscopy substrates was used to prepare SEIRA-active coatings [17].

In this work, we have investigated experimentally for the first time the possibility of using micro- and nanoporous Al and Cu layers as IR absorption enhancers. Adsorbed layers of *p*-nitrobenzoic acid $C_7H_5NO_4$ (*p*-NBA) served as markers in order to characterize the surface absorption properties. We have found before that different molecular groups of *p*-NBA on rough Au surface are enhanced differently. In particular, for SEIRA effect in reflection geometry, we succeeded in recording the spectra of 383 ng/cm^2 *p*-NBA [18, 19].

2. Sample preparation and experimental details

Al and Cu structured surfaces have been produced by steady-state near-equilibrium vapor condensation inside hollow cathode in the plasma-condensate system [20]. Al and Cu surface topology was studied using a SEM-102E scanning electron microscope.

Examination of the samples in visible spectrum was performed by monochromator DMR-4 (LOMO, Russia). IR absorption of *p*-NBA and its amplification on the obtained sample surfaces was studied by means of an IFS-66 (Bruker) FTIR spectrometer in 400–4000 cm^{-1} range using reflection and transmission geometry. The spectra were processed using the Opus-5.5 and OMNIC software.

The *p*-NBA powder (Sigma) was used without additional purification. The adsorbed layers on metal surfaces and dielectric CaF_2 substrate were formed by deposition and evaporation of *p*-NBA solutions in purified acetone at concentration of 0.5 mg/ml by 5 μl drops. The *p*-NBA molecules are chemically adsorbed on metals (Fig.1) and are able to form thin and homogeneous films [9, 10, 21]. The experimental enhancement factor was determined as the ratio of integral intensity of a specific molecular group absorption band on the metal surface to that of the same group on CaF_2 substrate: $g_{exp}(\omega) = I_m(\omega)/I_{CaF2}(\omega)$.

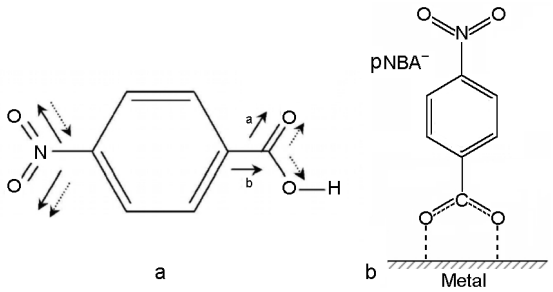

Fig. 1. Molecular structure of *p*-nitrobenzoic acid (a) and schematic image of its molecule adsorption on a metal (b).

3. Experimental results

Fig. 2 shows the electron microscope images of Al and Cu micro- and nanostructured surface obtained under different working gas pressure P_{Ar}, discharge power P_w, and deposition time t, as presented in the Table 1. The reflection spectra for Al and Cu surfaces in visible spectrum range depending on surface topology are given in Fig. 3(a,b). For well expressed dispersed structure Cu-18 with 0.1–1 μm size gran-

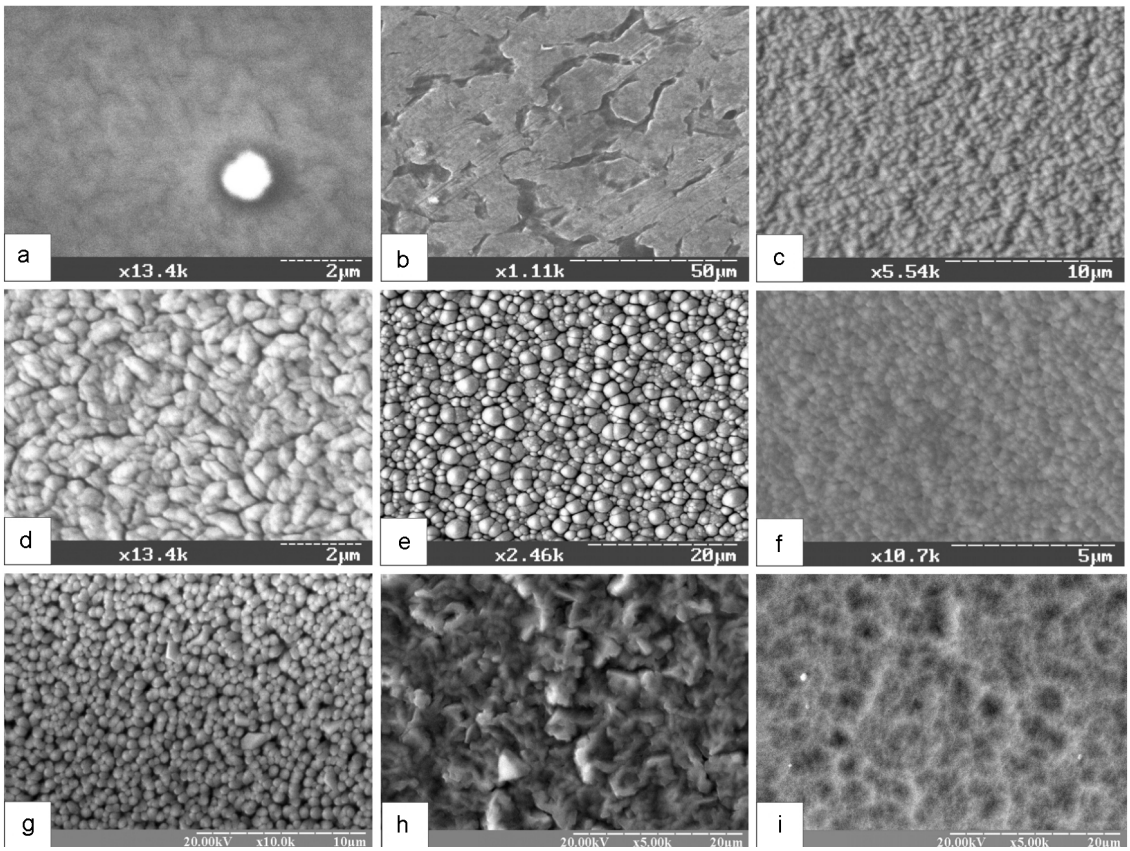

Fig. 2. SEM images of the studied surfaces: Cu-1 (a), Cu-6 (b), Cu-9 (c), Cu-18 (d), Cu-23 (e), Cu-19 (f), Al-3 (g), Al-9 (h), Al-18 (i).

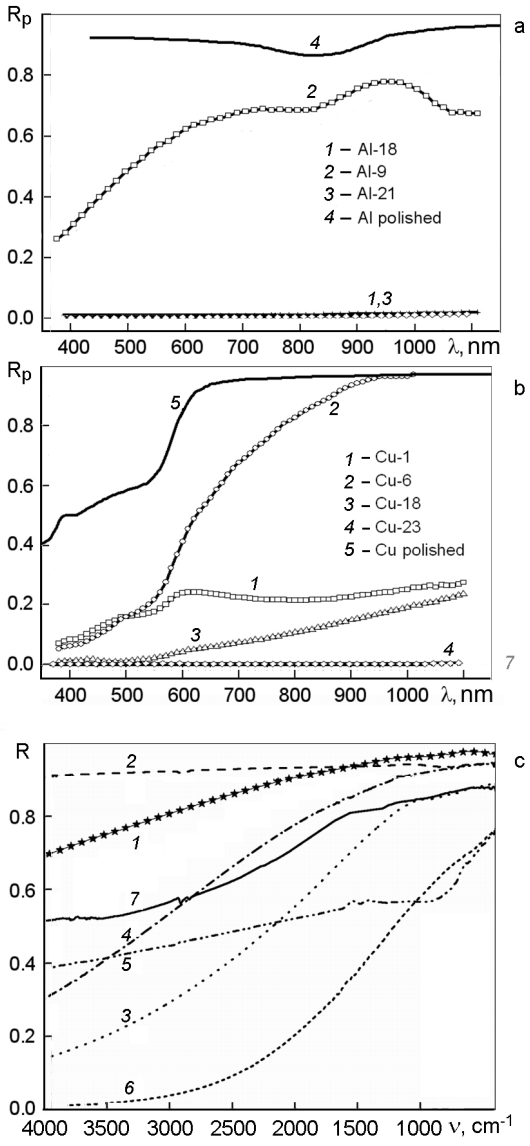

Fig. 3. Reflection of light from micro- and nanostructured Al - (a) and Cu - (b) metal surfaces in the visible spectral region (light incidence angle φ = 10°); (c) Cu–1 (*1*), Cu–6 (*2*), Al–3 (*3*), Al–9 (*4*), Cu–18 (*5*), Cu–23 (*6*), Al–18 (*7*), in the IR region (light incidence angle φ = 16.5°).

ules and high porosity, the lowest specular reflection coefficient is observed due to scattering losses. In the IR range, the reflection coefficient for metal surfaces (Fig. 3c) varies from 15 to 90 %, depending on their topology and the metal kind.

In Fig. 4, SEIRA spectra for vanishing quantity of *p*-NBA on metal and CaF_2 surfaces are presented. The best enhancement is observed for Cu-1, Cu-6, Al-18 samples.

Table 1. Operating parameters for fabrication of superporous structures

Fig.	Metal	P_{Ar} (Pa)	P_w (W)	t (hours)
a	Cu-1	10	4	3
b	Cu-6	20	9	9
c	Cu-9	20	9	4
d	Cu-18	15	9	6
e	Cu-23	3	1.3	9
f	Cu-19	3	1.3	4
g	Al-3	20	9	9
h	Al-9	15	3.2	2
i	Al-18	20	2	2

On certain substrates such as Al-9, Cu-18, Cu-23, the characteristic molecular vibration are not detected at all. The enhancement of *p*-NBA molecules absorption makes up 1.2–12 times for different molecular groups (Table 2). The enhancement factor for COO^- groups of *p*-NBA adsorbed in porous Cu substrates is close to that on rough gold substrate.

4. Conclusion

The consideration of the above experimental data allows concluding certain conditions necessary to enhance the *p*-NBA absorption on metal surfaces. (i) The reflection coefficient must exceed 50 % in IR range. (ii) The conditions of plasmon resonance long-wawe length shifting in metals to near infrared range must be realized that can be achieved if metal nanostructures having the size distribution in the 10–500 nm range. Such sizes of the metal structure correlate with the IR enhancement. The substrates possessing surface inhomogeneities <100 nm in size are the best to increase the IR absorption. The results obtained in this work can be of interest for proving the existing theories of SEIRA effects, and for its further using in IR spectroscopy for biology and medicine as well.

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Table 2. Enhancement factor of IR absorption for different molecular groups of *p*-NBA deposited on different surfaces

No	*p*-NBA adsorbed on CaF_2, frequency, cm^{-1}	*p*-NBA adsorbed on Al(18), frequency, cm^{-1}	Experim. enhancement factor	*p*-NBA adsorbed on Cu(1), frequency, cm^{-1}	Experim. enhancement factor	Assignement of absorption bands to molecular group vibrations
1	1689	1683	1.7	1689	2.4	C = O
2	1590	1604	2.5	1591	5.0	COO^- asymm. stretch.
3	1530	1529	1.8	1530	3.0	NO_2 asymm. stretch.
4	1407	1405	3.3	1411	12	COO^- symm. stretch.
5	1349	1348	2.0	1350	3.5	NO_2 asymm. stretch.

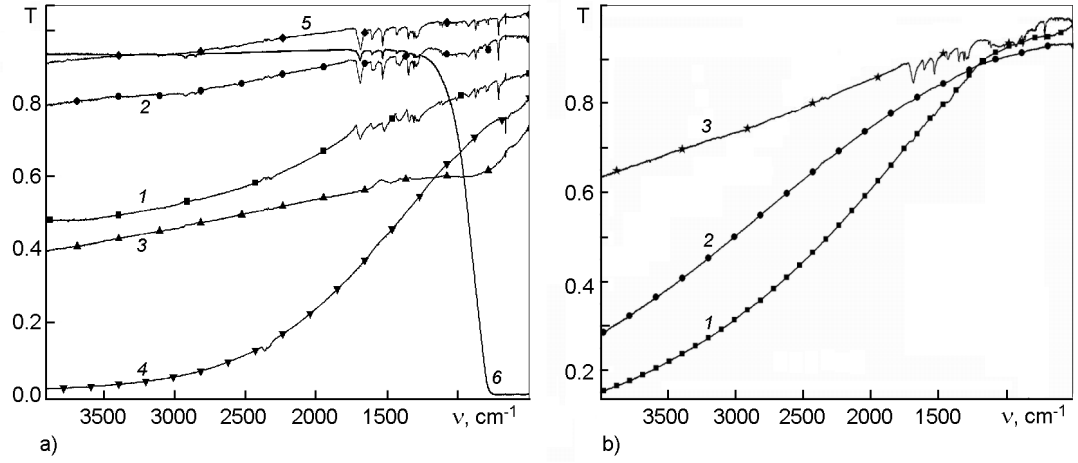

Fig. 4. SEIRA spectra of *p*-NBA molecules adsorbed on micro- and nanostructured sample surfaces: (a) copper (curve *1*– (Cu-1), curve *2*– (Cu-6), curve *3*–Cu-18), curve *4*– (Cu-23)), Au (curve *5*), CaF_2 substrate (curve *6*); (b) aluminum (curve *1*– *(*Al-3), curve *2* (Al-9), curve *3*– (Al-18).

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Пористі структури Al та Cu як підсилювачі ІЧ оптичних сигналів

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Досліджено оптичні властивості пористих шарів алюмінію та міді з адсорбованими молекулами *n*-нітробензойної кислоти (*n*-НБК). Спостерігалося підсилення поглинання окремими молекулярними групами у ІЧ спектрі поглинання *n*-НБК. Пористі мідні підкладки за фактором підсилення ІЧ-поглинання групи COO^- аналогічні до шорстких золотих підкладок.