Enhancement of NO$_2$ gas detection in hybrid silver nanoparticles-phthalocyanine thin films

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Abstract. Phthalocyanine-functionalized plasmonic sensing systems are typically based on Kretschmann configuration. Such scheme of detection utilizes spectral or angular modulation of reflected light, which is induced by surface plasmon’s excitation in the metal film on prism. Phthalocyanine’s layer plays a role of analyte adsorber. In present paper we offer another approach to phthalocyanine-plasmonic sensing, where both local surface plasmon resonance and optical absorption of phthalocyanines are simultaneously detected. Hybrid Ag nanoparticles (AgNps) – low symmetrical A3B zinc phthalocyanine (ZnPc) thin films were prepared, and their NO$_2$ gas sensitive properties were examined. Since the plasmon resonance of AgNps was properly tuned to charge-transfer band of ZnPc-NO$_2$ complex, we found out more than two-fold increase of the optical response to NO$_2$ exposure in AgNps-ZnPc thin films compared to ZnPc films without AgNps.

1. Introduction

Environmental safety and pollution prevention have always been a focus of leading science centers all over the world. As of today many different methods and techniques for detecting poisonous agents in gases and liquids have been developed—Particular attention among them is paid to methods based on excitation of surface and localized plasmons [1,2].

For detecting such gases as NO$_2$ and CO$_2$ plasmonic sensors, based on thin metal film covered by phthalocyanine layer, have been developed [3,4]. Phthalocyanine molecules serve as an adsorber of analyte molecules, providing changes in a permittivity of metal/phthalocyanine interface. As a consequence, conditions of surface plasmon resonance (SPR) are also changed. Kretschmann configuration is usually applied [5] to detect changes in SPR. Such scheme of surface plasmon excitation offers a possibility to detect SPR conditions by measuring angular or spectral distribution of reflected light. Significant response of SPR to alteration in the permittivity of metal/phthalocyanine interface results in high sensitivity of nitrogen dioxide detection close to 0.1 ppm. Moreover,
metal/phthalocyanine SPR sensors also provide fast, real-time gas analysis without any additional analyte preparation. However, there are some drawbacks in this approach which are associated with relative complexity and overall size of the detection setup in comparison to classic sensors based on phthalocyanine thin films.

In contrast with surface plasmons, localized surface plasmons in nanoparticles can be easily excited by plane electromagnetic wave without utilizing any special excitation scheme. The light, captured by the metal nanoparticles, is confined to quite a small volume, not much larger than the particle itself, which concentrates the energy gained from the incident field. Therefore, the localized field is much stronger than the incident field. The strong local field is commonly used to increase various photo-induced processes in chromophores. Particularly, considerable increase of optical absorption and decay rate of excited state of zinc phthalocyanines which are placed on a surface of gold nanoparticles have been demonstrated [6,7]. In our recent paper we have shown many-fold plasmonic enhancement of nonlinear saturable absorption effect in subphthalocyanines [8].

In present research we found out a two-times improvement in sensitive properties of AgNps-ZnPc thin films to nitrogen dioxide in a gas phase. We suppose that plasmonic enhancement of ZnPc-NO\textsubscript{2} charge-transfer complex’s absorption as well as red-shifting of LSPR are the most probable reasons of the improvement.

2. Formation of sensing structures

The synthesis of 2-((2′-hydroxymethyl)-benzyloxy)-9(10),16(17),23(24)-tri-tret-butyl- substituted low symmetrical A3B zinc phthalocyanine complex bearing hydroxyl group on the periphery (complex 1) was previously described [9]. Langmuir-Blodgett films of complex 1 were deposited onto two types of substrates: 1) hydrophilic glass (KnittelGlasser 20x20 mm), 2) plasmonic thin film based on silver nanoparticles. Plasmonic thin film was formed by a two-step process. At the first stage, 20 nm silver nanoparticles were deposited onto glass substrates through spin-coating technique. At the second stage, in order to stabilize and homogenize AgNps thin film, the structure was being annealed during 4 hours at 230°C. The annealing of AgNps has led to agglomeration of single nanoparticles to larger particles with an average size of 100-120 nm, as shown on Figure 1.

![Figure 1. SEM image of the plasmonic thin film based on Ag nanoparticles](image)

For preparation of Langmuir-Blodgett films KSV mini through system was applied. Ultrapure water with resistivity of 18 M\text{Ohm}\cdot\text{cm}, and temperature of 20°C was used as a subphase. Complex 1 was uniformly spread from chloroform solution (100 μl of concentration 2·10\textsuperscript{-4}M) onto the subphase. After evaporation of the solvent, the floating film was compressed to the surface pressure of 40 mN/m. Ten-monolayers films were deposited at the same surface pressure (40 mN/m) onto both hydrophilic glass and plasmonic thin film based on silver nanoparticles as well. For further convenience we introduced Sample 1 and Sample 2 abbreviations for 10-monolayers phthalocyanine films on the glass and on the plasmonic substrate respectively.
3. Optical properties of the samples
For spectral measurements Ocean Optics HR4000 spectrometer with 0.5 nm resolution and reflection/backscatter probe OceanOptics QR600-7-SR-125F were applied. Spectral measurements were carried out in reflectance mode with usage of the glass and the plasmonic substrate without phthalocyanine layers for reference measurements. Relative reflectance spectra are shown on Figure 2.

![Figure 2. Reflectance spectra of Sample 1 – a, and Sample 2 – b.](image)

Minimum in the reflectance spectrum of Sample 1 (Figure 2a) in a range of 600 – 700 nm is associated with strong Q-band absorption, where the dip at 682 nm is the main peak of the absorption band [9]. As can be seen from Figure 2b, Q-band absorption of Sample 2 is red-shifted in comparison with the band of Sample 1. Moreover, we obtained a new strong dip in the spectrum at 442 nm, which corresponds to LSPR of silver particles covered by phthalocyanine layers having a high real part of permittivity. Despite an overlap between Q-band and short-wavelength plasmonic band we see 10 nm red-shift of the Q-band absorption maximum. The reason of it is not clear. We suppose, that the charge transfer between ZnPc and AgNps, as well as some peculiarities in the molecular arrangement onto the plasmonic film, can be responsible for such non-additive behavior of the energy losses in the spectrum. New maximum of Q-band absorption of Sample 2 is located at 693 nm.

4. Results and discussions
4.1. Gas testing experiment
Experimental setup for gas testing is represented on Figure 3. Nitrogen dioxide was diluted with pure nitrogen (N₂) as inert carrier gas, the percentage of gases in amixture was regulated by mass flow controllers. In such way the concentration of nitrogen dioxide in the mixture was adjusted at the level of 10 ppm. Spectral measurements in relative reflectance mode were also performed.
4.2. Spectral changes induced by NO$_2$ exposure
The interaction of NO$_2$ with the Sample 1 results in considerable spectral modification of its reflectance properties. Figure 4A shows reflectance spectra of Sample 1 before and after NO$_2$ exposure (black and red line respectively). Additional losses in the spectrum at 470 – 580 nm after the gas exposure and increase of reflectance in the Q-band region clearly indicate a formation of the charge-transfer ZnPc-NO$_2$ complex, where ZnPc plays a role of electron-donating molecule. An absorption band at 470 – 580 nm is also well-known as a charge-transfer band (CT-band) [10]. In contrast to Sample 1, there is no well-resolved CT-band in reflectance spectrum of Sample 2, but we observe a red shift of LSPR as well as a considerable broadening of the dip (Figure 4B), which can be caused by superposition of CT-band and plasmonic shifting.

Since the reflectance is not linear function of losses, it is more convenient to consider absorption spectra which can be easily obtained from our reflectance measurement assuming, that absorption losses are dominant. Figure 5 shows effective absorption spectra of Sample 1 and Sample 2 before and after exposure of nitrogen dioxide.
Figure 5. Absorption spectra of Sample 1 – A, and Sample 2 – B. In both: black line – before NO\textsubscript{2} exposure, red line – after NO\textsubscript{2} exposure

Absorbance is a linear function to the number of molecules and therefore it can be utilized to adequate comparing responses of the samples to influence of nitrogen dioxide. Here we considered only CT-band (the range of 470 – 580 nm) because Q-band is not specifically sensitive to analyte molecules and can be easily altered during different external processes, such as heating. To evaluate enhancement factor we compared maxima of differential absorption of both samples in CT-band. While the maximum value of differential absorption of Sample 1 equals to 0.05, the maximum of Sample 2 is 0.11, that is more than 2-times larger. We suppose that the effect is induced by 2 factors. The first factor is the shifting of LSPR caused by altering phthalocyanine’s permittivity. Whereas the second one is plasmon-related enhancement of CT-band absorption. Of course, different chemical and photochemical processes, associated with interaction between silver particles and ZnPc molecules especially in the presence of nitrogen dioxide, cannot be excluded from consideration.

5. Conclusion

Here we proposed a new approach to designing of plasmonic phthalocyanine sensors which is based on simultaneous registration of LSPR spectral position and specific optical absorption of charge-transfer complex. Using Langmuir-Blodgett and spin-coating techniques, we fabricated hybrid thin-film sensitive structures based on novel A3B zinc phthalocyanine and silver nanoparticles, and found out more than two-fold improvement in the response of NO\textsubscript{2} exposure. As we are aware, this is the first time demonstration of plasmon-related enhancement in sensitive properties of phthalocyanines in similar hybrid structures. However, this is just a first step and it is required to conduct more research for further approach development.

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