ABSTRACT: The label-free detection of biomolecules by means of fluorescence spectroscopy and imaging is topical. The developed surface-enhanced fluorescence technique has been applied to achieve progress in the label-free detection of biomolecules including deoxynucleobase acid (DNA) bases. In this study, the effect of a strong enhancement of photoluminescence of S′-deoxyadenosine-monophosphate (dAMP) by the plasmonic nanocavity metasurface composed of the silver femtosecond laser-induced periodic surface structure (LIPSS) and gold nanorods or nanospheres has been realized at room temperature. The highest value of 1220 for dAMP on the Ag-LIPSS/Au nanorod metasurface has been explained to be a result of the synergetic effect of a strong enhancement of photoluminescence of 5′-adenosine-monophosphate (AMP) at low temperatures.11 Meanwhile, at room temperature, the quantum yield for 5′-adenosine-monophosphate (AMP) at low temperatures is of 10−3. Nevertheless, this method has some disadvantages concerning its labor- and time-consuming character. Therefore, the goal of label-free detection of biomolecules with fluorescence spectroscopy and imaging is highly possible.

INTRODUCTION
The development of various methods, techniques, and their combinations for high-sensitive detection and imaging of biomolecules in different biological systems at room temperature remains a topical objective for modern research. Fluorescence spectroscopy is one of the most sensitive spectroscopic techniques used for studying physical processes in living systems. It is even capable of identifying and imaging single molecules.1–3 High-sensitive fluorescence spectroscopy is successfully applied for the determination of deoxyribonucleic acid (DNA) sequencing, which is important for the study of physical and chemical processes occurring in living systems, in particular, genetic transcription/translation processes, etc.4,5 However, it should be noted that a high quantum yield of intrinsic fluorescence and phosphorescence of main nucleotides is achieved only at low temperatures, while at room temperature, it is of 10−5.−106.−1010 The quantum yields of fluorescence of ~0.4 and phosphorescence of ~0.6 were reported for 5′-adenosine-monophosphate (AMP) at low temperatures.11 Meanwhile, at room temperature, the quantum yield for 5′-deoxyadenosine-monophosphate (dAMP) is known to be 7 × 10−5.−6.7 Thereby, the task to enhance the fluorescence of nucleic acids and nucleotides at higher temperatures is of utmost relevance. To achieve an effective visualization of DNA sequencing and molecular and cellular bioimaging over different optical windows, additional labeling techniques of molecules with specific fluorescent dyes are frequently used.12–14 Nonetheless, this method has some disadvantages concerning its labor- and time-consuming character. Therefore, the goal of label-free detection of biomolecules with fluorescence spectroscopy and imaging is highly possible.

Some approaches have been elaborated to achieve an increase in the total quantum yield of fluorophores, namely, by its placing in close vicinity with metal nanostructures.15,16 The nanoscale metal structures could increase the excitation efficiency due to the enhancement of electromagnetic (EM)
field near the metal surface caused by the excitation of surface plasmon resonance (SPR). It has been shown that SPR excitation provides an increase in the radiative emission rate and, as a consequence, quantum yield of fluorophores. In addition, metal nanostructures characterized by the high directivity of radiation may cause an increase in collection efficiency. Therefore, the developed surface-enhanced fluorescence (SEF) technique has been applied for the label-free detection of biomolecules including DNA bases. However, most investigated metal nanostructures have been quite inhomogeneous. Respectively, certain imperfections of the obtained outcomes, namely, weak broad SPRs resulting in moderate signal enhancements, have been observed.

Some new methods have been applied to achieve a strong enhancement of biomolecule fluorescence: (i) metal nanostructures with densely packed sharp tips, (ii) periodically ordered metal nanostructures, and (iii) plasmonic cavities. All of these nanostructures have a similar feature, that is, the formation of so-called "hot spots", where the very strong EM field occurs. For this reason, plasmonic cavities have a very important place in this matter. In plasmonic cavities, hot spots emerge in a very thin gap between the components of such a cavity. This phenomenon originates from the SPR near-field coupling between the produced nanostructures. The EM field enhancement supports the processes, which in turn stimulates SERS and surface-enhanced Raman scattering (SERS) processes. The design of these cavities can be realized in different variants such as metal NPs on metal substrate–mirror (NPOM structures), nanopatch optical antennas, metal–insulator–metal resonators, etc. In particular, in NPOM structures, metal NPs are located in close vicinity to metal substrate–mirror. NPOM structures with metal NPs support a new collective plasmonic mode, the so-called gap mode, emerging due to the hybridization of the plasmonic mode of metal NP layer and the propagating surface plasmon polariton (SPP) of the metal substrate. At the excitation of the plasmonic gap mode, the EM field is squeezed into a very thin gap between the NP layer and the metal film, causing a strong field enhancement in the nanogap, i.e., the generation of hot spots. Moreover, the cavities containing nonspherical NPs with sharp edges should provide a higher signal enhancement for some processes than the cavities with spherical NPs.

Along with the mentioned structures, a rather high plasmonic enhancement has been achieved in the structures with gratings on metal surfaces. In particular, laser-induced periodic surface structures (LIPSS) on metal substrate represent such a type of plasmonic metasurface. The periodic surface structures are formed by the process of interference between the powerful incident laser plane wave and surface wave. For metals, this surface wave is determined by the grating-assisted excitation of SPP. It should be noted that the formed periodic surfaces also contain some nano-features and quasi-gratings of nanoscale dimensions. Nowadays, LIPSS is actively used for the fabrication of SERS/SEF substrates and plasmonic sensors. The application of LIPSS for the formation of plasmonic cavity may be promising due to the ability of biomolecules to bind to the edges of nanostructures, which leads to a stronger plasmonic enhancement.

Figure 1. Schemes of the studied structures with dAMP molecules precipitated on: (a) Ag smooth surface, (b) Ag LIPSS, (c) Ag smooth/Au NRs, (d) Ag LIPSS/Au NRs, (e) Ag smooth/Au NPs, and (f) Ag LIPSS/Au NPs. The schemes include the models depicting the formation of plasmonic hot spots and excitation of SPPs in the systems with (a) and (b) designs, and the excitation of plasmonic gap mode in the cavity systems with (c)–(f) designs. The inset to (a) presents the chemical structure of the dAMP molecule.
Recently, hybrid metal–dielectric micro- and nanocavities are intensively investigated. The structures of such metal–dielectric cavities possess the advantages of both metal and dielectric materials. Indeed, metal NPs highly support subwavelength plasmons with a strong local EM field; however, they are characterized by relatively high intrinsic material losses. \(^50\)–\(^52\) Meanwhile, dielectric structures support exquisite low-loss versatility, but only moderate confinement. \(^53\)–\(^55\) Recent attempts toward fabricating metal–dielectric hybrids were made to combine these two advantages, eliminating the mentioned limitations. \(^56\)–\(^59\) It has been shown that the hybrid approach can simultaneously exhibit a unique combination of plasmonic strong EM field and high confinement with dielectric small dissipative losses. In such hybrid cavity structures, the hybridized dielectric–metal resonances arise, leading to strong and highly tunable optical response, which thereby makes them suitable for different photonics applications. In the far field, they exhibit scattering stronger than that for all-metal and all-dielectric structures. In the near field, they provide high spontaneous emission enhancement and highly directional emission at visible and infrared wavelengths. The hybrid cavities of two types have been studied. The first one consists of the high-refractive-index (HRI) dielectric NPs located closely to metal plasmonic substrate (metal–dielectric NPOM structures). \(^56\)–\(^59\) Typically, the structures consisting of HRI dielectric (rare earth oxides and nitrides) or semiconductor (Si, Ge, GaP) NPs on the noble-metal (Ag, Au) substrates have been elaborated. The structures with nonspherical HRI NPs, e.g., rare-earth oxide (Nd\(_2\)O\(_3\)) \(^56\) and semiconductor (Si) \(^57\) nanorods (NRs), were reported to be most promising for surface-enhanced spectroscopy and sensing applications. The hybrids of the second type contain dielectric photonic crystals (PCs) combined with plasmonic metal NPs. \(^50\)–\(^62\) Metal NPs are used to increase the light-matter coupling in the PCs. The hybridization of localized SPRs of metal NPs and Bragg diffraction resonances of dielectric PC leads to a strong and tunable optical response of such structures, which allows us to use them for different applications such as surface-enhanced spectroscopy, \(^63\)–\(^65\) sensing, \(^66\) catalysis, \(^67\)–\(^68\) nonlinear optics, \(^69\)–\(^66\) etc.

In this study, we aim to develop the technique of label-free detection of biomolecule at room temperature with high sensitivity and reproducibility. Nucleotide dAMP was chosen for our research due to its high photostability compared to other nucleotides. \(^70\) We expected to obtain an effect of strong enhancement of photoluminescence (PL) (fluorescence and phosphorescence) of dAMP precipitated on plasmonic metasurface containing Ag LIPSS and Au nanorods (NRs) or spherical Au NPs for comparison. These materials have been used because (i) Ag supports the sharpest and most intense SPR in the visible and near-UV spectral ranges and (ii) SPR of Au NRs can be tuned over the visible and near-IR ranges by changing the NR aspect ratio. Thus, several types of metasurfaces have been studied: (1) Ag smooth substrate, (2) Ag LIPSS, (3) Ag smooth/Au NRs, (4) Ag LIPSS/Au NRs, (5) Ag smooth/Au NPs, and (6) Ag LIPSS/Au NPs (schematically depicted in Figure 1). The metasurfaces with both types of NPs are the plasmonic cavity nanostructures, where the near-field coupling of the localized SP mode of the layer of Au NRs or NPs and the propagating SPP mode of Ag surface arises. A quantitative comparative study of the quantum yield of dAMP PL on these metasurfaces was carried out, and the results are interpreted and discussed.

### RESULTS AND DISCUSSION

#### Structural Characterization

The procedures of the fabrication of Au NRs, Au NPs, Ag substrates, and metasurfaces are given in the Experimental Section, which also presents the features of optical measurements.

The shape and size of the fabricated Au NRs were analyzed by transmission electron microscopy (TEM), as presented in Figure 2a. The fabricated Au NRs have a perfect rod shape with an average length and diameter of 81 and 14 nm, respectively (aspect ratio is 5.8). The electric field simulation for Au NRs was finite-difference time-domain (FDTD) simulation (Lumerical Solutions). \(^71\) A mesh size of 0.5 nm in the NR region was used. The size of Au NR was set according to Figure 2b; the dielectric function of Au NR was taken from Au-CRC in the material library of the software. A perfectly matched layer was used as the boundary conditions in the FDTD simulation. The calculated electric field distribution is presented in Figure 2c. The fabricated Au NPs have a perfect spherical shape with an average diameter of 13 nm, as confirmed by the TEM images presented in Figure 2d.

The Ag LIPSS was fabricated by texturing the polished Ag thin plate with ultrashort laser pulses provided by an amplified Ti:sapphire femtosecond laser system. The morphology of the ultrashort laser-treated Ag surfaces, LIPSS, was analyzed using a scanning electron microscope (SEM). The SEM images in Figure 3a reveal a submicron LIPSS and a set of nanoscale features on the Ag surface. LIPSS consists of the surface ripples of two characteristic periods in perpendicular directions: \(L_1 = 0.62 \mu m\) and \(L_2 = 2.09 \mu m\).

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**Figure 2.** (a) TEM image of Au NRs, (b) the representative TEM image with a near-average size, and (c) the calculated electric field distribution in its vicinity. (d) TEM image of Au NPs.
The next stage of sample preparation was the formation of plasmonic cavity metasurface of Ag smooth/Au NRs (Figure 1c) and Ag LIPSS/Au NRs (Figure 1d). These cavity metasurfaces were prepared by drop-coating of the Au NR colloid on each of the substrates. It was previously shown that the drop-coating method could provide a uniform spread of molecules and NPs over the substrate. In that way, Au NRs are distributed over the substrate surface, forming a monolayer. The SEM morphology of the Ag LIPSS/Au NRs metasurface has confirmed the presence of Au NRs on the substrate (Figure 3b). Overall, Au NRs are spread quite evenly on the Ag surface with a density of about 0.8 μm⁻². It is seen that Au NRs are mainly located in the LIPSS hollows. The same procedure was used for the fabrication of Ag smooth/Au NP (Figure 1e) and Ag LIPSS/Au NPs (Figure 1f) metasurfaces containing spherical Au NPs.

Then, the method of drop-coating was used for the precipitation of dAMP solution on the respective dried metasurface substrate. In Figure 1, we schematically depicted the structure obtained metasurfaces along with the physical mechanisms explaining dAMP PL enhancement by such metasurfaces.

**Surface Plasmon Modes of Metasurfaces: Absorption and Reflection Experiments.** The absorption spectra of the water colloid of bare Au NRs and mixture colloid of Au NRs with dAMP molecules are presented in Figure 4 in comparison to that of spherical Au NPs. The spectrum of Au NRs, with an average length of 81 nm and a diameter of 14 nm, contains two peaks at 517 and 935 nm corresponding to the transversal (T) and longitudinal (L) localized surface plasmon (LSP) modes of NR. In contrast, spherical Au NPs, with an average diameter of 13 nm, show the LSP mode peaked at 520 nm. The spectrum of Au NRs and NPs as well as the mixed solution of Au NRs and NPs with dAMP, NR:L and NR:T denote the absorption peaks corresponding to longitudinal and transverse LSP modes of Au NRs; NP denotes the absorption peak of LSP mode of Au NPs. The absorption spectra of the dAMP solution is presented to show the absorption peak of dAMP molecules.

\[
k^2 - q_d^2 = \left(\frac{\omega}{c}\right)^2 \left(\epsilon' + \epsilon''\right) - \epsilon = -\left(\frac{\omega}{c}\right)^2 \epsilon' + \epsilon'' > 0
\]

Therefore, in the case of a smooth metal surface, \( k > q_d \), i.e., condition (1) cannot be fulfilled and, respectively, the SP polaritons cannot be excited on the smooth surface by the plane light wave. However, in the case of non-flat metal surface with high curvature or in the case of incident light wave with high curvature wavefront, the projection of incident photon wave vector on the metal surface is effectively increased by \( \Delta q_z \): \( q_z = \frac{\omega}{c} \sqrt{\epsilon'} \sin \varphi + \Delta q_z \). This makes the fulfillment of condition (1) possible. In the case of periodic surface structure

\[
\Delta q_z = \frac{2\pi}{d} m
\]

where \( d \) is the structure period and \( m \) is a natural number. In the case of the rough surface

\[
\Delta q_z = \frac{2\pi}{\langle d \rangle}
\]

where \( \langle d \rangle \) is the mean size of surface texture features. Thus, in the case of quasi-periodic submicron and nanosized surface texture, the grating excitation of SPPs takes place (schematically shown in Figure 1b). Meanwhile, on the smooth Ag substrate, the conditions of excitation of SPP modes are fulfilled due to the waves with large curvature wavefront. These waves arise due to the scattering of incident plane wave by Au NRs or NPs dispersed in the proximate vicinity of metal surface (Figure 1c,e).

In the case of Ag LIPSS/Au NRs or Ag LIPSS/Au NPs, depicted in Figure 1d,f, respectively, both the above-mentioned mechanisms take part under SPP mode excitation. LIPSS consists of submicron surface ripples in the perpendicular
Nanoscale features, namely, tips, nanocones, and other nanoprotrusions, are observed on the tops and slopes of the hills and on the slopes of the hollows. Thus, the analysis of the morphology of Ag LIPSS allows us to assume the role of the observed features in the interaction of such a modified surface and external excitation. LIPSS supports a rather efficient radiative excitation of the propagating SPP modes on its surface. Moreover, the observed nanoscale structures form additional plasmonic hot spots on ripples that will contribute to some physical processes.

The spectral manifestation of the excitation of propagating plasmon modes on the studied structures has been demonstrated by means of reflection spectroscopy (Figure 5). The reflection spectra were measured for P-polarized light, since in this case, the vector of electric field of incident beam lies in the plane formed perpendicular to the metal surface and in the direction of SP polariton propagation. Then, the electric field vector has both components perpendicular to the metal surface and parallel to the direction of SP polariton propagation, necessary for SP polariton excitation. For S-polarized light, the electric field vector is perpendicular to this plane, which makes the SP polariton excitation impossible. The distinct dips in the reflection spectra give evidence confirming the excitation of plasmonic propagating modes on Ag LIPSS, Ag smooth/Au NRs, Ag LIPSS/Au NRs, and metasurfaces with Au NPs.

The analysis of the reflection spectra (Figure 5) shows that the dip depths are the largest for the metasurfaces containing both LIPSS and layer of Au NRs or NPs, intermediate for bare Ag LIPSS, and the smallest for the hybrid metasurface based on smooth Ag surface and Au NRs or NPs. On the one hand, these data argue for the evidence of considerably higher efficiency of propagating plasmonic mode excitation for the structures that combines laser-treated surfaces and Au NRs or NPs, compared to the close levels of efficiencies for the metasurfaces with smooth Ag surface. The specified fact is caused by the synergetic effect of plasmonic propagating mode excitation by the quasi-grating on LIPSS surface and by waves scattered by Au NRs or NPs. On the other hand, the propagating mode excitation efficiency is higher for the metasurface containing nonspherical NRs than spherical NPs. This indicates that nonspherical particles are better for efficient cavity mode excitation than the spherical ones. As we have mentioned above, such plasmonic cavity mode is a plasmonic collective gap mode of the array of Au NRs or NPs and Ag substrate. Thus, a high-intensity plasmon gap mode is excited due to the plasmonic coupling in the system of Ag LIPSS Au NRs, as shown in Figure 1d. The space between the Au NRs and the LIPSS surface can be approximately evaluated by the thickness of the capping agent layer on Au NRs. Hereby, the gap between NRs and LIPSS of around 1 nm can provide a strong EM field that forms an extended hot spot in the gap. These hot spots determine the enhancement phenomena for the dAMP molecules discussed below.

Enhancement of dAMP Photoluminescence by Metasurfaces. The PL spectra of the dAMP molecules deposited on a polished quartz plate and on different metal metasurfaces under study are presented in Figure 6. The high-energy band peaked at 335 nm, marked as F, corresponds to the UV fluorescence of the dAMP molecules. The complex two-component band with maxima at 410 and 433 nm in the blue region, marked as P, is assigned to the dAMP phosphorescence.11 To confirm the nature of these PL bands, the PL excitation spectra at wavelengths of 335, 410, and 433 nm for the dAMP/Ag LIPSS/Au NRs structure have been measured (Figure 7). All of the excitation spectra contain the band centered at 260 nm. This specific feature confirms the enhancement phenomena for the dAMP molecules discussed below.
that the obtained emission spectra belong to the PL of dAMP molecules.

Figure 7. PL excitation spectra at wavelengths of 335 nm (F peak) and 410 and 433 nm (two peaks of P band) for dAMP on the Ag LIPSS/Au NR metasurface measured at room temperature.

One can see that the PL of dAMP molecules deposited on all of the studied Ag metasurfaces reveals a strong enhancement since the PL intensity of the dAMP deposited on a quartz plate (black curve in Figure 6) is fairly low. Note that only the fluorescence part of dAMP on quartz emission is observed and the intensity of dAMP phosphorescence in the blue range is too weak to be reliably measured. Meanwhile, the visible PL microscopy imaging of dAMP on the studied metasurfaces shows a high intensity in the blue range (Figure 6), while the PL of dAMP on quartz is undetectable. As it is known from the previous research,6,7 the quantum yield of dAMP PL is $7 \times 10^{-3}$ at room temperature. It is well known that the nature of low dAMP phosphorescence quantum yield is the capture of the majority of triplet excitations generated in the dAMP molecule by the surrounding oxygen molecules possessing the ground triplet state.

Now we consider possible physical mechanisms explaining the PL enhancement of dAMP molecules for all of the studied metasurfaces. The observed PL enhancement for the dAMP molecules deposited on the smooth Ag surface (green curve in Figure 6) and Ag LIPSS (dark green curve in Figure 6) is caused by the local EM field enhancement near the corresponding surface, arising due to the SPP excitation at this surface. At the smooth Ag surface, SPPs are generated by near-field waves emitted by dAMP molecules. Meanwhile, an additional mechanism of the SPP excitation at LIPSS occurs due to its direct excitation on the formed diffraction gratings, as shown in Figure 3. It is well known that the direct SPP excitation on metal gratings becomes possible due to the fulfillment of the matching condition for exciting photon and SPP. In the case of a smooth metal surface, the matching condition cannot be implemented, as SPPs are nonradiative modes for this case. Naturally, a higher PL enhancement for dAMP deposited on the Ag LIPSS than on the smooth surface is experimentally observed in Figure 6. Moreover, the phosphorescence intensity is sufficiently higher for dAMP deposited on the Ag LIPSS than on the smooth Ag surface, while the fluorescence intensities differ slightly for these surfaces. The most probable reason for a stronger plasmonic enhancement of the phosphorescence than the fluorescence is the closer location of the phosphorescence spectrum to the SPP spectral region (see Figure 5). Indeed, the noble-metal (silver and gold) structures are characterized by surface plasmonic response in the visible spectral region, where the dAMP phosphorescence is spectrally located (380–480 nm).

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The PL spectra of dAMP molecules deposited on different metasurfaces containing Au NRs also reveal a strong PL enhancement (Figure 6). Au NRs in the metasurface structure stimulate the process of the plasmonic near-field coupling of the Au NR LSP modes with the propagating SPPs of Ag surface (smooth or LIPSS) that results in the excitation of collective SP mode or plasmonic gap mode.33,36–40 Consequently, the plasmonic gap mode generates a very intense EM field in the cavity, where the dAMP molecules are located, that causes a stronger enhancement compared to the metasurfaces without Au NRs. Such an effect is observed experimentally (see Figure 6 and Table 1). At the same time, the enhancement in the structures with spherical NPs was a few times lower, which indicates the central role of the strong electric field in hot spots near the tips of nonspherical NRs in the plasmonic enhancement phenomenon (the calculated electric field near the tips of an NR is presented in Figure 2c).75 Note that the PL spectra of the dAMP deposited on the bare metasurfaces and the other two containing Au NRs or NPs demonstrate a significant difference. Namely, in the presence of Au NRs or NPs, the fluorescence is much more intense than the phosphorescence (Figure 6).

To conclude about the effect of the incorporation of specific nanoscale components onto the metasurfaces and to evaluate the levels of enhancement factors of spectroscopic characteristics, we quantitatively analyze the PL enhancement of dAMP on the studied metasurfaces. An enhancement factor of PL is determined as the ratio of the total intensity of the PL spectrum of the dAMP molecules deposited on a metasurface to the one on the quartz plate. Let us note that because of the transparency of quartz, the emission distribution pattern of emitters on quartz can be significantly different from those on the metal metasurfaces.76 This would lead to different spectrophotometer collection efficiencies that can cause bias in the quantum efficiency measurement. Thus, the dAMP PL enhancement factors obtained in our work are not the enhancement factors of the quantum yield of the dAMP molecules.

Table 1. Enhancement Factors of the Fluorescence and Total PL (Fluorescence + Phosphorescence) of the dAMP Molecules Deposited on Different Substrates

| Substrate | Fluorescence | Total PL (Fluorescence + Phosphorescence) |
|-----------|--------------|------------------------------------------|
| quartz    | 1            | 143                                      |
| Ag smooth | 108          | 850                                      |
| Ag LIPSS  | 143          | 1050                                     |
| Ag smooth/Au NRs | 850 | 154                                      |
| Ag LIPSS/Au NRs | 1050 | 366                                      |
| Ag smooth/Au NPs | 295 | 366                                      |
| Ag LIPSS/Au NPs | 808 | 430                                      |
molecules. Those are the values of PL enhancement of the dAMP species provided by different metal metasurface substrates compared to the common nonluminescent dielectric substrate (quartz), which can be obtained directly by a standard spectrophotometer.

The obtained enhancement factors for total PL (fluorescence + phosphorescence) and for fluorescence separately are given in Table 1. The PL enhancement factor of dAMP deposited on the studied metasurfaces ranges from 295 for dAMP deposited on smooth Ag surface to 1220 on Ag LIPSS/Au NRs metasurface. It is seen that the enhancement factor values of fluorescence fit in the range of 108 for dAMP deposited on the smooth Ag surface to 1050 on the Ag LIPSS/Au NRs metasurface. The presented data elucidate the crucial role of the plasmonic gap mode and, accordingly, the plasmonic coupling in the enhancement of fluorescence. Moreover, a higher enhancement for the dAMP on the Ag LIPSS/Au NR metasurface in comparison to the dAMP on the Ag smooth/Au NR one should be emphasized. The nature of this difference is caused by a higher efficiency of gap mode excitation and a higher concentration of hot spots formed at the metasurface based on LIPSS.

Finally, it should be accentuated that the highest value of the dAMP PL enhancement factor of 1220 achieved in the plasmonic cavity metasurface is due to the two main components: LIPSS and NRs. The indicated value of the PL enhancement factor of 1220 is 15 times higher than the maximum value of 80 previously known from the literature for Al nanoparticle array. At the same time, it is similar by value to the 1120-fold PL enhancement for the dAMP molecules obtained by us hybridizing Ag LIPSS with Ag nanoprisms. The key factors providing these results are the following: (i) the highest plasmonic near-field coupling for the LIPSS substrate together with the consequent formation of plasmonic gap mode and (ii) the highest concentration of hot spots on the textured metal surface and at the tips of nonspherical NPs.

## CONCLUSIONS

The levels of plasmonic enhancement for the PL of dAMP have been analyzed depending on the plasmonic nanocavity metasurface structures, namely, Ag smooth substrate and LIPSS combined with Au NRs or NPs. The deposition of Au NRs on different Ag substrates forms the plasmonic cavity nanosystems with strong near-field coupling of the LSP modes of Au NRs and the propagating SPP modes of Ag surface (smooth or laser structured). The obtained values of the PL enhancement factor of dAMP deposited on the studied metasurfaces fell in the range of 295–1220 depending on the metasurface type. The highest 1220-fold enhancement has been achieved for the Ag LIPSS/Au NR metasurface. This sufficient enhancement is shown to arise due to the synergistic effect of the generation of a high concentration of the hot spots near the sharp edges of the LIPSS ripples and the tips of NRs, together with the excitation of the collective gap mode due to the strong plasmonic near-field coupling in the formed plasmonic cavity. The phosphorescence intensity is essentially higher for dAMP on the Ag LIPSS than on the smooth Ag surface, whereas the fluorescence intensities differ slightly for these Ag metasurfaces. This is explained by a greater overlap of the phosphorescence spectrum in the SPP spectral region. The visible PL microscopy imaging of dAMP on the studied metasurfaces shows high intensity in the blue range, while the PL of dAMP on quartz is undetectable.

Thus, we have demonstrated that the combination of laser-textured metal surface (i.e., LIPSS) and nonspherical metal NPs with sharp tips (NRs, in particular) forms the plasmonic cavity metasurfaces promising for rather simple high-sensitive detection and imaging of biomolecules in ambient air at room temperature. It should be emphasized that in the case of the presented plasmonic cavity metasurfaces, there is no need to use any auxiliary dye labels for nucleotide PL imaging. These findings will be very useful for the development of plasmonic metasurfaces having the possibility to control the enhancement of separate PL components by changing the form and material of metal substrate and NPs. Also, in light of obtained results and recent trends in the elaboration of hybrid metal–dielectric nanocavity structures, the next challenge in the future is the design and fabrication of the metasurfaces consisting of metal LIPSS and HRI dielectric nonspherical NPs or dielectric photonic crystals for surface-enhanced spectroscopy applications, high-sensitive detection and imaging of biomolecules in particular.

## EXPERIMENTAL SECTION

### Au Nanorods

The used Au NRs were synthesized according to the following procedure. A solution of 1 mL of 0.5 mM HAuCl4 (5 mL, 0.5 mM) was mixed with the cationic surfactant hexadecyltrimethylammonium bromide (CTAB; 5 mL, 0.2 M) solution. Then, 1 mL of fresh 6 mM NaBH4 was injected into the as-prepared solution under vigorous stirring. After 2 min stirring, the seed solution was aged at room temperature and under weak room light illumination for 30 min.

**Seed Solution Preparation.** HAuCl4 (5 mL, 0.5 mM) was mixed with the cationic surfactant hexadecyltrimethylammonium bromide (CTAB; 5 mL, 0.2 M) solution. Then, 1 mL of fresh 6 mM NaBH4 was injected into the as-prepared solution under vigorous stirring. After 2 min stirring, the seed solution was aged at room temperature and under weak room light illumination for 30 min.

**Growth Solution Preparation.** CTAB (9.0 g) and 5-bromosalicylic acid (1.1 g) were dissolved in 250 mL of warm water. After the resulting solution was cooled to 30 °C, 4 mM AgNO3 solution was added. The mixture was kept undisturbed for 15 min. Then, 250 mL of 1 mM HAuCl4 solution and 37 wt % HCl were added. After 15 min of slow stirring, 0.064 M ascorbic acid was added and the solution was vigorously stirred to colorless for 30 s.

Finally, 0.4 mL of the seed solution was injected into the as-prepared growth solution. The resultant mixture was stirred for 30 s and left undisturbed for 12 h. Au NRs were collected by centrifugation at 9000 rpm for 20 min, followed by the removal of the supernatant. The precipitates were redispersed in water to obtain the resultant NR solution with a concentration of about 0.05 mg/mL.

### Au Spherical Nanoparticles

Under vigorous stirring, 5 mL of 1% sodium citrate was added into 100 mL of 0.3 mM HAuCl4 at 100 °C. After 30 min stirring, the mixture was cooled to room temperature. Au NPs were collected using centrifugation at 13 000 rpm for 20 min, followed by the removal of the supernatant. The precipitates were redispersed in water to obtain the resultant NP solution with a concentration of about 0.05 mg/mL.

### Ag LIPSS Substrate

A pure Ag thin plate of size 1.5 × 2.5 cm, polished mechanically to the residual roughness less than 150 nm, was used for the texturing with ultrashort laser pulses provided by an amplified Ti:sapphire femtosecond laser system (Coherent, Inc.). The main characteristic parameters of high-intensity femtosecond laser pulses were as follows: a central wavelength of 800 nm, the pulse duration of horizontally polarized beam from the amplifier of 140 fs, and the pulse energy of about 0.77 mJ at a repetition rate of 1 kHz. The experimental setup also included a quartz lens with a 100.0 mm
focal length, a vertically standing sample stage, an electromechanical shutter to vary the number of laser shots applied to the sample. During the laser treatment, the sample holder moved at a velocity of 1 mm/s. The diameter of the laser beam spot on the sample surface was 8.5 × 10^-2 cm. The power density of the incident radiation varied by changing the distance between the focusing lens and the sample. The laser processing was performed in air at atmospheric pressure.

Ag LIPSS/Au NR Metasurface. These cavity metasurfaces were prepared by drop-coating 3 μL of the Au NR colloid on each of the substrates. The solution spread into a circular area of about ~5 mm in diameter. We used the Au NR and NP solutions with concentrations of 0.05 mg/mL, providing approximately the same optical density in the SP spectral range of absorption spectra.

A dAMP stock solution of 1.7 mM was obtained by dissolving a dAMP powder in distilled water. For PL measurements, the solution concentration was reduced to 0.17 mM. Then, the method of drop-coating was used for the precipitation of 2 μL of the dAMP solution on the respective dried metasurface substrate. As a result, a circular area of about 3 mm in diameter was obtained. In Figure 1, we schematically depicted the structure of the obtained metasurfaces along with the physical mechanisms explaining dAMP PL enhancement by such metasurfaces.

Optical Characterization. The spectra of the optical density (light extinction) of Au NR or Au NP water colloids as well as the mixture of Au NPs or Au NRs and dAMP molecules were recorded with a Cary 60 UV−Vis spectrophotometer (Agilent Technologies, Inc.). The reflection spectra of the metasurfaces were measured with a double-grating spectrometer DFS-12 (LOMO) equipped with a tungsten−halogen incandescent lamp as the excitation source. The reflection measurements were carried out at the light incidence angle of 20°. The PL spectra were recorded with a Shimadzu RF-6000 spectrofluorophotometer (Shimadzu Corp.). The excitation wavelength of 260 nm was chosen for the measurements due to its coincidence with the maximum of the dAMP absorption peak. Let us note that an area covered by dAMP varied in diameter from about 2.5 to 3.5 mm in different metasurface samples. However, the cross section of the exciting beam of the spectrofluorophotometer was quite large and the dAMP area was entirely illuminated by the exciting beam. The corresponding PL signal was collected from the same amount of dAMP molecules in experiments with different metasurface samples. At the same time, the emission was collected over a rather large angle by a large-scale focusing mirror; thus, the modification of scattering varied in different sample surfaces might negligibly affect the collection efficiency. Therefore, no calibration factors were applied when calculating the dAMP PL enhancement factors for different metasurface samples. All samples were inspected at the same parameters of luminescence imaging, exploiting a Nikon Eclipse Ti-U inverted microscope at 20× optical magnification equipped with a Nikon Digital Sight DS-Fi2 camera (Nikon). UV excitation over the whole imaging area of about 0.5 × 0.5 mm and a long-pass 405 nm filter were used. Luminescence imaging was used only for the qualitative inspection of sample emission. All of the optical measurements were carried out in ambient air at room temperature.

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**Notes**

The authors declare no competing financial interest.

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