ІНФОКОМУНІКАЦІЙНІ ТЕХНОЛОГІЇ ТА ЕЛЕКТРОННА ІНЖЕНЕРІЯ
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NANOCOMPOSITE MATERIALS BASED ON GRAPHENE, GRAPHENE OXIDE, AND SILVER NANOPARTICLES

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In this work, plasmon characteristics of nanocomposite materials based on graphene, graphene oxide, and silver nanoparticles have been studied. The effective dielectric constant and absorption coefficient of the nanocomposites based on graphene-silver and graphene oxide – silver depending on the concentration and size of nanoparticles have been calculated. A change in the silver nanoparticles filling factor by 5 percent leads to significant changes in both the real and imaginary parts of the effective dielectric constant of the nanocomposite material. A pronounced absorption peak is observed in the case of graphene-based nanocomposite with a silver filling factor of 0.2. At the same time, the absorption peak can be indicated at a silver filling factor of 0.1 for the graphene oxide-based nanocomposite. The maximum absorption is observed for the nanocomposite material with nanoparticles having a radius of 5 nm in both cases. The researched nanocomposite materials can be successfully used for various organic electronics applications.

Key words: *nanocomposite materials; graphene; oxide graphene; silver nanoparticles; effective dielectric permittivity; absorption.*
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1. Introduction

Nowadays, the development and production of new electronic elements and devices are aimed not only at achieving high economic efficiency but also at ensuring sustainable industrial development. Various approaches such as adsorption, progressive oxidation processes, flocculation and coagulation, and others are used [1–3]. The materials used are the main factors determining the effectiveness of these methods. Researchers from all over the world are trying to improve the material's characteristics by combining them with other materials, which allows for reducing defects and improving the properties of the original materials [4–6].

Recently, graphene as well as graphene products and precursors for its production have attracted the increasing attention of researchers due to their mechanical strength, electrical conductivity, and unique optical and thermal properties [7, 8]. Nanosystems based on graphene or graphene oxide exhibit electrochromic behavior, allowing linear and ultrafast optical properties to be tuned. Composites containing graphene are characterized by increased noise absorption, reduced band gap, larger surface area, limited recombination, and improved charge carrier migration speed [9]. Recent studies have shown that composite materials based on graphene and graphene products (foams, flakes, nanotubes, quantum dots) and metal nanostructures have a high potential for use in electronics (energy storage technologies), optics, electrochemistry, and catalysis [10–12]. Nanocomposites based on graphene and silver nanoparticles have proven to be promising materials due to their unique physical and chemical properties and can potentially be used in many areas of science and technology. Each of the system components individually has a significant potential for application in various fields, however, in the form of composite material, they show a synergistic, significantly improved photo effect [13]. Graphene-based composites can also increase the ability to decompose organic compounds due to the enhancement of ultra-broad spectral response, which significantly expands the range of their practical application, as well as through the generation of free oxygen forms by graphite oxide, or hydrogen and free electrons by graphene structures during the catalytic photolysis of water. It can be used in practice for whitening surfaces, in water and air filtration systems, and even for creating bacteriostatic coatings, etc. [14, 15].

It should be noted that graphene is not a plasmonic material, however, it can be successfully combined with materials that exhibit plasmonic effects at the interface, such as gold or silver. For instance, a graphene layer on gold or silver thin films can cause significant changes in the surface plasmon resonance signal compared to an uncoated metal film, mainly due to charge transfer from the porous graphene to the surfaces [16]. Graphene oxide is usually desorbed through absorption by the plasmon field. Creating a powerful electric field at the boundary between two materials is extremely important for generating surface plasmon waves. Graphene, which has the highest electronic structural configuration, serves to generate such waves. The effect of localized surface plasmon resonance is realized through the interaction between plasmonic nanoparticles and a light wave on the graphene surface, improving their optical characteristics. Among all transition elements, silver is the material with the highest conductivity and reactivity [17]. Recently, publications appeared in which silver was also used for doping graphene oxide, which has favorable properties for the target applications: low resistance, good dispersion, and increased mechanical strength, against the background of significantly better electrochemical and photocatalytic properties. Changes in the size, structure, and shape of nanoparticles determine their physical and chemical properties, thus, their optical characteristics [18]. It is the possibility of manufacturing silver nanoparticles of various shapes and sizes, such as nanodiscs, nanostrips, nanorods, nanowires, dendrites, and nanoantennas, that opens up new opportunities for their wide application. Different nanostructure morphology showed their specific behavior in the visible and infrared spectral regions.

It is worth noting that despite the excellent reinforcement, silver is difficult to use in an acidic environment or at higher temperatures in an oxidizing environment due to the processes of dissolution or oxidation of silver. Graphene is highly resistant to chemicals, acting (in particular, graphite oxide) as a matrix with special centers of silver crystallization (GO-supported Ag NPs synthesis), and graphene coatings or the very presence of a graphite matrix largely prevent the rapid oxidation of silver even in a rather aggressive environment with preservation, and even simultaneous enhancement of the silver nanoparticles plasmonic properties. Therefore, graphene, like graphite oxide, fits quite well as a material for dispersing and stabilizing silver, because they combine a large specific surface, and graphite oxide also has many oxygen-containing functional groups that serve as crystallization centers for silver nanoparticles and landfill for possible further chemical modification, with unique physical and chemical properties. The graphene matrix and silver nanoparticles in the nanocomposite material work synergistically, improving their properties, such as higher antimicrobial, catalytic activity, and, for example, light absorption and emission or thermal conductivity [19]. The synergistic properties of these hybrid materials have proven their suitability in electronics, for example in OLED and OPV [20–22].

Even though promising results have already been obtained from the application of nanocomposite materials based on the graphene matrix and nanoparticles, the search for a universal solution to increase the efficiency of electronic elements continues. Synthesis and properties of nanoparticles are active areas of research that are developing rapidly. Synthesis and properties of nanoparticles are active areas of research that are developing rapidly. Thus, many new possible approaches remain to be explored. For instance, the size, shape, and concentration of nanoparticles are crucial for OLEDs and OPVs, as they affect light output for OLEDs, and light capture for OPVs. In summary, we can say that the design of nanocomposite materials based on highly oxidized and reduced (graphene) forms of graphite encrusted with silver nanoparticles is an urgent task and is of significant interest to various fields of science and technology.

2. Results and discussions

It is necessary to optimize both the matrix parameters and the parameters of the inclusions for the manufacture of the above-mentioned nanocomposites with the given characteristics. It is known that incorrectly chosen parameters can lead to a decrease in the sensitivity of the surface plasmon resonance, therefore, enhancement absorption or scattering is impossible. In this work, we limited ourselves to the study using theoretical calculation of only the inclusions parameters, namely spherical silver nanoparticles.

The optical properties of a nanocomposite material (when one of the components can be considered as a matrix in which metal inclusions are dispersed), can be described using the approximate Maxwell-Garnett theory [23]. The effective permittivity ε_{MG} of the nanocomposite medium is determined as follows:

$$\varepsilon_{MG} = \varepsilon_h \frac{1+2f\dfrac{\varepsilon_i-\varepsilon_h}{\varepsilon_i+2\varepsilon_h}}{1-f\dfrac{\varepsilon_i-\varepsilon_h}{\varepsilon_i+2\varepsilon_h}} = \varepsilon_h \frac{\varepsilon_h+\dfrac{1+2f}{3}\left(\varepsilon_i-\varepsilon_h\right)}{\varepsilon_h+\dfrac{1-f}{3}\left(\varepsilon_i-\varepsilon_h\right)}, \tag{1}$$

where, ε_h is permittivity of the host medium, ε_i is permittivity of the inclusions, and f is the volume fraction of inclusions. It should be noted that equation (1) is valid when the concentration of nanoparticles does not exceed 30 percent.

Equation (1) is derived under the assumption that the inclusions are spherical in shape. However, equation (1) does not contain information about the shape of inclusions. It contains only the values of dielectric constants of the main substance (host medium) and inclusions and the volume fraction (filling factor) of the latter. Therefore, it can be assumed that this equation is a valid approximation for inclusions of any shape if the medium is spatially homogeneous and isotropic on average.

The absorption coefficient of the nanocomposite material was calculated according to the next equation:

$$\alpha(\lambda) = \frac{4\pi}{\lambda}\sqrt{\frac{1}{2}}\sqrt{\sqrt{\left(\mathrm{Re}\left(\varepsilon_{MG}(\lambda)+\mathrm{Im}\left(\varepsilon_{MG}(\lambda)-\mathrm{Re}(\varepsilon_{MG}(\lambda))\right)\right)\right)}}, \tag{1}$$

where λ is wavelength.

Graphene-based composite materials can be conditionally divided into three types, namely: graphene-based nanocomposites, graphene oxide-based composites, and reduced graphene oxide-based composites. In the work, we limited ourselves to the first two cases, to get a qualitative picture for comparison. Graphene oxide-based nanocomposites have been widely used.

The dependence of the real and imaginary parts of the effective dielectric permittivity of the nanocomposite material on the wavelength for the different values of the silver nanoparticles filling factor is shown in Fig. 1.

The filling factor was used from 0.05 to 0.2. The radius of the nanoparticle was 15 nm. The data from the experimentally obtained complex refractive index was used from work [24] for graphene and from [25] for graphene oxide. The value of the silver complex dielectric permittivity was used from [26].

As can be seen from Fig. 1, an increase in the content of nanoparticles leads to an increase in the imaginary part of the effective dielectric permittivity in the entire spectral range. It is worth noting that a noticeable increase is observed only at a filling factor of 0.2.

The dependence of the absorption coefficient of the nanocomposite material on the wavelength is shown in Fig. 2, *a* at three values of the silver nanoparticles filling factor. The dependence curve of the absorption coefficient contains two peaks. The first peak at a wavelength of about 320 nm corresponds to the absorption peak of silver nanoparticles. The second peak is observed at a wavelength of 600 nm and is responsible for absorption by the nanocomposite, namely graphene with spherical silver nanoparticles dispersed in it.

The maximum absorption was observed at the nanoparticle filling factor of 0.20. Thus, for this concentration, the dependences of the absorption coefficient of the nanocomposite material on the wavelength at different values of the metal nanoparticles radius were calculated (Fig. 2, *b*). The nanoparticle's radius varied from 5 to 20 nm, in steps of 5 nm. Absorption decreases with increasing nanoparticle size.

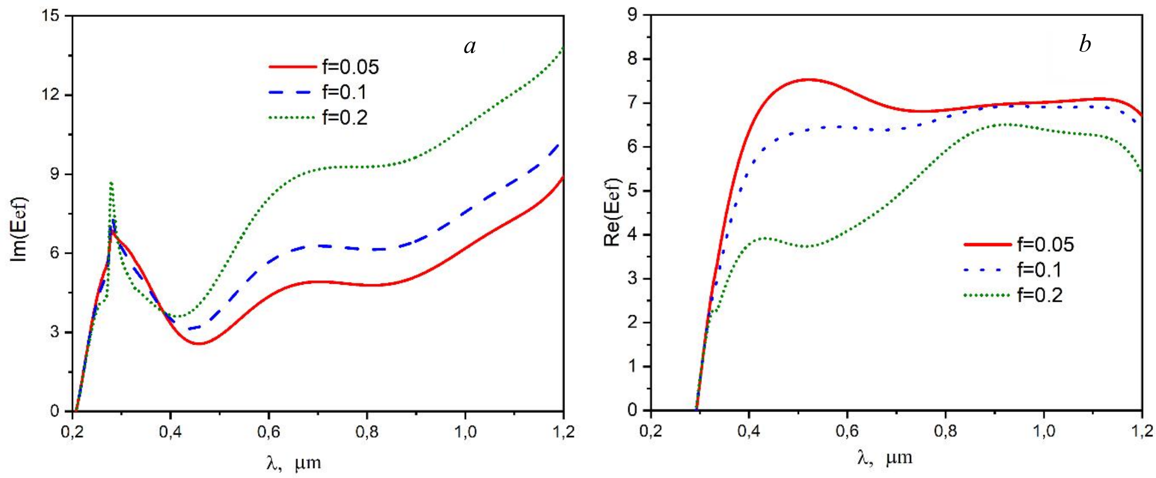

Fig. 1. The dependence of the imaginary part (a) and the real part (b) of effective dielectric permittivity of the nanocomposite material based on graphene and silver nanoparticles on the wavelength for the different values of the silver nanoparticles filling factor

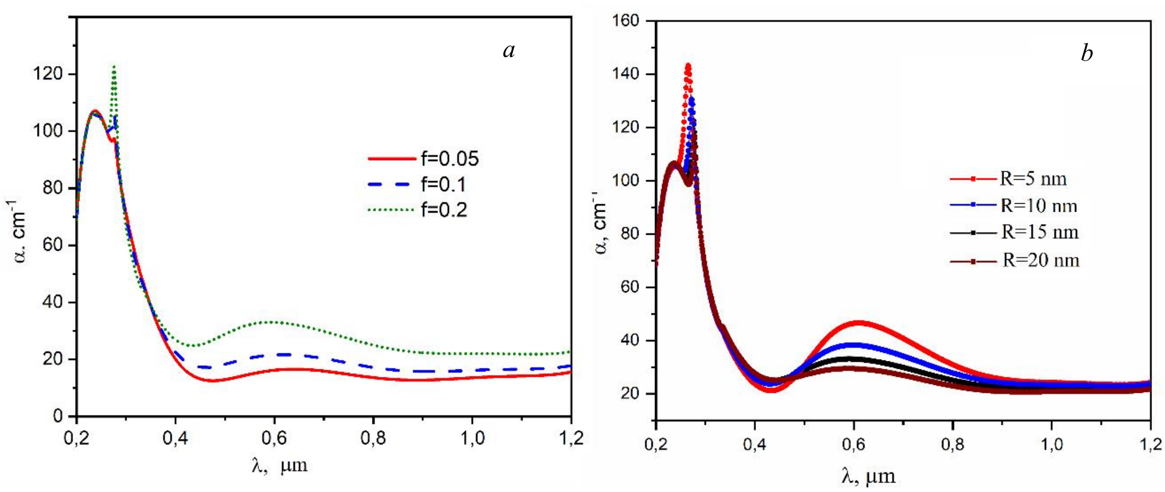

Fig. 2. The dependence of the nanocomposite material absorption coefficient on the wavelength for the different values of the silver nanoparticles filling factor (a) and radius (b)

The dependences of the real and imaginary parts of the effective dielectric constant of the nanocomposite material based on graphene oxide and silver nanoparticles on the wavelength were calculated, using the same values as for the previous case (Fig. 3).

As can be seen from Fig. 3, a change in the silver nanoparticle filling factor by 5 percent leads to significant changes in both the real and imaginary parts of the effective dielectric constant of the nanocomposite material based on graphene oxide and silver nanoparticles. As in the case of the graphene-based composite material, an increase in the silver filling factor leads to an increase in the complex part of the dielectric constant, which in turn leads to an increase in the absorption coefficient.

The dependence of the absorption coefficient and the nanocomposite material on the wavelength is shown in Fig. 3 at three values of the silver nanoparticles filling factor. Simulation results show that increasing the filling factor to 0.1 practically does not change the shape of the absorption coefficient curve only increases it. However, with a silver filling factor of 0.2, a pronounced absorption peak at a wavelength of about 430 nm is observed in the spectrum.

The maximum absorption was observed, as for graphene, at the nanoparticle filling factor of 0.20. The dependence of the absorption coefficient of the nanocomposite material on the wavelength at different values of the metal nanoparticles' radius was calculated for this concentration (Fig. 4, *b*). The radius of the nanoparticles varied from 5 to 20 nm, in steps 5 nm. The maximum absorption is observed for the nanocomposite material with inclusions with a radius of 5 nm in both cases, both for graphene and for graphene oxide. As the size of the nanoparticles increases, the amplitude of the absorption spectrum decreases, and the absorption peak shifts to the short-wavelength region.

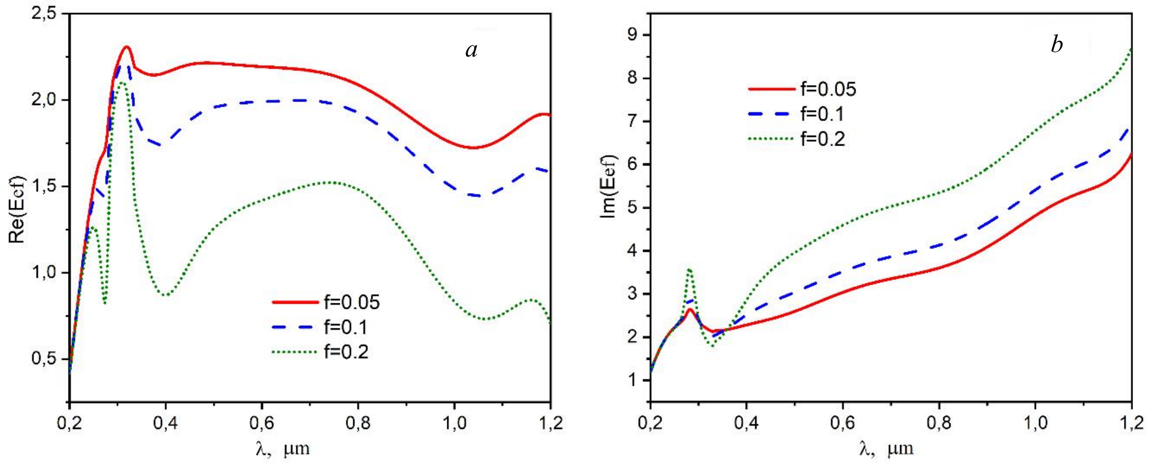

Fig. 3. The dependence of the imaginary part (a) and the real part (b) of effective dielectric permittivity of the nanocomposite material based on graphene oxide and silver nanoparticles on the wavelength for the different values of the silver nanoparticles filling factor

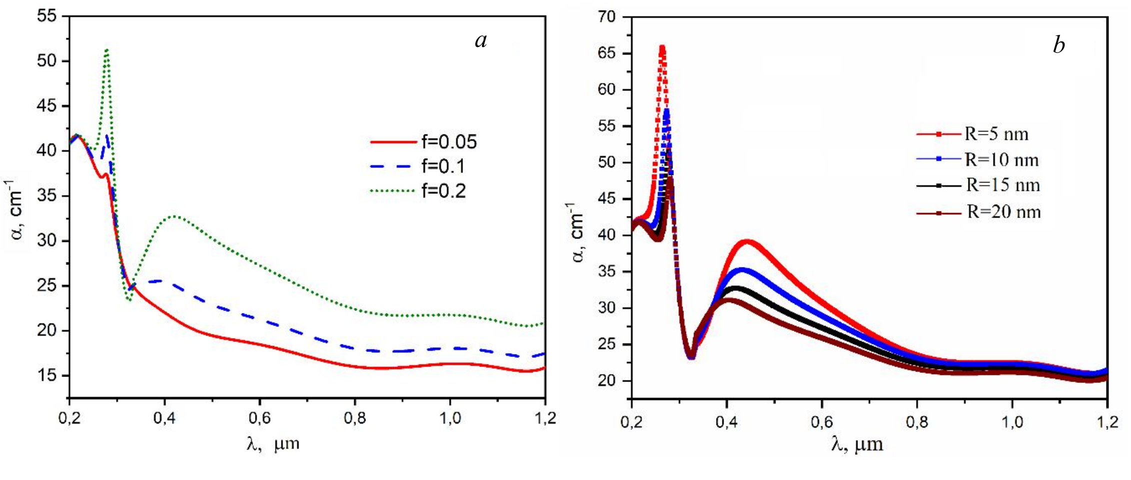

Fig. 4. The dependence of the nanocomposite material absorption coefficient on the wavelength for the different values of the silver nanoparticles filling factor

Nanoparticles of different sizes cause different surface plasmon effects in organic optoelectronic devices. Therefore, it is worth remembering that the size of plasmonic nanoparticles that demonstrate forward scattering is usually between 30 and 70 nm. As the particle size increases, more light is scattered, and light-out coupling for OLED devices improves accordingly. However, large nanoparticles embedded in the layer are detrimental to the device due to the morphology of the bottom layer and strong metal absorption. In the case of plasmonic nanoparticles smaller than 30 nm, absorption occurs mainly due to the localized surface plasmon effect instead of scattering, and such particles enhance light trapping for OPVs. However, the size, shape, and concentrations of nanoparticles are crucial for OLED and OPV applications.

Complex optical processes are difficult to simulate only using numerical simulations; therefore, extensive experimental work is required. A combination of both experimental results and numerical analysis can contribute to a better understanding of the behavior of charge carriers induced by the use of a plasmonic nanocomposite layer.

Conclusion

Plasmon characteristics of nanocomposite materials based on graphene, graphene oxide, and silver nanoparticles have been studied. A change in the silver nanoparticles filling factor by 5 percent leads to significant changes in both the real and imaginary parts of the effective dielectric constant of the nanocomposite material. The simulation results show that increasing the filling factor to 0.1 does not change the shape of the absorption coefficient curve only increases it. However, a pronounced absorption peak at the wavelength of about 450 nm is observed on the spectrum with a silver filling factor of 0.2. Thus, it is possible to obtain the maximum absorption at the given wavelength by selecting the concentration of nanoparticles in the composite. Therefore, such nanocomposite materials can be successfully used for different electronic applications.

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НАНОКОМПОЗИТНІ МАТЕРІАЛИ НА ОСНОВІ ГРАФЕНУ, ОКСИДУ ГРАФЕНУ ТА НАНОЧАСТИНОК СРІБЛА

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У роботі досліджено плазмонні характеристики нанокомпозитних матеріалів на основі графену, оксиду графену та наночастинок срібла. Розраховано ефективну діелектричну проникність та коефіцієнт поглинання нанокомпозитів на основі графен – срібло та оксид графену – срібло залежно від концентрації та розміру наночастинок. Зміна коефіцієнта заповнення наночастинок срібла на 5 % призводить до істотних змін як дійсної, так і уявної частин ефективної діелектричної проникності нанокомпозитного матеріалу. Яскраво виражений пік поглинання спостерігається у випадку композиту на основі графену з коефіцієнтом заповнення срібла 0,2. Водночас для композиту на основі оксиду графену пік поглинання можна ідентифікувати, якщо коефіцієнт заповнення срібла дорівнює 0,1. Максимальне поглинання спостерігається для нанокомпозитного матеріалу із включеннями радіусом 5 нм в обох випадках. Досліджувані нанокомпозитні матеріали можна успішно використовуватись для різних застосувань органічної електроніки

Ключові слова: *нанокомпозитні матеріали; графен; оксид графену; наночастинки срібла; ефективна діелектрична проникність; поглинання.*