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Effect of Silver Nanoparticles on the Optoelectronic Properties of Graphene Oxide Films

The effect of Ag nanoparticles (NPs) on the optical and optoelectronic properties of films based on graphene oxide has been studied. In the presence of Ag NPs, the morphology, as well as the thickness of graphene oxide films, were not changed. When Ag NPs were added, a change in the shape and position of the absorption bands and Raman spectra of graphene oxide was observed. It is shown that with the addition of Ag NPs, the G band of graphene oxide shifts to low frequencies, which may be the result of the absence of separate double bonds, while the I_D/I_G ratio was not changed, as did the number of Gr layers. In the absorption spectrum of the films, along with the absorption band of graphene oxide, a shoulder was registered, which can be associated with the absorption of Ag NPs. The optical density of Gr films with plasmonic NPs is higher than without them. Measurements of the optoelectronic characteristics showed that, in the presence of Ag NPs, an increase in the values of the photocurrent of graphene oxide is observed. The sensitivity of graphene oxide films was increased by almost 20 times when plasmonic NPs were added to them, and the detection ability increased by 25 times. The results obtained can be used in the development of new photosensitive devices for optoelectronic and photocatalytic applications.

Keywords: graphene oxide, silver nanoparticles, plasmon, properties, absorption, Raman spectra, optoelectronic properties, photodetectors.

Introduction

Graphene is one of the most widely used ultrathin two-dimensional materials that have had a huge impact on supercapacitors, biosensors [1] and is used in the development of optoelectronics [2], photovoltaics [3], and photocatalysis [4] devices. Graphene with surface oxygen-containing groups is called graphene oxide. Graphene oxide and its modifications, in contrast to graphene, are a more convenient material for researchers, since it is easy to obtain and use for practical purposes. Graphene oxide (GO) is rich in oxygen-containing functional groups such as carboxyl, hydroxyl, epoxy and carbonyl on its surface and edges compared to graphene, which improves solubility and provides many reactive sites for further functioning [5, 6]. Meanwhile, graphene oxide saves the characteristics of graphene. Thus, graphene oxide has great potential for applications [7].

In recent years, long-range photodetectors have attracted wide interest due to their large civilian and military applications, including biological and chemical analysis, environmental monitoring, remote control, and missile launch detection [8, 9]. Ultraviolet photodetectors are usually made from wide-gap semiconductor materials or from graphene nanostructures. Photodetectors based on graphene have a number of advantages, such as better efficiency of charge-transport processes and low cost [10, 11, 12]. However, photovoltaic devices based on graphene and graphene oxide has limitation lies in their low sensitivity.

The introduction of plasmonic silver nanoparticles into graphene layers will make it possible to overcome this limitation. It is known that the inclusion of metallic nanostructures in graphene enhances the light–substance interaction [13]. Recently, plasmonic nanostructures have been used for surface enhanced Raman spectroscopy (SERS), single molecule spectroscopy, improved photodetection, photovoltaics, and light emitting devices. Near-field enhancement of the photoconversion efficiency in graphene was demonstrated by placing Au nanostructures on the surface of a graphene sheet [13]. This approach has also been reported to provide better spectral sensitivity, which enables multicolor photodetection [14].

The amplification of the photocurrent in graphene-Ag hybrid devices is the result of the amplification of graphene electronic vibrations in the near field, as well as the scattering effect of Ag nanoparticles [15]. In addition, scattering from Ag NPs can also play a vital role in increasing the photocurrent, which is similar to the plasmon enhancement effect observed in a nanoantenna-based optical photodetector [16]. The results of the review clearly demonstrate that Ag nanoparticles embedded in graphene with several layers can be an active material to improve the interaction of light and matter. Thus, new hybrid 2D plasmonic nanostructures may be very attractive for future graphene-based optoelectronic devices.

In this work, the effect of silver nanoparticles on the optoelectronic properties of graphene oxide films prepared by the method of airbrush spraying was studied. This method makes it possible to obtain graphene films of a larger area with less time spent, which can be used in practical applications.

Experimental

To obtain films, single layer graphene oxide (SLGO, Cheaptubes) was dispersed in deionized water in an ultrasonic bath for 30 minutes. The Gr concentration in solutions was equal to 2 mg/mL. To remove large particles, the dispersions were centrifuged at 3000 rpm.

Ag nanoparticles (NPs) were synthesized by laser ablation using a Nd: YAG laser with λ_{gen}=532 nm, τ_{pulse}=10 ns, and E_{pulse}~16 J/cm^2 [17]. The ablation time was equal to 10 minutes. The height of the ablated liquid was equal to 0.8 cm. The average NPs diameter determined by dynamic light scattering (Nanosizer S90, Malvern) was equal to 18±5 nm. NPs were added to the prepared dispersion of graphene oxide at a concentration of 10^{-12} mol/L.

The films were deposited with a graphic airbrush with a nozzle diameter of 0.9 mm. The distance from the airbrush to the substrate surface was equal to 15.5 cm. The thickness of the films was 25 layers. The resulting films were dried at 80 °C in a drying oven for at least 3 hours to completely remove the solvent. In the study of optoelectronic properties, FTO coated glasses (fluorine-doped tin oxide, ~7 Ω/sq, Sigma-Aldrich) were used.

The structural and morphological properties of the prepared films were studied using a Mira 3 LMU (Tescan) scanning electron microscope (SEM).

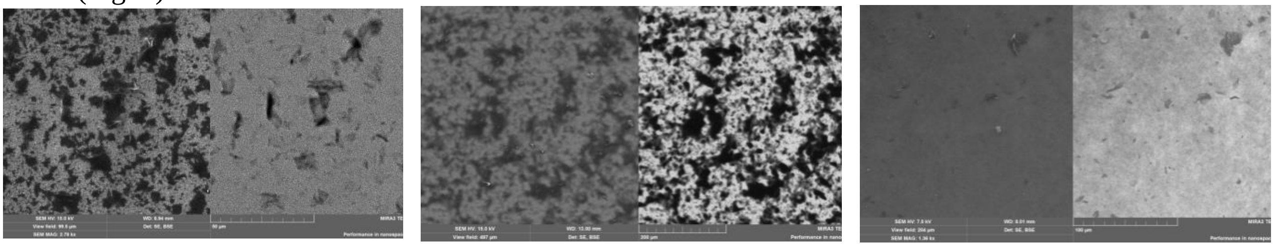
Absorption spectra were measured using a Cary 300 spectrometer (Agilent). The Raman spectra were recorded using a Confotec MR520 microscope (Sol Instruments) with laser excitation at a wavelength of 632.8 nm.

Measurements of the current-voltage characteristics (CVC) of the prepared samples were carried out using an Elins P-20X (Elins) potentiostat-galvanostat when the samples were irradiated with Xe lamp with 35 mW/cm^2.

FTO glasses were used to assemble the photodetector. On the surface of the substrates, interdigitated tracks were cut out using a BLS0503MM (Bodor) laser scribing machine. The distance between the tracks is 1.5 mm, the length of the tracks is 10 mm. The view of the photodetector can be found in [18].

Results and Discussion

The study of the structure on SEM (Tescan Mira-3) showed that when Gr is deposited, an islet film is formed (Fig. 1).



5 layers 10 layers 20 layers

Figure 1. SEM images of Gr films obtained by airbrushing

In this case, the image clearly shows multilayer particles located on the periphery of the sprayed film. With an increase in the number of sprayed layers, the film occupies a larger area and is more uniform. The SEM images (right) recorded with a reflected electron detector (BSE) show that as the number of layers increases the number of multilayer particles also grow. The structure of Gr+Ag NPs films does not differ from that for films with graphene oxide due to the fact that the concentration of plasmon NPs in them is too low.

To study the optical properties of the prepared films, the spectra shown in Figure 2 were obtained. A band with a maximum at about 230 nm is observed in the absorption spectrum of the films. It is known that the absorption band at 230 nm is formed by transitions between $\pi\pi^*$–nature orbitals in aromatic C–C bonds [18, 19]. The addition of silver NPs did not practically change the optical density at the maximum. A shoulder that is observed at 350 nm, can be associated with the absorption of Ag NPs. The maximum absorption spectrum of plasmonic NPs exhibits at 400 nm. In the wavelength range from 350 to 600 nm, the optical density of Gr films with plasmon NPs is higher than without them.

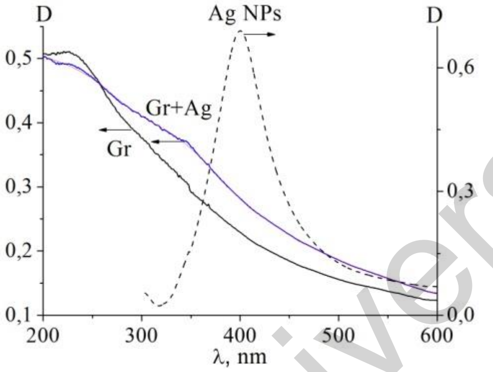


Figure 2. Absorption spectra of Gr films deposited by airbrushing with the addition of Ag NPs

The plasmonic effect of Ag NPs also leads to an increase in the intensity of Raman scattering of Gr films (Fig. 3). In the Raman spectra of Gr film, the G band exhibits at 1595–1605 cm^{-1} and it is shifted to higher frequencies compared to the position of this band (1581 cm^{-1}) in graphite [20].

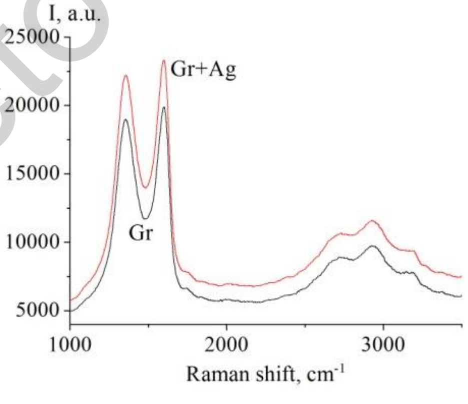


Figure 3. Raman spectra of Gr films deposited by airbrushing with the addition of Ag NPs

The Raman spectrum of Gr films also contains a D band at about 1360 cm^{-1}, which characterizes the degree of defectiveness, and a 2D band in the region of about 2700–2900 cm^{-1} is clearly distinguishable, which indicates the possible presence of disordered regions in the structure of the synthesized Gr films. As can be seen from the data (Table 1), with the addition of Ag NPs, the G-band of graphene oxide shifts to the low-frequency region, which may be the result of the absence of individual double bonds that resonate at higher frequencies [21]. At the same time, the I_D/I_G ratio did not change, as the number of Gr layers, which can be obtained from the I_{2D}/I_G value [21]. However, the value of this parameter indicates that the number of layers in Gr in the films under study varies from 4 to 8.

Table 1

Position and intensity of Raman bands of Gr films with Ag NPs

Sample	D, cm^{-1}	I, a.u.	G, cm^{-1}	I, a.u.	I_D/I_G	2D, cm^{-1}	I, a.u.	I_{2D}/I_G
Gr	1350	18940	1600	19923	0.95	2733	8910	0.45
Gr +Ag	1355	22203	1598	23346	0.95	2740	10588	0.45

The optoelectronic properties of graphene oxide films were studied by measuring the current-voltage characteristics (CVC) of the films under study, as well as by determining the photocurrent I_{ph}, sensitivity R, and detectivity D* of the obtained films according to the procedure of [18].

The current-voltage characteristics of the prepared samples were measured both at a positive voltage bias (up to +30 V) and at negative values — up to -30 V. The I(U) dependence curves have a non-linear shape. In this case, even in the absence of illumination of the samples, currents are recorded. The values of the generated photocurrent I_{ph} of the detector, shown in Table 2, were estimated from the difference between the dark and light values of *I*.

The maximum photocurrent value recorded for graphene oxide without plasmonic NPs is equal to 10 nA (at +25 V), while at a reverse polarity voltage it is only 0.048 nA. The I_{ph} values for films based on Gr+Ag NPs are almost 20 times higher. It can be seen that both dark and light currents increased almost proportionally (Fig. 4).

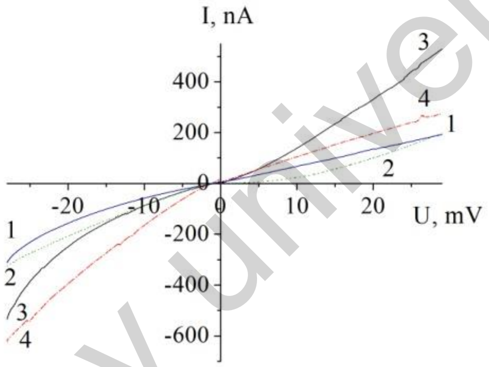


Figure 4. I — V characteristics of Gr films without (1, 2) and with Ag NPs (3, 4): 1.3 — light; 2.4 — dark curves

Table 2

Optoelectronic parameters of Gr-based films

Sample	I_{ph}, nA at + 25 V	I_{ph}, μA at –25 V	R, A/W	D*, Jones
Gr	10	0.048	$2.86\cdot10^{-7}$	$0.12\cdot10^{7}$
Gr+Ag	196	0.120	$56\cdot10^{-7}$	$3.01\cdot10^{7}$

When evaluating the responsivity R of the prepared films, the formula R = I_{ph}/P was used, where P is the power of the incident light. From Table 2, it can be seen that the responsivity of graphene oxide films increased significantly (almost 20 times) with the addition of plasmon NPs to them.

Further, the specific detectivity D* of the prepared samples was estimated, which determines the ability of the device to detect weak light signals and can be determined from expression (1) [22, 23]:

$$D^* = \frac{RA^{1/2}}{\sqrt{2*e*I_{dark}}}, \tag{1}$$

where R is the responsivity of the films, A is the illuminated area of the sample, e is the modulus of the electron charge, Idark is the value of the dark current at +25 V.

Calculations showed that the specific detectivity of Gr films is equal to $1.2\cdot10^{6}$ Jones, while in the presence of silver NPs D* increased 25 times and is equal to $3.01\cdot10^{7}$ Jones. It can be explained by the fact that, for pure Gr films, the value of the calculated sensitivity of the films is almost the same time smaller.

Comparing the results obtained with other authors, it can be noted that values of the R and D* parameters for pure Gr films are very small and differ by an order of magnitude from the values of [23, 24], where graphene oxide was used to prepare photodetectors. However, it can be noted that, in this work, graphene oxide films were deposited by dip-coating and were subjected to further high-temperature annealing, which, as is known from our studies [25], leads to partial reduction of graphene oxide and removal of oxygen-containing groups. As a result, the charge-transport characteristics of graphene oxide films also increase. However, the optoelectronic characteristics of graphene oxide films can be increased due to the plasmon effect of Ag NPs. Moreover, their value is comparable to the values obtained by other groups for both Gr and pure graphene [23]. The enhancement of the photocurrent can be explained both by the enhancement of the electric field near Ag NPs [26], [27] and by the scattering of light by silver NPs. This field can increase the absorption of the Gr films in the visible region of the spectrum [27].

Conclusions

Films based on graphene oxide and plasmonic NPs have been synthesized. It is shown that in the presence of Ag NPs, the morphology, as well as the thickness of graphene oxide films, does not change. When Ag NPs were added, a change in the shape and position of the absorption bands and Raman spectra of graphene oxide was observed. In particular, with the addition of Ag NPs, the G band of graphene oxide is shifted to low frequencies, which may be the result of the absence of individual double bonds. At the same time, the I_D/I_G ratio did not change, as did the number of Gr layers. In the absorption spectrum of the films, along with the absorption band of graphene oxide, a shoulder was registered, which can be associated with the absorption of Ag NPs. The optical density of Gr films with plasmonic NPs is higher than without them.

Measurements of the optoelectronic characteristics showed that, in the presence of Ag NPs, an increase in the values of the photocurrent of graphene oxide is observed. The sensitivity of graphene oxide films increased by almost 20 times when plasmonic NPs were added to them. The detectivity of Gr films is equal to $1.2{\cdot}10^6$ Jones, whereas in the presence of LPR silver NPs D* increased by 25 times and is equal to $3.01{\cdot}10^7$ Jones. The enhancement of the photocurrent can be explained both by the enhancement of the electric field near the Ag NPs and by the scattering of light by silver NPs.

The results obtained can be used in the development of new photosensitive devices for optoelectronic and photocatalytic applications.

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Күміс нанобөлшектерінің графен оксиді пленкаларының оптоэлектрондық қасиеттеріне әсері

Ag нанобөлшектерінің (НБ) графен оксиді негізіндегі пленкаларының оптикалық және оптоэлектрондық қасиеттеріне әсері зерттелді. Графен оксиді құрамында Ag НБ бар пленкаларының морфологиясы мен қалыңдығы өзгермейді. Ag НБ қосқанда графен оксидінің Раман-спектрлерінің пішіні мен жұтылу жолақтарының өзгерісі байқалады. Ag НБ-нің қосылған кезде графен оксидінің G-жолағы төмен жиіліктерге ауысатыны көрсетілген, бұл жеке қос байланыстың болмауының нәтижесінде болуы мүмкін, ал Gr қабаттарының санымен қоса I_D/I_G қатынасы да өзгермеген. Пленкалардың жұтылу спектрінде графен оксидінің жұтылу спектрлерімен қатар, Ag НБ-нің жұтылуына байланысты болуы мүмкін иин тіркелді. Gr пленкаларының оптикалық тығыздығы плазмондық НБ қоспағанға қарағанда жоғары болды. Оптоэлектрондық сипаттамаларды өлшеу кезінде Ag НБ қосылған графен оксидінің фототок мәндерінің жоғарылауы байқалатынын көрсетті. Графен оксиді пленкаларының сезімталдығы оларға плазмондық НБ қосылған кезде 20 есе, ал детекторлық қабілеті 25 есе өсті. Алынған нәтижелерді оптоэлектронды және фотокаталитикалық қосымшалар үшін жаңа жарыққасезімтал жаңа құрылғыларды жасауда пайдалануға болады.

Кілт сөздер: графен оксиді, күміс нанобөлшектері, плазмон, қасиеттері, жұтылу, КШ спектрлері, оптоэлектрондық қасиеттер, фотодетекторлар.

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Влияние наночастиц серебра на оптоэлектронные свойства пленок оксида графена

Изучено влияние наночастиц (НЧ) Ag на оптические и оптоэлектронные свойства пленок на основе оксида графена. В присутствии НЧ Ag морфология, как и толщина пленок оксида графена, не изменяется. При добавлении НЧ Ag наблюдается изменение формы и положения полос поглощения и Раман-спектров оксида графена. Показано, что с добавлением НЧ Ag G-полоса оксида графена сдвигается в область низких частот, что может быть результатом отсутствия отдельных двойных связей, при этом соотношение I_D/I_G не изменилось, как и количество слоев Gr. В спектре поглощения пленок, наряду с полосой поглощения оксида графена, зарегистрировано плечо, которое может быть ассоциировано с поглощением НЧ Ag. Оптическая плотность пленок Gr с плазмонными НЧ выше, чем без них. Измерения оптоэлектронных характеристик показали, что в присутствии НЧ Ag наблюдается рост значений фототока оксида графена. Чувствительность пленок оксида графена увеличилась почти в 20 раз при добавлении в них плазмонных НЧ, а детектирующая способность — в 25 раз. Полученные результаты могут быть использованы при разработке новых светочувствительных устройств для оптоэлектронных и фотокаталитических приложений.

Ключевые слова: оксид графена, наночастицы серебра, плазмон, свойства, поглощение, спектры КР, оптоэлектронные свойства, фотодетекторы.