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Synthesis and study of photoelectrical properties of planar ensembles based on TiO_2 and graphene oxide

In this paper, planar structures of various configurations based on TiO_2 and graphene oxide are synthesized. Using SEM, it is shown that graphene oxide forms an insular film both on the surface and under the TiO_2 layer during deposition. As well as SEM images show that TiO_2 nanoparticles on the surface of graphene oxide are distributed as evenly as on the surface of FTO glass. The absorption spectra of synthesized films are a combination of the absorption curves of the original components. In this case, there is a shift of the absorption band of the planar structure nanocomposite to the longwave region. It is shown that in planar ensembles, the photoelectrochemical activity of films is higher only for the first lighting cycle. Research shows that the amount of graphene oxide affects not only the optical and photoelectrochemical properties, but also the electrical parameters. The latter, in turn, show that the resistance decreases by 1.3 times in the planar structure of graphene oxide with 30 layers. It was found that in planar structures of nanocomposite materials, the location of graphene oxide also affects the overall properties of the material. Research shows that the best indicators of photoinduced current generation are registered for the FTO/GO/TiO_2 structure. Thus, a nanocomposite material in a planar structure based on TiO_2 and graphene oxide depends on the architecture of the location and deposited volume of graphene oxide.

Keywords: semiconductors, graphene oxide, TiO_2, planar structure, SEM image, photoinduced current, impedance spectra, photocatalysis.

Introduction

Titanium dioxide (TiO_2) is one of the most affordable photocatalysts due to its physicochemical properties. This semiconductor is distinguished by its strong oxidizing ability, non-toxicity, high chemical stability, photoconversion efficiency and photostability. Currently, it is a very attractive material for photocatalysis, photovoltaics, and optoelectronics. [1–3].

Graphene and its derivatives are very popular due to their electronic, mechanical, thermal and optical characteristics [4–6]. Graphene has found application in nanoelectronics, chemical and biochemical sensing, photocells and in photocatalysis [7–9].

Currently, graphene oxide (GO) is a very promising material for the development of hybrid structures that can combine the properties of both GO and nanosized particles of metal oxide. Hydrothermal synthesis is often used to create these structures. The resulting materials have higher photoelectric, photoelectrochemical, and catalytic properties [10–13] compared to the initial semiconductor.

When used in photocatalytic cells, semiconductor nanoparticles easily form agglomerates in which the generation and transport of charge carriers to the pick-off electrodes decreases. When using graphene oxide, TiO_2 nanoparticles are uniformly distributed over the surface of graphene «sheets» and easily form chemical bonds along the folds of their folds or other defects. The result is a material with improved photocatalytic and photodetecting parameters [14].

In this paper, we propose a method for preparation of planar nanocomposite material based on films of graphene oxide and TiO_2. It is assumed that the addition of graphene oxide to the TiO_2 will improve the photoelectrochemical properties of the semiconductor, which can be used to increase the efficiency of the photocatalyst based on it.

Experiment

To prepare a material with a planar structure, single-layer graphene oxide (GO, Cheaptubes) and TiO_2 (d>21 nm, anatase, 99.7 %, Sigma Aldrich), deionized water (purified using the AquaMax water treatment system), ethanol (anhydrous) were used. The films were deposited on the surface of glass substrates coated with a FTO conductive layer (Fluorine doped tin oxide coated glass slide, ~ 7Ω / sq, Sigma Aldrich).

Graphene oxide films were prepared by airbrushing from water-isopropanol dispersion. The preparation of the GO water-isopropanol dispersion was performed as follows: 4 mg of graphene oxide was mixed with

1.8 ml of isopropanol (C_3H_8O) and 0.4 ml of deionized water. The resulting mixture was sonicated for 2 hours. For film deposition, a graphic airbrush was used, the nozzle diameter of which was equal to 0.2 mm. The resulting films were dried at 80 °C in an oven for at least 3 hours to completely remove the solvent.

TiO_2 semiconductor films were deposited on the surface of FTO substrates by spin-coating method from ethanol-based paste at a substrate rotation speed of 3000 rpm.

To create a planar structure, 2 types of samples were prepared. In the first type, the GO film was sprayed directly onto the FTO surface, and a semiconductor film was deposited over it. In the second type, thin films of graphene oxide were deposited on top of a TiO_2 film. The thickness of the graphene oxide films was different — 2 and 30 layers. The prepared samples of the first type (FTO/GO/TiO_2 structure) with 2 layers of graphene oxide are denoted as 1a, and with 30 layers as 1b. Samples of the second type (FTO/TiO_2/GO structure) with 2 layers of graphene oxide marked as 2a and with 30 layers — as 2b. Next, the obtained films were annealed in an Ar inert atmosphere at 450 °C.

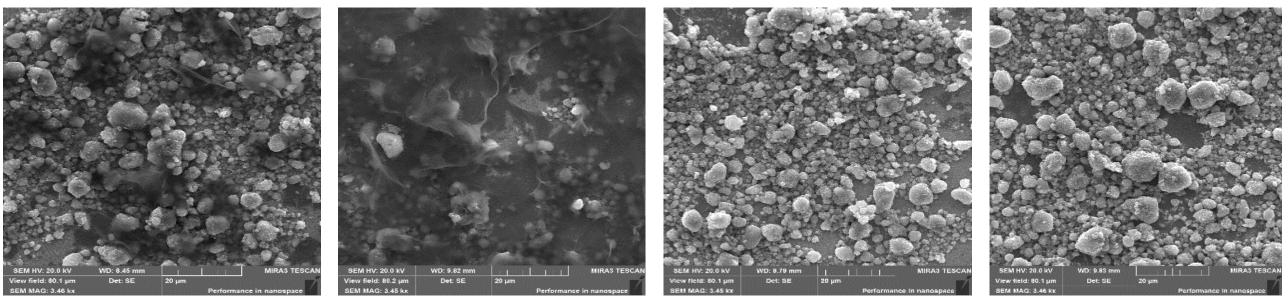
The surface morphology of the obtained composite materials was investigated using a Tescan Mira-3 (Tescan) scanning electron microscope (SEM).

The optical properties of the films were recorded using a Cary-300 spectrophotometer (Agilent). To measure the optical characteristics of the film, they were deposited on quartz substrates. To study the kinetics of transport and recombination of charge carriers, the samples were illuminated with a xenon lamp with a radiation power of 100 mW/cm^2 (Cell Tester Model#CTAAA, Photo Emission Tech. Inc., USA) in a standard two electrode cell. Z–500PRO impedance meter (Elins) was used for this purpose. The amplitude of the applied signal was 25 mV, and the frequency was varied from 1 MHz to 100 MHz. Platinum films deposited by the electrochemical method from an ethanol solution of H_2PtCl_6 onto glass substrates with a conductive layer of FTO were used as counter electrode. The electrodes were glued together. Meltonix polymer film was used as a gasket between the working and counter electrode in the cell. Iodolyte was used as the electrolyte. The area of the illuminated area was equal to 0.16 cm^2. In all samples, the electrolyte volume in the cells, as well as the thickness and area of the films were the same. The measured impedance spectra were analyzed using the EIS analyzer program. The equivalent electrical circuit of the electrochemical cell used for analysis was shown in ref. [15].

The transition photocurrent characteristics of the obtained materials were studied by recording the photocurrent in a standard three electrode photoelectrochemical cell with a quartz window on a P–30J potentiostat-galvanostat (Elins). Ag/AgCl electrode was used as a reference. The radiation source was served a diode lamp with a power of 35 mW/cm^2. The studied samples were deposited by centrifugation on the surface of substrates with FTO, which were connected to the working electrode. A platinum electrode was connected to the negative potential. The measurements were carried out in an electrolyte of 0.1 M NaOH.

Results and its discussion

During the study of the structural characteristics of the synthesized samples by using of SEM (Figure 1), it was found that in planar structures, as in samples of pure TiO_2, titanium dioxide particles are aggregated.



1a 1b 2a 2b

Figure 1. SEM image of planar structures

From SEM images of films 1a and 2a, in which the thickness of the graphene oxide films was equal to 2 layers, it can be seen that GO is deposited in the form of an island film. In the film with 30 layer of GO, graphene oxide almost completely covers the substrate. At the same time, «folds» and «wrinkles» that are formed during the deposition of graphene oxide are clearly distinguishable on the surface of TiO_2.

The data, obtained under study of optical characteristics, are shown in Figure 2. It is known that the absorption spectrum of TiO_2 appears in the UV region of the spectrum at about 380 nm. Graphene oxide also absorbs in the UV range; its absorption spectrum reaches a maximum at 230 nm. In this case, GO films are almost transparent in the wavelength range from 400 to 800 nm [16, 17].

In the planar structures of GO/TiO_2 and TiO_2/GO the absorption band of the semiconductor broadens to the visible spectral range up to 510 nm (Figure 2). It is also seen that the nanocomposite actively absorbs light in the UV region of the spectrum. Previously, it was shown in refs. [12, 18] that the semiconductor band gap changes in the nanocomposites. This contributes to a wider spectral sensitivity of nanocomposite materials, as well as improving their photoelectrochemical properties.

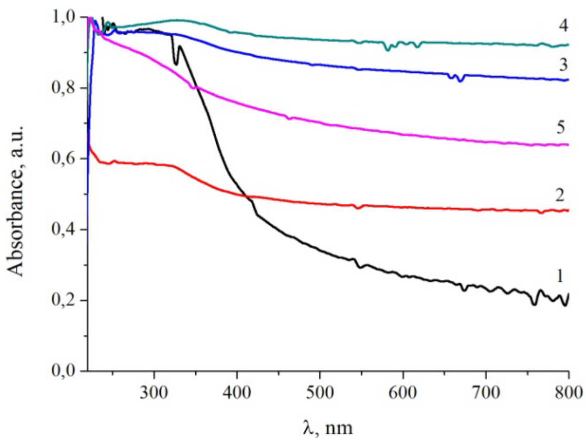
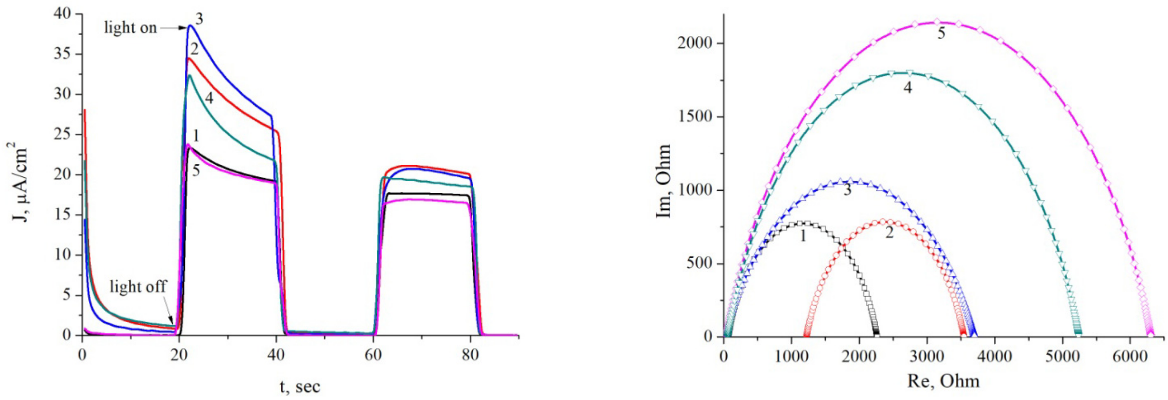


Figure 2. Normalized absorption spectra of films of: 1 — TiO_2; 2 — 1a, 3 — 1b, 4 — 2a, 5 — 2b

Next, the photoelectric characteristics of TiO_2 and planar structures were studied, with the help of which their photocatalytic activity can be estimated. The photoinduced current values was measured for 20 seconds when the light was turned on and off cyclically.

The photocurrent of a TiO_2 — based film was equal to ~23 μA (Figure 3a). When sample 1b was irradiated, the photocurrent was increased of 1.5 times. Also, a high photocurrent generation for the first switching cycle was recorded for films 1a, where the film thickness of graphene oxide was 2 layers. Thinner films generate a little less current. At the same time, for samples where graphene oxide was deposited on top of the conductive layer, the parameters were lower on 10 %.

Since the efficiency of the photocatalytic splitting of water into molecular oxygen and hydrogen will directly depend on the number of photoinduced electrons, it can be assumed that when using planar structures based on TiO_2 and graphene oxide, hydrogen generation will be higher compared to other similar nanocomposites.



a) b)

Figure 3. Transient characteristics of the photocurrent (a) and impedance spectra in the Nyquist plot (b) of films: 1 — TiO_2; 2 — 1a, 3 — 1b, 4 — 2a, 5 — 2b.

It should be noted that lower photocurrent generation for thinner graphene oxide films is related to their structure. As was shown earlier in [19], thin GO films are inhomogeneous, which leads to large values of the transport resistance of charge carriers. Nevertheless, it can be unequivocally stated that the presence of graphene oxide in the planar structure leads to an increase in the photocatalytic activity of semiconductor coatings. It is much more efficient when graphene oxide is located under a TiO_2 layer.

Further, the electrophysical characteristics of planar structures and nanocomposite material were studied. The impedance spectra in the Nyquist coordinates based on the films are presented in Figure 3b. Based on the obtained impedance spectra, the main electric transport properties of the films were calculated. Parameters, such as R_k — charge-transfer resistance related to recombination of electron, R_w — electron transport resistance in TiO_2-GO, k_{eff} — effective rate constant for recombination and τ_{eff} — effective lifetime of electrons [20] were obtained.

Figure 3b shows that the diameter of the hodograph of a TiO_2 film is smaller than that of most other films. This means that the studied samples have a smaller amount of charge transfer resistance. The addition of graphene oxide makes it possible results in lower the resistance values R_k and R_w of semiconductor samples.

Table 1 shows the values of the electrophysical parameters of the TiO_2 film and planar structures. Using the EIS — analyzer software package, R_k and R_w w are calculated, and k_{eff} — is determined by the maximum of the hodograph arc according to the formula $\omega_{max} = k_{eff}$. The film thickness was determined using a TESCAN Mira3 scanning electron microscope.

Table 1

The value of the electrophysical parameters of TiO_2 films and planar structures

Sample	k_{eff}, s^{-1}	τ_{eff}, ms	R_k, Ohm	R_w, Ohm
TiO_2	13.895	72	2194.0	69.3
1a	5,1795	193	2327,9	1221,8
1b	3,7276	268	3693,7	11,8
2a	2,6827	373	6274,8	30,8
2b	2,6827	373	5185,2	54,8

In the sample 1a, the charge transfer resistance is R_k = 2327.9 Ohms and is the smallest value among planar structures were obtained. But R_w in this film is equal to 1221.8 Ohms, which means that the resistance to electronic transport in the film is very large compared to other samples. With an increase in the number of graphene oxide layers to 30, the charge transfer resistance also increases by 1.6 times. Nevertheless, this sample characterizes the best electrophysical parameters compared to other planar structures.

When the GO film was deposited onto TiO_2surface, the resistance of both charge transfer and electron transport of such a structure were also increased. In sample 2a, R_k = 6274.8 Ohms and in 1.7 times more than in sample 1b. Also in sample 2b, the value of the charge transfer resistance is R_k = 5185.2 Ohms, which is in 1.4 times higher than the value for the more optimal sample 1b. Thus, it was shown that the architecture of a planar nanocomposite (the location of GO on the surface or under TiO_2) affects its electrophysical parameters. At the same time, improved properties show samples where GO films are deposited between TiO_2 and FTO. However, when graphene oxide is added to TiO_2 in planar structures, the electrophysical characteristics do not decreases with respect to resistance. This is due to the high resistance values of graphene oxide itself.

Conclusion

Samples based on graphene oxide and TiO_2 were prepared in the form of a planar structure and their photoelectric and electrophysical characteristics were studied. SEM studies have shown that graphene oxide forms an island film during deposition, both on the surface and under the TiO2 layer. SEM images clearly show graphene oxide sheets. Measurements of the optical characteristics of the synthesized material showed that the absorption spectrum of planar structures corresponds to the spectra of the starting components. In this case, a slight shift of the absorption band of the nanocomposite to the long-wavelength region was observed. The transient characteristics of the photocurrents of planar structures show an increase in the photoinduced current only for the first illumination cycle, and in the future the photocurrent decreases. Studies of the impedance spectra showed that the addition of graphene oxide in the form of a planar structure does not contribute to a decrease in the resistance of semiconductor films due to the high resistance value of graphene oxide itself.

The results can be used for development of photocatalytic materials for the UV and visible spectral ranges, as well as relevant in areas requiring photodegradation of organic compounds.

Acknowledgment

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TiO_2 және графен оксиді негізіндегі планарлық ансамбльдердің фотоэлектрлік қасиеттерін зерттеу және синтездеу

Мақалада TiO_2 және графен оксиді негізінде әртүрлі конфигурациялы планарлы құрылымдар синтезделген. СЭМ көмегімен графен оксиді тозаңдағанда TiO_2 қабатының астында аралдық пленканы түзеді. Сондай-ақ, графен оксиді бетінде TiO_2 нанобөлшектері FTO шыны бетінде біркелкі бөлінген. Синтезделген пленкалардың сіңіру спектрлері бастапқы компоненттердің сіңіру қисықтарының комбинациясын білдіреді. Бұл ретте жоспарлы құрылымның нанокомпозит жұту жолағының ұзын толқынды аймаққа ауысуы байқалған. Планарлық ансамбльдерде пленкалардың фотоэлектрохимиялық белсенділігі жарықтандырудың бірінші циклі үшін ғана жоғары екендігі көрсетілген. Зерттеу нәтижесі көрсеткендей, графен оксидінің саны оптикалық және фотоэлектрохимиялық қасиеттерге ғана емес, сонымен қатар электр параметрлеріне де әсер етеді. Соңғылары өз кезегінде, 30 қабатты графен оксидінің жоспарлы құрылымында 1,3 есе кедергінің азайғанын көрсетті. Нанокомпозитті материалдардың планарлы құрылымдарында графен оксидінің орналасуы да материалдың жалпы қасиеттеріне әсер ететіні анықталған. FTO/GO/TiO_2 құрылымы үшін фотоиндуцирленген ток генерациясының ең жақсы көрсеткіштері тіркелгенін көрсеткен. Осылайша, TiO_2 және графен оксиді негізіндегі планарлық құрылымдағы нанокомпозиттік материал орналасу архитектурасына және графен оксиді жағылған көлеміне байланысты.

Кілт сөздер: жартылай өткізгіштер, графен оксиді, TiO_2, планарлық құрылым, СЭМ суреті, фотоиндуцирленген ток, импеданс спектрі, фотокатализ.

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Синтез и исследование фотоэлектрических свойств планарных ансамблей на основе TiO_2 и оксида графена

В статье синтезированы планарные структуры различной конфигурации на основе TiO_2 и оксида графена. При помощи СЭМ показано, что при напылении оксид графена формирует островковую пленку как на поверхности, так и под слоем TiO_2. А также СЭМ-изображения показывают, что наночастицы TiO_2 на поверхности оксида графена распределены так же равномерно, как и на поверхности FTO стекла. Спектры поглощения синтезированных пленок представляют комбинацию кривых поглощения исходных компонентов. При этом наблюдается сдвиг полосы поглощения нанокомпозита планарной структуры в длинноволновую область. Показано, что в планарных ансамблях фотоэлектрохимическая активность пленок выше только для первого цикла освещения. По результатам исследования видно, что количество оксида графена влияет не только на оптические и фотоэлектрохимические свойства, но и на электрические параметры. Последние, в свою очередь, показывают, что происходит уменьшение сопротивления в 1,3 раза в планарной структуре оксида графена с 30-м слоем. Установлено, что в планарных структурах нанокомпозитных материалов расположение оксида графена также влияет на общие свойства материала. Определено, что для структуры FTO/GO/TiO_2 зарегистрированы наилучшие показатели генерации фотоиндуцированного тока. Таким образом, можно заключить, что нанокомпозитный материал в планарной структуре на основе TiO_2 и оксида графена зависит от архитектуры расположения и нанесенного объема оксид графена.

Ключевые слова: полупроводники, оксид графена, TiO_2, планарная структура, СЭМ-изображение, фотоиндуцированный ток, импеданс-спектры, фотокатализ.