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Preparation and study of electrophysical and optical properties of TiO_2-GO nanocomposite material

Nanocomposite material TiO_2–GO was synthesized by hydrothermal method. The formation of nanocomposite was confirmed by FTIR analysis. It is shown that the functional groups characteristic of graphene oxide partially disappear in TiO_2–GO, which indicates its partial reduction during synthesis. In addition, the appearance of a wide band below 1000 cm^{-1} also indicates the formation of bonds between TiO_2 and GO. EDS analysis showed the presence of titanium, oxygen and carbon in the powder of nanocomposite material. Raman spectra of nanocomposite contain peaks typical for both TiO_2 and graphene oxide. Measurements of the optical characteristics of the synthesized material showed that the absorption spectrum of the nanocomposite shifted in the long-wave region relative to the absorption spectrum of the original components, which may be the result of changes in the band gap of the semiconductor. Measurements of electrophysical characteristics showed that the resistance to electronic transport of nanocomposite material is much less than the value of this parameter obtained for pure TiO_2, which leads to an increase in the efficiency of the photocurrent conversion.

Keywords: titanium dioxide, graphene oxide, TiO_2-GO, nanocomposite material, impedance spectra.

Introduction

Titanium dioxide (TiO_2) occupies a special place among semiconductor materials due to its physical and optical properties, such as high melting point, chemical inertness, high efficiency of phototransformation and photostability [1–3]. Titanium dioxide with a band gap of 3.2 eV is only sensitive to light with wavelengths below 380 nm, which are in the UV range. However, it is one of the most popular photocatalysts [4] due to its high oxidation capacity and chemical stability in relation to the high acidity environment.

Semiconductor nanoparticles are aggregated, which leads to a decrease in the generation and transport of charge carriers to the counter electrodes in photocatalytic and photodetecting cells. When used with graphene, this problem can be solved. In this case, TiO_2 nanoparticles are evenly distributed in graphene and easily form chemical bonds along the folds of graphene sheets or other defects.

Graphene with sp^2 hybridization has recently been widely used in almost all branches of science due to its high mobility of charge carriers, high specific surface area and the possibility of chemical functionalization and mechanical strength. Graphene also absorbs both UV radiation and 1–2 % of light in the visible spectrum [5–8].

In this paper, a nanocomposite material based on TiO_2 and graphene oxide was synthesized. It is assumed that the addition of graphene oxide will improve the electrophysical properties of the semiconductor material, which can be used for photocatalysis and photovoltaics.

Method of experiment

Preparation of TiO_2–GO nanocomposite material by hydrothermal synthesis was carried out as follows: 10 mg of graphene oxide (GO, Cheaptubes, USA) was mixed with 30 ml of deionized water purified by Aquamax water purification system and 10 ml of ethanol in ultrasonic bath for 1 hour. Then, 1 g of TiO_2 was added to the suspension of graphene oxide and the sonication and stirring were sequentially alternated for 2 hours, for each procedure for 30 minutes, until a uniform suspension of light gray color was achieved. After that, the suspension is poured into a Teflon coated 100 ml autoclave and heated at 120 ºC during 24 hours for the synthesis of the composite. This process simultaneously restores graphene oxide (GO) to reduced graphene oxide (rGO) by «taking» the electron from ethanol and forming Ti–O–C bonds of TiO_2 and rGO. After cooling to room temperature, the suspension was filtered several times with deionized water and the product was dried at 60 ºC [9]. Under these conditions the ratio of GO to TiO_2 was equal to 1 % in nanocomposite material.

To measure the electrophysical properties of the TiO_2-GO nanocomposite material, films were prepared by the «spin-coating» method (Vacuum Spin Coater, MTI Co, USA). The finished paste was applied to the surface of a rotating substrate with a conductive layer of FTO. The substrate was rotating at a constant speed. Speed mode was varied from 500 to 4000 rpm, rotation time — 10 s. It allowed to change the thickness of the films obtained by varying the speed of rotation of the substrates. After application and drying, the film was annealed in Ar atmosphere for 2 hours. Under the same conditions, films based on pure TiO_2 paste were obtained.

The surface of morphology of the obtained nanocomposite materials was studied using a scanning electron microscope (SEM) Tescan Mira3. Also EDS of the samples was carried out on the SEM. The Confotec MR520 microscope (3D Scanning Raman Confocal Microscope, Sol Instruments) with laser excitation at a wavelength of 632.8 nm was used to record the Raman spectrum. The FTIR spectra were recorded using the Fourier spectrometer FSM 1201 and the electronic absorption spectra were recorded using the Cary-300 spectrophotometer (Agilent). To measure the absorption of nanocomposite films, the samples were deposited on quartz substrates.

The method of impedance spectroscopy was used to study the kinetics of transport and recombination of charge carriers. Measurement of impedance spectra was carried out under illumination of samples by xenon lamp light with radiation power of 100 mV/cm^2 (Cell Tester Model # CTAAA, Photo Emission Tech. Inc., USA) on Z–500PRO impedancemeter (Elins, Russia). The amplitude of the applied signal was 25 mV, and the frequency was ranged from 1 MHz to 100 mHz.

Platinum films deposited by an electrochemical method from an ethanol solution of H_2PtCl_6 on glass substrates with a conductive layer of FTO were used as a counter electrode. The electrodes were glued together. The 25 μm thick polymer film Meltonix (Solaronix, Switzerland) served as a gasket between the working electrode and the counter electrode in the cell. The electrolyte used was Iodolyte H30 (Solaronix, Switzerland).

Results and its discussion

Figure 1 shows SEM images of neat materials and nanocomposites. The figure shows that nanoparticles aggregated in the bulk sample of titanium dioxide. However, in the pictures a small number of micropores can be distinguished. Graphene oxide has a layered structure, which is formed by separate sheets. In the synthesis of nanocomposite material, titanium dioxide particles tend to be less aggregated. In the picture the interparticle pores can be distinguished.

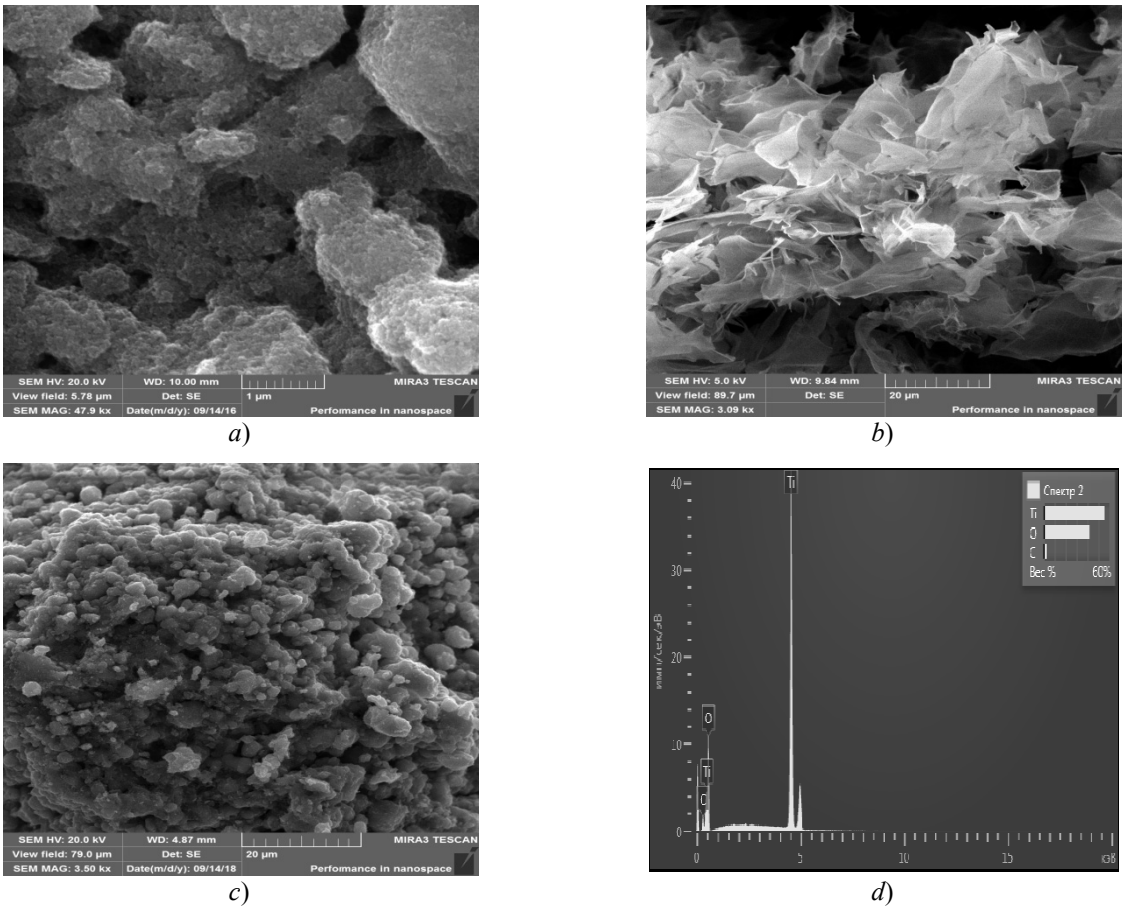
The presence of graphene oxide in the synthesized sample can be confirmed both visually and according to the EDS analysis (Fig. 1*d*). Figure 1*d* shows that most part of the studied sample is represented by atoms of titanium and oxygen. The carbon content of the sample is low, due to the low GO concentration relative to TiO_2 (1:100) in the sample.

The measured Raman spectra are shown in Figure 2. Ttitanium dioxide with anatase structure has six combination-active peaks in the vibrational spectrum (Fig. 2*a*): three Eg peaks centered at about 149, 183 and 630 cm^{-1} (Eg(1), Eg(2) and Eg(3) peaks respectively), and two B1g peaks at 397 and 506 cm^{-1} (denoted by B1g(1) and B1g(2)), and A1g peaks at 481 cm^{-1} [10].

In the Raman spectra of graphene oxide several bands can be clearly distinguished: D-band, which characterizes the degree of defectiveness of graphene ($\bar{\nu}$ = 1350 cm^{-1}), G-band, which characterizes the graphene in-plane vibrational modes of sp^2 hybridization — this parameter displays the degree of crystallization of the material ($\bar{\nu}$ = 1586 cm^{-1}) and 2D band, which indicates the degree of graphitization and displays the number of graphene layers ($\bar{\nu}$ = 2700 см$^{-1}$) [11].

Both TiO_2 and graphene oxide peaks are present in the Raman spectra of the synthesized material. This confirms by the data obtained by EDS analysis of the samples.

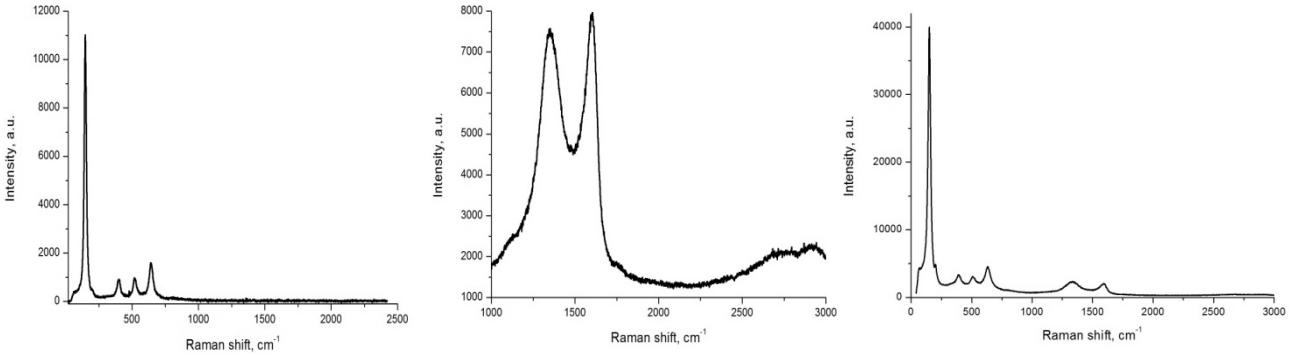
Figure 3 shows the FTIR spectra for pure TiO_2 and graphene oxide powders, as well as for the TiO_2–GO nanocomposite material. FTIR spectra of graphene oxide shows the oscillations of bonds characteristic of chemical groups: C-O (1095 cm^{-1}), C-O-C (1261 cm^{-1}), C-OH (1454 cm^{-1}), C=O (1728 cm^{-1}). The intense peak at 3000–3500 cm^{-1} (3441 cm^{-1}) characterizes fluctuations of O-H groups in the composition of C-OH and water. The peak at 1628 cm^{-1} is called skeletal vibration of graphene oxide [12]. Figure 3 shows that the functional groups characteristic for graphene oxide are absent.



a) *b*) *c*) *d*)

a — TiO_2; *b* — graphene oxide; *c* — TiO_2–GO

Figure 1. SEM images of powders



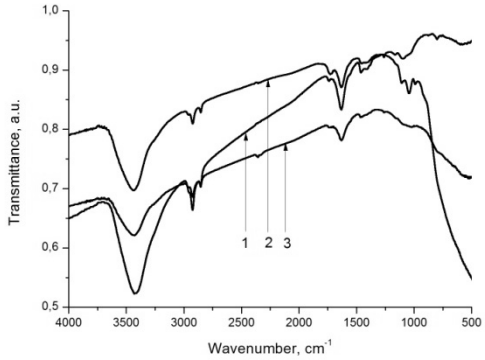
a) *b*) *c*)

a — TiO_2; *b* — graphene oxide; *c* — TiO_2–GO

Figure 2. Raman spectra of powders

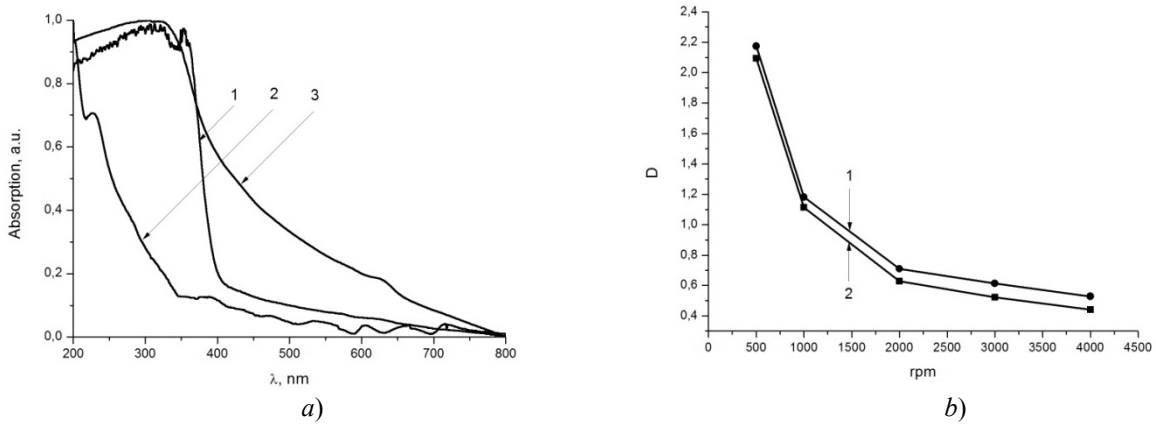
The pure powder TiO_2 has a low-frequency mode of about 500 cm^{-1}, which corresponds to the vibration of Ti-O-Ti bonds. Also, as can be seen from the spectrum, at 3440 cm^{-1} there is an intense band, which indicates that on the surface of titanium dioxide particles adsorbed OH group.

The nanocomposite material TiO_2–GO exhibits absorption below 1000 cm^{-1}. This peak can be considered as a combination of oscillations of Ti-O-Ti and Ti-O-C bonds (about 792 cm^{-1}). The presence of Ti-O-C bonds indicates that during hydrothermal reduction graphene oxide with residual functional groups of carboxylic acid strongly interacts with surface hydroxyl groups of TiO_2 nanoparticles and, ultimately, a TiO_2–GO nanocomposite material is formed.



a — TiO_2; *b* — graphene oxide; *c* — TiO_2–GO

Figure 3. FTIR spectra of powders



a) *b*)

a) *1* — TiO_2; *2* — graphene oxide; *3* — TiO_2–GO; *b*) at *1* — 390 nm; *2* — 700 nm

Figure 4. Absorption spectra (*a*) and the dependence of the optical density of nanocomposite films on the substrate rotation speed (*b*)

As is known, the edge of the TiO_2 absorption band appears in the UV region of the spectrum about 380 nm. Graphene oxide also absorbs in the UV region, the maximum of its absorption spectrum is 230 nm. GO films are practically transparent in the wavelength range from 400 to 800 nm [8, 13]. Figure 4*a* shows that the TiO_2–GO nanocomposite actively absorbs light in the UV region of the spectrum. Along with this, there is a broadening of the absorption band in the visible range of the spectrum. As shown in [14], this is due to the fact that nanocomposite materials shift the edge of the band gap of the material in the long-wavelength region of the spectrum.

Figure 4(*b*) shows the dependence of the optical density of TiO_2–GO nanocomposite films on the substrate rotation speed. As can be seen from the figure, the increase in speed leads to a decrease in the optical density of the samples, which indicates a decrease in the thickness of the films.

Next, the electrophysical characteristics of the material of the nanocomposite of TiO_2–GO and pure TiO_2 were studied. To obtain an equivalent circuit, the data of the measured impedance spectra were processed in the EIS analyzer program. The resulting equivalent electrical circuit of the electrochemical cell is shown in Figure 5 [15].

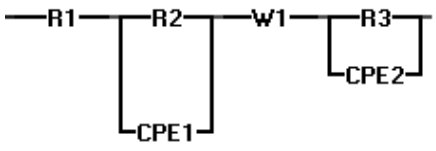
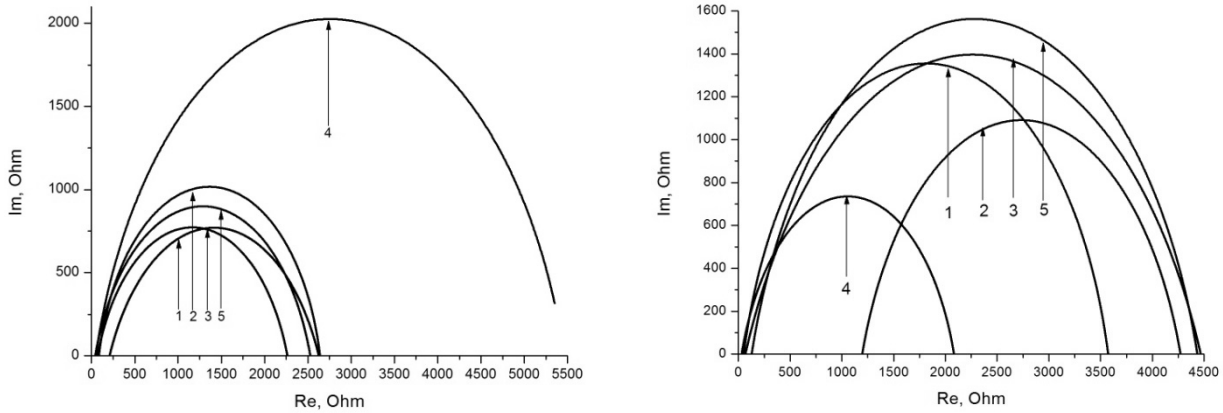


Figure 5. Equivalent electric diagram

On the basis of the obtained data (Fig. 6) the basic electrotransport properties of films were calculated, where: k_{eff} — effective rate constant for recombination, $\tau_{eff.}$ — effective lifetime of the electron, electron transport resistance in the film of titanium dioxide is R_w, charge-transfer resistance R_k ($R_k = R_{w\max} - R_{w\min}$), related to recombination of electron.



a) *b*)

a) TiO_2; *b*) TiO_2-GO: *1* — 500 rpm; *2* — 1000 rpm; *3* — 2000 rpm; *4* — 3000 rpm; *5* — 4000 rpm

Figure 6. Impedance of spectra

Table 1

Values of electrophysical parameters of TiO_2 films

Film speed	k_{eff}, s^{-1}	τ_{eff}, s	R_k, Ohm	R_W, Ohm
500 rpm	10	0.1	2417.4	208.3
1000 rpm	13.895	0.072	2554.5	84.9
2000 rpm	13.895	0.072	2194.0	69.3
3000 rpm	5.1795	0.193	5411.7	48.2
4000 rpm	26.822	0.037	2485.5	42.3

From Table 1 it is seen that the best electro transport and conducting properties were recorded for TiO_2 film deposited at a speed of 2000 rpm. For this sample, there is a minimum resistance value of the electro transport 2194 Ohm. The maximum value of the resistance of electro transport are films deposited at a speed of 3000 rpm.

Table 2

Values of electrophysical parameters of TiO_2–GO films

Film speed	k_{eff}, s^{-1}	τ_{eff}, s	R_k, Ohm	R_W, Ohm
500 rpm	10	0.1	3521.5	48.4
1000 rpm	26.822	0.037	3075.9	1196
2000 rpm	7.1969	0.139	4400.7	66.9
3000 rpm	51.767	0.02	2052.9	30.5
4000 rpm	10	0.1	4307.2	127.5

Table 2 shows the electrophysical parameters of the TiO_2-GO nanocomposite material. As can be seen from Table 2, that in films deposited at a rotation speed of 3000 rpm, the resistance of electronic transport is equal to R_k = 2052.9 Ohm, which is the minimum value compared to other samples. The minimum value of the resistance of electronic transport when measuring the impedance means that the films have large values of electrical conductivity, since the resistance is inversely proportional to the conductivity. R_w — in the film TiO_2-GO 3000 rpm is 30.5 Ohms and shows that in the nanocomposite material resistance to electronic transport is negligible. And in the sample applied at a speed of 1000 rpm, R_w is equal to 1196 Ohm, which is

much more than the above value. This suggests that electronic transport in thick films is carried out with low efficiency.

Effective lifetime of the electron ($\tau_{eff.}$) in a sample of 2000 rpm is more than in the other samples. For films deposited at a speed of 4000 rpm, the electrophysical parameters are close in value to that, obtained at 2000 rpm. Studies have shown that the best mode for deposition of TiO_2-GO films is the rotation speed of 3000 rpm.

Thus, studies have shown that hydrothermal synthesis forms a bond between the particles of TiO_2 and graphene oxide sheets, which indicates the production of nanocomposite material. This was confirmed by the EDS analysis data on the presence of titanium, oxygen and carbon in the powder of nanocomposite material. The Raman spectra of the nanocomposite show peaks characteristic of both TiO_2 and graphene oxide. According to the FTIR spectra in TiO_2–GO functional groups characteristic of graphene oxide partially disappear, which confirms its partial recovery during synthesis. In addition, the appearance of a wide band below 1000 cm^{-1} indicates the formation of a connection between TiO_2 and GO.

Measurements of the optical characteristics of the synthesized material have shown that the absorption spectrum of the TiO_2–GO nanocomposite is shifted to the long-wave region relative to the absorption spectrum of the initial components, which may be the result of changes in the band gap of the semiconductor.

Measurements of the electrophysical characteristics of the nanocomposite material showed that the resistance to electronic transport is much less than in pure TiO_2, which leads to an increase in the efficiency of the photocurrent conversion.

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А.Ж. Жумабеков, Н.Х. Ибраев, Е.В. Селиверстова, Г.Б. Камалова

TiO_2-GO нанокомпозиттік материалды алу мен оның электрфизикалық және оптикалық қасиеттерін зерттеу

TiO_2–GO нанокомпозиттік материалы гидротермалды әдіспен синтезделді. Нанокомпозиттің құрылуы ИҚ-талдау мәліметтері арқылы расталды. TiO_2–GO нанокомпозитінде графен оксидіне тән функционалды топтар жарым-жартылай жоғалады, яғни синтез барысында оның жартылай қалпына келетіні көрсетілген. Сонымен қатар 1000 $см^{-1}$ төмен кең жолақтың пайда болуы да, TiO_2 және GO арасында байланыстың құрылуын дәлелдейді. ЭДС талдау нанокомпозитті материалдың ұнтағында титанның, көміртектің және оттегінің бар болуын көрсетті. Синтезделген материалдың оптикалық сипаттамаларының өлшеулері нанокомпозиттің жұтылу спектрі, бастапқы компоненттердің жұтылу спектрлеріне қарағанда, ұзынтолқынды аймаққа қарай жылжығанын көрсетті, яғни оның нәтижесі жартылайөткізгіштің тыйым салу зонасының өзгеруі болуы мүмкін. Электрфизикалық сипаттамаларының өлшеулері кезінде нанокомпозиттік материалдың электрон тасымалдануы кедергісі таза TiO_2 мәндерімен салыстырғанда көп есе төмендігін көрсетті және фототокты түрлендіруде тиімділігін жоғарылатуға әкеліп соқтырады.

Кілт сөздер: титан диоксиді, графен оксиді, TiO_2–GO, нанокомпозиттік материал, импеданс спектрі.

А.Ж. Жумабеков, Н.Х. Ибраев, Е.В. Селиверстова, Г.Б. Камалова

Получение и исследование электрофизических и оптических свойств нанокомпозитного материала TiO_2–GO

Гидротермальным методом синтезирован нанокомпозитный материал TiO_2–GO. Образование нанокомпозита было подтверждено данными ИК-анализа. Показано, что в TiO_2–GO частично исчезают функциональные группы, характерные для оксида графена, что свидетельствует о его частичном восстановлении в ходе синтеза. Кроме того, появление широкой полосы ниже 1000 $см^{-1}$ также свидетельствует о формировании связи между TiO_2 и GO. ЭДС анализ показал наличие титана, кислорода и углерода в порошке нанокомпозитного материала. В Раман спектрах нанокомпозита имеются пики, характерные как для TiO_2, так и оксида графена. Измерения оптических характеристик синтезированного материала показали, что спектр поглощения нанокомпозита сдвинут в длинноволновую область относительно спектра поглощения исходных компонентов, что может являться результатом изменения ширины запрещенной зоны полупроводника. Измерения электрофизических характеристик показали, что сопротивление электронному транспорту нанокомпозитного материала намного меньше значения этого параметра, полученного для чистого TiO_2, что приводит к повышению эффективности преобразования фототока.

Ключевые слова: диоксид титана, оксид графена, TiO_2–GO, нанокомпозитный материал, импеданс спектры.