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ФИЗИКА КОНДЕНСИРОВАННОГО СОСТОЯНИЯ
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Article

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A. Zhumabekov*, A. Kassanova, N. Ispulov, K. Dossumbekov,
Zh. Ospanova, T. Dossanov, A. Kurmanov

Toraighyrov University, Pavlodar, Kazakhstan
**Corresponding author's e-mail: almar89-89@mail.ru*

High responsivity UV detector based on TiO_2-rGO nanocomposite material

The influence of reduced graphene oxide and the optoelectronic characterictics of a nanocomposites based on rGO and TiO_2 were studied. Surface morphology and Raman spectra of nanocomposite materials indicate the presence of initial components. It has been illustrated that during hydrothermal synthesis further reduction of rGO occurs, i.e. the variety of oxygen-containing groups decreases. Studies of current-voltage characteristics have displayed the availability of rGO in the nanocomposite leads to an increase in the photo induced current to more than 40 μA. Next, the photoresponsivity of the samples was determined, which is three orders of value higher than pure titanium dioxide for nano-composite material. And the detectivity also increased 9 times. This parameter allows you to identify the performance of the device. In this regard, the UV detector based on nanocomposite has a higher performance. Studies also show a decrease in reaction time to light irradiation. When irradiated, the nanocomposite material reacts to light three orders of magnitude faster than TiO_2.

Keywords: graphene oxide, titanium dioxide, Raman spectra, optoelectronic properties, UV detectors.

Introduction

Photodetectors originated as incident light sensors, which were mainly used to convert the energy of a falling photon into an electrical signal. Typically, the sensing capacity of incident radiation can be significantly assessed by measuring the current or voltage signal generated in the device. Therefore, there is great interest in developing photodetectors. So far, many researchers have reported various photodetector mechanisms included in the ultraviolet, visible and infrared regions. Therefore, it is necessary to develop a strategic device architecture using various composite materials to improve the perception of incident light. Therefore, achieving excellent photoresponsibility and photoresponsivity mechanism of a photodetector is primarily due to photoconductive, photoreflective and photoelectric effects.

Due to their improved physical and chemical properties, nanostructures have become attractive materials in the area of nanoelectronics, energy, optoelectronics, photocatalysis, sensors, drug delivery, biomedicine, lasers, and flexible technologies [1–3]. In particular, photodetector technology is practically applied in the ultraviolet region for ozone detection, pollution detection, gas sensors and flame detection; in the visible region for energy, fiber optic communications, video imaging and artificial vision, and infrared (IR) for biomedical imaging, defence, space telescopes and meteorology.

Wide bandgap metal oxide materials (ZnO, SnO_2, Ga_2O_3, WO_3 and TiO_2) provide outstanding processing approaches such as ease of fabrication, scalability, crystal orientation control, uniformity and reproducibility in the UV detector community. Thus, all the above features demonstrate that metal oxide semiconductors can be widely used in high-responsivity UV photodetectors.

In the last decade, works have been appeared where multicomponent and hybrid materials based on graphene and TiO_2 nanoparticles [4–6]. Materials received in these works mostly focus on creating TiO_2 nanocrystals with the desired size and morphology, followed by their modification and applying on the surface of graphene sheets. However, these hybrid materials have disadvantages. Their size is too small to be easily agglomerated. Moreover, during the process of photodecomposition of organic compounds, the effective surface area of TiO_2 and graphene of such a hybrid material can considerably decrease.

Titanium dioxide (TiO_2) is one of the most researched semiconductors due to its high potential of application in photocatalysis, photovoltaic cells and gas sensors. Titanium dioxide, with a bandgap of 3.2 eV, is responsivity to light with wavelengths below 380 nm. This allows it to be used for the manufacture of photodetectors for the UV-A range. TiO_2 with a Schottky barrier have high-speed UV detection, but have low photoresponsivity. This limits its use in UV detection. At the same time, oxygen vacancies in TiO_2 can lead to strong tunneling of carriers, this can increase the dark current. Thus, the properties of TiO_2 with excellent structural transformation and non-stoichiometric phase transitions ensure its importance in optoelectronic sensors and imaging systems [7–11].

Recently, graphene based photo-electric devices have drawn the attentions because of its superior optical and electrical properties [12]. Graphene has an almost flat absorption to the specific optical spectrum, and has ballistic electronic transport and ultrahigh carrier mobility, which may lower the recombination possibility of electrons and holes [13, 14]. Those properties make graphene an ideal material for photodetecting devices when combining it with other photoresponsivity responsivity materials.

One of the most important graphene derivatives is graphene oxide, an excellent carbon material with a high specific surface area, good dispersion and a surface rich in functional groups. Go contains a large number of oxygen-containing functional groups (hydroxyl, epoxy, carbonyl and carboxyl) on its basal plane and edges; these groups allow combining GO with other modified nanomaterials and provide ample opportunities for creating hybrid nanocomposites based on GO [15–17].

In addition, it is believed that the combination of TiO_2 and graphene oxide GO has synergistic effects and improves the photodegradation of organic compounds in both gaseous and aqueous media. Meanwhile, in [18] it was shown that the reduced graphene oxide (rGO) has a higher photocatalytic activity and electrical conductivity compared to graphene oxide.

In this work, an ultraviolet detector of a nanocomposite material based on rGO and TiO_2 was obtained. It is expected that the addition of rGO and TiO_2 in a complex will improve the optoelectronic characteristics of the detector, since their use has led to an increase in the effectiveness of photocatalytic properties [19].

Experimental

Preparation of nanocomposite materials was synthesized by the hydrothermal method according to the methods of work [19, 20]. The preparation were carried out on the basis of rGO (Cheaptubes, USA), TiO_2 (Sigma Aldrich), deionized water and ethanol. The concentration of rGO in the resulting nanocomposite material is 10%, since studies have shown that at this concentration the materials have highly efficient catalytic activity [19].

All reagents were analytically pure and used without further purification.

The surface morphology of the resulting composite materials was examined using a JEM-2100F transmission electron microscope with an accelerating voltage of 120 kV. To record Raman spectra, a Confotec MR520 microscope (Sol Instruments) with laser excitation at a wavelength of 632.8 nm was used. TiO_2 or TiO_2-rGO nanocomposite films were prepared from a paste obtained by constantly mixing $TiO_2$of 150 mg and TiO_2-rGO with 1 mL of ethanol for 24 hours.

The finished paste was applied to the surface of the substrates using the “spin-coating” method at a rotation speed of 2000 rpm. After application, the film was annealed in an argon atmosphere for 2 hours at a temperature of 450 ℃.

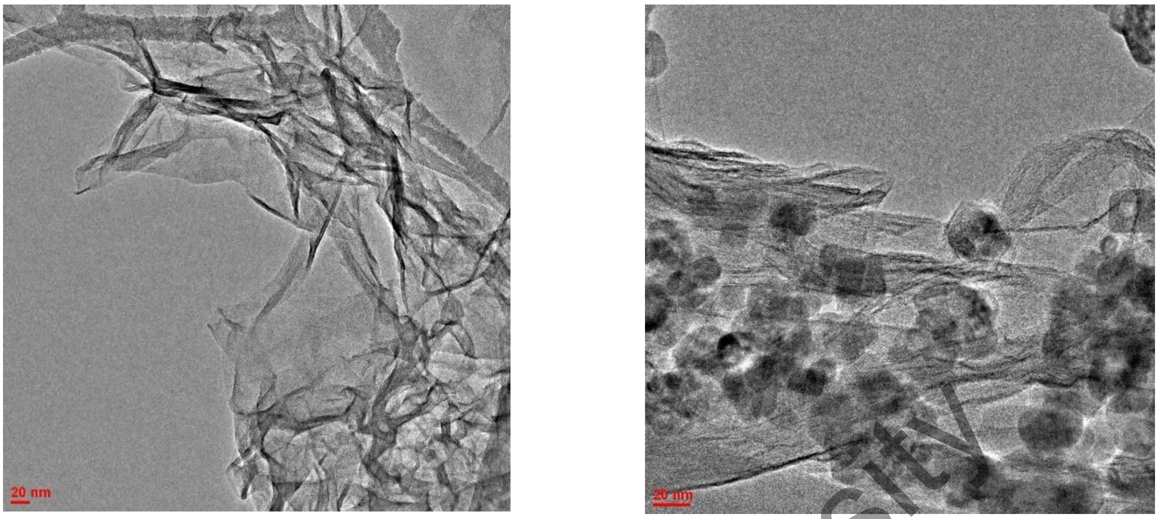
The photodetector was assembled on glass with a conducting layer of fluorinated tin oxide (FTO, Sigma Aldrich). Interdigitated tracks were cut on the surface substrates using a laser scriber BLS0503MM (Bodor) [21].

Measurements of the current-voltage characteristics (CVC) of the prepared samples were carried out using a potentiostat-galvanostat Elins P-40X (Elins) when the samples were irradiated with light from a xenon lamp with a power of 35 mW/ cm^2.

To study the response time of the samples, we used a setup and a pulsed laser LQ215 (Solar) with a third harmonic generator with 355 nm and a pulse duration of 7 ns [21].

Results and Discussion

A TEM study of the structure of prepared films showed that when rGO is applied, an island film is formed (Fig. 1).

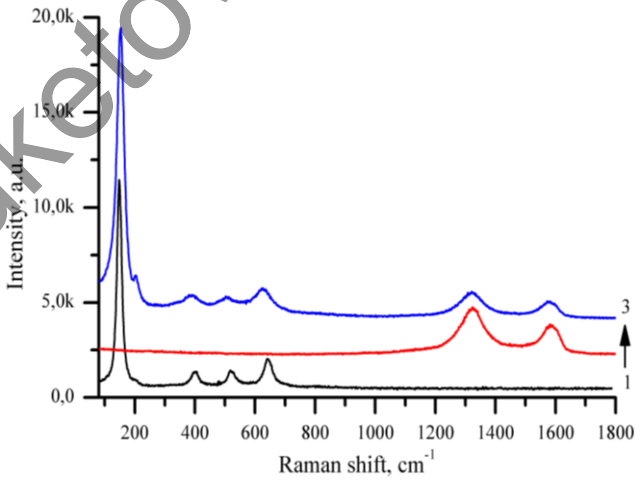


a) *b*)

Figure 1. TEM images of rGO (*a*) and TiO_2-rGO (*b*) powders

TEM images (Fig. 1) show rGO sheets and TiO_2 particles dispersed on a surface of individual rGO sheets. In this case, a slight agglomeration of TiO_2 particles is also observed. Figure 1b shows larger flakes of thin translucent rGO enveloping TiO_2 particles.

TEM studies demonstrate that reduced graphene oxide sheets are dispersed throughout the synthesized composites. This can promote the formation of a conductive network between TiO_2 particles and more efficient injection of photogenerated electrons into graphene sheets, ensuring their further transfer to FTO layer and recording.



1 — TiO_2; *2* — rGO; *3* — TiO_2–rGO

Figure 2. Raman shift of samples

Raman spectra were recorded to identify the materials. According to the Raman spectra, the nanocomposite material contains TiO_2 and rGO peaks. Titanium dioxide of the anatase structure has six Raman-active peaks in the vibrational spectrum [19, 22]. The spectrum of reduced graphene oxide contains two characteristic bands: D- and G-bands (Table 1).

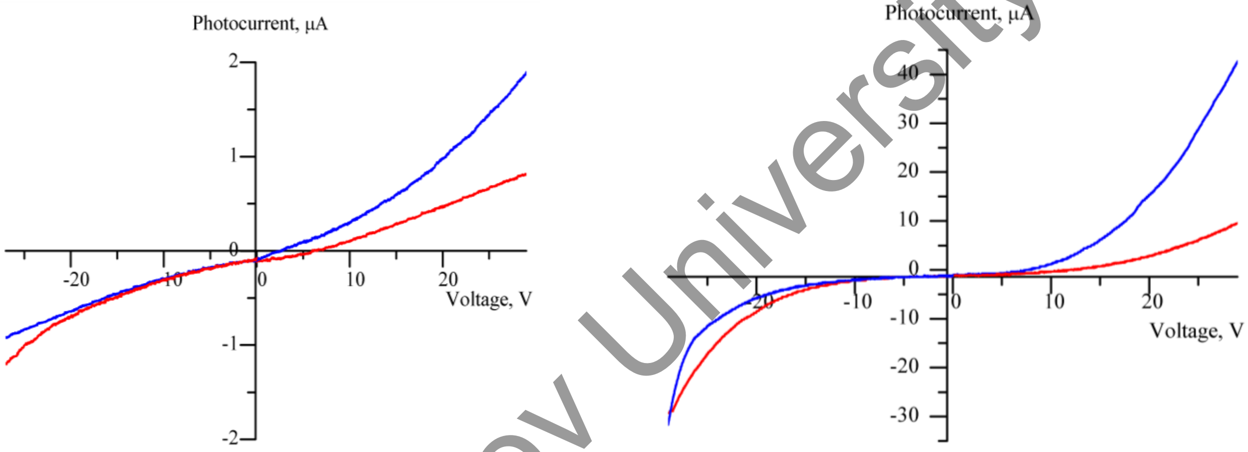
Table 1

Position and intensity of the RC shift

Sample	D, cm^{-1}	I, o.e.	G, cm^{-1}	I, o.e.	I_D/I_G
rGO	1326,83	2708	1582,79	1789	1,51
TiO_2-rGO	1321,22	1584	1571,97	1079	1,47

A decrease in the I_D/I_G intensity ratio in the nanocomposite material indicates the process of further reduction of graphene oxide during synthesis, where the formation of sp^2 carbon domains and a decrease in the amount of oxygen-containing groups can occur [23].

The main parameters for determining an ultraviolet detector are current-voltage characteristics (volt-ampere characteristics), with the help of which light and dark photocurrents are found, as well as responsivity and detectability. Figure 3 shows the CVC of light and dark photo-induced current for TiO_2 and TiO_2-rGO. The CVC of the samples were measured at a voltage of +30 V and at –30 V. The dependence of current on voltage has a nonlinear form. At the same time, even without illumination of the samples, so-called dark currents are recorded. The values of the generated photocurrent I_{ph} of the detector, shown in Table 2, were assessed from the difference in light and dark values.



TiO_2 TiO_2-rGO

Figure 3. CVC of samples: blue — light, red — dark

The maximum photocurrent value was recorded in the TiO_2-rGO nanocomposite material, which is 46.83 μA (at +30 V), and the current is 29.76 μA at –30 V. It is also clear from Figure 3 that at +8V there is an intense increase photocurrent compared to dark current. This shows the response of the samples to irradiation. The difference between light and dark current is equal to the background photocurrent. The figure shows the current-voltage characteristics for pure TiO_2, where upon irradiation the photocurrent is only 1.9 μA, and the dark current is only 0.8 μA. Table 2 shows that the background current at +30V voltage in TiO_2-rGO is 36 times higher than in TiO_2. And at –30V this value only increases by almost 2 times.

The photoresponsivity of the detector is determined by the formula:

$$R = \frac{I_{ph}}{P}, \tag{1}$$

where P is the incident radiation power.

Table 2 shows, it is clear that the responsivity of TiO_2-rGO nanocomposite films has increased by almost three orders of magnitude. Next, the specific detection ability of the prepared samples D* was estimated, which determines the ability of the device to detect weak light signals and can be determined from expression (1) [24, 25]:

$$D^* = \frac{R\sqrt{A}}{\sqrt{2 \cdot e \cdot I_{dark}}}, \tag{2}$$

where R is the responsivity of the films, A is the illuminated area of the sample, e is the electron charge modulo, I_{dark} is the value of the dark current at +30 V.

Table 2

Optoelectronic characteristics UV detectors based on TiO_2 and nanocomposite TiO_2-rGO

Sample	I_{ph}, μA+30 V	I_{ph}, μA–30 V	R, A/W	D^*, Jones	τ_1, s	τ_2, s
TiO_2	1.10	2,98	$31.4\cdot10^{-6}$	$6.03\cdot10^{7}$	$17\cdot10^{-3}$	3,3
TiO_2-rGO	36.1	4,03	$1.03\cdot10^{-3}$	$55{,}9\cdot10^{7}$	$7\cdot10^{-6}$	$0{,}31\cdot10^{-3}$

According to the calculations that the specific detection ability of TiO_2 films is $6.03\cdot10^7$ Jones, while in the presence of rGO D* increased to $55.9\cdot10^7$ Jones. This can be explained by the fact that the responsivity of pure TiO2 films has a very low value. Table 2 shows the rise and fall times of the samples. The rise time for TiO_2-rGO is three orders of magnitude longer than that for TiO_2. Thus, the nanocomposite material reacts faster to the incident light. However, the decay time in the nanocomposite material also passes faster and is equal to 0.31 ms.

Thus, the optoelectronic characteristics of a UV detector based on a nanocomposite material are improved by the addition of reduced graphene oxide.

Conclusions

Thus, a nanocomposite material based on rGO and TiO_2 was obtained using a hydrothermal synthesis method. The surface morphology of the nanocomposite is shown and the rGO sheets and TiO_2 nanoparticles are clearly visible. The Raman spectrum also confirms the presence of initial components in the nanocomposite material. The intensity ratio shows that further reduction of rGO occurs in the nanocomposite material. Studies of current-voltage characteristics have shown that in the nanocomposite material the background photocurrent is 36 μA, and in pure TiO_2 it is only 1.1 μA. Accordingly, the responsivity of the nanocomposite UV detector is three orders of magnitude greater and is equal to 1 mA, whereas for TiO_2 it is 31 μA. The detectability also shows the best results for TiO_2-rGO. Studies of the timing characteristics of the nanocomposite material show rise and fall reaction times of 7 μs and 0.31 ms, respectively.

Thus, the results obtained show that the optoelectronic characteristics of the UV detector of the TiO_2-rGO nanocomposite material are much higher than those of pure TiO_2.

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А. Жумабеков, А. Қасанова, Н. Испулов, К. Досумбеков,
Ж. Оспанова, Т. Досанов, А. Құрманов

TiO_2-rGO нанокомпозиті негізіндегі жоғарысезімтал ультракүлгін детектор

Мақалада титан диоксиді мен rGO негізіндегі нанокомпозиттік материалдың оптоэлектрондық қасиеттеріне қайта құрылған графен оксидінің әсері зерттелген. Нанокомпозиттік материалдардың бетінің морфологиясы және рамандық спектрлері бастапқы компоненттердің болуын көрсетеді. Гидротермалдық синтез кезінде rGO одан әрі қайта құрылады, яғни оттегі бар топтардың саны азаятындығы көрсетілген. Вольт-ампер сипаттамаларының зерттеуі бойынша нанокомпозитте rGO-ның болуы фотоиндукцияланған токтың 40 мкА-дан жоғары мәнге әкелетінін көрсетті. Осыдан нанокомпозиттік материал үшін таза титан диоксидімен салыстырғанда үш ондықтан артық асатын үлгілердің сезімталдығы анықталды. Ал детекторлау қабілеті де 9 есе өсті. Бұл параметр құрылғының өнімділігін анықтауға мүмкіндік береді. Осыған байланысты нанокомпозит негізіндегі ультракүлгін детектордың өнімділігі жоғары. Сондай-ақ, зерттеулер жарық сәулеленуінде реакция уақытының азаюын көрсетеді. Сәулеленген кезде нанокомпозиттік материал TiO_2-ге қарағанда үш реттік шамадағы жарыққа тез әрекет етеді. Алынған нәтижелерді оптоэлектрондық және фотокаталитикалық қосымшаларға арналған жарыққа сезімтал жаңа құрылғыларды жасауда қолдануға болады.

Кілт сөздер: графен оксиді, титан диоксиді, КШ спектрі, оптоэлектрондық қасиеттері, ультракүлгін детекторы.

А. Жумабеков, А. Касанова, Н. Испулов, К. Досумбеков,
Ж. Оспанова, Т. Досанов, А. Курманов

Высокочувствительный УФ детектор на основе нанокомпозита TiO_2–rGO

Изучено влияние восстановленного оксида графена на оптоэлектронные свойства нанокомпозитного материала на основе диоксида титана и rGO. Морфология поверхности и Раман-спектры нанокомпозитных материалов показывают наличие исходных компонентов. Показано, что при гидротермальном синтезе происходит дальнейшее восстановление rGO, то есть уменьшается количество кислородсодержащих групп. Исследования вольт-амперных характеристик показали, что наличие rGO в нанокомпозите приводит к увеличению фотоиндуцированного тока к более 40 мкА. Отсюда была определена чувствительность образцов, которая для нанокомпозитного материала превысила уровень на три порядка по сравнению с чистым диоксидом титана. А детектирующая способность также увеличилась в 9 раз. Данный параметр позволяет выявить производительность устройства. В связи с этим УФ детектор на основе нанокомпозита обладает более высокой производительностью. Также исследования показывают уменьшение времени реакции на облучение светом. При облучении нанокомпозитный материал реагирует на свет на три порядка быстрее, чем TiO_2. Полученные результаты могут быть использованы при разработке новых светочувствительных устройств для оптоэлектронных и фотокаталитических приложений.

Ключевые слова: оксид графена, диоксид титана, спектр КР, оптоэлектронные характеристики, УФ детектор.

Information about authors

Zhumabekov, Almar — PhD, Associate Professor, Computer Science Faculty, Toraighyrov University, Pavlodar, Kazakhstan; e-mail: almar89-89@mail.ru; ORCID ID https://orcid.org/0000-0003-2360-3747

Kassanova, Assiya — PhD, Assoc. Professor, Department of Chemistry and Chemical Technologies, Toraighyrov University, Pavlodar, Kazakhstan; asiyakass@mail.ru; ORCID ID https://orcid.org/0000-0002-9563-5521

Ispulov, Nurlybek — Candidate of physical and mathematical sciences, Professor, Computer Science Faculty, Toraighyrov University, Pavlodar, Kazakhstan; nurlybek_79@mail.ru, https://orcid.org/0000-0003-4703-1413

Dossumbekov, Kairat — Master, Senior teacher, Computer Science Faculty, Toraighyrov University, Pavlodar, Kazakhstan; kairat_83@inbox.ru; ORCID ID https://orcid.org/0000-0002-9695-8154

Ospanova, Zhulduz — PhD student, Toraighyrov University, Pavlodar, Kazakhstan; zhulduz-ospan@mail.ru

Dossanov, Talgat — Candidate of physical and mathematical sciences, Computer Science Faculty, Toraighyrov University, Pavlodar, Kazakhstan; dosts81@mail.ru

Kurmanov, Almas — Senior teacher, Master, Computer Science Faculty, Toraighyrov University, Pavlodar, Kazakhstan; almaskurmanov@mail.ru