Торайғыров университетінің
ҒЫЛЫМИ ЖУРНАЛ

НАУЧНЫЙ ЖУРНАЛ
Торайгыров университета

ТОРАЙҒЫРОВ УНИВЕРСИТЕТІНІҢ ХАБАРШЫСЫ

Физика, математика және компьютерлік ғылымдар сериясы

1997 жылдан бастап шығады

ВЕСТНИК ТОРАЙГЫРОВ УНИВЕРСИТЕТА

Серия: Физика, математика и компьютерные науки

Издается с 1997 года

ISSN 2959-068X

№ 2 (2023)
Павлодар

НАУЧНЫЙ ЖУРНАЛ
ТОРАЙГЫРОВ УНИВЕРСИТЕТА

Серия: Физика, математика и компьютерные науки
выходит 4 раза в год

СВИДЕТЕЛЬСТВО
о постановке на переучет периодического печатного издания,
информационного агентства и сетевого издания
№ KZ91VPY00046988
выдано
Министерством информации и общественного развития
Республики Казахстан

Тематическая направленность
публикация материалов в области физики, математики,
механики и информатики

Подписной индекс – 76208

https://doi.org/10.48081/GGBG9646

СЕКЦИЯ «ТЕОРЕТИЧЕСКАЯ И ЭКСПЕРИМЕНТАЛЬНАЯ ФИЗИКА»

SRSTI 29.19.31, 29.31.26

https://doi.org/10.48081/UXBI7290

***A. Zh. Zhumabekov**[1]
[1]Toraighyrov University, Republic of Kazakhstan, Pavlodar
*e-mail : almar89-89@mail.ru

THE INFLUENCE OF GRAPHENE OXIDE ON THE PHOTOCATALYTIC ACTIVITY OF NANOCOMPOSITE MATERIAL

In this paper, is investigated the photocatalytic activity of a nanocomposite material based on titanium and graphene oxides. The sample was obtained by hydrothermal synthesis. The photoactalytic activity of nanocomposites was studied by the transient responce of the photoinduced current. Charge transfer resistances were also investigated using electrochemical impedance spectroscopy. Identification of nanocomposite materials was carried out using Raman and FTIR spectroscopy. This combination shows that there is a connection between the original components. Raman spectroscopy shows that the peaks obtained are characteristic of both titanium dioxide and graphene oxide. At the same time, the I_D/I_G *ratio shows the reduction of graphene oxide during hydrothermal synthesis. And FTIR spectroscopy shows that there is a Ti-O-C bond below the 1000* cm^{-1} *mode.*

The absorption ability also affects the increase in the photocurrent of the nanocomposite material. Absorption spectra show a shift to the long-wavelength region of light due to the transparency of graphene oxide in the visible region.

The concentration of graphene oxide plays an important role in increasing the efficiency of the nanocomposite material. In this work, the concentration of the graphene oxide is equal to 7 wt% with respect to titanium dioxide.

Keywords: nanocomposite material, titanium dioxide, graphene oxide, hydrothermal synthesis, photocatalytic activity.

Introduction

Titanium dioxide (TiO_2) has attracted a lot of attention due to its unique properties, such as high chemical stability, non-toxicity, low cost, highly efficient photocatalytic activity, ease of synthesis, etc. [1–3]. Currently used in catalysts, dye-sensitive solar cells, water splitting, water purification, optical sensors and rechargeable lithium-ion batteries, etc. Among other semiconductors, it has such advantages, but TiO_2 absorbs only in the UV region, since the band gap is about 3.0–3.2 eV.

Therefore, to solve this disadvantage, various methods have been used to improve them, for example, alloying with noble metals and nonmetals, sensitization with dyes, semiconductor compounds and layered semiconductors [4–8].

Graphene, a planar, hexagonal arrangement of carbon atoms, was the starting point in all calculations for graphite, carbon nanotubes and fullerenes. The unique physical properties of graphene (high surface area, excellent conductivity, mechanical strength, transparency in the visible spectrum, etc.) make it very promising for use in various fields of science and technology, such as electronics, energy, biotechnology, etc. Along with graphene itself, its derivatives are of great interest: graphene oxide (GO), reduced graphene oxide and graphene doped with nitrogen. Theoretical and experimental studies show that graphene doping opens up new possibilities for the physics and chemistry of this unique material.

Over the past decade, papers have been published reporting the production of complexes based on graphene and TiO_2 nanoparticles [9–11]. Thus, nanocomposite materials based on graphene oxide and TiO_2 are synthesized by various methods that show high adsorption capacity, high photodegradation of dyes, high efficiency of hydrogen decomposition.

One of the important properties of obtaining nanocomposite materials is the concentration of the initial components. The concentration of graphene oxide in TiO_2 strongly affects the electrophysical, photocatalytic and optical characteristics of the nanocomposite. There are many works using different concentrations in the synthesis of nanocomposites. Studies in this direction have shown that the optimal concentration is the ratio of 5 wt % graphene oxide to TiO_2 [12].

In this work, nanocomposite materials based on titanium dioxide and graphene oxide with a concentration of carbon-containing material equal to 7 wt % relative to TiO2 were prepared. Also, this work is an intermediate experiment, which determines that the efficiency of graphene oxide concentration of 5 wt % is the most optimal concentration for the application [13].

Materials and methods

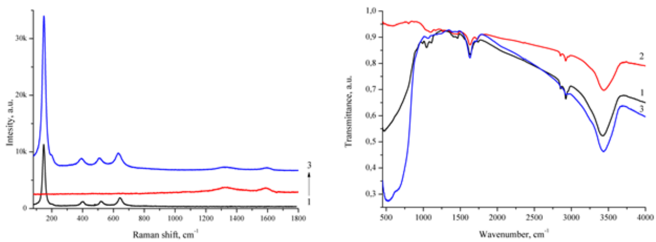
To prepare 7 wt % nanocomposite based on TiO_2 and GO, the following was performed: 70 mg of graphene oxide was mixed with 210 mL of deionized water and 210 mL of ethanol. Then the suspension was sonicated for 1 hour. After that, 1 g of TiO_2 was added. The resulting mix was sonicated and stirred progressively for 2 hours with 30 min for each step until a homogeneous suspension was achieved, which shows a uniform light gray color. The suspension was then poured into a Teflon-lined autoclave and left for 24 hours at 120 °C for the synthesis of the composite. After cooling to room temperature, the suspension was filtered and rinsed with deionized water several times. The resulting product was dried at a temperature of 60 °C.

The film of nanocomposite material was deposited onto the surface of the FTO substrates with the spin-coating method. The deposited paste was prepared from synthesized powder and ethanol. After application and drying, the film was annealed in the Ar atmosphere for 2 hours at a temperature of 450 °C.

Identification of the initial components in the nanocomposite material was carried out using a microscope the Confotec MR520 microscope (Sol Instruments) with a wavelength 632.8 nm laser excitation was used to register Raman spectra. FTIR spectroscopy (FSM 1201, Infraspec) was used to record the IR spectra of the composite material.

Results and discussions

Graphene oxide is characterized by two bands: D- and G-. The D-band of about 1350 cm^{-1} characterizes the degree of graphene defectiveness and is active only if the defects participate in double resonance scattering near the Brillouin zone [14]. The G-band is centered about 1590 cm^{-1}. And TiO_2 of anatase structure has six combinationally active peaks in the vibrational spectrum [15]. The ratio of the intensities of D- and G-bands in the nanocomposite material was calculated to be ID/IG equal to 1.4 for 7 wt %. The increase in ID/IG may be associated with an increase in bond defects or the formation of a large number of small sp2-bound carbon domains during the reduction process [16].



a) b)

Figure 1 – Raman (a) and FT-IR (b) spectra:
1 – graphene oxide, 2 – TiO_2, 3 – TiO_2-GO/3 %

In the IR spectrum (Figure 1, b) of graphene oxide, there are bands characterizing the fluctuations of oxygen-containing bonds: C–O (1095 cm^{-1}), C-O-C (1261 cm^{-1}),C-OH(1454cm^{-1}), C=O (1728 cm^{-1}). An intense peak at 3441 cm^{-1} characterizes the fluctuations of OH groups in the composition of C-OH and water. The peak at 1628 cm^{-1} is associated with skeletal oscillations of graphene oxide [17]. The same bands were registered in the spectrum. In a pure TiO_2 sample, there is 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, an intense band appears around 3440 cm^{-1}, which indicates that OH groups are adsorbed on the surface of titanium dioxide particles. The TiO_2–GO nanocomposite exhibits absorption below 1000 cm^{-1}. For the TiO_2-GO nanocomposite, this band is very pronounced, and its intensity increases with increasing GO concentration. This band is usually considered as a combination of bands corresponding to the fluctuations of Ti-O-Ti (695 cm^{-1}) and Ti-O-C (about 792 cm^{-1}) bonds [17]. This indicates that during the hydrothermal reaction, graphene oxide interacts through the residual functional groups of carboxylic acid with the surface hydroxyl groups of TiO_2 nanoparticles.

After the preparation of solid films of the nanocomposite material, the absorption spectra, impedance spectra and transient characteristics of the photocurrent of the nanocomposite material TiO_2-GO and pure TiO_2 were studied. The methods of sample preparation and the measurement technique are described in detail in [18,19].

When studying the absorption spectra of nanocomposites, the data shown in Figure 2 were obtained. It is known that the absorption spectrum of TiO_2 manifests itself in the UV region of the spectrum of about 380 nm. Graphene and its modifications are also absorbed in the UV range, and for graphene oxide, the maximum of its absorption spectrum is 230 nm. At the same time, graphene oxide films are practically transparent in the wavelength range from 400 to 800 nm [20].

When measuring the optical properties of the prepared films, it was found that the absorption band of the semiconductor broadens into the visible range of the spectrum in the nanocomposite material (Figure 2). A change in the absorption spectrum in the long-wavelength region affects the width of the band gap of the nanocomposite material, i.e. its decrease occurs.

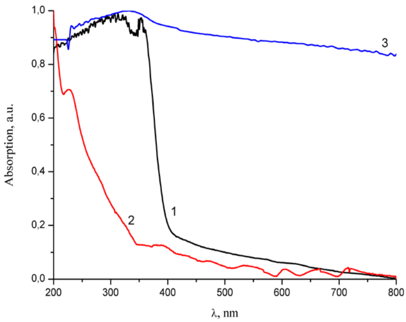
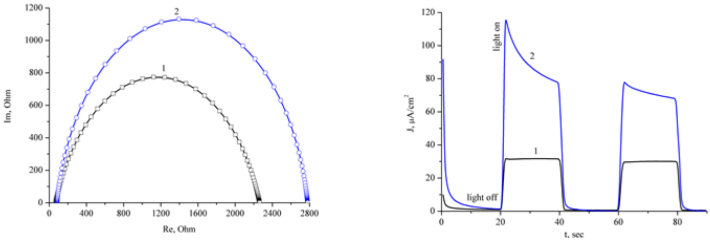


Figure 2 – Normalized absorption spectra of films:
1 – TiO_2, 2 – graphene oxide, 3 – TiO_2-GO/7 %

Next, the impedance spectra of the nanocomposite material were studied. Impedance spectra in Nyquist coordinates based on films are shown in Figure 3a. Based on the obtained impedance spectra, the main electric transport properties of the films were calculated. The following parameters were determined: R_k, R_w, k_{eff}, τ_{eff}, где R_k – charge-transfer resistance related to recombination of electron, Rw – electron transport resistance in TiO_2-GO, keff – effective rate constant for recombination and τ_{eff} – effective lifetime of electrons [21].

Figure 3a shows that the diameter of the TiO_2-GO/7 % film hodograph is much smaller than that of TiO_2 films. This means that the studied samples have a smaller amount of charge transfer resistance. The addition of graphene oxide makes it possible to reduce the resistance values R_k и R_w of semiconductor samples.

In TiO_2, the charge transfer resistance is equal to R_k=2294.0 Ohms, and in TiO_2-GO/7 % is equal to R_k=2696.8 Ohms. Thus, the data show that when graphene oxide is added by 7 wt %, the charge transfer resistance decreases by 5 times. It is also seen that the Rw – in the film is 82.7 Ohms, which means that the resistance to electronic transport is almost 1.5 times higher than in TiO_2. This can be explained by the fact that with an increase in the content of graphene oxide at the «TiO_2-GO/electrolyte» interface, the number of injected electrons increases, which undoubtedly increases the rate of charge recombination. But in this case, there is an increase in the resistance of electronic transport in the film itself between the electrons. And the lifetime of electrons in a nanocomposite film shows that the electrons are not in an excited state for a long time.



a) b)

Figure 3 – Impedance spectra in Nyquist plots (a) and (b) Transient response of the photocurrent of samples: 1 – TiO_2, 2 – TiO_2-GO/7 %.

Table 1 shows the values of the electrophysical parameters of the TiO_2 film and the nanocomposite material. Using the EIS–analyzer software package, R_k and R_w are calculated, and k_{eff} is determined by the maximum of the hodograph arc using the formula $w_{max}=k_{eff}$. The thickness of the films was determined using a TESCAN Mira3 scanning electron microscope.

Таблица 1 – Electric transport parameters of TiO_2 and TiO_2-GO/7%

Sample	**k_{eff}, s^{-1}**	**τ_{eff}, ms**	**R_k, Ohm**	**R_W, Ohm**
TiO_2	13.895	72	2194.0	69.3
TiO_2-GO/7%	1148.7	0.9	2696.8	82.7

The transient characteristics of the photoinduced current are shown in Figure 3, b. Photoelectric characteristics of TiO_2 and TiO_2-GO/7 % with which their photocatalytic activity can be estimated.

The magnitude of the photocurrent of a TiO_2-based film is ~30 µA (Figure 3b). When the sample was irradiated, the magnitude of the photocurrent increased by 2.5 times. Also, a high generation of photoinduced current for the first turn-on cycle was recorded for nanocomposite films. Since the efficiency of photocatalytic splitting of water into molecular oxygen and hydrogen will directly depend on the magnitude of photoinduced electrons, it can be assumed that when using synthesized nanocomposites, hydrogen generation will be higher compared to other similar nanocomposites.

Conclusion

Samples based on TiO_2 and graphene oxide with the addition of 7 wt% were prepared and their optical, photoelectric and electrophysical characteristics were studied.

Measurements of the optical characteristics of the synthesized material showed that the absorption spectrum of the nanocomposite material corresponds to the spectra of the initial components. At the same time, there is a slight shift of the absorption band of the nanocomposite to the long-wavelength region. The transient characteristics of the photocurrents show an increase in the photoinduced current of the nanocomposite material. Studies of impedance spectra have shown that when graphene oxide with a concentration of 7 wt % is added, it has the opposite effect, i.e. the resistances of nanocomposite films increase. This work shows once again that there is an optimal concentration of graphene oxide. In previous studies, it was shown that the optimal concentration is 5 wt % [13]. This work was carried out while searching for such a ratio and these results do not affect any previous experiments.

Thus, when determining the optimal concentration, such ratios as 1,3,5,7,10 wt % [21] of graphene oxide with respect to TiO_2 were chosen. A comprehensive study of these samples shows that the best effect in terms of electrophysical and photocatalytic characteristics shows 5 mass %.

REFERENCES

1 **Sasan, K., Zuo, F.** Self-doped Ti^{3+}–TiO_2 as a photocatalyst for the reduction of CO_2 into a hydrocarbon fuel under visible light irradiation // Nanoscale. – 2015. – Vol. 7. – P. 13369–13372.

2 **Oluwafunmilola, O., Maroto-Valer M.** Review of material design and reactor engineering on TiO_2 photocatalysis for CO_2 reduction // Journal of Photochemistry and Photobiology C : Photochemistry Reviews – 2015. – Vol. 24. – P. 16–42.

3 **Mills, A., Hunte, S.** An overview of semiconductor photocatalysis // Journal of Photochemistry and Photobiology A : Chemistry. – 1997. – Vol. 108. – № 1. – P. 1–35.

4 **Kowalska, E., Remita, H., Colbeau-Justin, C., Hupka, J., and Belloni, J.** Modification of Titanium Dioxide with Platinum Ions and Clusters : Application in Photocatalysis // J. Phys. Chem. C. – 2008. – Vol. 112. –P. 1124.

5 **Ohno, T., Akiyoshi, M., Umebayashi, T., Asai, K., Mitsui, T., and Matsumura, M.** Preparation of S-doped TiO_2 Photocatalysis and their Photocatalytic Activities under Visible Light. Applied Catalysis A : General. – 2004. – Vol. 265(1). – P. 115–121.

6 **Fuldner, S., Mild, R., Siegmund, H. I., Schroeder, J. A., Gruber, M., and Konig, B.** Green-light photocatalytic reduction using dye-sensitized TiO_2 and transition metal nanoparticles. // Green Chem. – 2010. – Vol. 12. – P. 400–406.

7 **Xu, J., Wang, W., Sun, S., and Wang, L.** Enhancing visible-light-induced photocatalytic activity by coupling with wide-band-gap semiconductor : A case study on Bi_2WO_6/TiO_2. // Appl. Catal. B Environ. – 2012. – Vol. 111–112. – 126–132.

8 **Cui, W., Guo, D., Liu, L., Hu, J., Rana, D., and Liang, Y.** Preparation of $ZnIn_2S_4/K_2La_2Ti_3O_{10}$ composites and their photocatalytic H_2 evolution from aqueous Na_2S/Na_2SO_3 under visible light irradiation. // Catal. Commun. – 2014. – Vol. 48. – P. 55–59.

9 **Bahadur, J., Pal, K.** Structural and magnetic properties of reduced graphene oxide-TiO_2 nanoflower composite. // Physica E : Low-dimensional Systems and Nanostructures – 2017. – Vol. 90. – P. 98–103.

10 **Manzoor M., Rafiq A., Ikram M., Nafees M., Ali S.** Structural, optical, and magnetic study of Nidoped TiO_2 nanoparticles synthesized by sol–gel method. // Inter. Nano Lett. – 2018. – Vol. 8. – № 1. – P. 1–8.

11 **Aqeel, M., Anjum, S., Imran, M.** TiO_2@RGO (reduced graphene oxide) doped nanoparticles demonstrated improved photocatalytic activity. // J. Mater. Res. Express – 2019. – Vol. 6. – P. 086215.

12 **Fan, W., Lai, Q., Zhang, Q., Wang, Ye.** Nanocomposites of TiO_2 and Reduced Graphene Oxide as Efficient Photocatalysts for Hydrogen Evolution // J. Phys. Chem. : C – 2011. – Vol. 115. – P. 10694–10701.

13 **Ibrayev, N., Ghyngazov, S., Lysenko, E., Zhumabekov, A.** Synthesis and study of the properties of nanocomposite materials TiO_2-GO and TiO_2-rGO. // Material Research Express. – 2019. – Vol. 6. – № 11. – P. 1–11.

14 **Swamy, V., Kuznetsov, A., Dubrovinsky, L. S., Caruso, R. A., Shchukin D. G., Muddle B. C.** Finite-size and pressure effects on the Raman spectrum of nanocrystalline anatase TiO_2 // Phys. Rev. B. – 2005. – Vol. 71 – P. 184302–12.

15 **Wang, S. J., Geng, Y., Zheng, Q., Kim, J.-K.** Fabrication of highly conducting and transparent graphene films // Carbon. – 2010. – Vol. 48. – P. 1815–1823.

16 **Xu, Y., Bai, H., Lu, G., Li, C., Shi, G.** Flexible graphene films via the filtration of water-soluble noncovalent functionalized graphene sheets // J. Am. Chem. Soc. – 2008. – Vol. 48. – P. 5856–5857.

17 **Kamat, P. V.** Graphene-based nanoassemblies for energy conversion // J. Phys. Chem. Lett. – 2011. – Vol. 2. – P. 242–251.

18 **Zhang, W., Cui, J., Tao, C-an., Wu, Y., Li, Z., Ma, L.** A strategy for producing pure single-layer graphene sheets based on a confined self-assembly approach : Angew. Intern. Edit. Chem. – 2009. – Vol. 48. – P. 5864–5868.

19 **Fan, Z.-J., Kai, W., Yan, J., Wei, T., Zhi, L.-J., Feng, J., Ren, Y.-m., Song, L.-P., Wei, F.** Facile Synthesis of graphene Nanoshets via Fe reduction of exfoliated graphite oxide // ACS Nano. – 2010. – Vol. 5. – P. 191–198.

20 **Adachi, M., Murata, Y., Takao, J., Jinting, J.** Highly efficient dye–sensitized solar cells with a titania thin–film electrode composed of a network structure of single–crystal–like TiO_2 nanowires made by the «oriented attachment» mechanism // J. Am. Chem. Soc. – 2004. – P. 126.

21 **Zhumabekov, A. Zh.** Improving the electrophysical properties of nanocomposite materials based on graphene oxide and TiO_2, Bulletin of Toraighyrov University. Physics, mathematics and Computer Science series, № 3. – 2022. – P. 66–78.

Material received on 16.05.23

А. Ж. Жумабеков[1]
[1]Торайғыров университеті, Қазақстан Республикасы, Павлодар қ.
Материал 16.05.23 баспаға түсті.

ГРАФЕН ОКСИДІНІҢ НАНОКОМПОЗИТТІК МАТЕРИАЛДЫҢ ФОТОКАТАЛИТИКАЛЫҚ БЕЛСЕНДІЛІГІНЕ ӘСЕРІ

Аталмыш жұмыста титан және графен оксидтеріне негізделген нанокомпозиттік материалдың фотокаталитикалық белсенділігі зерттелді. Үлгі гидротермиялық синтез әдісімен алынды. Нанокомпозиттердің фотокаталитикалық белсенділігі фотоиндукцияланган токтың өтпелі сипаттамалары бойынша алынды. Сондай-ақ электрохимиялық импеданс спектроскопиясының көмегімен зарядты тасымалдау кедергісі зерттелді. Нанокомпозиттік материалдарды анықтау Комбинациялық шашырау және ИҚ Фурье түрлендіру спектроскопиялары арқылы жүзеге асырылды. Осындай комбинациялық зерттеу бастапқы компоненттер арасында байланыс бар екенін көрсетеді. Комбинациялық шашырау спектроскопиясы нәтижесінде пайда болган шыңдар титан диоксиді мен графен оксидіне тән екенін көрсетеді. Бұл жагдайда I_D/I_G қатынасы гидротермиялық синтез кезінде графен оксидінің қалпына келтіруін көрсетеді. ИҚ спектроскопиясы 1000 см$^{-1}$ модасынан төмен Ti-O-C байланысы бар екенін көрсетеді.

Нанокомпозиттік материалдың фотоагынының жогарылауына жұту қабілеті де әсер етеді. Жұтылу спектрлері көрінетін аймақтагы графен оксидінің мөлдірлігі арқылы жарықтың ұзын толқындық аймагына ауысуын көрсетеді.

Графен оксидінің концентрациясы нанокомпозиттік материалдың тиімділігін арттыруда үлкен рөл атқарады. Бұл *жұмыста графен оксидінің концентрациясы титан диоксидіне қатысты 7 масса % құрайды.*

Кілтті сөздер: нанокомпозиттік материал, титан диоксиді, графен оксиді, гидротермиялық синтез, фотокаталитикалық белсенділік.

***А. Ж. Жумабеков[1]**
[1]Торайгыров университет, Республика Казахстан, г. Павлодар.
Материал поступил в редакцию 16.05.23.

ВЛИЯНИЕ ОКСИДА ГРАФЕНА НА ФОТОКАТАЛИТИЧЕСКУЮ АКТИВНОСТЬ НАНОКОМПОЗИТНОГО МАТЕРИАЛА

В данной работе исследована фотокаталитическая активность нанокомпозитного материала на основе оксидов титана и графена. Образец был получен методом гидротермального синтеза. Фотоакталитическая активность нанокомпозитов были получены по переходным характеристикам фотоиндуцированного тока. А также с помощью электрохимической импедансной спектроскопией были исследованы сопротивления переноса зарядов. Идентификацию нанокомпозитных материалов проводили с помощью Раман и ИК с преобразованием Фурье спектроскопии. Данная комбинация показывает, что имеется связь между исходными компонентами. Раман спектроскопия показывает, что полученные пики характерны как для диоксида титана так и для оксида графена. При этом соотношение I_D/I_G показывает восстановление оксида графена при гидротермальном синтезе. А ИК-спектроскопия показывает, что имеется связь Ti-O-C ниже моды 1000 $см^{-1}$.

На увеличение фототока нанокомпозитного материала также влияет абсорбционная способность. Спектры поглощения показывают сдвиг в длинноволновую область света за счет прозрачности оксида графена в видимой области.

Большую роль в повышении эффективности нанокомпозитного материала играет концентрация оксида графена. В данной работе концентрация оксида графена равна 7 масс % по отношению к диоксиду титана.

Ключевые слова: нанокомпозитный материал, диоксид титана, оксид графена, гидротермальный синтез, фотокаталитическая активность.

Теруге 16.05.2023 ж. жіберілді. Басуға 31.05.2023 ж. қол қойылды.
Электрондық баспа
7,50 Mb RAM
Шартты баспа табағы 10,01. Таралымы 300 дана. Бағасы келісім бойынша.
Компьютерде беттеген: Е. Е. Калихан
Корректор: А. Р. Омарова, Д. А. Кожас
Тапсырыс № 4081

Сдано в набор 16.05.2023 г. Подписано в печать 31.05.2023 г.
Электронное издание
7,50 Mb RAM
Усл.печ.л. 10,01. Тираж 300 экз. Цена договорная.
Компьютерная верстка Е. Е. Калихан
Корректор: А. Р. Омарова, Д. А. Кожас
Заказ № 4081

«Toraighyrov University» баспасынан басылып шығарылған
«Торайғыров университеті» КЕ АҚ
140008, Павлодар қ., Ломов к., 64, 137 каб.

«Toraighyrov University» баспасы
«Торайғыров университеті» КЕ АҚ
140008, Павлодар қ., Ломов к., 64, 137 каб.
+7(718)267-36-69

e-mail: kereku@tou.edu.kz
www.vestnik.tou.edu.kz
https://vestnik-pm.tou.edu.kz/