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T.M. Serikov, P.A. Zhanbirbayeva, A.S. Baltabekov, A.B. Kuanyshbekova

Karaganda University of the name of academician E.A. Buketov, Kazakhstan
*(*e-mail: serikov-timur@mail.ru)*

Photocatalytic activity of the TIO_2/Ag/rGO nanocomposite

The paper presents the results of a study of the photocatalytic activity of films formed by titanium dioxide nanorods doped with silver nanoparticles and reduced graphene oxide. The obtained nanocomposite materials were studied by optical spectroscopy, scanning electron microscopy, X-ray diffractometry, and Raman spectroscopy. The photocatalytic activity of the samples was evaluated by generating a photocurrent when the surface was illuminated by a modulated light source of a xenon lamp. In addition, the photocatalytic activity of the samples was evaluated by the degradation of the methylene blue dye, which is a model. It was found that the introduction of silver nanoparticles and reduced graphene oxide into the pores of films made of titanium dioxide nanorods leads to an increase in the spectral sensitivity of the sample in the region of 400-500 nm. The increased sensitivity of the sample to visible light leads to an increase in photocurrent generation and is 2.3 times higher than that of the original sample. Degradation of the methylene blue dye after 100 minutes of irradiation in the presence of a TiO_2/Ag/rGO sample was 19 %. This is 3 times higher than in TiO_2 nanorods films and 2.3 times higher than TiO_2/Ag films. The results of the conducted studies have shown that the improvement of photocatalytic activity is associated with a decrease in film resistance, an expansion of spectral sensitivity and an increase in the surface area of the nanorods.

Keywords: titanium dioxide nanorods, silver nanoparticles, reduced graphene oxide, photocatalysis

Introduction

Recently, semiconductors based on metal oxides with high photosensitivity and excellent physicochemical properties have attracted wide attention due to their widespread use for environmental restoration and solar energy conversion [1-3]. As one of the promising semiconductors, TiO_2 nanostructures have been extensively investigated for photocatalysis and photocatalytic splitting of water, due to availability, low cost and good stability [4]. The most commonly used structures in photocatalysis are titanium dioxide nanoparticles, but they have a significant disadvantage associated with the implementation of 3–dimensional electron transport. In addition, when films are made from nanoparticles, unformed contacts between them affect the possibility of electron transfer from one nanoparticle to another [5]. One-dimensional nanostructures, such as titanium dioxide nanorods, may have a number of advantages over nanoparticles. For example, in nanorods, electron transport is carried out in one direction — along the walls. This can lead to a decrease in the electron travel time from the charge generation centers to the current-removing electrodes [6]. Despite the advantages of TiO_2 (TNR) nanorods over nanoparticles, the wide band gap (~ 3.0–3.2 eV) and the rapid recombination of photogenerated electron-hole pairs in TiO_2 still limit its widespread use in photocatalysis. Increasing the sensitivity of TiO_2 in the visible region of the spectrum and reducing the recombination rate can be achieved by adding nanoparticles of noble metals, such as silver and carbon nanostructures, such as graphene. It has been reported that alloying with noble metals is an effective way to improve the optical and photoelectrochemical properties of the TiO_2 photocatalyst.

LF of noble metals with surface plasmon resonance (SPR) not only contributes to the generation of electron-hole pairs by electromagnetic fields, but also increase light scattering in order to capture most of the light for bonded semiconductors [7-10]. Numerous successful systems have been created using TiO_2 in combination with various noble metals, and represent great potential for electrochemistry and photocatalysis.

Graphene with a two-dimensional planar structure has many advantages, such as high electron mobility, ease of solution synthesis, unique optical, thermal and mechanical properties, with a wide range of applications from photocatalysis, electrochemical detection, transparent electrodes to lithium-ion batteries. Graphene in its pure form is rarely used in photocatalysis, as it is hydrophobic. Therefore, it is more convenient to use graphene oxides, for example, reduced graphene oxide (rGO), since it forms stable dispersions in water. It is noteworthy that nanocomposite photocatalysts based on reduced graphene oxide (rGO) can quickly transfer electrons and prolong the lifetime of charge carriers, which leads to an increase in quantum efficiency. Graphene or its derivatives can also significantly improve the adsorption capacity of the target molecule due to its large specific surface area. In addition, due to the adjustable band gap and high transparency, the light intensity practically does not change before it reaches the surface of the catalyst.

Thus, the creation of a triple hybrid system combining noble metal, TiO_2 and nanolists (rGO) to improve the photocatalytic characteristics of the photocatalyst and the study of their mechanisms of action is a very urgent task.

The aim of this work is to synthesize and study the photocatalytic activity of a nanocomposite material, which consists of a film of titanium dioxide nanorods doped with silver nanoparticles and reduced graphene oxide deposited on their surface.

Experimental

Films formed by TiO_2 nanorods were obtained on FTO substrates (7 ohms/cm^2, Sigma–Aldrich) by hydrothermal synthesis in a sealed autoclave with a volume of 50 with a solution content containing 15 ml of deionized water (H_2O), 15 ml of hydrochloric acid (HCl) (36.5–38.0 %, Sigma–Aldrich) and 0.25 ml of titanium butylate $C_{16}H_{36}O_4Ti$ (titanium butoxide, 97 %, Sigma–Aldrich) at a temperature of 180^{0}C and a synthesis duration of 18 hours. Then the samples were calcined at a temperature of 500 ^{0}C for 2 hours. Silver nanoparticles were recovered on the surface of TiO_2 nanorods in a solution containing 0.2 g of polyvinylpyrrolidone (PVP, molecular weight 40,000), 40 ml of deionized water and ethylene glycol, with the addition of 2 mmol $NaBH_4$. Then the film from the nanorods was immersed to the bottom of the vessel with the rods up and kept in an oven at a temperature of 70 °C for 1 hour, removed and dried at room temperature. rGO (99 %, Cheaptubes) was deposited on the surface of a film made of titanium dioxide nanorods containing silver nanoparticles from a phosphate solution (0.5 g/l) by electrochemical method using a standard three-electrode system. After 5 minutes of deposition, the films were removed and washed several times with deionized water. The deposition time is optimal, at which the maximum photocatalytic activity of the samples is observed [11, 12].

The phase composition of the samples was studied by X-ray diffraction using an automatic powder diffractometer STOE STADI-P (STOE & Cie GmbH) in the angle range 2 ° 5-80°. X-ray images were analyzed using the PDF-2 powder database, as well as the standard WinXPow software package. The morphology of the surface was studied using a MIRA 3LMU scanning electron microscope (Tescan, Czech Republic). The optical density of all samples was recorded on a CM 2203 spectrofluorimeter (Solar, Belarus). Raman spectra were studied using a Confotec MR520 microscope (Sol Instruments), laser wavelength λ=532 nm. The photocatalytic activity of the samples was evaluated by measuring the magnitude of the photoinduced current with an illuminated area of 1 cm^2 in a standard three-electrode cell using a CS350 potentiostat/galvanostat with a built-in EIS analyzer (Corrtest Instruments, China) in an electrolyte of 0.1 M NaOH. In addition, the photoactivity of the films was evaluated by photodegradation of the methylene blue (MV) dye. A xenon lamp with a power of 300 W/cm^2 (Newport, USA) served as a laboratory light source. The surface area of the samples was estimated by the number of adsorbed dye molecules as follows: an aqueous solution of methylene blue dye with a concentration of 10 — ^{6} mol/l was poured into three containers with a volume of 25 ml. Then, the films were lowered into the solutions for 20 hours. At the same time, the optical density of the dye was determined every 1 hour and the concentration of adsorbed molecules was calculated by the formula

$$C = \frac{N_A C' V}{S}\left(1 - D_1 / D_2\right)$$

where N_A is the Avogadro constant, C′ is the concentration of dye molecules in the solution, V is the volume of the solution, S is the area of the adsorbent, D1 and D2 are the optical densities of the solution before and after sorption. The active surface of the films was calculated from the calculation of the area of one molecule of methylene blue 130 Å2.

Results and Discussion

Figure 1 shows SEM images of TiO_2 nanorods (a), TiO_2 nanorods with the addition of silver nanoparticles (b) and deposited sheets of reduced graphene oxide (c).

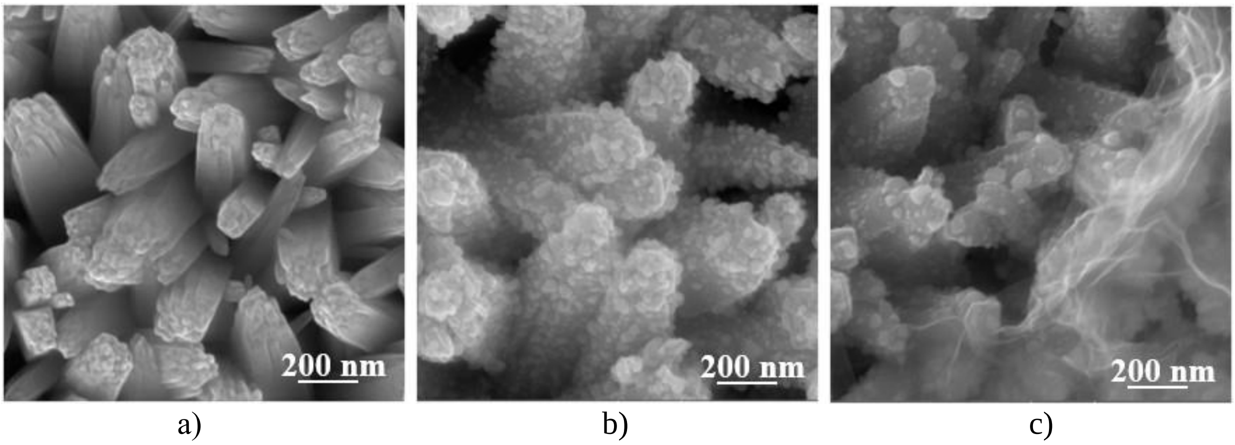


Figure 1. SEM images TNR (a), TNR/Ag (b), TNR/Ag/rGO (c)

Figure 1a shows that TNRS is formed on the surface of the FTO substrate as a result of hydrothermal synthesis. As a result of image processing, it was found that the diameter of the nanorods varies from 100 to 180 nm. TiO_2 nanorods are mainly located perpendicular to the substrate surface and have a length of about 4.1 microns. As a result of the chemical reduction of silver nitrate, silver nanoparticles are formed on the surface of the nanorods. The diameter of silver nanoparticles varies from 20 to 40 nm. In addition, the sizes of silver nanoparticles were confirmed by the method of dynamic light scattering on Zeta Seizer (Malvern) (Figure 2b). Electrochemical deposition of rGO on the surface of TNT/Ag films leads to the formation of rGO sheets on its surface. Figure 1c shows that graphene oxide sheets partially envelop the surface of the rods.

Figure 2a shows the spectrum of maps of the presence of chemical elements in the TNR/Ag/rGO sample.

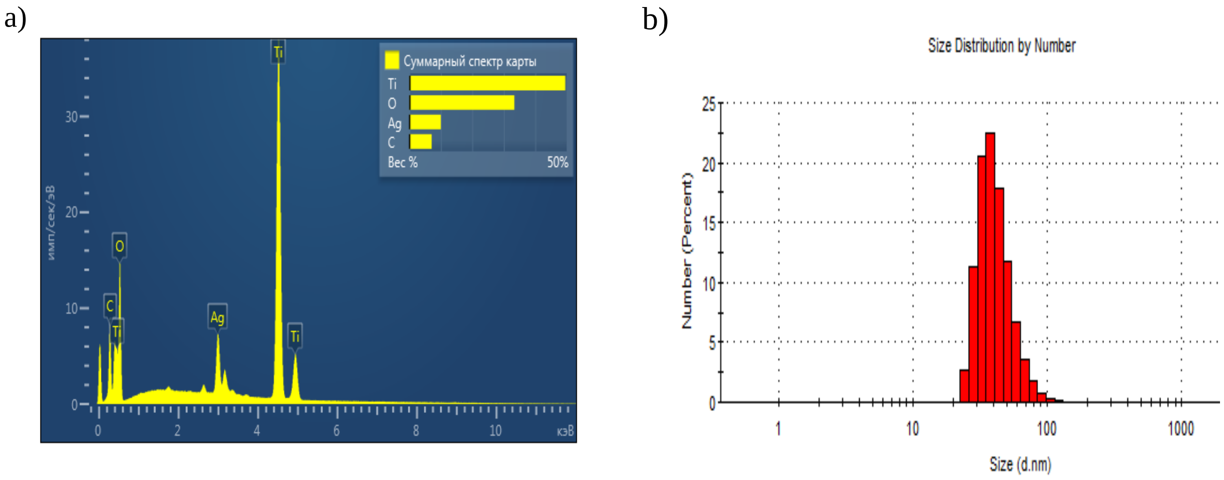


Figure 2. EDX analysis of TNR/Ag/rGO (a) and size distribution of silver nanoparticles determined on Zeta Seizer

According to the results of studies of the elemental composition of the TNR/Ag/rGO sample, it was shown that 4 elements were identified in the samples, such as Ti, O, Ag and C. The elements Ti and O belong to titanium dioxide, which form the basis of the film, therefore its percentage ratio is significantly greater than the rest and amounts to 50 and 32 % respectively. The presence of Ag (10 %) and C (8 %) is a confirmation of the formation of silver and nanoparticles on the surface of the semiconductor film.

Figure 3 shows the mapping of chemical elements on the TNR/Ag/rGO surface.

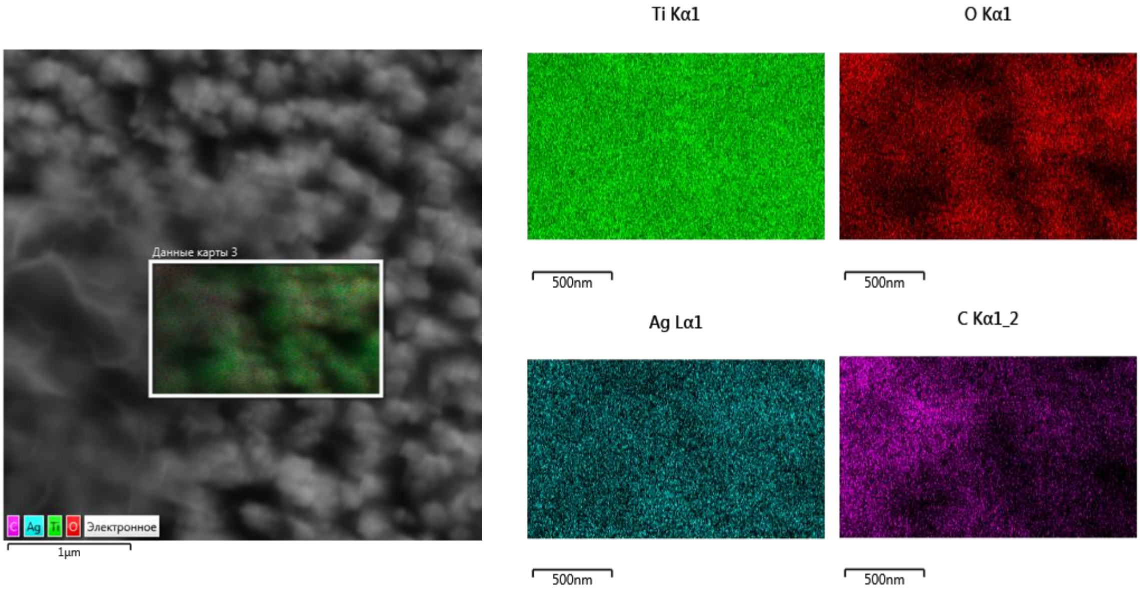


Figure 3. Mapping of chemical elements on the TNR/Ag/rGO surface

It can be seen from the presented data that Ag is evenly distributed over the entire surface and excludes aggregation of nanoparticles.

Figure 4 shows the X-ray diffraction of the studied samples. It was found that the films formed by TNR belong to the tetragonal modification of rutile (JCPDS, No. 21-1276), which is characterized by reflexes in the 27.4°, 36.1°, 41.3°, 54.4°, 62.9° and 69.9°. When silver nanoparticles are deposited, four additional peaks appear on the X-ray at 38.11°, 44.27°, 64.42° and 77.47° corresponding to the lattice planes (111), (200), (220) and (311) (JCPDS No. 07-0783). There was no registration of peaks corresponding to graphene in our experiments, due to the low detection limit.

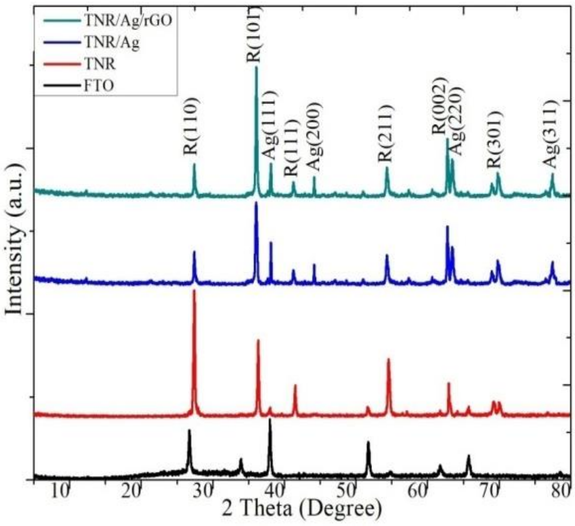


Figure 4. X-ray diffraction patterns of TNR, TNR/Ag, and TNR/Ag/rGO samples

Figure 5 shows the Raman spectra of TR, TNR/Ag and TNR/Ag/rGO. For TNR, intense three combinationally active optical phonon modes 144, 445 and 610 cm-1 are observed, which belong to the B1g, Eg, A1g modes.

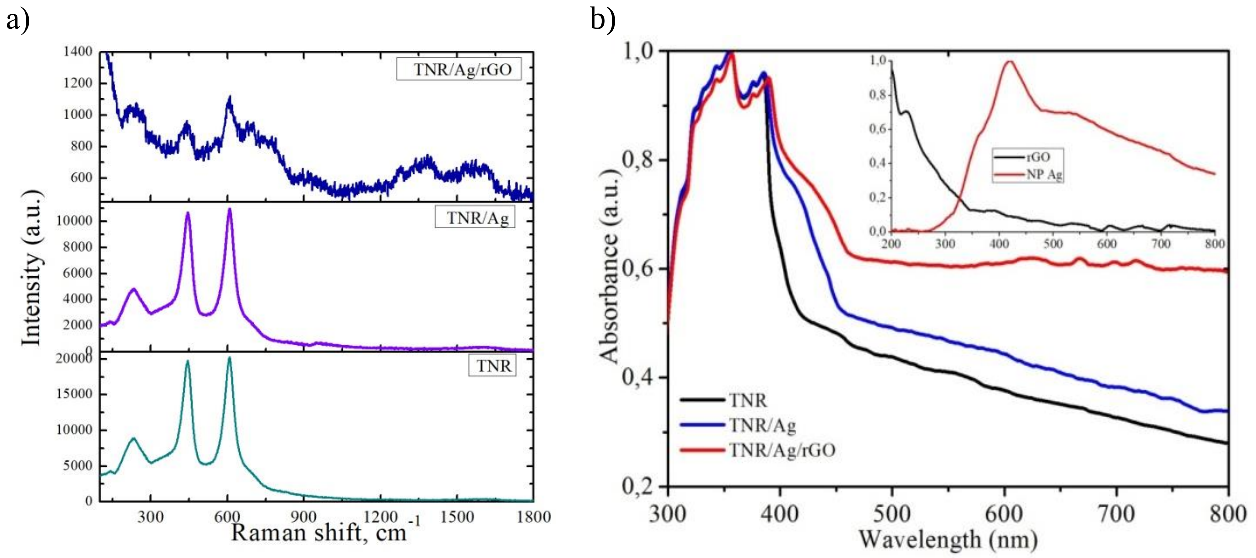
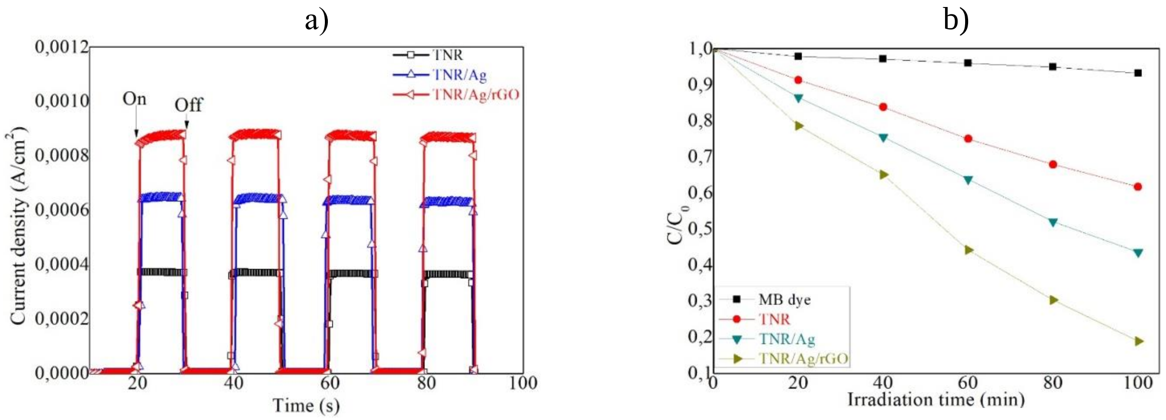


Figure 5. Raman spectra (a) and absorption spectra (b) of TR, TNR/Ag and TNR/Ag/rGO samples

The addition of silver nanoparticles to the structure of titanium dioxide nanorods does not lead to the appearance of new bands, since metals are not combinationally active. However, we observed a 2-fold decrease in the intensity of the bands compared to the original sample, which may be due to the partial blocking of the surface of the nanorods by silver nanoparticles, preventing excitation by laser radiation. With the deposition of rGO, the peaks of raman scattering from the nanorods noticeably decreased, while peaks of raman scattering of light from rGO appear in the region of 1350, 1590 cm^{-1}, which characterize the degree of graphene defectiveness.

Figure 5b shows the normalized absorption spectra of nanostructured films. The absorption of TiO_2 nanorods is in the ultraviolet region, the edge of the spectrum is in the region of 380-400 nm. The introduction of Ag nanoparticles leads to a change in the absorption spectrum and is characterized by the presence of a small shoulder in the region of 420-430 nm. Obviously, this is due to the absorption capacity of Ag nanoparticles in this area. It can be seen from the insertion of Figure 4b that the maximum absorption spectrum of Ag nanoparticles is in the region of 410-430 nm. The TNR/Ag/go nanocomposite material allows to absorb much more light in the visible region of the spectrum compared to pure titanium dioxide and with doped Ag nanoparticles. The edge of the absorption band of the nanocomposite is shifted relative to the TiO2 band, which indicates a decrease in the band gap of the composite material.

Figure 6a shows the dependence of the density of the generated current when the surface is illuminated by a light source and when it is turned off. The samples demonstrate excellent stability over the time period presented. When the surface is illuminated, the current density instantly reaches its maximum. From the data obtained, it can be seen that sensitization of the surface of the nanorods by Ag and rGO nanoparticles leads to an increase in photocurrent, as for TNR. Thus, for TNR/Ag/rGO, the photocurrent density is 2.3 and 1.3 times higher than TN and TNR/Ag, respectively.



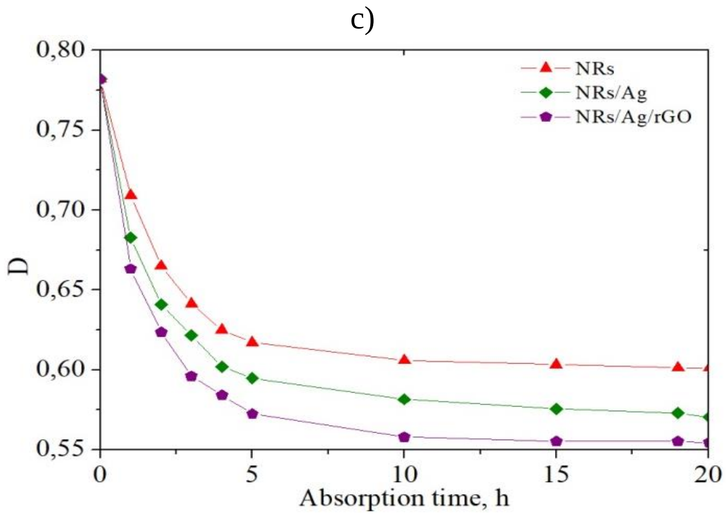


Figure 6. Photocurrent density (a), degradation of the dye MV (b) and the dependence of the optical density of the dye on the sorption time (c) for TNR, TNR/Ag and TNR/Ag/rGO

The photocatalytic activity of the samples was studied by observing the discoloration of the heterocyclic dye MV under the action of UV radiation. The photodegradation curves of MG are shown in Figure 6b, where C0 is the initial concentration, and C is the dye concentration at the time of measurement. MV itself shows almost no self-decomposition during prolonged irradiation. In contrast, MB demonstrates a clearly positive degradation process in the presence of TR, TNR/Ag and TNR/Ag/rGO nanocomposite. The degradation of MV after 100 min of irradiation in the presence of a TNR/Ag/rGO sample was 19 %, which is 3 times higher than in TNR and 2.3 times higher than TNR/Ag. It is obvious that the nanocomposite TNR/Ag/rGO exhibits a significant increase in photocatalytic activity than individually. Next, the active surface area of the samples was estimated. To do this, the samples were kept in a container with a dye with a known concentration for 20 hours. At the same time, the optical density of the dye was measured at certain intervals (Figure 6c). It can be seen from the figure that after 5 hours of sorption, the change in the optical density of the dye is insignificant, which indicates their saturation. Thus, it was found that 36.18*1014 were sorbed in TNR films, and 44.66*1014 and 49.37*1014 molecule/cm^2 respectively were sorbed in TNR/Ag and TNR/Ag/rGO. If we take into account, that the area occupied by 1 MV dye molecule is 130 A2, then the active surface area for TNR will be 4.7*1017 A2, for TNR/Ag 5.8*1017 A2 and for TNR/Ag/rGO 6.4*1017 A2. The results obtained indicate that the addition of Ag and rGO nanoparticles leads to an increase in the active surface area of the nanorods.

Conclusion

Thus, the influence of Ag nanoparticles and rGO impurities on the structural, optical, structural and photocatalytic properties of films formed by TiO$_2$ nanorods has been studied. The formation of Ag nanoparticles with a cubic structure and gan layers on the TNR surface is confirmed by the presence of reflexes on X-ray and sRaman spectra, respectively. Measurements of the optical characteristics of the synthesized material showed that the absorption spectrum of the TNR/Ag/rGO and TNR/Ag nanocomposite is shifted to the long-wavelength region relative to the absorption spectrum of TNR, possibly as a result of changes in the band gap of the semiconductor and the absorption capacity of Ag. The synthesized TNR/Ag/rGO nanocomposite showed a significant increase in photocatalytic activity with respect to the degradation of MV under the action of UV light and generation of photocurrent. In the presence of TNR/Ag/rGO film, MG degradation was 19 %, which is 3 times higher than in TNR and 2.3 times higher than TNR/Ag. The increase in photocatalytic activity is associated with an expansion of spectral sensitivity and an increase in the active surface area of the samples.

Acknowledgments

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References

1 Zhang, L., Hu, J.S., Huang, X.H., Song, J., & Lu, S.Y. (2018). Particle-in-box nanostructured materials created via spatially confined pyrolysis as high performance bifunctional catalysts for electrochemical overall water splitting. *Nano Energy, 48,* 489-499.

2 Ito, S., Murakami, T.N., Comte, P., Liska, P., Grätzel, C., Nazeeruddin, M.K., & Grätzel, M. (2008). Fabrication of thin film dye sensitized solar cells with solar to electric power conversion efficiency over 10 %. *Thin Solid Films, 516,* 4613-4619.

3 Lee, J., Hong, K.S., Shin, K., & Jho, J.Y. (2012). Fabrication of dye-sensitized solar cells using ordered and vertically oriented TiO2 nanotube arrays with open and closed ends. *Journal of Industrial and Engineering Chemistry, 18,* 19-23.

4 Blanco-Vega, M.P., Guzmán-Mar, J.L., Villanueva-Rodríguez, M., Maya-Treviño, L., Garza-Tovar, L.L., Hernández-Ramírez, A., & Hinojosa-Reyes, L. (2017). Photocatalytic elimination of bisphenol A under visible light using Ni-doped TiO2 synthesized by microwave assisted sol-gel method. *Materials Science in Semiconductor Processing, 71,* 275-282.

5 Serikov, T.M., Ibrayev, N.Kh., Ivanova, T.M., & Savilov, S.V. (2021). Influence of the hydrothermal synthesis conditions on the photocatalytic activity of titanium dioxide nanorods. *Russian Journal of Applied Chemistry, 94*(4), 438-445.

6 Serikov, T.M., Ibrayev, N.Kh., Isaikina, O.Ya., & Savilov, S.V. (2021). Nanocrystalline TiO2 films: synthesis and low-temperature luminescent and photovoltaic properties. *Russian Journal of Inorganic Chemistry, 66*(1), 117-123.

7 Patil, S.S., Mali, M.G., Tamboli, M.S., Patil, D.R., Kulkarni, M.V., Yoon, H., Kim, H., Al-Deyab, S.S., Yoon, S.S., Kolekar, S.S., & Kale, B.B. (2016). Green approach for hierarchical nanostructured Ag-ZnO and their photocatalytic performance under sunlight. *Catalysis Today, 260,* 126-134.

8 Hajkova, P., Matousek, J., & Antos, P. (2014). Aging of the photocatalytic TiO2 thin films modified by Ag and Pt. *Applied Catalysis B: Environmental, 160,* 51–56.

9 Liu, Y., Chi, M., Dong, H.L., Jia, H.S., Xu, B.S., & Zhang, Z.X. (2014) Ag/CdS heterostructural composites: fabrication, characterizations and photocatalysis. *Applied Surface Science, 313,* 558–562.

10 Gao, W.Y., Wang, M.Q., Ran, C.X., Yao, X., Yang, H.H., Liu, J., He, D.L., & Bai, J.B. (2014). One-pot synthesis of Ag/r-GO/TiO_2 nanocomposites with high solar absorption and enhanced anti-recombination in photocatalytic applications. *Nanoscale, 6,* 5498-5508.

11 Zhumabekov, A.Z., Ibrayev, N.K., & Seliverstova, E.V. (2020). Photoelectric properties of a nanocomposite derived from reduced graphene oxide and TiO2. *Theoretical and Experimental Chemistry, 55,* 398-406.

12 Serikov, T.M. (2020). The effect of electric transport properties of titanium dioxide nanostructures on their photocatalytic activity. *Bulletin of the University of Karaganda-Physics,* 3, 13-21.

Т.М. Сериков, П.А. Жанбирбаева, А.С. Балтабеков, А.Б. Куанышбекова

TIO_2/Ag/rGO нанокомпозитінің фотокаталитикалық белсенділігі

Мақалада күміс нанобөлшектерімен және тотықсыздандырылған графен оксиді тұндырылған титан диоксиді наноөзекшелерінен түзілген қабыршақтардың фотокаталитикалық белсенділігін зерттеу нәтижелері келтірілген. Алынған нанокомпозиттік материалдар оптикалық спектроскопия, сканерлеуші электронды микроскопия, рентгендік дифрактометрия және Раман спектроскопиясы арқылы зерттелді. Үлгілердің фотокаталитикалық белсенділігі бетіне ксенон шамының модуляцияланған жарық көзімен жарықтандырылған кездегі фототоктың генерациясынан бағаланды. Сонымен қатар үлгілердің фотокаталитикалық белсенділігі мысал ретінде қолданылған метилен көк бояғышының ыдырауы арқылы бағаланған. Титан диоксиді наноөзекшелерінен түзелген қабыршақтардың кеуектеріне күміс нанобөлшектерін және тотықсыздандырылған графен оксидін енгізу 400–500 нм аймағында үлгінің спектрлік сезімталдығының жоғарылауына әкелетіні анықталды. Үлгінің көріну облысында жарыққа сезімталдығының жоғарылауы фототок генерациясының жоғарылауына әкеледі және бастапқы үлгіге қарағанда 2,3 есе жоғары екені көрсетілді. TiO_2/Ag/rGO үлгісінің қатысуымен 100 минут сәулеленуден кейін метилен көк бояғыштың ыдырауы 19 % құрады. Бұл TiO_2 наноторлы қабыршақтарына қарағанда 3 есе және TiO_2/Ag қабыршақтарына қарағанда 2,3 есе жоғары. Жүргізілген зерттеулердің нәтижелері фотокаталитикалық белсенділіктің жақсаруы қабыршақтардың кедергісінің төмендеуімен, спектрлік сезімталдықтың кеңеюімен және қабыршақтардың бетінің ұлғаюымен байланысты екенін көрсетілді.

Кілт сөздер: титан диоксидінің наноөзекшелері, күміс нанобөлшектері, тотықсыздандырылған графен оксиді, фотокатализ.

Т.М. Сериков, П.А. Жанбирбаева, А.С. Балтабеков, А.Б. Куанышбекова

Фотокаталитическая активность нанокомпозита TIO2/Ag/rGO

В статье представлены результаты исследования фотокаталитической активности пленок, образованных наностержнями диоксида титана, допированных наночастицами серебра и восстановленного оксида графена. Полученные нанокомпозитные материалы исследованы методами оптической спектроскопии, сканирующей электронной микроскопии, рентгеновской дифрактометрии, раман-спектроскопии. Фотокаталитическую активность образцов оценивали по генерации фототока при освещении поверхности модулированным источником света ксеноновой лампы. Кроме того, фотокаталитическая активность образцов была оценена по деградации красителя метиленового голубого, который является модельным. Установлено, что внедрение в поры пленок из наностержней диоксида титана наночастиц серебра и восстановленного оксида графена приводит к повышению спектральной чувствительности образца в области 400–500 нм. Повышенная чувствительность образца к видимому свету приводит к росту генерации фототока и в 2,3 раза выше, чем у исходного образца. Деградация красителя метиленового голубого после 100 мин облучения в присутствии образца TiO_2/Ag/rGO составила 19 %. Это в 3 раза выше, чем в пленках из наностержней TiO_2 и 2,3 раза выше, чем пленках TiO_2/Ag. Результаты проведенных исследований показали, что улучшение фотокаталитической активности связано с понижением сопротивления пленки, расширением спектральной чувствительности и ростом величины площади поверхности наностержней.

Ключевые слова: наностержни диоксида титана, наночастицы серебра, восстановленный оксид графена, фотокатализ.