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Effect of TNR/Ag/rGO film area on its photocatalytic activity

This paper presents the results of a study of the effect of the area of nanocomposite films formed by titanium dioxide nanorods, silver nanoparticles and reduced graphene oxide (TNR/Ag/rGO) on its photocatalytic activity. The active area of the nanocomposite films was $S=1\text{cm}^2$, $S=1.5\text{cm}^2$, $S=2\text{cm}^2$, $S=3\text{cm}^2$. The photocatalytic activity of the samples was assessed by the value of the generated photocurrent per unit surface of the film and the photodegradation of the methylene blue dye when the surface was illuminated with a light source from a xenon lamp (300 W). A film with an area of 1cm^2 generated 0.00042 A/cm^2 . With increasing film area $S=1.5\text{ cm}^2$, $S=2\text{cm}^2$, $S=3\text{cm}^2$, the photocurrent density was 0.00035 A/cm^2 , 0.00028 A/cm^2 , 0.00013 A/cm^2 , respectively. It was found that in the absence of a nanocomposite film, the degradation of the dye is negligible. When the TNR/Ag/rGO film was immersed in a dye solution, the degradation of the dye increased and amounted to 32, 59, 70 and 81 % for $S=1\text{cm}^2$, $S=1.5\text{ cm}^2$, $S=2\text{cm}^2$, $S=3\text{cm}^2$ with an irradiation duration of 240 minutes. The results obtained suggested that as the active surface area of the films increases, their photocatalytic activity decreases. The decrease in photocatalytic activity is associated with surface defects and an increase in film resistance.

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

Introduction

Titanium dioxide (TiO_2) is a promising semiconductor material in photocatalysis due to its optical, structural, electrical characteristics, high chemical stability, low toxicity, low cost and high photocatalytic activity [1-4]. Among the variety of TiO_2 nanostructures, such as nanoparticles, nanostitches, nanotubes and nanothreads, materials with one-dimensional transport of charge carriers are more promising [5]. One of these is titanium dioxide nanorod (TNR), obtained by hydrothermal synthesis. By controlling the synthesis conditions, for example, temperatures, concentrations of chemical reagents and the number of synthesis stages, it is possible to control the geometric characteristics of TNR and films based on them [6]. Along with the above advantages, films based on TNR have a number of disadvantages, the main of which are low absorption capacity in the visible range of the electromagnetic wave and the high rate of recombination of electron-hole pairs [7]. There are many methods and approaches to expand the spectral sensitivity of TNR, for example, introducing into the structure semiconductors with a narrower band gap, such as CdS CdSe CuO, etc. [8-10]. The introduction of nanoparticles of noble metals Au, Ag, Cu is also promising, while the absorption capacity is enhanced due to hot electrons of the metals and due to surface plasmon resonance [11-13]. To suppress the rate of recombination of electron-hole pairs, graphene nanostructures are applied to the surface or into the pores of TiO_2 nanostructures by electrochemical deposition or airbrush sputtering [14]. Graphene can serve as both an effective conductor, facilitating efficient charge transfer, and absorb visible light, which

increases sensitivity to it. By integrating TiO₂ with graphene, an improvement in the electronic and photoelectric behavior of the material is achieved. This method can overcome some of the disadvantages of one-dimensional TNR structures and create more efficient photocatalysts with reduced recombination and a wider spectrum of light sensitivity [15, 16].

In our previous works, as well as in a number of other sources, it was shown that the introduction of nanoparticles of noble metals Ag and reduced graphene oxide (rGO) into the TiO₂ structure significantly improves its photocatalytic activity [17-21]. When assessing the photocatalytic activity of TNR or TNR/Ag/rGO films, a film area of the order of 1 cm² was typically used. If the cost of the materials used is reduced, this technology can potentially be commercialized. In this case, there will be a need to create films on an industrial scale, which will lead to an increase in its area. However, a literature review showed that the published works lack information on the effects of film area on its photocatalytic activity, which is the goal of this work.

Experimental

To obtain TNR/Ag/rGO films with different areas, glass substrates with a conductive FTO layer (8 Ohm/cm², Sigma–Aldrich) were cut into geometric dimensions, as shown in Figure 1.

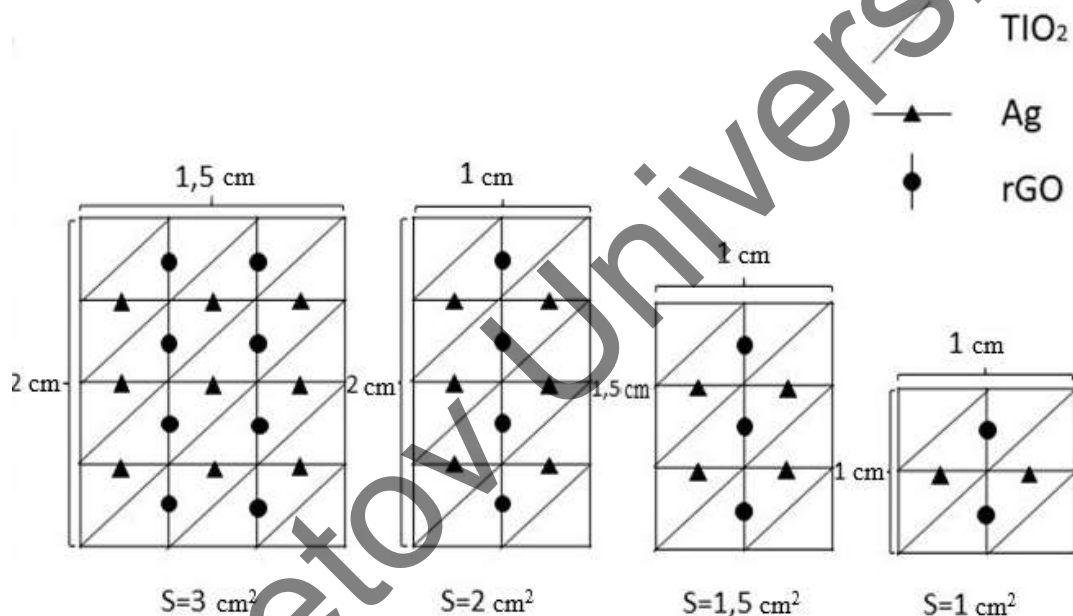


Figure 1. Schematic representation of films with different areas.

TNR with a rutile phase was obtained by hydrothermal synthesis in a stainless steel autoclave with a fluoroplastic vessel. To do this, 12 ml of deionized water, 12 ml of hydrochloric acid (36.5 %, Karagandareaktivsbytt), 0.275 ml of C₁₆H₃₆O₄Ti (97 %, Sigma-Aldrich) were poured into a vessel with a volume of 50 ml and mixed in an ultrasonic bath for 3 minutes. Then, the pre-cleaned FTO glass substrates were placed into a vessel with the conductive side up, sealed tightly and placed in an electronic oven (8.2/1100, SNOL) for 6 hours at a temperature of 180°C. After cooling, the samples were removed, thoroughly washed with deionized water and subjected to heat treatment in an oven at a temperature of 500°C for 2 hours. The introduction of silver (Ag) nanoparticles was carried out by chemical deposition. To 0.2 g of polyvinylpyrrolidone (PVP), 20 ml of H₂O and 20 ml of C₂H₆O₂ and 2 mmol of NaBH₄ were added. The substrates were kept in an oven at 70 °C for 2 minutes, washed with deionized water and dried at room temperature. rGO (99 %, Cheaptubes) was deposited onto the surface by electrochemical deposition. The rGO powder was dispersed in a phosphate solution (0.5 g/L), then treated in an ultrasonic bath for 2 hours. The deposition of rGO onto the TNR/Ag surface was carried out using a standard three-electrode system. The working electrode was TNR/Ag, the counter electrode was Pt foil, and the reference electrode was Ag/AgCl. After 5 minutes of deposition, the films were removed and washed several times with deionized water.

The surface morphology and microstructure of the resulting composite was studied using a Mira 3MLU scanning electron microscope (SEM) (Tescan). Spectrophotometric measurements were carried out on a Solar CM 2203 scanning spectrophotometer (Solar) in the wavelength range 190-750 nm. The film resistance was determined using the impedance spectroscopy method in the frequency range from 1 MHz to 100 MHz. For this purpose, the working electrode (test samples) and the counter electrode made of Pt (Platisol T/SP, Solaronix) deposited on FTO were glued together with a polymer film 25 μm thick (Melotonix, Solaronix). The electrolyte used was iodide/triiodide electrolyte (Iodolyte Z-150, Solaronix). The photocatalytic activity of the samples was assessed by measuring 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). Platinum foil served as the counter electrode, and an AgCl electrode was used as the reference electrode. The measurements were carried out in a 0.1 M NaOH electrolyte in a specially manufactured photoelectrochemical cell with a quartz window. In addition, the photoactivity of the films was assessed by photodegradation of the methylene blue (MB) dye. Methylene blue dye is used as a model pollutant. A xenon lamp with a power of 300 W/cm^2 was used as a radiation source in all experiments (Newport, USA).

Results and discussion

Figure 2 (a, b) shows micrographs of the surface morphology of the TNR film before and after deposition of Ag and rGO nanoparticles. Figure 2a shows that as a result of hydrothermal synthesis, titanium dioxide nanorods are formed on the surface of the FTO substrate, mainly perpendicular to the surface of the substrate. The length of the nanorods is about 2.1 microns, the average diameter of the nanorods is 80-90 nm. As a result of the chemical reduction of silver nitrate, Ag nanoparticles are formed on the TNR surface. The deposited Ag nanoparticles are evenly distributed over the entire surface of the samples and envelope the walls of TNR films, at the same time creating roughness. The average diameter of nanoparticles is 25-30 nm. Also, on the surface of TNR/Ag films, rGO sheets are visible, which were deposited by electrochemical method. The figure shows that graphene sheets partially envelop the TNR/Ag surface.

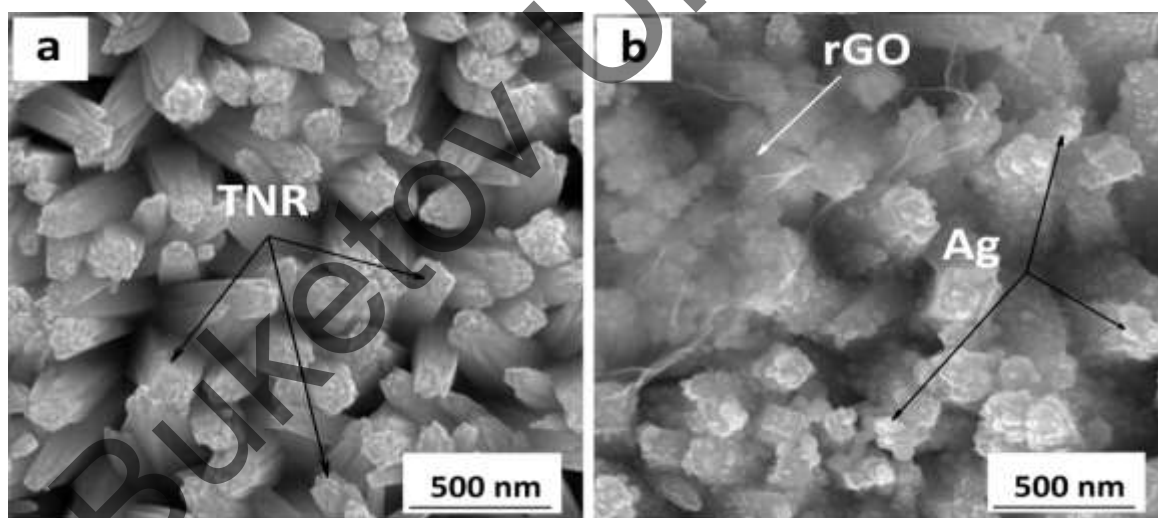


Figure 2. SEM images of the TNR surface before (a) and after (b) deposition of Ag and rGO.

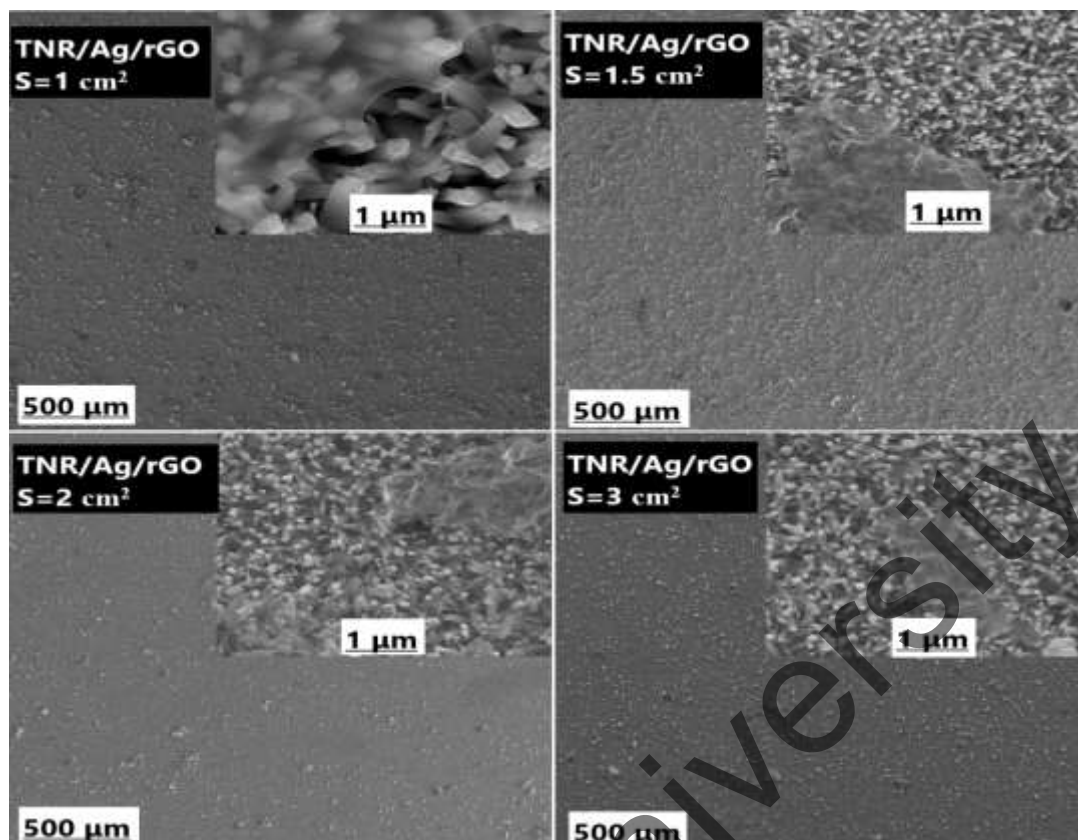


Figure 3. Surface morphology of samples.

Figure 3 shows micrographs of TNR/Ag/rGO films with different areas. The figure shows that increasing the area of the TNR/Ag/rGO film obtained by hydrothermal synthesis does not lead to significant changes in the structure. The film surface is smooth, without visible surface defects.

The photocatalytic activity of the nanocomposites was assessed by the degradation of methylene blue (MB) dye. MB is used as a model dye, which is the source of any contaminants. When films placed in an aqueous solution of this dye are irradiated with light rays, a decrease in the optical density of the dye is observed, which indicates the gradual degradation of molecules in the solution under the influence of light rays. For each sample, an aqueous solution of MB dye with a concentration of 10^{-6} mol/L was poured into a container with a different volume, and the optical density of the dye was determined at certain time intervals.

MB volume
 $S = 3.0 \text{ cm}^2 \rightarrow 60 \text{ ml}$
 $S = 2.0 \text{ cm}^2 \rightarrow 40 \text{ ml}$
 $S = 1.5 \text{ cm}^2 \rightarrow 30 \text{ ml}$
 $S = 1.0 \text{ cm}^2 \rightarrow 20 \text{ ml}$.

Figure 4a shows an example of dye photodegradation. At the absorption peak of 662 nm, a change in the absorbance of the MB dye was observed. The photodegradation curve is shown in Figure 4b. As can be seen from the figure, with long-term irradiation, the degradation of MB without a film is less pronounced. In the presence of the film formed by TNR/Ag/rGO, significant degradation of the methylene blue dye is observed (Fig. 4b). In the presence of a film with an area of 3 cm^2 , the degradation of the dye over a time period of 240 minutes reached 81 %, and when using a film with an area of 2 cm^2 , 1.5 cm^2 and 1 cm^2 , this parameter in the specified period of time was only 70, 59, 32 %. The results obtained indicate that in a film with an area of 3 cm^2 , the rate of dye degradation increases in relation to films with an area of 2 cm^2 , 1.5 cm^2 and 1 cm^2 .

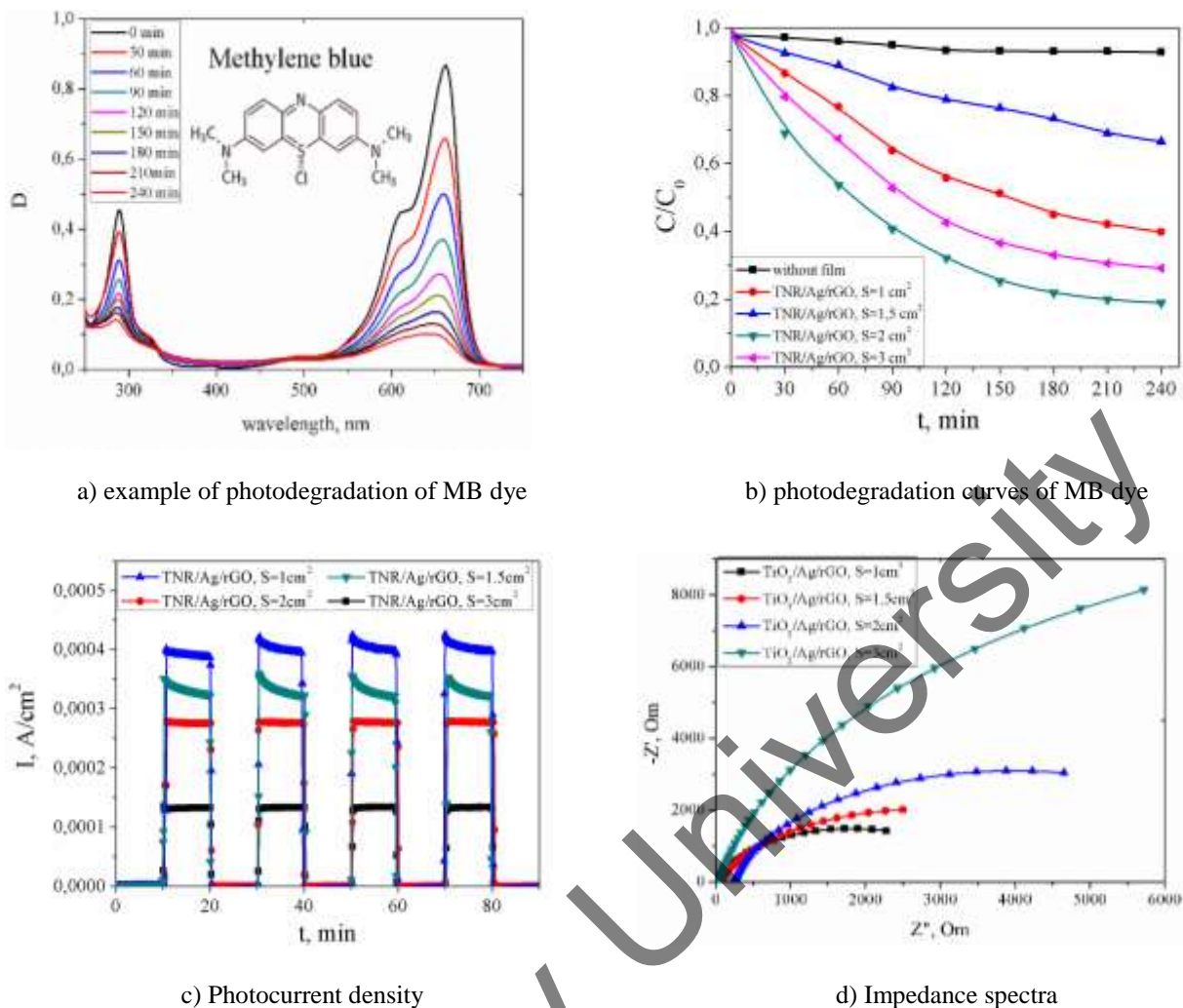


Figure 4. Photocatalytic properties of TNR/Ag/rGO films at different areas.

And also, the photocatalytic activity of the samples was assessed by the response of the photocurrent when irradiated with artificial sunlight with periodic on-off for 10 s. In the absence of lighting, the photocurrent is zero, but when the light is turned on, its density instantly increases. From Figure 4c it can be seen that the maximum value under illumination for a sample with an area of 1 cm² is 0.00042 A/cm², for a sample with an area of 1.5 cm² it is 0.00035 A/cm², for a sample with an area of 2 cm² it is 0.00028 A/cm² and 0.00013 A/cm² for a sample with an area 3 cm². All samples show stability over time when recording photocurrent. From the results of the study, we can see that as the area increases, its photocatalytic activity also increases. This means that it increases the likelihood of reactions and allows them to interact better with the catalyst.

Figure 4d shows impedance hodographs as a function of Nyquist coordinates for all samples studied. Using the central arc of the hodograph, which characterizes the processes occurring in the nanocomposite, the main electrical transport properties of the film were calculated using methods described in the literature [22].

The resistance to electron transport in a nanocomposite R_w and the charge transfer resistance R_k will depend directly on the number of electrons received from the number of free electrons. If we take into account that the dimensions and thickness of the semiconductor film are identical for all systems, accordingly, only the deposited layers of graphene oxide will affect the resistance value. The brief calculations performed are presented in Table.

Electrical transport properties of films based on nanocomposite materials

Name of samples and measurement error	R_w , Ohm	R_k , Ohm	ω_{\max} Hz	τ_{eff} , SEC
TNR/Ag/rGO -1cm ²	71.4	2345.5	295.9	0.003
Error, %	9.2	2.0	-	-
TNR/Ag/rGO-1.5cm ²	55.8	2669.9	12.2	0.082
Error, %	0.7	2.6	-	-
TNR/Ag/rGO -2cm ²	242.2	4733.5	2.6	0.377
Error, %	0.9	3.7	-	-
TNR/Ag/rGO -3cm ²	43.0	5934.2	1.7	0.573
Error, %	1.6	4.1		

The resistance of TNR/Ag/rGO films with an area of 3 cm² is 3 times greater than that of a film with an area of 1 cm² and is 1902 Ohm and 5733 Ohm. And for films with an area of 1.5 cm², the resistance value was 2496 Ohm, and 3878 Ohm for a film with an area of 2 cm². Based on the hodograph, the electron lifetime τ_{eff} was calculated in films and nanocomposite materials. According to the results obtained, the effective lifetime of an electron in a sample with an area of 3 cm² is 0.573 seconds. Samples with an area of 2, 1.5 and 1 cm² with a time of 0.377, 0.082 and 0.003 seconds, respectively. It follows that as the area of the films increases, the effective lifetime of the electron in the sample increases. A long electron lifetime increases the probability of electron recombination in trap states associated with both structural and surface structural defects. In addition, as the film area increases, the film resistance also increases, which also impedes the transport of photogenerated electrons. The table also shows the measurement error values as percentages. In general, the magnitude of errors is in the confidence interval from 0.5 to 5 %.

Conclusions

Thus, it was found that as the active area of the TNR/Ag/rGO nanocomposite increases, its photocatalytic activity decreases. It was found that with the same duration of irradiation (240 min) of the dye in the presence of films, the degree of its degradation is different. In the presence of a film with an area of $S=3\text{cm}^2$, during the above period of time the dye reached 66 % degradation, and with $S=1\text{cm}^2$ the degree of dye degradation was 83 %. It should be noted that the volume of dye increased with increasing film area. Similar results were obtained for the magnitude of the generated photocurrent per unit surface of the sample.

The results obtained led to the conclusion that as the active surface area of the films increases, their photocatalytic activity decreases. The decrease in photocatalytic activity is associated with an increase in film resistance, associated with surface defects. Since the charge transfer resistance R_k increased with increasing area of the nanocomposite.

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TNR/Ag/rGO қабыршақтары ауданының фотокаталикалық белсенділігіне әсері

Мақалада титан қостотығы, күміс наноөзекшелері және қайта қалпына келтірілген графен оксиді (TNR/Ag/rGO) нанокөпозиттік қабыршақтар ауданының, оның фотокаталикалық белсенділігіне әсері туралы зерттеу нәтижелері келтірілген. Нанокөпозиттік қабыршақтардың белсенді аудандары $S=1\text{ см}^2$, $S=1.5\text{ см}^2$, $S=2\text{ см}^2$, $S=3\text{ см}^2$ құрайды. Үлгілердің фотокаталикалық белсенділігі қабыршақ бетінің бірлігінен алынған фототок мөлшері және ксенон шамының (300 Вт) жарық көзімен бетті жарықтандыру кезінде метилен көк бояғыштың фотодеградациясы бойынша бағаланды. 1 см^2 ауданды қабыршақтың фототок тығыздығы 0.00042 А/см^2 құрады. Қабыршақтар ауданының ұлғаюымен $S=1.5\text{ см}^2$, $S=2\text{ см}^2$, $S=3\text{ см}^2$ фототоктың тығыздығы сәйкесінше 0.00035 А/см^2 , 0.00028 А/см^2 , 0.00013 А/см^2 құрады. Нанокөпозиттік қабыршақ болмаған кезде бояғыштың деградациясы шамалы екендігі анықталды. TNR/Ag/rGO қабыршағының бояғыш ерітіндісіне батырылған кездегі бояғыштың деградациясы $S=1\text{ см}^2$, $S=1.5\text{ см}^2$, $S=2\text{ см}^2$, $S=3\text{ см}^2$ аудандарында сәулелену ұзақтығы 240 минут болғанда 32, 59, 70 және 81 % өсті. Нәтижелер қабыршақтардың аудан бетінің өсуімен, олардың фотокаталикалық белсенділігі төмендейтінін көрсетті. Фотокаталикалық белсенділіктің төмендеуі беткі ақаулармен және қабыршақтардың кедергілерінің жоғарылауымен байланысты.

Кілт сөздер: титан қостотығының наноөзекшелері, күміс нанобөлшектері, қайта қалпына келтірілген графен оксиді, қабыршақ ауданы, фотокатализ.

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Влияние площади и пленки TNR/Ag/rGO на её фотокаталитическую активность

В статье представлены результаты исследования влияния площади нанокompозитных пленок, образованных наностержнями диоксида титана, наночастицами серебра и восстановленного оксида графена (TNR/Ag/rGO), на её фотокаталитическую активность. Активная площадь нанокompозитных пленок составила $S=1\text{ см}^2$; $S=1,5\text{ см}^2$; $S=2\text{ см}^2$; $S=3\text{ см}^2$. Фотокаталитическая активность образцов оценивалась по величине генерируемого фототока с единицы поверхности пленки и фотодеградации красителя метиленового голубого при освещении поверхности источником света от ксеноновой лампы (300 Вт). Пленка площадью 1 см^2 генерировала $0,00042\text{ А/см}^2$. С ростом площади пленок $S=1,5\text{ см}^2$; $S=2\text{ см}^2$; $S=3\text{ см}^2$ плотность фототока составила $0,00035\text{ А/см}^2$; $0,00028\text{ А/см}^2$; $0,00013\text{ А/см}^2$, соответственно. Было установлено, что при отсутствии нанокompозитной пленки деградация красителя незначительна. При погружении в раствор красителя пленки TNR/Ag/rGO деградация красителя возросла и составила для $S=1\text{ см}^2$; $S=1,5\text{ см}^2$; $S=2\text{ см}^2$; $S=3\text{ см}^2$ 32, 59, 70 и 81 % при длительности облучения 240 мин. Полученные результаты позволили предположить, что с ростом активной площади поверхности пленок их фотокаталитическая активность уменьшается. Снижение фотокаталитической активности связано с поверхностными дефектами и ростом сопротивления пленок.

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