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EFFECT OF THE CONCENTRATION OF SILVER NANOPARTICLES ON THE PHOTOCATALYTIC ACTIVITY OF TITANIUM DIOXIDE NANORODS

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In this paper the results of a study of the effect of the concentration of silver nanoparticles in films of titanium dioxide nanorods on their photocatalytic activity are presented.Titanium dioxide nanorods with a rutile structure was obtained usingthe method of hydrothermal synthesis. Due tochanging with the amount of substance of the transition metal silver salt ($AgNO_3$) and chemical reduction on the surface of the titanium dioxide nanorods, Ag nanoparticles of different concentrations were obtained. The photocatalytic activity of the samples was assessed by the amount of photocurrent obtained from a unit of film surface and photodegradation of methylene blue dye when illuminating the surface with a light source of a Xenon lamp.Surface morphologies and energy dispersive X-ray studies showed that Ag nanoparticles were uniformly distributed and anchored on the titanium dioxide nanorods surface.

Keywords: nanorods, titanium dioxide, silver nanoparticles, Ag, photocatalysis

1. Introduction

Titanium dioxideTiO_2 is one of the most researched and widely used materials for water purification, air purification, hydrogen production and solar cells due to its many advantages and unique physical and chemical properties [1-4]:

1. Low cost: TiO_2 is cheap and readily available, making it attractive for mass production.
2. Chemical stability: TiO_2 is chemically stable and does not degrade in aggressive environments, which allows it to be used in various conditions.
3. Suitable zone position: TiO_2 zones are suitable for inducing oxidation and reduction reactions, making it effective for a variety of catalyst processes.
4. Non-toxic and biocompatible: TiO_2 is a non-toxic and biocompatible material, which is important for medical and biological applications.
5. Possibility of controlling the geometric structure, depending on the synthesis method, for example nanorods, nanotubes, nanofilaments and TiO_2 nanoparticles [5-9].

However, despite the many structures, TiO_2 has two main disadvantages: firstly, it can only absorb ultraviolet radiation due to its wide band gap (~3.2 eV), secondly, its high photogenerated carrier recombination rate leads to low quantum efficiency [10, 11].

Among the variety of nanostructures, titanium dioxide nanorods (TNR) are the most promising because they have one-dimensional electron transport, high specific surface area and high crystallinity [12-14]. At the same time, the possibility of using one-dimensional electron transport will make it possible to somehow reduce the recombination rate of photogenerated TNR charge carriers, but the problem of the absorption capacity of only the ultraviolet region has not yet been resolved.

The spectral sensitivity of TNR in the visible range can be expanded by adding noble metal nanoparticles [15, 16], sensitization with dye molecules [17], and adding nanomaterials with lower band gap energy [18-20]. The introduction of Ag nanoparticles into the TiO_2 structure is an effective method for improving its photocatalytic properties. The introduction of Ag nanoparticles into TiO_2 is an effective method for improving its photocatalytic properties. On the one hand, a Schottky barrier can form between TiO_2 and Ag nanoparticles [21, 22], restraining the reverse current of injected electrons from TiO_2 to Ag and thereby suppressing the recombination of electron-hole pairs.On the other hand, Ag nanoparticles generate localized surface plasmon resonance (LSPR) effect under visible light, and excited hot electrons can be

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injected onto the TiO_2 surface [23, 24].Thus, the performance of TiO_2 /Ag composite is superior to that of TiO_2 [25]. Despite the huge number of published works on the photocatalytic activity of TNR and the use of LSPR in these processes, there is no information on the optimal concentration of Ag nanoparticles on the surface of TiO_2 nanorods obtained by chemical method.

The purpose of this work is to determine the optimal concentration of Ag nanoparticles on the surface of TNR films at which the best photocatalytic activity will be observed.

2. Experimental part

TNRs are synthesized by hydrothermal synthesis. Cleaned fluorine-doped tin oxide(FTO) substrates were prepared from a solution containing 7.5 ml - of deionized water, 7.5 ml of hydrochloric acid, and 0.25 ml of titanium butoxide $C_{16}H_{36}O_4Ti$ - in a 25 ml fluoroplastic embedded stainless steel tube was placed in an autoclave. The solution was kept in a furnace for 6 hours at a temperature of 180^0C. The samples were then removed and washed with deionized water. To improve crystallization and remove synthesis byproducts, the nanorods films were heated in a high temperature oven at 500^0C for 2 hours.

Ag nanoparticles were prepared by chemical deposition method. 0.2 g of polyvinylpyrrolidone was added to 40 ml of H_2O and $C_2H_6O_2$ (1:1% by volume), then 2 mmol of $NaBH_4$ was added to the solution mixture with vigorous stirring. The resulting mixture was stirred for about 5 minutes. Then 0.5, 0.75, 1 and2 mmol $AgNO_3$ were added at different concentrations. Substrates containing TNR were dipped upwards into the bottom of the dish and kept in an oven at 70°C for 2 minutes. The sample was then washed with deionized water and dried at room temperature.

Using a scanning electron microscope Mira 3MLU from Tescan at a voltage of 20 kV, a study of surface morphology, energy dispersive X-ray analysis (EDX) analysis and distribution of elements on the surface was carried out.Spectrophotometric measurements were carried out on a Solar CM 2203 scanning spectrophotometer (Solar) in the wavelength range 190-750 nm.

The resistance of the films was determined using impedance spectroscopy. 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).Iodide/triiodide electrolyte (Iodolyte Z-150, Solaronix) was used as the electrolyte.

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 mmol NaOH electrolyte in a specially manufactured photoelectrochemical cell with a quartz window. In addition, the photoactivity of the films was assessed by the photodegradation of the dye methylene blue (MB), which is used as a model pollutant. The radiation source used in the experiments was a xenon lamp with a power of 300 W/cm^2 (Newport, USA).

3. Results and discussion

Figure 1 shows micrographs of the surface morphology of the TNR film before and after deposition of Ag nanoparticles. From Figure 1a, it can be seen that hydrothermal synthesis produces titanium dioxide nanorods on the surface of the FTO substrate, predominantly perpendicular to the substrate surface. The length of the nanorods is about 1.48 μm, the average diameter of the nanorods is 50-60 nm. Chemical reduction of silver nitrate resulted in the formation of Ag nanoparticles on the surface of TNR (see Figure 1 b, c, d and f). The deposited Ag nanoparticles are uniformly distributed over the entire surface of the samples and envelop the walls of the TNR films, thereby creating roughness. It can be seen from the figures that with an increase in the concentration of $AgNO_3$ from 0.5 to 2 mmol used in reduction, the number of Ag nanoparticles increases.

This is especially noticeable from Figure 1d and 1f, where the concentration is 1 and 2 mmol. At the same time, the number of Ag nanoparticles is so large that the presence of TNR underneath is practically invisible. The sizes of silver nanoparticles were measured using the dynamic light scattering method on a Zetasizer Nano ZS. For this purpose, solutions were used from which Ag nanoparticles were deposited. It was found that the average diameter of nanoparticles is 25-30 nm, which is also confirmed by SEM image processing.

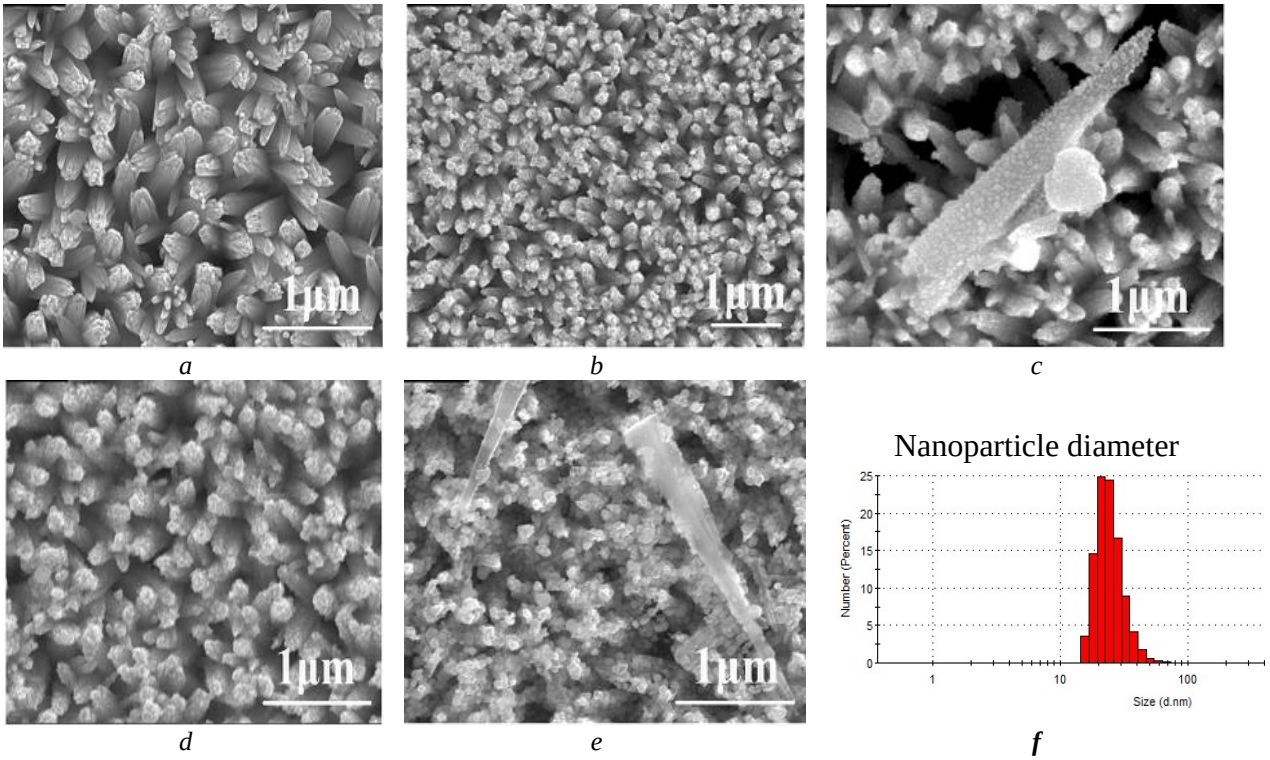

Fig.1.SEM images of the TNR surface before and after Ag deposition:

a) TNR; b) TNR/Ag_0.5 mmol; c) TNR/Ag_0.75 mmol; d) TNR/Ag_1 mmol; e) TNR/Ag_2 mmol; f) Diameter of nanoparticles measured on Zetasizer Nano

Surface mapping and EDX spectrum of TNR doped with Ag nanoparticles of different concentrations are presented in Figure 2.In all samples, 5 elements were identified, such as Ti, O, Ag, Na and Si. The elements Ti and O belong to the titanium dioxide nanorods that form the basis of the film, so its percentage is much higher than the others. The presence of peaks in the energy ranges from 3.4 to 4 keV and 1.8 keV, 1 keV correspond to the peaks of Sn, Si and Na, respectively, which belong to the FTO substrates. Peaks in the 3 keV region correspond to Ag nanoparticles.

Five spectra were taken from the surface of each sample: at the center and at the corners. The inset in Figure 2 shows the content of elements (in percentage) relative to the entire total spectrum of the map. From the data obtained, it is clear that with an increase in the amount of silver transition metal salt ($AgNO_3$) used in chemical reduction, the concentration of reduced Ag nanoparticles on the TNR surface increases. Thus, with an amount of substance of 0.5 mmol $AgNO_3$, the proportion of Ag nanoparticles relative to the entire total spectrum was 2.3%, for 0.75, 1 and 2 mmol it was 2.8, 6.5 and 6.8%, respectively.

The normalized absorption spectra of the samples are presented in Figure 3. From the absorption spectra presented in Figure 3 it is clear that doping Ag NPs significantly expands the absorption spectrum of the photocatalyst relative to undoped TiO_2. The absorption peak of silver nanoparticles in the spectrum is located in the range of 410-420 nm. The introduction of Ag nanoparticles into TNR structures leads to an expansion of spectral sensitivity in the visible range.

This is confirmed by the pronounced small peaks of Ag nanoparticles in TNR/Ag nanocomposite materials in the region of 420–480 nm. In addition, TNR/Ag nanocomposites effectively absorb light in the ultraviolet region of the spectrum.

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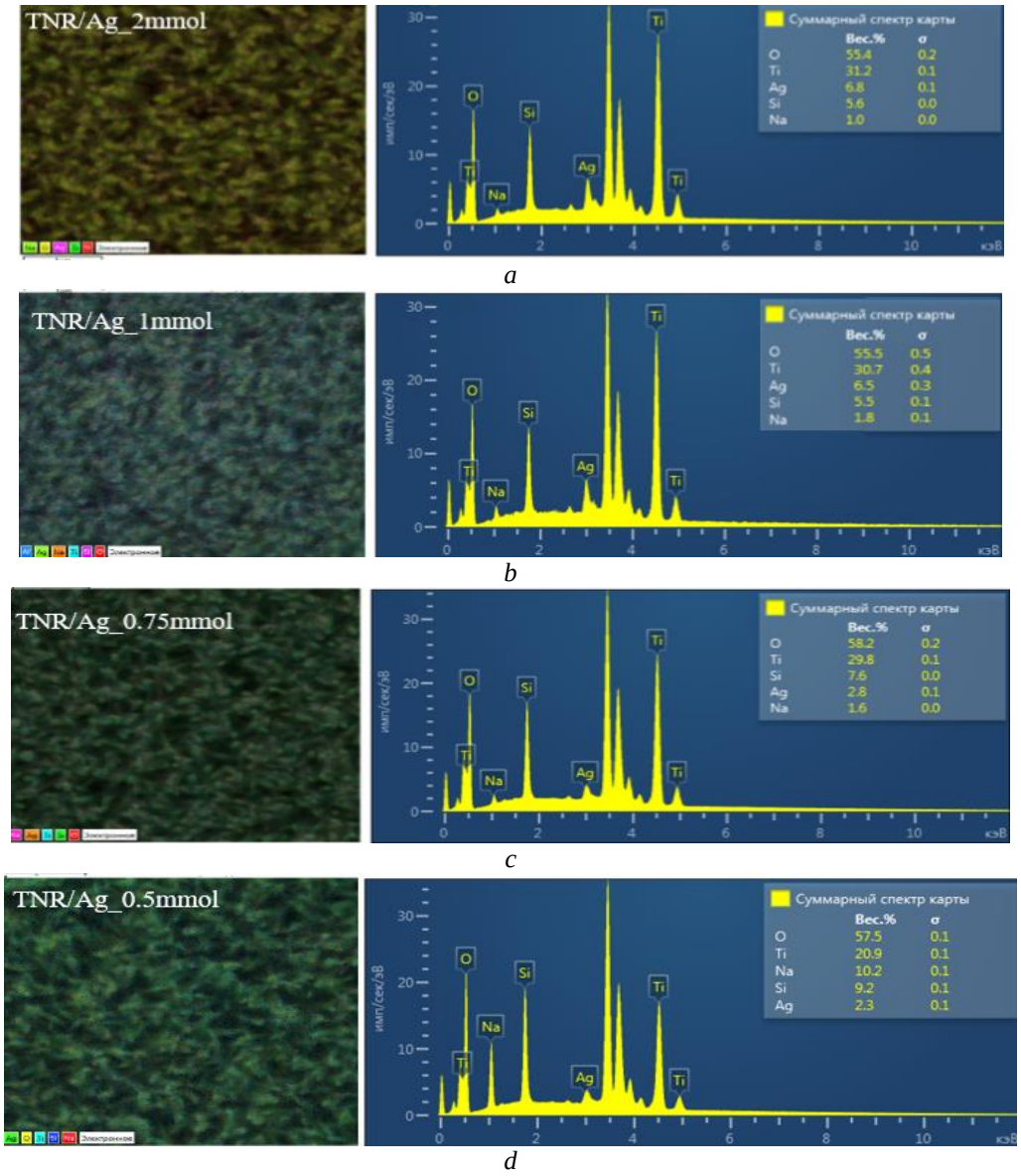

Fig. 2. Surface mapping and EDX spectrum of TNR doped with Ag nanoparticles of different concentrations: a) TNR/Ag_2 mmol; b) TNR/Ag_1 mmol; c) TNR/Ag_0.75 mmol; d) TNR/Ag_0.5 mmol.

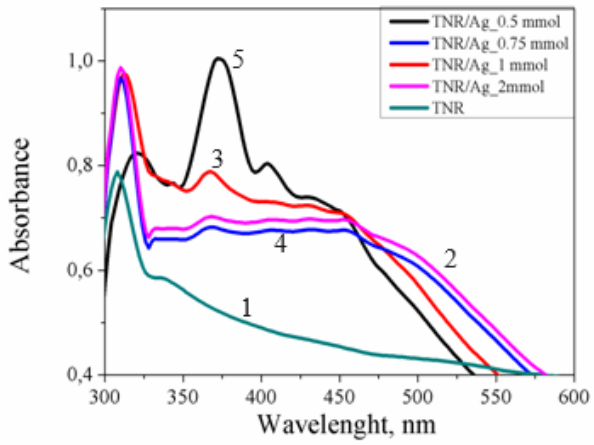

Fig. 3. Absorption spectrum of TNR/Ag at different concentrations:
1-TNR, 2- TNR/Ag_2 mmol, 3-TNR/Ag_1 mmol, 4-TNR/Ag_0,75 mmol, 5-TNR/Ag_0,5 mmol

The photocatalytic activity of the samples was assessed by the decomposition reaction of the dye methylene blue (MB) and it is a model pollutant. The process of photocatalytic oxidation is as follows: after irradiation and excitation of electrons from the valence band of the photocatalyst, photogenerated holes can directly oxidize the dye to a reactive intermediate (reaction 1) or lead to the formation of highly reactive oxidative hydroxyl radicals (OH•), leading to degradation and discoloration dye (reactions 2 and 3).

$$TNR/Ag+hv \rightarrow TNR/Ag\ (e_{CB}^{-}+h_{VB}^{+}) \qquad \textit{(reaction 1)}$$

or

$$h_{VB}^{+}+MB \rightarrow MB^{+} \rightarrow \textit{dye oxidation} \qquad \textit{(reaction 2)}$$

or

$$h_{VB}^{+}+H_2O(OH^{-}) \rightarrow OH+H$$

$$OH+MB \rightarrow CO_2+H_2O \qquad \textit{(reaction 3)}$$

The initial concentration of the MB dye was 10^{-6} mol/L.Before the experiment, the samples were kept in a different solution of the MB dye for 8 hours to eliminate errors associated with the adsorption of the dye on its surface. The original optical density of the MB dye was 0.55 at the wavelength of its 662 nm absorption maximum and was obtained per unit.

An example of the degradation process of the MV dye and its assessment by optical density are presented in Figure 4a. From this figure it can be seen that with an increase in the duration of radiation, the optical density of the dye decreases, which leads to its discoloration and degradation of molecules. Further, at the absorption peak of 662 nm, a change in the absorbance of the MB dye was observed in the presence of TNR and TNR/Ag films with different silver concentrations. The curves for changes in optical density or dye concentration in the absence and presence of nanocomposite films are presented in Figure 4b. From the presented data it is clear that during long-term irradiation of the dye without immersed films, its degradation is insignificant and amounts to only 7%. In the presence of the film formed by TNR, the degradation rate increased significantly and reached 40% in 180 minutes of radiation. In the presence of TNR films with condemned Ag nanoparticles, the rate of dye degradation increased. Thus, when using a TNR/Ag film with an amount of reduced silver nitrate of 0.5 mmol, the degradation was 48%, and for 0.75, 1 and 2 mmol it was 60, 81 and 70%, respectively (see Fig. 4b) for a similar irradiation time.

Also, the photocatalytic activity of the samples was assessed by the photocurrent response when irradiated with artificial sunlight with periodic switching on and off of the light. In the absence of illumination, the photocurrent of the samples is zero; when the light was turned on, the photocurrent density instantly increased for all samples. It can be seen from Figure 4c that the maximum photocurrent value under light illumination for the TNR/Ag_1mmol sample is 890 μA/cm^2 and is the highest among all samples. It is clear from the data that with an increase in the amount of reduced $AgNO_3$ and, accordingly, reduced Ag nanoparticles on the surface, TNR first increases the photocurrent density and then decreases, indicating the presence of an optimal concentration.

Figure 4d shows the impedance hodographs in the Nyquist coordinates for all the samples under study. According to the godograph M. Adachi, M. Sakamoto, J. Jiu, et al. according to the methodology proposed in his works, the main electrical transfer properties of films were calculated [26]. The electron transport resistance in the R_w nanocomposite and the R_k charge transport resistance will directly depend on the number of electrons coming from the number of free electrons. The charge transfer resistance R_k of TNR/Ag films at a concentration of 1 mmol is 2.5 times less than in a film with a concentration of 0.5 mmol and is 1748 Ohm and 685 Ohm. Effective electron lifetime τ_{eff}in films and nanocomposite materials. According to the results obtained, the duration of the effective lifetime of an electron in a sample with a concentration of 1 mmol is also 2 times less than the other samples. As the silver concentration increases, the effective lifetime of an electron in the sample increases. Long electron lifetimes increase the probability of electron recombination. Ag on the surface of TNR can resist oxidizing agents from solution or, conversely, are oxidized, since silver is a strong oxidizing agent. Unlike other noble metals such as Pt or Au, when Ag nanoparticles are combined with TNR, the Fermi level of the metal is located near the conduction band of TiO_2, and a Schottky barrier cannot be formed.

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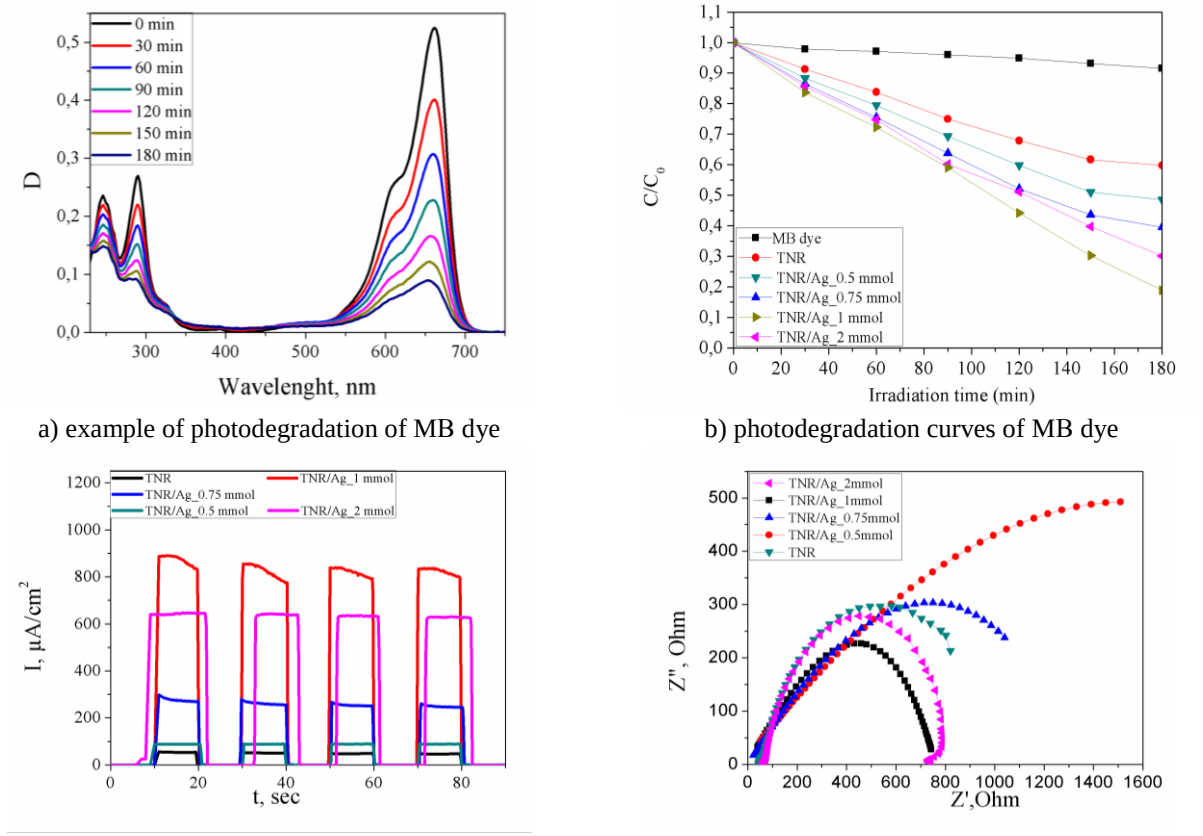

a) example of photodegradation of MB dye

b) photodegradation curves of MB dye

c) Photocurrent density

d) Impedance spectra

Fig. 4. Photocatalytic properties of TNR/Ag films at different concentrations.

Therefore, electrons can flow in both directions, allowing holes to be effectively captured by the silver particle. Researchers presented possible mechanisms of decomposition of various substances on the surface of TiO_2 at different concentrations of silver nanoparticles [27]. However, they used TiO_2 in nanoparticle form. The increase in photocatalytic activity of TNR in the presence of Ag may be due to the unusual electronic properties of silver and hot electrons, which are efficiently transferred to the conduction band of TiO_2 and participate in photochemical reactions. The results obtained can be useful in creating effective photocatalysts for wastewater treatment and water splitting to produce hydrogen gas.

4. Conclusions

Thus, the work compares TiO_2 nanorods with a rutile structure, which were used to create composite materials with different concentrations of $AgNO_3$. From the results of the study, we can see that as the concentration of $AgNO_3$ increases, its photocatalytic activity also increases. As the concentration of Ag nanoparticles on the TNR surface increases to 1 mmol, the photocatalytic activity increases and then decreases at 2 mmol, indicating the presence of an optimal concentration.The photocurrent density generated by a TNR film with a concentration of Ag nanoparticles of 1 mmol is 10 and 1.4 times higher than 0.5 mmol and 2 mmol, respectively. In the presence of a TNR film with a concentration of Ag nanoparticles of 1 mmol, the degradation of the dye reached 71%, which is 1.7 times higher than without Ag nanoparticles. The resistance of TNR/Ag films at a concentration of 1 mmol is 2.5 times less than that of a film with a concentration of 0.5 mmol.

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