

Article

Facile Synthesis of Ti/TiN/TiON/TiO₂ Composite Particles for Plasmon-Enhanced Solar Photocatalytic Decomposition of Methylene Blue

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Abstract: The present work studies the interrelation of the structural-phase composition and morphology of composite Ti/TiN/TiON/TiO₂ microparticles with their catalytic properties under UV, visible, and solar light irradiation. An efficient method for the synthesis of composite Ti/TiN/TiON/TiO₂ microparticles is proposed. The method uses the effect of low-temperature nitrogen plasma of an electric arc in an open atmosphere on titanium microparticles. Photocatalytic activity of fabricated composite microparticles under visible and sunlight irradiation is demonstrated. The mechanism of photocatalysis is proposed.



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Keywords: titanium; composite particles; titanium nitride; rutile; titanium oxynitride; photocatalysis; visible and sunlight radiation; methylene blue photodegradation; plasmon enhancement

1. Introduction

The rapid development of industry inevitably leads to the deterioration of the ecological situation and environmental pollution. The volumes of waste from industrial enterprises, oils, phenol, and chlorobenzene derivatives, and artificial dyes requiring disposal increase daily. Despite the high cost, traditional methods of purification and mineralization of contaminants are not always effective, and the use of photocatalytic methods is required [1,2]. However, the transition to environmental photocatalysts is hampered by their low efficiency. For example, today’s most popular photocatalyst TiO₂ (P25 from Degussa) is active exclusively in the ultraviolet (UV) range, which occupies no more than 5% of the solar spectrum. In addition, many catalytic processes require high temperature and pressure, and expensive catalysts using gold, platinum, and silver are used to increase activity [3,4]. The increase in activity is associated with the injection electrons from metal particles in TiO₂ due to their surface plasmon resonance, or by charge transfer mechanism in the interface metal/oxide. This anisotropic electron flow significantly retarded the charge recombination of these electrons with the holes in metal particles. New approaches are required to develop low-cost photocatalysts operating under normal conditions using solar energy. At present, studies in the field of photocatalysis are mainly focused on the search for new photocatalytic materials. For example, in [3], a three-phase nanocomposite CuO–MgO–ZnO obtained from a mixture of nitrates by the method of homogeneous precipitation with long treatment at various temperatures (up to 700 °C) was shown to be effective under sunlight. Another approach is proposed in [5]. The effect of electrolyte composition on photocatalytic properties was investigated. The addition of

two common electrolytes that are not hydrolyzing (NaCl and CaCl_2) into the dye solution was correlated with the chemical stability of the $\text{CIS}/\text{TiO}_2/\text{SnO}_2$ hetero-structure and the removal/mineralization efficiencies. The highest photodegradation efficiency (99%) was reached when 3.5% NaCl was used. A series of works [6–9] is devoted to the synthesis of nanocomposite photocatalysts based on hexacyanoferrates and other compounds, which also demonstrated efficiency under sunlight. Another type of nanocomposite photocatalyst based on graphite carbon nitride ($\text{g-C}_3\text{N}_4$) was proposed in [10–12]. The use of tellurium-containing solid solutions of the β -pyrochlore structure type [13] can be considered as a new direction of photocatalysis, however, their efficiency under sunlight is currently not high. In [14], the photocatalytic activity of the $\text{g-C}_3\text{N}_4\text{-TiO}_2$ nanocomposite under sunlight irradiation was demonstrated. Despite the pronounced photocatalytic properties, the synthesis of nanocomposites is a complex technological process that requires careful selection of materials and many hours of processing. In addition, the problem of transitioning from laboratory synthesis of nanomaterials to their mass production is not trivial. In this regard, the most promising composites for photocatalysis on an industrial scale, in our opinion, are microparticles of the TiN-TiO_2 system. The absorption spectrum of TiN [15] extends from the UV to the near infrared (NIR) range, which confirms the metallic conductivity. Due to this, pronounced plasmon effects are observed in titanium nitride nanoparticles [16] in the visible and NIR regions. In [17], a localized surface plasmon resonance in TiN nanoparticles embedded in a TiN_xO_y matrix was studied. It was found that the plasmon absorption peak is located at the wavelengths of ~ 800 nm (~ 1.55 eV) and ~ 1200 nm (~ 1.03 eV), depending on the particle size. Thus, photosensitivity in the TiN-TiO_2 system can be implemented in a wide spectral range, including the UV, visible, and NIR regions, which allows one to expect its high efficiency under solar irradiation. In general, the effectiveness of the composite depends on the area of the interface boundary. In particular, in [18], a TiN@TiO_2 nanocomposite is proposed as a photosensitizer with improved characteristics due to plasmon effects. Thus, a new approach may consist not in the search for a new material, but in the search for a productive and economically accessible method for the synthesis of TiO_2 -based microcomposites. A convenient technique is an electric arc plasma treatment [19]. Its advantages include the possibility of modifying the surface of objects of any complexity, the mechanical strength of the resulting coating, as well as the control of the chemical composition using plasma gas and the surrounding atmosphere. In the presence of a reliable low-temperature plasma generator [20], in the discharge gap of which a high-enthalpy plasma flow of working gases with a temperature of thousands to tens of thousands of degrees is created, it is possible to oxidize and nitride the injected metal microparticles. The advantage of plasma treatment of metal microparticles is preserving the metal due to the high speed of flight. This is important in the case of plasma treatment of titanium in an open atmosphere, since the formation of microparticles with titanium increases the photocatalytic activity. The additional use of nitrogen plasma will create conditions for the formation of nitrogen-containing phases. The disadvantage of the proposed synthesis method is the formation of a high-temperature TiO_2 phase (rutile) characterized by low photoactivity. This disadvantage is supposed to be compensated for by charge transfer between the metal and semiconductor phases, as well as by plasmon enhancement in nitrogen-containing phases.

In the present work, the interrelation of the structural-phase composition and morphology of composite microparticles with their catalytic properties under UV, visible, and solar light irradiation was studied. Resonant amplification processes were investigated. Composite microparticles were synthesized by treating titanium microparticles in low-temperature nitrogen plasma in an open atmosphere. The mechanism of photocatalysis of the obtained composite microparticles was studied. It should be noted that the synthesis of nanoparticles is a complex and lengthy process. In our case, a short-term effect on microparticles is used, the synthesis of which is cheaper.

2. Materials and Methods

High purity commercial titanium powder was used as an initial sample. At the first stage, microscopic and X-ray diffraction analysis of the initial powder were carried out. Microscopic studies were performed using the JEOL (Tokyo, Japan) scanning electron microscope (SEM) equipped with an energy dispersive X-ray (EDX, Cambridge, MA, USA) microanalyzer. X-ray diffraction (XRD) patterns were obtained using the PANalytical Empyrean diffractometer (Almelo, the Netherlands) in the Bragg–Brentano geometry. Radiation from a copper anode ($\text{CuK}\alpha_2 = 1.54 \text{ \AA}$) was used. To determine the band gap by UV/VIS spectroscopy, a spectrometric complex based on the MDR-41 monochromator (NPO “Spektr”, Rostov-on-Don, Russia) was used. A commercial titanium microparticle powder (brand PTM-A, OCHV, St. Petersburg, Russia, fraction of impurity not more than 0.1%) was used as the initial sample. The microparticles had a large spread in lateral size: 20–100 μm . The titanium microparticles were treated in the anode region of the nitrogen plasma generator using a plasmatron with vortex stabilization and an expanding channel. Plasma treatment was carried out in an open atmosphere. The technique and theoretical calculations of the process of plasma treatment of particles are described in detail in [21]. The generator’s parameters during the treatment process were as follows. Nitrogen and carrier gas consumption were 1.5 and 0.2 g/s, respectively, powder consumption was 10 g/min, arc current was 150 A, plasma temperature in the powder supply zone was ~8–10 kK, and speed of particles flight through the treatment zone was $50 \div 60 \text{ m/s}$.

X-ray photoelectron spectroscopy (XPS) using the SPECS spectrometer (Specs, Berlin, Germany) equipped with Al and Mg anodes was used to determine the chemical composition of the titanium oxide powder surface. The spectrometer was metrologically verified and included in the register of measuring instruments of the Russian Federation (FSIS “Arshin”). The spectra were recorded in the binding energy range from 0 to 1200 eV. To estimate the dependence of the powder composition on the depth of the near-surface layer, the samples were etched with Ar^+ ions with an energy of 4 keV.

The photocatalytic characteristics of the samples were evaluated using the photodegradation of methylene blue (MB) in an aqueous solution (1 mg L^{-1}). Photocatalytic experiments were carried out in a 50 mL glass beaker. In this case, visible, UV-Visible, and solar light were used. A 250 W high-pressure mercury lamp (Phillips, Amsterdam, The Netherlands) without cutoff filters was used as a source of UV-Visible light, and a 70 W metal halogen lamp (Osram, Munich, Germany) was used as a visible light source. A constant temperature in the reaction vessel of 26°C was maintained by ventilation and controlled by a thermometer. To carry out the photocatalytic reaction, 20 mg of a photocatalyst was added to 20 mL of an MB aqueous solution. Before turning on the light, the cuvette was placed in the dark for 75 min to achieve adsorption–desorption equilibrium. Before the start of the experiment, the suspension was subjected to ultrasonic treatment to degas the photocatalyst. The whole process was carried out by stirring on a magnetic stirrer. The light source was placed above the reactor at a distance of 10 cm. Collection of samples (5 mL) was performed every 15 min. The particles were separated from the solution by centrifugation at 14,000 rpm for 2 min in a PE-6926 laboratory centrifuge (Ekroskhim LLS, St. Petersburg, Russia). The MB concentration was measured using an SF-2000 spectrophotometer (NPO “Spektr”, Rostov-on-Don, Russia) from the characteristic MB absorption peak at a wavelength of 663.7 nm. After the measurement, the solution was poured back into the reactor and the process continued. For comparison, the MB solution was tested under similar conditions without a photocatalyst (photolysis). The MB concentration was determined using Beer–Lambert law.

3. Results

3.1. Study of Morphology, Elemental, and Structural-Phase Compositions of Microparticles

The initial titanium powder consisted of microparticles (Figure 1a). According to XRD data (Figure 2), the initial powder was a low-temperature Ti α -phase with a hexagonal close-packed lattice (JCPDS card no. 44-1294).

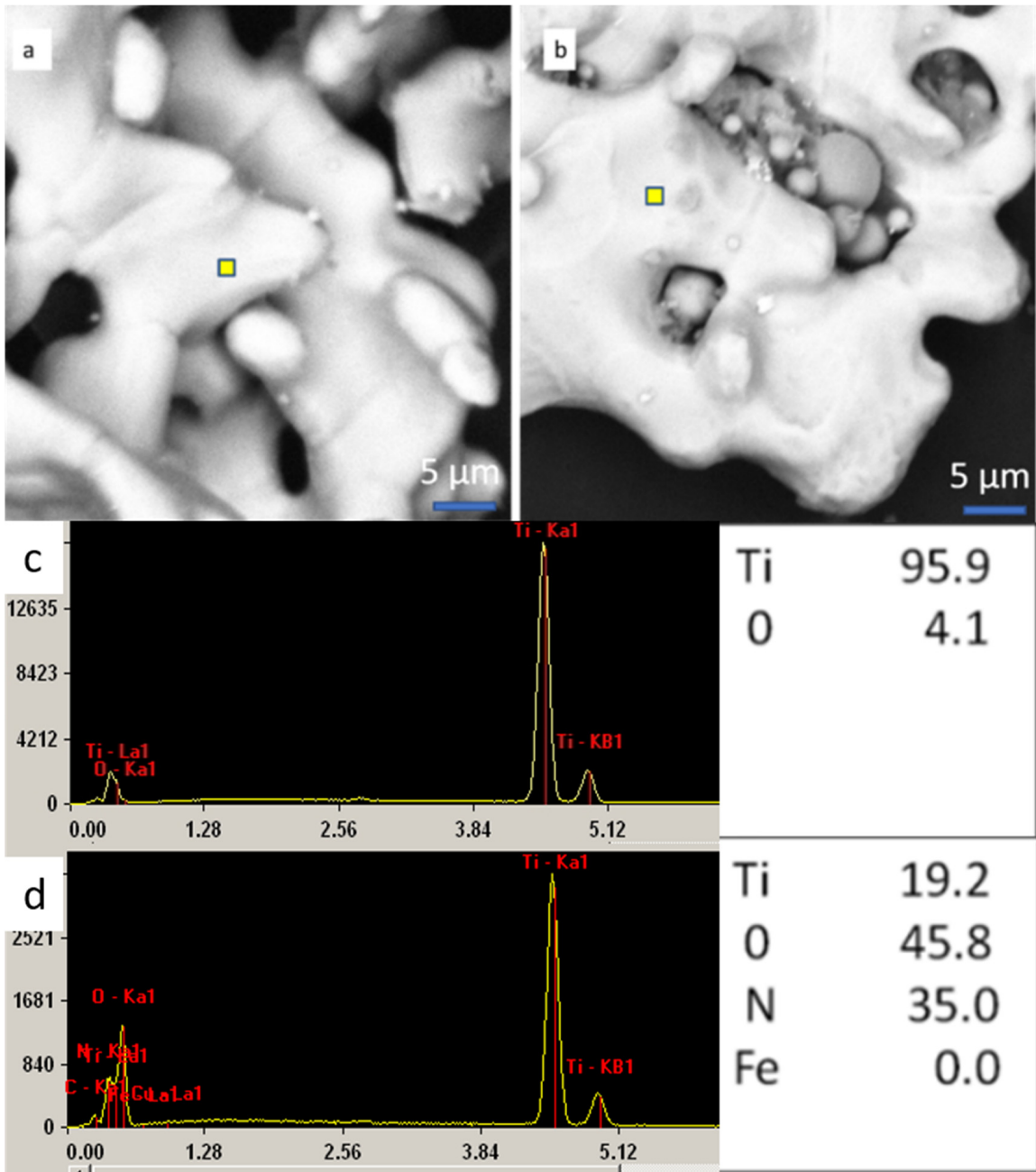


Figure 1. Typical SEM images and the results of EDX analysis of titanium microparticles before (a,c) and after (b,d) plasma treatment.

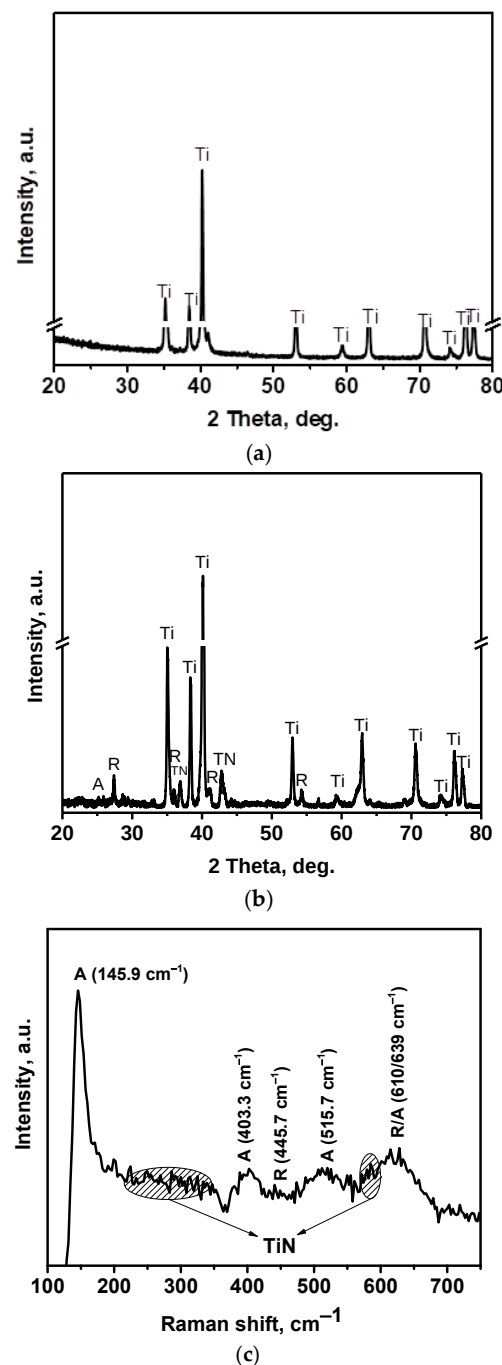


Figure 2. (a) XRD patterns of Ti microparticles before (a) and after (b) plasma treatment. Designations: R—Rutile TiO_2 , A—Anatase TiO_2 , TN—TiN, Ti—Titanium. (c) Raman spectra of Ti microparticles after plasma treatment.

According to the SEM data (Figure 1), the morphology of the microparticles changes after treatment, and the surface became less uniform. Treatment causes agglomeration of titanium microparticles. The results of EDX analysis demonstrate a low oxygen content in the original sample, which is associated with the oxidation of the titanium surface during long-term storage. During the treatment of titanium microparticles, the oxygen content increases many times, and nitriding of the microparticles is also observed. According to the XRD data (Figure 2), the α -phase of Ti remains the main one in the microparticles, which indirectly confirms the preservation of the metallic titanium. In addition, there was a high-temperature phase of rutile TiO_2 (JCPDS card no. 21-1276). In addition to the original

picture, two new diffraction peaks centered at 36.9° and 43.1° are clearly visible, which are characteristic of the (111) and (200) crystal planes of titanium nitride TiN (JCPDS card no. 38-1420). A very weak signal from the TiO₂ anatase phase can also be seen in the spectrum (JCPDS card no. 21-1272). The anatase phase is likely retained in deeper layers because, during the very short time of high-temperature treatment in nitrogen plasma, only the near-surface layer manages to form the rutile phase. In addition, it is practically impossible to quantify the content of the phases using X-ray phase analysis, since many peaks of anatase, rutile, and titanium nitride overlap. This is clearly seen from the asymmetry of many peaks. For our composite, the band gap optically measured and calculated by the Tauc plot was 2.83 eV. The ERM data confirm the presence of nitrogen in titanium powder microparticles after plasma treatment; however, its exact quantitative content is difficult to estimate, since the spectral lines of nitrogen and titanium partially overlap. For a more accurate understanding of the structure, the Raman spectra were studied. The data are shown in Figure 2c. The Raman spectrum also shows the presence of modes characteristic of titanium dioxide in the anatase and rutile phases and titanium nitride. The Raman peaks observed at 145.9, 403.3, 515.7, 521.0, and 639.0 cm⁻¹ belong to the E_g, B_{1g}, B_{1g}, and E_g modes of the anatase phase. Rutile TiO₂ showed characteristic stretch peaks at 445.7 and 610 cm⁻¹, which correspond to the symmetry of E_g and A_{1g}, respectively [22]. Two broad bands at 200–300 cm⁻¹ and about 550 cm⁻¹ are due to acoustic transitions (LA and TA) and optical modes (LO and TO) of TiN, respectively [23]. The results indicate successful formation of the Ti/TiN/TiO₂ hybrid multicomponent structure.

Of great interest is the dependence of the chemical composition of the powder on the depth of the near-surface layer. For this, XPS studies were carried out (Figure 3) with successive etching of the powder (the etching rate calculated for a planar structure is ~1 nm/min).

The spectra of the ground level Ti 2p are shown in Figure 3a–d. The spin-orbit splitting of the Ti 2p_{1/2} and Ti 2p_{3/2} peaks located near 464.7 and 458.6 eV corresponds to the Ti 2p_{1/2} and Ti 2p_{3/2} binding energies. These peaks are consistent with Ti⁴⁺ in the TiO₂ lattice [24]. Figure 3b–d shows the spectra of the main level Ti 2p depending on the etching time 5–10–15 min. Now, the XPS spectra of Ti 2p are described by 3 doublets: Ti 2p_{3/2} (454.9 eV)—Ti 2p_{1/2} (461.2 eV), Ti 2p_{3/2} (456.6 eV)—Ti 2p_{1/2} (462.4 eV), and Ti 2p_{3/2} (458.6 eV)—Ti 2p_{1/2} (464.2 eV), typical for TiN [25], TiON [26], and TiO₂ [27], respectively. The appearance of peaks specific for TiON indicates that TiO₂ is doped with nitrogen, which replaces oxygen in the TiO₂ sublattice. It can also be seen that with the depth of etching, the proportion of TiN increases and TiON decreases. The high thermodynamic stability of TiN is known. However, under the action of oxygen or air heated to high temperatures, an oxide layer is easily formed on the TiN surface: the negative free Gibbs energy for the TiN oxidation reaction (582 kJ/mol) [28]. At the same time, the formation of a transition layer similar to TiON at the TiO₂/TiN interface has already been reported [29].

The presence of TiON bonds, indicating that TiO₂ is doped with nitrogen, suggests the inevitable formation of oxygen vacancies to maintain the electroneutrality of the system. This can be confirmed by the high resolution XPS spectra of the O 1s peak. The O 1s spectrum shown in Figure 3e is characterized by three spectral positions: 530.14 eV, 531.4 eV, and 533.14 eV. The peak at 531.4 eV corresponds to chemisorbed (–OH) groups. Different authors report different spectral positions of this peak: from 530.8 eV [30] to 532.3 eV [31], which depends on the experimental conditions. The peaks at 530.14 eV and 533.14 eV are determined directly by the features of the sample. According to [30], the peaks at 528.7 eV and 529.0 eV are related to the Ti–O bond and oxygen defects, respectively. They are shifted towards low energies relative to those obtained in our study. A similar bias was obtained in [32], where the effect of vacuum treatment on the photocatalytic properties of titanium dioxide was studied. Thus, the peaks at 530.14 eV and 533.14 eV characterize the Ti–O bond and oxygen vacancies, confirming the presence of the Ti³⁺–V_O bond.

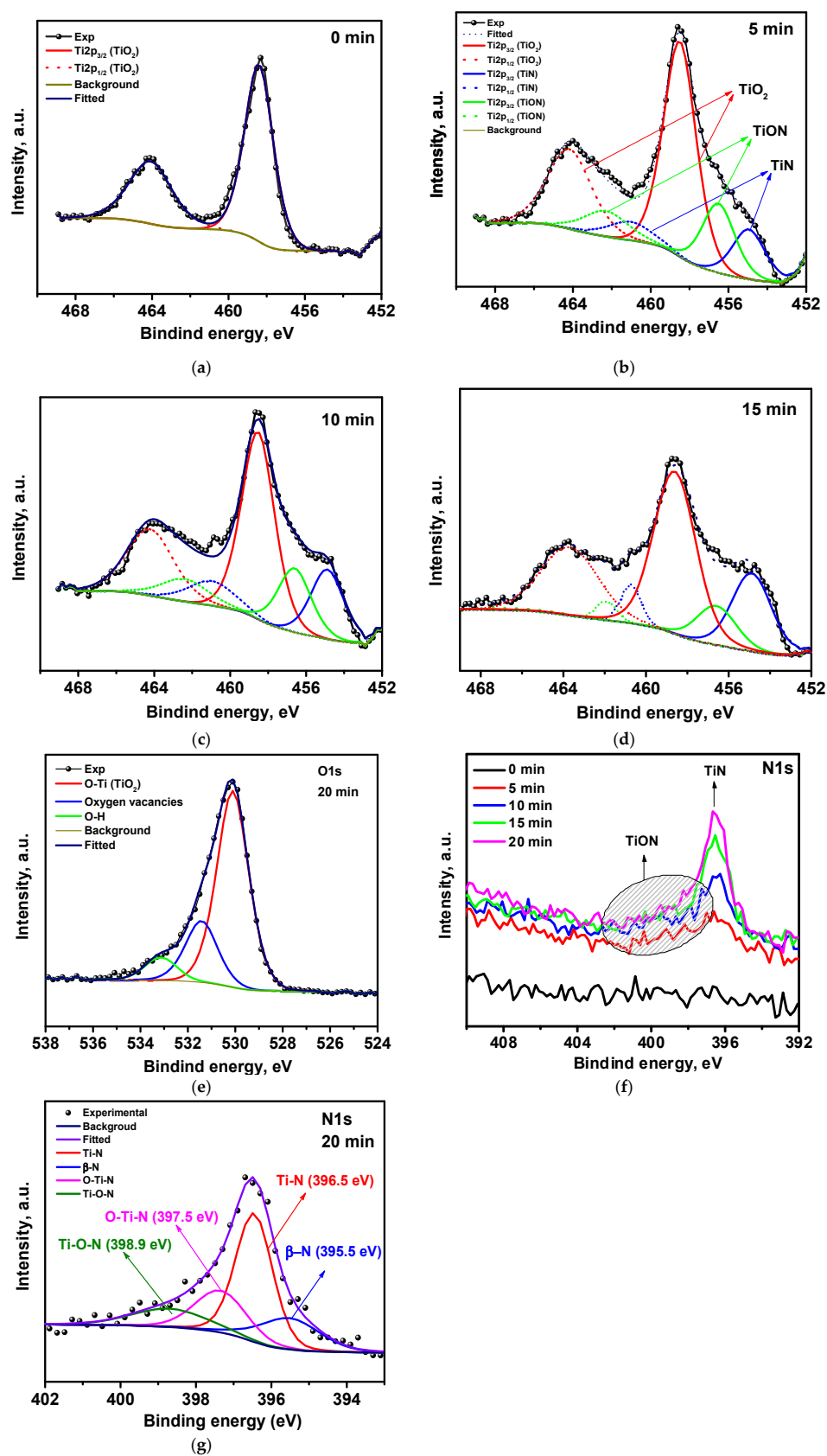


Figure 3. Ti 2p (a–d), O 1s (e), and N 1s (f,g). XPS spectra of plasma treated titanium microparticles for different etching time.

The high-resolution XPS spectra of the N 1s level obtained at various depths during etching are shown in Figure 3f,g. It can be seen that the nitrogen content increases with depth. The N 1s peaks can be well-described by four components (Figure 3f,g). In particular, components at 498.9 eV, 397.5 eV, and 396.5 eV are related to the Ti-O-N [33,34], O-Ti-N [35], and Ti-N bonds, respectively. The peak in the lower energy range of 395.5 eV can be attributed to β -N, which replaces oxygen in the TiO_2 sublattice [36]. It was suggested in [36] that the presence of β -N plays a main role in the charge accumulation of TiN due to the creation of oxygen vacancies on the upper surface.

An analysis of the spectra revealed an interesting result (Table 1): as far as deepening into surface layers of titanium powder microparticles as a result of etching by plasma treatment, the oxygen content decreases, while the nitrogen content, on the contrary, increases. Further, the content of Ti^{3+} increases while deepening into the sample, which indicates the diffusion activity of oxygen and nitrogen atoms within a certain near-surface layer and, in addition to XRD data, the retention of the metallic titanium. It is also interesting that the content of the intermediate layer between titanium nitride and titanium oxynitride remains practically unchanged. Perhaps this is due to the peculiarity of the oxidation of titanium nitride [37]: the oxidation process proceeds in several stages, including the formation of TiON followed by the delayed formation of TiO_2 . In addition, the oxidation of TiN begins at temperatures above 600 °C, and both phases can coexist in the range of 600–800 °C [28]. In titanium microparticles moving in plasma, only the surface in direct contact with the plasma has time to heat up to high temperatures. At the initial stage, active atomic nitrogen ions penetrate into the near-surface layers with the formation of titanium nitride. Further, when leaving the plasma, the microparticles enter the open atmosphere with hot active oxygen. In the near-surface region of high-temperature microparticles, titanium nitride is completely oxidized, while in deeper layers with low temperature, the titanium nitride phase is retained. In this case, a TiO_xN_y phase with a different ratio of oxygen and nitrogen is present in the volume of the fully reacted titanium layer, except for the surface. In general, titanium microparticles after treatment in a low-temperature nitrogen plasma in an open atmosphere can be represented by a Ti/TiN/TiON/ TiO_2 composite structure.

Table 1. Concentrations (at. %) of the components in the near-surface layer of titanium powder after plasma treatment depending on the etching time.

Binding Energies, eV	Ti 2p _{1/2} -464.2 Ti 2p _{3/2} -458.6	Ti 2p _{1/2} -461.2 Ti 2p _{3/2} -454.9	Ti 2p _{1/2} -462.4 Ti 2p _{3/2} -456.6
Etching Time, min	TiO ₂ , at. %	TiN, at. %	TiON, at. %
0	100	0	0
5	64.4	14.9	20.7
10	58.4	21.7	19.9
15	52.3	25.1	22.6
20	48.2	29.9	21.9

3.2. Photocatalytic Properties of Ti/TiN/TiON/ TiO_2 Composite Microparticles

3.2.1. Study of Photocatalytic Properties of Ti/TiN/TiON/ TiO_2 Composite Microparticles

To assess the photocatalytic characteristics of the samples, the MB dye was chosen as a typical pollutant. Figure 4 shows the results of photocatalytic experiments under irradiation with UV-Visible light.

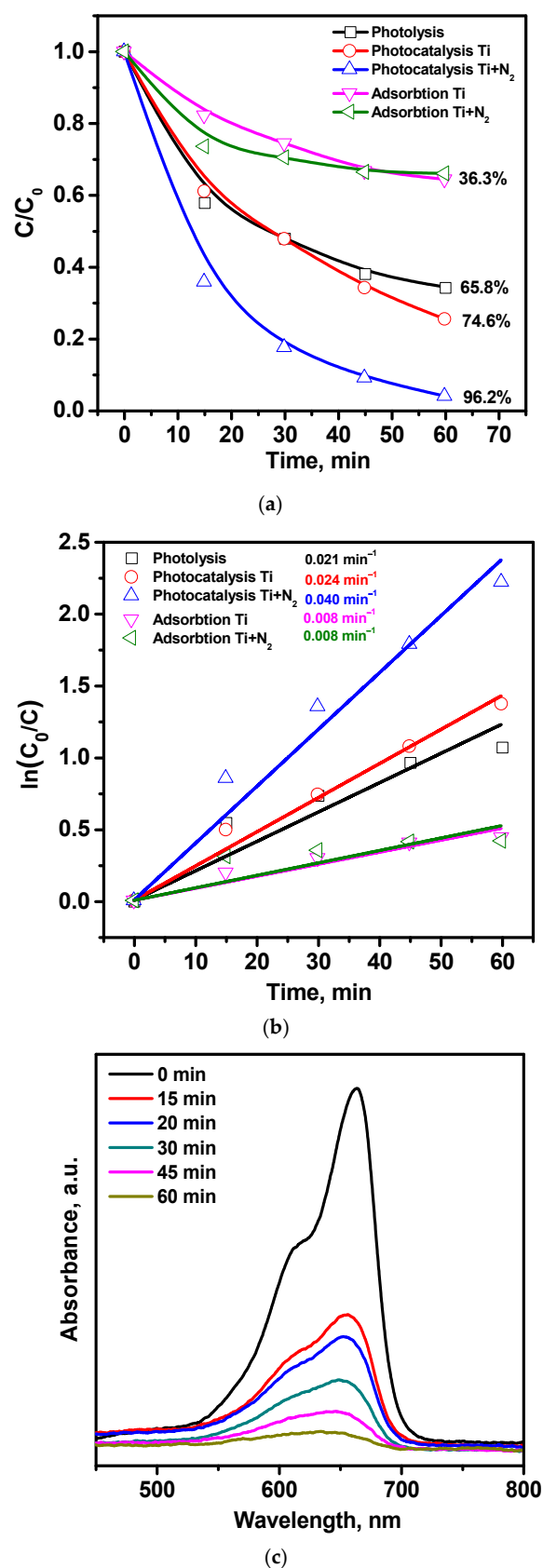


Figure 4. Kinetic curves of MB degradation ($1 \text{ mg} \cdot \text{L}^{-1}$, 20 mL) under UV-Visible light irradiation (a); semilogarithmic plots of MB degradation versus time (b); MB absorbance spectra during photocatalysis using titanium microparticles treated in nitrogen plasma (c).

Since the first act of photocatalytic reactions is surface adsorption, the contribution of dark adsorption of MB to the decrease in its concentration was preliminarily estimated. From Figure 4a, one can see that, in the first 15 min, a rather intense sorption of MB occurs on the surface of the titanium powder both untreated and treated with nitrogen plasma. Further, after 30 min, the concentration of the dye is almost constant, which indicates the achievement of adsorption–desorption equilibrium. Moreover, it can be noted that the plasma treatment has practically no effect on the efficiency of MB adsorption, and the concentration decreased by about 36.3% in 75 min. Since it is known that MB can also be degraded upon its direct exposure to light, the contribution of photolysis in the absence of catalysts was evaluated. During 1 h of the experiment, the MB concentration decreased by approximately 66%. A sample of pure titanium powder, as expected, did not show photocatalytic activity, and the apparent increase in the degree of MB degradation to 74.6% is due to the effects of photolysis. This is clearly seen from the semilogarithmic anamorphoses of the degradation kinetic curves in Figure 4b, where the photocatalytic degradation rate constant is almost equal to the photolysis rate constants. The increase in the degradation degree to almost 97% and of the rate constant in the case of titanium microparticles treated with nitrogen plasma confirms the photocatalytic activity of the sample due to the presence of photoactive phases of rutile and titanium nitride in the surface region.

Since no optical filters were used with a high-pressure mercury lamp in the experiment, it was important to understand the contribution to photocatalytic activity made by UV and visible light separately. For this purpose, experiments were carried out on the photocatalytic oxidation of MB under irradiation by visible light emitted by a metal–halogen lamp. The data are shown in Figure 5.

As shown in Figure 5, in a blank experiment without any photocatalyst, only a slight change in the MB concentration was observed, which indicates that the MB is sufficiently stable to visible light. Untreated Ti microparticles showed no photocatalytic activity. In the case of the treated Ti microparticles, the degradation characteristics improved markedly—about 69% of the MB decomposed within 60 min of irradiation by visible light. It can be concluded that nitrogen plasma treatment creates conditions for increasing photocatalytic activity in visible light. However, the photocatalytic activity is much lower than that in the case of UV-Visible light irradiation.

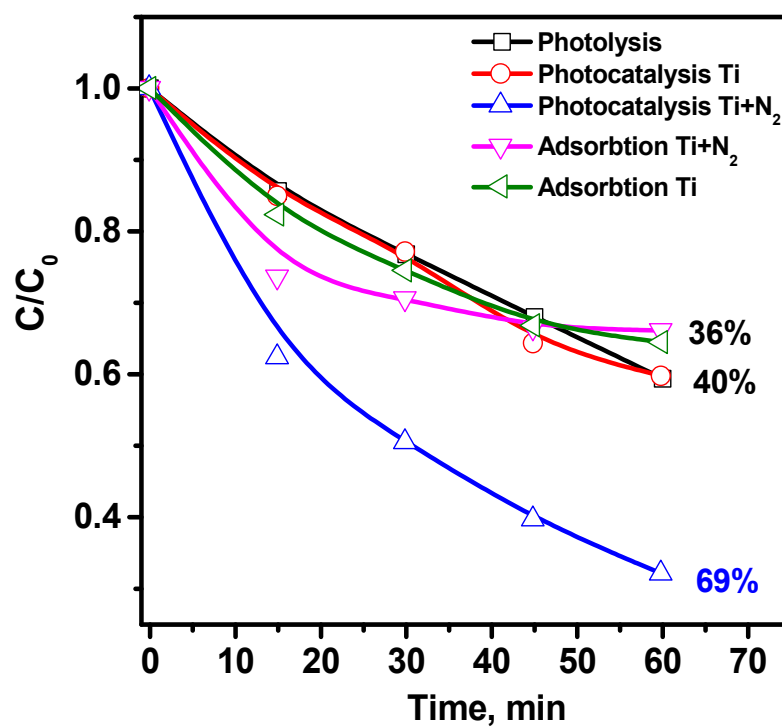
From a practical point of view, photocatalysts that are active in direct sunlight are of greatest interest in photocatalysis. Figure 6 shows data on MB photocatalytic degradation under direct sunlight. The experiments were carried out in Makhachkala, RF (42.97939 N 47.49659 E) from 4 July 2022 to 10 July 2022 from 12:00 P.M. to 16:00 P.M. Moscow time.

As one can see from Figure 6, the photocatalytic activity under direct sunlight is significantly higher than that in the case of visible light irradiation (83% vs. 69% per hour of the experiment), but lower than that in the case of UV-Visible irradiation (96%). This may be due to the presence of about 5% UV radiation in the solar spectrum. To understand the role of UV radiation in solar photocatalysis, an additional experiment with the use of a UV cut filter was carried out. The decrease in activity up to 60% in this case confirms the high role of UV radiation.

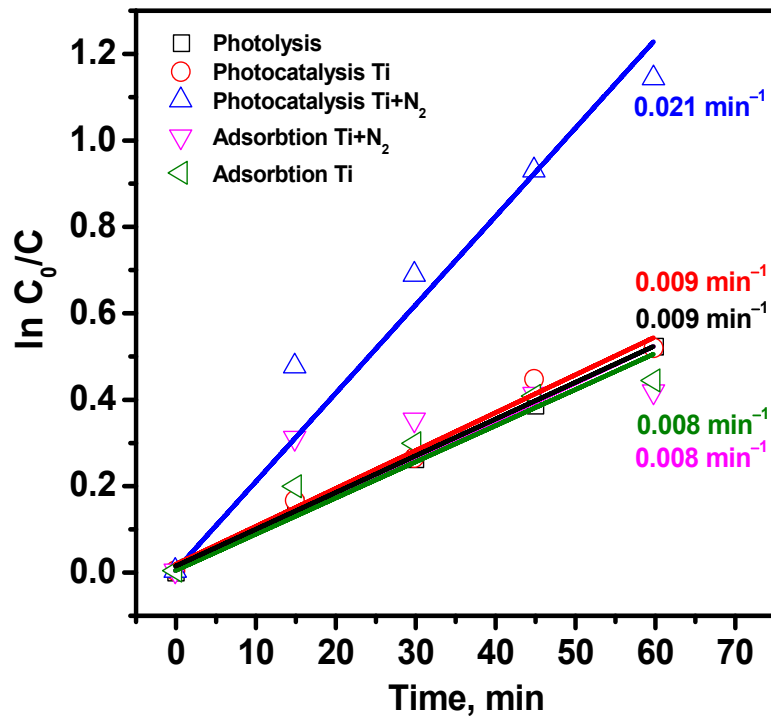
3.2.2. Photocatalysis Mechanism

The X-ray diffraction analysis results, as well as XPS data obtained during the etching of the sample, confirm the fabrication of a composite Ti/TiN/TiON/TiO₂ photocatalyst. Moreover, the coexistence of these structures in a relatively thin surface layer indicates good interfacial contact. The results show that the presence of UV part in the light source spectrum significantly increases the activity of the composite. This may be due to a number of factors. For example, this can be explained by the generation of a large number of carriers due to the excitation of TiO₂ and TiON in the rutile phase by UV light and by the presence of interband transitions in TiN. Moreover, it is unlikely that TiN acts as a sink

for photogenerated electrons generated in TiO_2 due to the lower work function of TiN compared to rutile.



(a)



(b)

Figure 5. Cont.

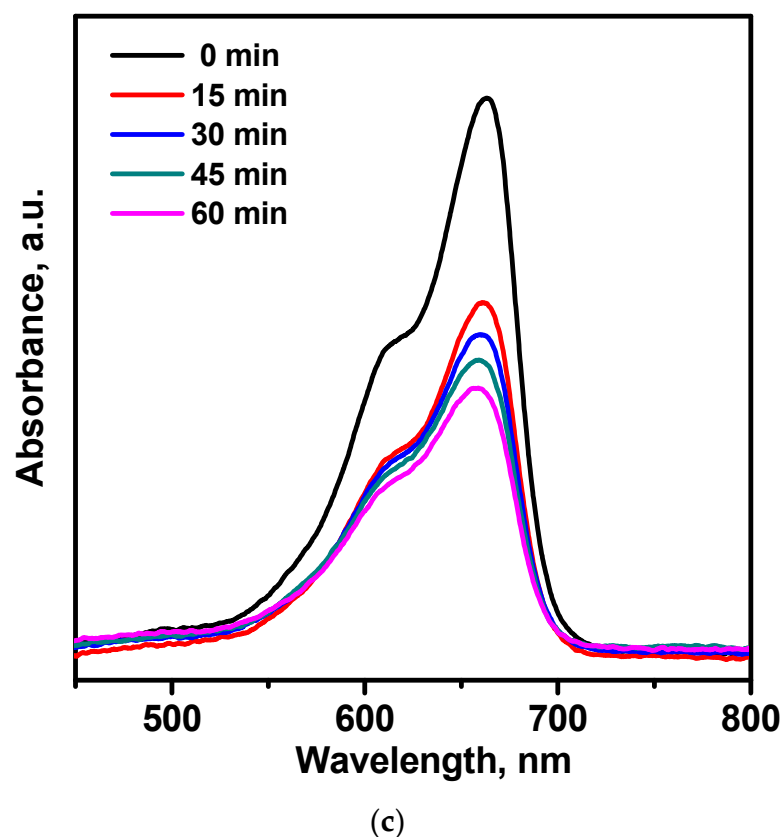


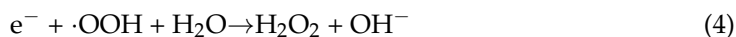
Figure 5. Kinetic curves of MB degradation ($1 \text{ mg}\cdot\text{L}^{-1}$, 20 mL) under visible light irradiation (a); semilogarithmic plots of MB degradation versus time (b); MB absorbance spectra during photocatalysis using titanium microparticles treated in nitrogen plasma (c).

It is more interesting to understand the activity of a photocatalyst under irradiation with only visible light. To understand the possible mechanism, experiments with scavengers on active oxidizing particles were carried out. Figure 7a,b shows obtained data on photocatalysis under visible light irradiation.

Figure 7a shows that the addition of isopropanol (IP) as scavengers for hydroxyl radicals ($\cdot\text{OH}$) slightly reduced the photocatalytic activity. This indicates a weak contribution of $\cdot\text{OH}$ to the overall process and may be due to the fact that only surface-bound $\cdot\text{OH}$ are formed in rutile, as was shown in [38]. As a result, their role is limited only to surface reactions. It is known that the main way of generating $\cdot\text{OH}$ is according to the reaction 1:



However, for (1) to occur, the generation of electron–hole pairs in TiO_2 upon visible light irradiation is necessary, which is impossible given the band gap of TiO_2 on the order of 3 eV. Possibly, such excitation occurs in nitrogen-doped rutile. However, in the literature there are quite contradictory results regarding the change in the energy levels of rutile upon doping with nitrogen [39]. In our opinion, a small amount of surface $\cdot\text{OH}$ in the system can still be formed according to the mechanism:



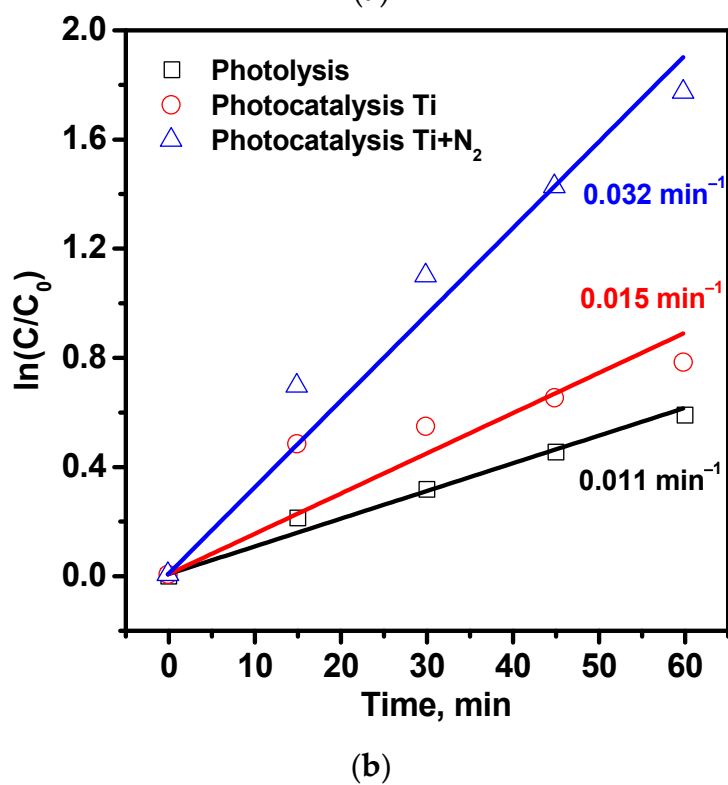
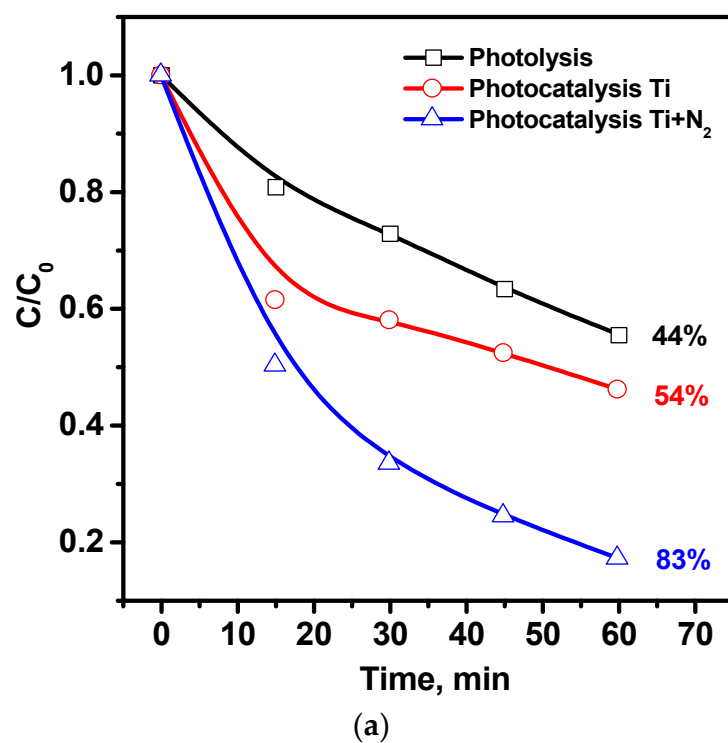


Figure 6. Cont.

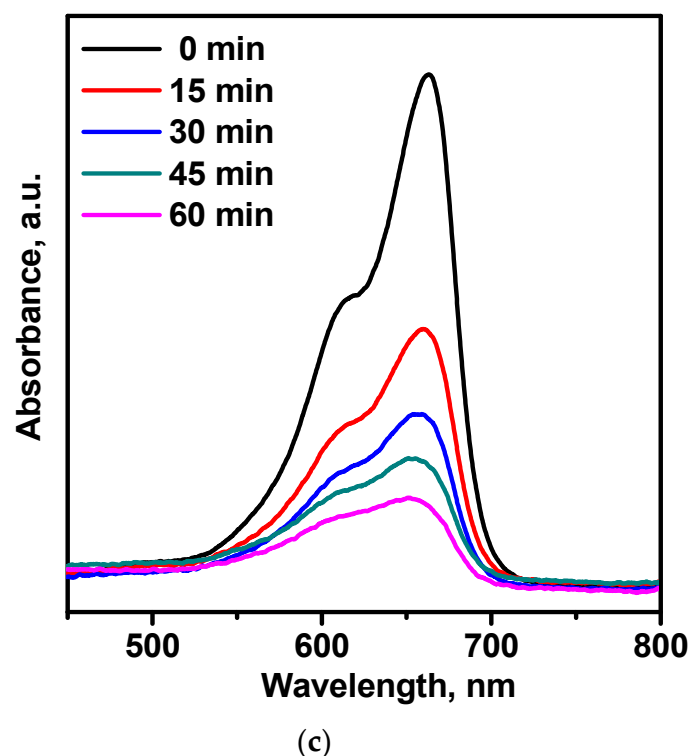


Figure 6. Kinetic curves of MB degradation ($1 \text{ mg}\cdot\text{L}^{-1}$, 20 mL) under direct sunlight irradiation (a); semilogarithmic plots of MB degradation versus time (b); MB absorbance spectra during photocatalysis using titanium microparticles treated in nitrogen plasma (c).

The predominant occurrence of the mechanism (2–5) should also indicate a significant role of superoxide anion radicals ($\cdot\text{O}_2^-$) in the photocatalytic activity. This was shown in [15]. The addition of hole scavengers (EDTA) leads to acceleration of the reaction. This may indicate that electron–hole pairs are nevertheless generated in the system upon visible light irradiation. However, the rate of their recombination is too high for the holes to enter into chemical reactions. A high rate of charge recombination in rutile was previously reported [40]. Thus, hole trapping limits recombination and, as a consequence, causes an increase in photocatalytic activity. The presence of an electron scavengers (AgNO_3) also leads to a photocatalytic process acceleration, which is probably also due to the weakening of the electron–hole recombination, changing the course of the reaction to the hole mechanism. Another possible reason for the enhancement of photocatalytic activity upon the addition of AgNO_3 may be that photocatalytic reduction of silver nanoparticles occurs on the surface. The possibility of such an effect was mentioned earlier [41]. This, in turn, proves that photoexcitation generates a large number of hot electrons on the surface.

To better understand the mechanism, experiments in the presence of several e^-/h^+ ($\text{AgNO}_3 + \text{EDTA}$), $\text{e}^-/\cdot\text{OH}$ ($\text{AgNO}_3 + \text{IP}$) and $\cdot\text{OH}/\text{h}^+$ ($\text{IP} + \text{EDTA}$) scavengers were carried out. The results are shown in Figure 7b. Since a separate addition of scavengers for electrons or holes resulted in photocatalytic activity increase, to confirm the hypothesis about the reaction acceleration due to hindering of e–h recombination, an experiment with the simultaneous addition of scavengers for both electrons and holes was carried out ($\text{AgNO}_3 + \text{EDTA}$). One can see from Figure 7b that, in this case, the photocatalytic process almost completely stopped, confirming the conclusions about the recombination hindering when scavengers are added separately. The addition of both e^- and $\cdot\text{OH}$ scavengers ($\text{AgNO}_3 + \text{IP}$) also significantly suppressed the activity. At the same time, electron trapping prevents reactions 2–5 from proceeding, and trapping of hydroxyl radicals inhibits reaction 1. To determine which radicals play a main role in MB degradation, we decided to carry out the process by adding hole and hydroxyl radicals scavengers ($\text{IP} + \text{EDTA}$). The results showed

that the activity increased significantly, which confirms the conclusion that superoxide anion radicals play a decisive role in the decomposition of MB.

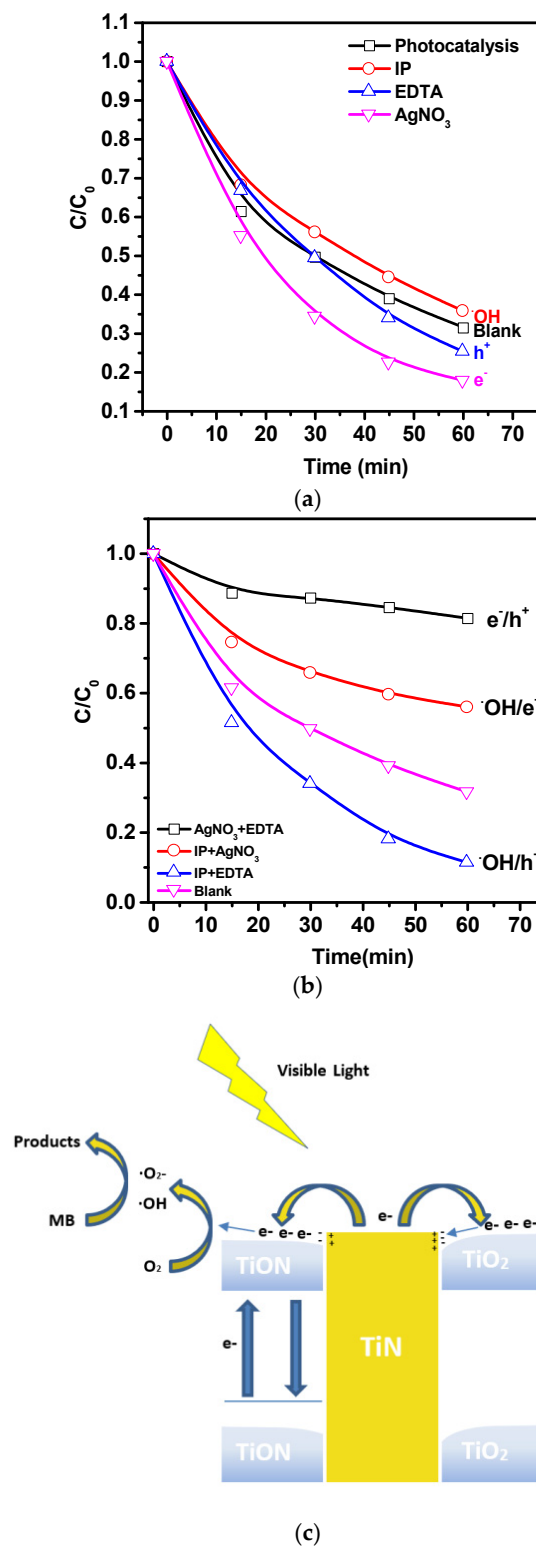


Figure 7. Kinetic curves of MB degradation ($1 \text{ mg}\cdot\text{L}^{-1}$, 20 mL) under visible light irradiation, using titanium microparticles treated in nitrogen plasma combined with scavengers—(a) and combinations of different scavengers—(b). The proposed mechanism of the photocatalytic activity of Ti/TiN/TiON/TiO₂ composite photocatalyst under visible light illumination—(c).

Figure 7c shows the process schematically. When a metal and an n-type semiconductor come into contact, a barrier usually forms at their interface, the energy of which can be calculated as $\varphi = \varphi_M - \chi_S$, where φ_M is the work function of the metal, and χ_S is the semiconductor's electron affinity. Metal electrons can be injected into a semiconductor if their energy is greater than φ . The experimentally determined work functions for rutile and TiN are 4.9 eV and 3.74 eV, respectively; the electron affinity of rutile is 4.8 eV [42]. Based on this, the barrier energy is -0.9 eV. Theoretically, in this case, the TiON/TiN and TiO₂/TiN contacts can provide an electron transfer from TiN to TiON and TiO₂, creating a negative charge accumulation layer on the TiO₂ surface and downward band bending from TiON and TiO₂ to the interface with TiN. In the absence of external perturbation, the transfer process will continue until the Fermi levels of the titanium nitride and titanium oxide-oxy-nitride are aligned. It is assumed that excitation of the band gap of TiON under visible light illumination will contribute to a decrease in the band bending at the TiON/TiN interface. In this case, TiN electrons flow from the TiON/TiN interface to the TiON/solution interface, and this is the main component of photoactivity in the visible range. The enhancement of photoactivity under sunlight irradiation can be associated with several factors: the generation and excitation of carriers in TiO₂ under the UV light irradiation; the heating of electrons in the TiN-TiO₂ composite matrix due to plasmon effects in the visible and NIR regions. The presence of a Ti metal inclusion can also contribute to the spatial separation of photoinduced electron-hole pairs due to the partial delocalization of electrons at the metal-semiconductor interface. Thus, hot electrons injected into the conduction band of TiON and TiO₂ from TiN react with oxygen to form $\cdot\text{O}_2^-$ radicals in aqueous solution, followed by the formation of $\cdot\text{OH}$ radicals. These highly reactive radicals cause the degradation of organic pollutants. In addition, recent results indicate the possibility of direct photocatalysis on plasmonic nanoparticles due to processes such as elastic radiative reemission of photons, nonradiative Landau damping, and chemical interface damping (CID) [15].

Comparison of photocatalytic properties of composite Ti/TiN/TiON/TiO₂ microparticles of under UV and visible light irrigation with the results of works [43,44] shows that their efficiency is not worse, and in some cases even better. In [44,45], nanoparticles whose active surface is many times larger than microparticles were used. It should be noted that the synthesis of nanoparticles is a complex and lengthy process. In our case, a short-term effect on microparticles is used, the synthesis of which is cheaper.

4. Conclusions

In the present work, the interrelation of the structural-phase composition and morphology of composite microparticles with their catalytic properties under UV, visible, and solar light irradiation was studied. The titanium powder was treated in the anode region of the nitrogen plasma generator using a plasmatron with vortex stabilization and an expanding channel. Mass average plasma temperature in the powder supply zone was ~ 10 kK, speed of particles flight through the treatment zone was $50 \div 60$ m/s. After treatment, the morphology of microparticles changes: porosity decreases and roughness increases. According to XRD data, the α -phase Ti remains the main one in microparticles; in addition, the high-temperature phase of rutile TiO₂ and titanium nitride TiN are formed. Based on the data of XRD analysis and XPS with depth etching, it was concluded that a tandem composite Ti/TiN/TiON/TiO₂ photocatalyst was formed during plasma treatment. It is shown that the main components of photoactivity under visible light irradiation are electrons from TiN migrating from the TiON/TiN interface to the TiON/solution interface. The enhancement of photoactivity under sunlight is associated with several factors: the generation and excitation of carriers in TiO₂ under the UV light irradiation and the heating of electrons in the TiN-TiO₂ composite matrix due to plasmon effects in the visible and NIR regions.

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