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Photocatalytic properties in the visible region of light of composite microparticles of Ti/TiN/TiO_2 obtained by electric arc synthesis

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Method of electric arc synthesis of composite microparticles metal−semiconductor−dielectric based on titanium, titanium nitride and rutile with productivity up to 10 g/min is proposed. Using diffraction and microscopic methods, the morphology and structural-phase composition of the synthesized microparticles were studied. Using the example of methylene blue degradation, the photocatalytic activity of synthesized microparticles in the visible radiation range was demonstrated and its possible mechanism was proposed.

Keywords: titanium, rutile, titanium nitride, microparticles, photocatalysis, visible light.

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The development of visible-range photocatalysts of a new class with an elevated efficiency in degradation of organic pollutants is one of the relevant trends in ecological catalysis. The TiO_2 photocatalyst (P25, Degussa), which is currently being used on an industrial scale, is active only in the ultraviolet range that covers no more than 5% of the solar spectrum. Several approaches to increasing the sensitivity of TiO_2-based photocatalysts in the visible range have been proposed. One of them consists in forming composite metal/TiO_2 structures, where the efficiency increases due to charge transfer between the metal and TiO_2 [1,2]. For example, the Au/TiO_2 composite structure [3] features an elevated photosensitivity in the visible range due to a resonance energy transfer mechanism [4] based on the surface plasmon resonance at Au nanoparticles: intensification of the local electromagnetic field facilitates the production of e^-/h^+ pairs at defects and their clusters in the vicinity of the semiconductor surface [5]. Another approach involves doping TiO_2 with a non-metal impurity. The highest photocatalyst efficiency was obtained by doping TiO_2 with N [6], since O and N have close structural parameters (polarizability, electronegativity, and ionic radii). The photosensitivity of TiO_2 doped with N increases in the visible range due to the formation of a new energy state $N2p$ in the bandgap of TiO_2. This state induces a reduction in the bandgap width, which decreases to 2.5 eV [7]. A more thorough analysis [8] revealed that a bandgap narrowing of this magnitude is achieved when impurity nitrogen is incorporated into the TiO_2 lattice. In the case of incorporation of nitrogen atoms into a substitutional position in the TiO_2 lattice, the bandgap width decreases to 3.06 eV. The option of retrograde doping of TiN nanoparticles with oxygen [9] was also discussed, but it was demonstrated in the same study that a TiN/TiO_2 hybrid photocatalyst has higher values of the absorption coefficient in the visible range and the photocatalytic (PC) activity in this range. The conductivity of TiN is near-metallic, and one of the plasmon absorption bands is located in the visible range [10]; therefore, the PC activity of the TiN/TiO_2 system is typical of metal−TiO_2 systems. It should be noted that nanoparticles and nanocomposites were the most efficient in all the considered examples. At the same time, high productivity and economic feasibility are no less important requirements, which are hard to satisfy when nanoobjects are used. In our view, the application of composite microobjects with a metal−semiconductor−insulator structure and a sufficiently high efficiency may be advantageous in terms of the price/performance ratio. In this light, the technique of surface modification of titanium microparticles with the formation of a Ti/TiN/TiO_2-type composite structure may be the optimum one. Electric arc plasma processing is one of the efficient and cost-effective methods for surface modification. Its advantages include the potential to modify surfaces of objects of any degree of complexity, mechanical stability of the coating, and control over the chemical composition with the use of plasma-forming gas and the ambient atmosphere. If a reliable low-temperature plasma generator [11], which produces a high-enthalpy plasma flow of working gases with temperatures ranging from several thousand to tens of thousands of degrees in its discharge gap, is available, one may oxidize and nitrogenize metallic microparticles.

In the present study, we examine the potential for application of electric arc plasma in synthesis of composite photosensitive titanium-based metal−semiconductor−insulator microparticles. Their morphology, structural and phase composition, and photoactivity in the visible range are investigated.

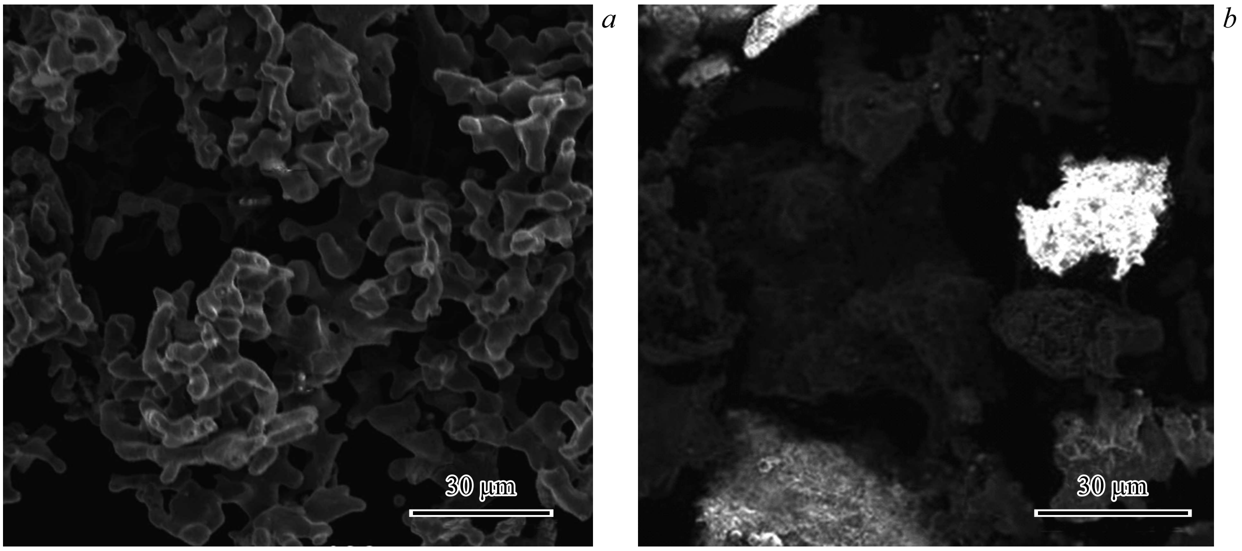

Figure 1. SEM images of titanium microparticles before (*a*) and after (*b*) plasma processing.

Commercial high-purity titanium powder was used as a sample for studies. Microscopic and X-ray diffraction analysis of the initial powder was performed first. Microscopic studies were carried out using a JEOL (Japan) scanning electron microscope (SEM) fitted with an energy-dispersive X-ray microanalyzer. X-ray diffraction patterns were recorded with an Empyrean PANalytical (Netherlands) diffractometer in the Bragg–Brentano geometry. Copper anode radiation ($\mathrm{Cu}K_{\alpha 2}$, 1.54 Å) was used. The titanium powder sample was then processed in the anode region of a plasma generator using a plasmatron with vortex stabilization and an expanding channel. Plasma processing was performed in the ambient atmosphere. The procedure of plasma processing of particles and theoretical calculations for this process were discussed in sufficient detail in [12]. The generator processing parameters were as follows: nitrogen flow, 1.5 g/s; transport gas flow, 0.2 g/s; powder consumption rate, 10 g/min; arc current, 150 A; plasma temperature in the powder feed zone, ~ 10 kK; velocity of particles at the plasma nozzle exit, 50–60 m/s.

The photocatalytic characteristics of samples were estimated in the process of photodegradation of methylene blue (MB) in an aqueous solution ($1\,\mathrm{mg}\cdot\mathrm{l}^{-1}$). A glass beaker with a volume of 50 ml was used. Experiments were performed under irradiation by visible light (70 W Osram metal-halogen bulb). A constant temperature (26°C) was maintained in the reaction vessel by ventilation and was monitored with a thermometer. In order to induce a photocatalytic reaction, 20 mg of the photocatalyst were added to 20 ml of the aqueous solution of MB. Prior to irradiation, the beaker was introduced into a dark box and kept there for 75 min to achieve adsorption equilibrium. The suspension was subjected to ultrasonic treatment (for photocatalyst degassing) before the experiment. The entire process was accompanied by mixing with a magnetic stirrer. A light source was located above the reactor at a distance of 10 cm. Sampling (5 ml) was performed in 15 min intervals. Particles were separated from the solution by centrifuging at 14 000 rpm for 2 min with a PE-6926 (LLC „Ekroskhim“) laboratory centrifuge. The MB concentration was measured using an SF-2000 spectrophotometer by the characteristic MB absorption peak at a wavelength of 663.7 nm. Following measurements, the solution was poured back into the reactor, and the process continued. The MB solution was also tested in similar conditions without the photocatalyst (photolysis) for comparison. The MB concentration was determined in accordance with the Beer–Lambert–Bouguer law.

The initial titanium powder consisted of solid and porous microparticles of various shapes (Fig. 1, *a*). These particles had a large spread of lateral sizes (20–120 μm). According to the XRD data (Fig. 2), the initial powder consisted of the low-temperature α TI phase with a hexagonal close-packed lattice (JCPDS card N 44-1294). SEM images (Fig. 1, *b*) reveal that the morphology of porous microparticles changes after processing: the porosity decreases, while their roughness increases. In contrast, the morphology of solid particles remains almost unchanged. Since particles spend just a minimum amount of time in the plasma-affected region (the flight velocity is 50–60 m/s), only porous microparticles become heated. Plasma processing induces changes in the composition of the near-surface microparticle layer, which is altered by high-intensity thermochemical processes, and in the morphology of porous microparticles. The XRD data from Fig. 2 confirm that the composition changes after processing. The α TI phase still remains dominant in composite microparticles. The high-temperature phase of rutile TiO_2 (JCPDS card N 21-1276), titanium nitride TiN (JCPDS card N 38-1420), and the low-temperature phase of anatase TiO_2 (JCPDS card N 21-1272), which was identified in additional studies with the use of surface-sensitive methods, also form.

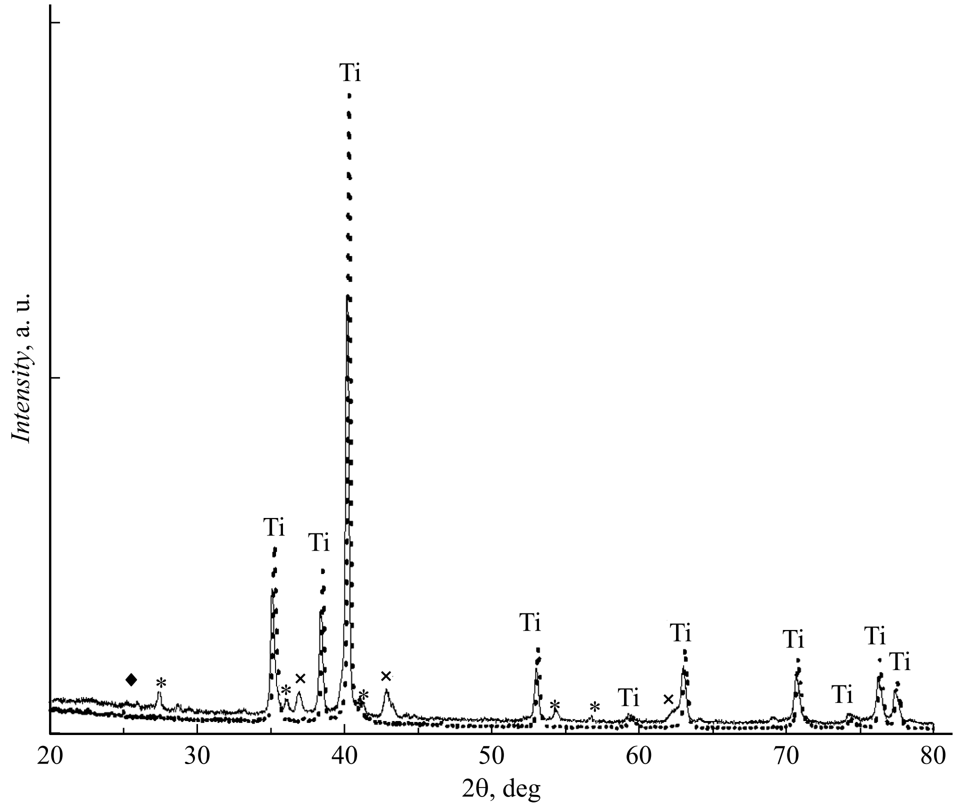

Figure 2. XRD curves of titanium powders before (dotted curve) and after (solid curve) plasma processing. Rutile TiO_2, anatase TiO_2, and TiN are denoted by asterisks, the diamond, and crosses.

The results of energy-dispersive X-ray microanalysis confirm the presence of nitrogen (2.6 at. %) in titanium powder microparticles after plasma processing. However, it is hard to estimate its quantitative content accurately, since the spectral lines of nitrogen and titanium partially overlap. Thus, the obtained data provide indirect evidence of the formation of composite Ti/TiN/TiO_2 microparticles with near-surface layers dominated by the rutile phase and cores composed of metallic titanium in the course of processing of titanium microparticles in electric arc nitrogen plasma. Although the temperature is very high, short-term plasma processing does not induce sufficient heating of deep titanium microparticle layers, and the anatase phase is preserved partially in them.

The photocatalytic activity of synthesized composite microparticles was examined next. The process of photocatalytic MB oxidation under irradiation with visible light from a metal–halogen bulb was studied (Figs. 3, *a*, *b*). The results of a preliminary experiment on dark adsorption in similar conditions revealed a 36% reduction in the MB concentration within 75 min for both unprocessed Ti microparticles and Ti microparticles after plasma processing. Figure 3, *a* demonstrates that the MB concentration in a blank experiment without any photocatalyst (photolysis) decreases by 40%. Unprocessed titanium microparticles (Ti in Fig. 3) did not reveal any PC activity. A 40% MB degradation is attributable to photolysis. The degradation was significantly more pronounced for composite microparticles: approximately 71% of MB decomposed under irradiation with visible light within 60 min (Ti+N_2 *plasma* in Fig. 3). It may be concluded that the rearrangement of the structural and phase composition of titanium microparticles with the formation of a metal—semiconductor—insulator composition establishes the conditions for enhancing the PC activity in visible light.

It is vital to understand the probable mechanism of photocatalyst activity under irradiation with visible light. Experiments with active oxidizing „particle“ absorbers were performed for this purpose (Fig. 3, *c*). The absorbers of hydroxyl radicals (·OH), electrons (e^-), and holes (h^+) were 0.1 mM of isopropyl alcohol (IP), $AgNO_3$, and ethylenediaminetetraacetic acid (EDTA), respectively. Figure 3, *c* presents the data on PC activity under irradiation with visible light. It can be seen that the addition of isopropyl alcohol as an OH absorber led to a slight reduction in PC activity. Therefore, OH is likely to produce only a minor contribution to the overall process. This is attributable to the formation of only surface-bound OH on the rutile component (see [13]). Consequently, their contribution is limited to surface reactions. It is known that hydroxyl radicals are generated primarily in reaction

$$h^+ + H_2O \rightarrow \cdot OH + H^+. \qquad (1)$$

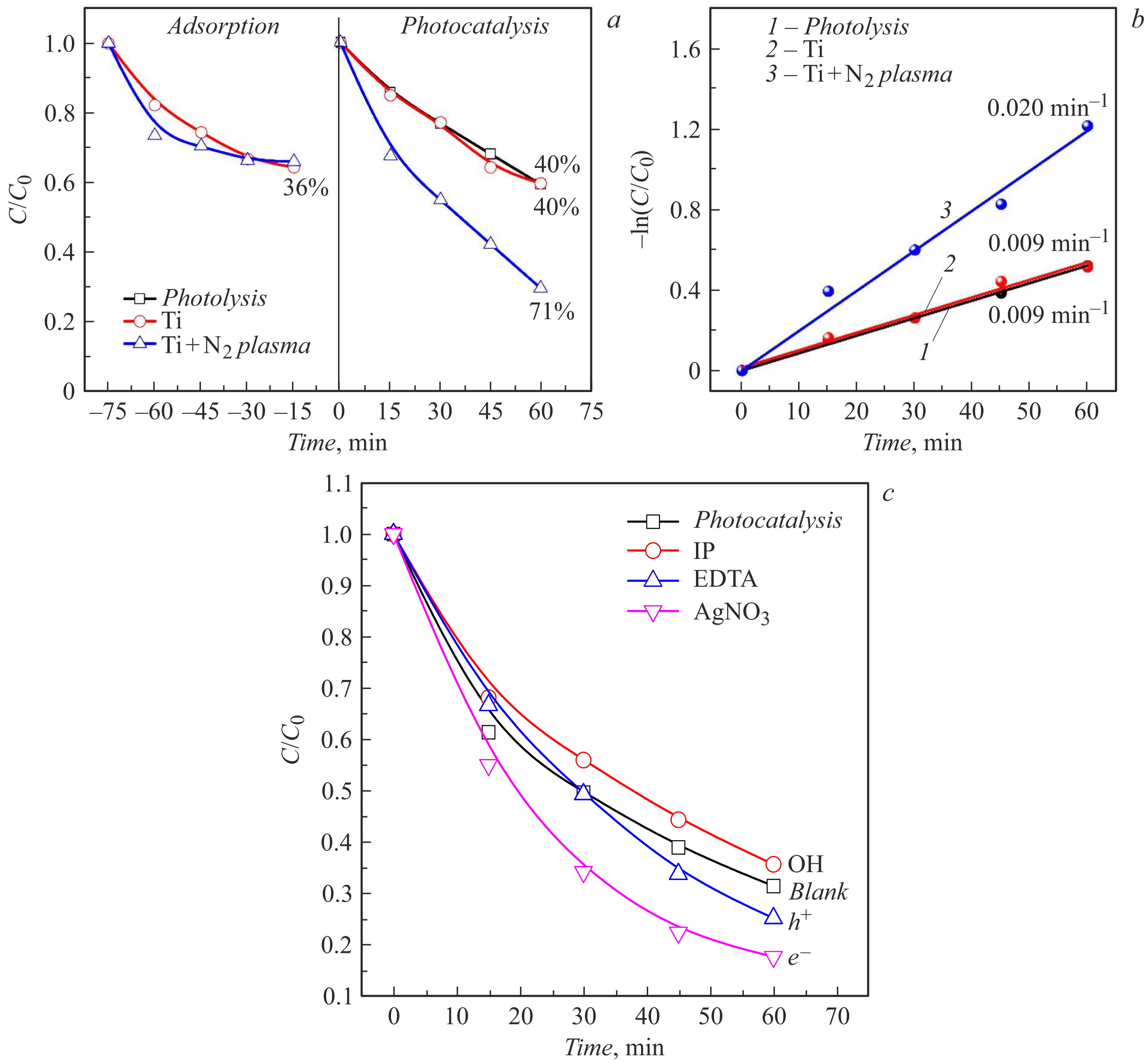

Figure 3. *a* — Kinetic curves of MB decomposition ($1\,\mathrm{mg}\cdot \mathrm{l}^{-1}$, 20 ml) in the dark and under irradiation by visible light; *b* — semi-logarithmic anamorphoses of the kinetic curves of MB decomposition; *c* — kinetic curves of MB decomposition ($1\,\mathrm{mg}\cdot \mathrm{l}^{-1}$, 20 ml) under irradiation by visible light with the use of composite microparticles and different absorbers.

However, the probability of this reaction is low. Electron–hole pairs need to be generated in TiO_2 under irradiation with visible light for this reaction to proceed, but the bandgap width of rutile (approximately 3 eV) makes the production of these pairs infeasible. In our view, an insignificant amount of surface hydroxyl radicals may form in the system in the following process:

$$e^- + O_2 \rightarrow \cdot O_2^-, \tag{2}$$

$$O_2^- + H^+ \rightarrow \cdot OOH, \tag{3}$$

$$e^- + \cdot OOH + H_2O \rightarrow H_2O_2 + OH^-, \tag{4}$$

$$e^- + H_2O_2 + H^+ \rightarrow \cdot OH + H_2O. \tag{5}$$

The predominance of this mechanism should also be indicative of a significant contribution of superoxide anion radicals ($\cdot O_2^-$) to PC activity (see [14]). A large number of electrons may be generated in this case due to surface plasmon resonance in TiN. The addition of hole absorbers results in a slight intensification of the reaction. This may indicate that, after all, electron-hole pairs are generated in the system under irradiation with visible light. However, the recombination rate is so high that holes have no time to enter into reactions. A high charge recombination rate in rutile has already been reported in [15]. Thus, hole trapping sets limits to recombination and, consequently, enhances PC activity. The addition of electron absorbers also speeds up the PC process. This is likely attributable to the quenching of recombination of $e{-}h$ pairs; the reaction shifts toward the hole mechanism. The photocatalytic reduction of silver nanoparticles on the surface of composite microparticles is another possible cause of enhancement of PC activity observed after the addition of $AgNO_3$. This possibility has been mentioned earlier in [16] and provides additional proof of generation of a large number of hot electrons on the surface of microparticles under photoexcitation.

A method for electric arc synthesis of metal–semiconductor–insulator composite microparticles based on titanium, titanium nitride, and titanium oxide with a productivity on the order of 10 g/min was proposed. The morphology and the structural and phase composition of synthesized microparticles were examined using diffraction and microscopic techniques. The photoactivity of synthesized microparticles in the visible range was demonstrated through the example of MB degradation, and a probable photoactivity mechanism was proposed. If a way to increase the productivity of the presented technique for synthesis of photoactive composite microparticles is found, it may become widely used in industrial-scale production of inexpensive and readily available photocatalysts of the visible range.

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Conflict of interest

The authors declare that they have no conflict of interest.

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