ABSTRACT

of the dissertation for the degree of Doctor of Philosophy (PhD) on the educational program 8D05301—Chemistry by Orazov Zhandos Kanatuly

on the topic: "Doped TiO_2 nanoparticles and TiO_2-based heterostructures preparation for visible-light promoted photocatalysis"

General overview of the work.

The dissertation is devoted to the preparation of TiO_2 nanoparticles and TiO_2-based heterostructures by thermolysis of synthesized titanium-based metal-organic framework structures (MIL-125). Various synthesis conditions for metal-organic framework structures were studied. The optimal conditions for obtaining titanium(IV) dioxide-based nanoparticles were determined, their photocatalytic properties were evaluated, and the role of photogenerated species (e^-, h^+, $^1O_2$, $\bullet O_2^-$ and $\bullet OH$) in the decomposition reactions of aqueous solutions of various dyes was established.

Relevance of the research topic. Purification of water resources from persistent organic pollutants such as pharmaceuticals, dyes, and pesticides remains a relevant problem. Existing purification methods have a number of disadvantages: they do not ensure complete removal of compounds, often require high energy consumption, and are characterized by low removal efficiency under real operating conditions (for example, a decrease in adsorption capacity at high humidity, a limited service life of membranes, high energy consumption of thermocatalytic processes, and the formation of toxic by-products under irradiation). A promising direction in this field is the use of visible-light driven photocatalysis for the removal of organic compounds from water objects.

The practical application of photocatalysis is limited by a number of factors. The main problem is associated with the fast recombination of photogenerated electron-hole pairs, which reduces the efficiency of compound removal. In addition, photocatalysts often have a narrow spectral response region, a low charge transfer rate, and insufficient stability during long-term operation. To overcome these limitations, various types of heterostructures are being actively developed. The attention is paid to Z- and S-schemes, which provide effective separation of charge carriers and preserve the redox potential. Type II heterostructures and multicomponent hybrid systems are also being investigated, which make it possible to expand the spectral range of radiation absorption and increase photocatalytic activity.

Degree of Development of the Topic.

Titanium dioxide (TiO_2) is a key compound for the photocatalytic decomposition of organic pollutants due to its advantages: non-toxicity, photostability, high corrosion, physical and chemical resistance, as well as low production cost. Nevertheless, its efficiency under visible or solar light is limited by the band gap (~3.2 eV for anatase) and the high recombination rate of photogenerated electron-hole pairs. Various strategies for modifying TiO_2 are used, including control of the anatase-to-rutile phase ratio, doping with metals and/or nonmetals, and heterostructure formation. In this regard, the preparation of TiO_2 nanoparticles from metal-organic framework structures is promising, which provides a high specific surface area of the catalyst and a tunable surface morphology, promoting more efficient charge transfer in photoprocesses.

In the study (*Science. 2001. Vol. 293, P. 269–271*), it was demonstrated that nitrogen doping leads to a decrease in the TiO_2 band gap and the appearance of photoactivity in the visible region of light. Further studies were aimed at using metal-organic framework compounds as precursors, which made it possible to combine modification of the band structure with developed porosity of the material. In this direction, (*Chem. Eng. J. 2019. Vol.*

360, P. 75–88) showed the possibility of obtaining iron-doped TiO_2 from MIL-125 by impregnation with iron ions followed by calcination. Publications in the Scopus database over the past two decades indicate an increase in the number of publications on the topic "doping TiO_2 with metals". Along with doping with metals and nonmetals, the synthesis of TiO_2-based heterostructures is also actively developing. Thus, (*ACS Mater. Au 2021, Vol.1(1), P. 37–54*) showed the promise of using graphene oxide (GO) as a second semiconductor: its introduction reduces e^-/h^+ recombination and improves absorption in the visible region.

The aim of the research is to prepare TiO_2 nanoparticles and TiO_2-based heterostructures by thermal decomposition of metal-organic framework structures of the NH_2-MIL-125 type and to perform characterization.

Research objectives:

- Determine the optimal synthesis conditions for N-TiO_2 nanoparticles from NH_2-MIL-125-type metal-organic framework structures by varying the following parameters: calcination temperature and precursor ratio.
- Determine the catalyst with the maximum photocatalytic activity in model pollutant solutions, ciprofloxacin and Orange II.
- Characterize the selected photocatalyst, identify photoactive species, and propose a photocatalysis scheme.

Objects of the study: TiO_2 nanoparticles doped with Fe^{3+} ions and TiO_2/GO-type heterostructures.

Subject of the study: Preparation of nitrogen-doped TiO_2 and its modification (graphene oxide, Fe^{3+} ions), along with the study of their structure, characteristics, and photocatalytic activity for the decomposition of organic pollutants.

Methods of investigation: Solvothermal synthesis, impregnation method, X-ray phase analysis (XRD), UV–visible diffuse reflectance spectroscopy (DRS), Fourier-transform IR spectroscopy, scanning electron microscopy (SEM), transmission electron microscopy (TEM), energy-dispersive X-ray spectroscopy (EDS), X-ray photoelectron spectroscopy (XPS), photoluminescence spectroscopy (PL), thermal analysis (TG/DTA), UV-visible spectrophotometer, potentiostat-galvanostat, BET analysis.

Scientific novelty:

- A relationship was revealed between the synthesis parameters of TiO_2 nanoparticles: "calcination temperature → structure → photoactivity." At 450 °C, the main anatase phase is formed without a noticeable presence of the rutile phase, with pore sizes in the range of ~3.8–10 nm.
- For the first time, an optimal concentration was determined at which the photocatalytic activity (determined by the rate constant) exceeds the values of N-TiO_2 without iron due to suppression of the recombination of photogenerated charge carriers.
- It is shown that the introduction of GO improves the performance of the photocatalyst due to: (i) more efficient separation of photogenerated electrons and holes; (ii) increased adsorption capacity toward organic molecules; (iii) accelerated electron transfer through the conductive π-system of GO. It was established that the obtained heterostructures are characterized by higher rate constants under visible-light irradiation compared to the initial N-TiO_2 and anatase.

Theoretical significance: It is shown that modification of semiconductor TiO_2 by iron doping or by forming heterostructures of the N-TiO_2/GO type promotes interfacial charge transfer, reduces the carrier recombination rate, and ensures stability of catalytic activity upon repeated use. At the same time, exceeding the optimal concentrations of dopants can

lead to the formation of recombination centers and traps for electron-hole pairs, which reduces the photocatalytic efficiency of the material. Based on the results of experiments with scavengers of active species, a scheme of photocatalytic reactions was proposed, according to which, under visible-light irradiation, charge carriers are generated in N-TiO_2: electrons transition to the conduction band and then transferred to GO, where they reduce O_2 with the formation of $\bullet O_2^-$ (and subsequent oxygen-containing radicals), while holes in the valence band oxidize H_2O/OH^- with the formation of •OH; the combined action of $\bullet O_2^-$/•OH ensures accelerated decomposition of organic molecules. The obtained optimal synthesis conditions for metal-organic framework structures and photocatalysts based on them are valuable theoretical information in inorganic synthesis. In addition, the obtained data on the mechanisms of photocatalytic oxidation contribute to the theory of photocatalysis involving heterostructures in the visible-light region.

The practical significance lies in the fact that the obtained photocatalysts, photoactive in the visible-light region, can be used for the removal of organic compounds (dyes, pharmaceuticals) from wastewater and surface waters. The obtained optimal synthesis conditions for metal-organic framework structures and photocatalysts based on them can be applied to obtain efficient titanium dioxide-based photocatalysts.

Main provisions submitted for defense:

- Calcination of NH_2-MIL-125-type MOFs (molar ratio NH_2-BDC:$Ti(OPr)_4$ = 3.3:1) at 450 ℃ in an air atmosphere is the optimal temperature for the formation of the anatase phase, which exhibits photocatalytic activity under visible light (ciprofloxacin degradation rate constant $k = (13.30 \pm 0.29) \times 10^{-3}$ min^{-1} at I_0 = 30 mW/cm^2).
- The incorporation of iron ions or graphene oxide into N-TiO_2 leads to an increase in photocatalytic activity in the visible-light region compared to the pristine N-TiO_2. The highest visible-light photocatalytic activity is observed for N-TiO_2/GO samples obtained by thermolysis at 450 ℃ of an MOF (NH_2-MIL-125)-based mixture with the addition of 20 wt.% graphene oxide (Orange II degradation rate constant $k = (16.2 \pm 1.4) \times 10^{-3}$ min^{-1} at I_0 = 30 mW/cm^2).
- Superoxide radicals ($\bullet O_2^-$), hydroxyl radicals (•OH), and singlet oxygen ($^1O_2$) are the main reactive species involved in the photodegradation of organic compounds during the photocatalysis of heterostructures based on N-TiO_2/30 wt.% GO.

The main results of the dissertation research were published in 9 scientific papers, including:

- Bakhadur, A., Alem, H., Carré, V., Gries, T., Balan, L., Cantin, J. L., Ghouti Medjahdi, Orazov Z., Uralbekov B., Schneider, R. Porous nitrogen-doped TiO_2/graphene oxide derived from H_2N-MIL-125 (Ti)/graphene oxide composites as highly efficient visible light active photocatalysts for the degradation of dyes and carbamazepine. Applied Surface Science, 164466, 714 (2025). https://doi.org/10.1016/j.apsusc.2025.164466 (WoS — Q1, Impact Factor 6.9; Scopus — Percentile 90%, CiteScore 13.4 according to 2024). Personal contribution of the doctoral candidate: conducting experimental work on the synthesis of NH2-MIL-125 metal–organic frameworks and selecting solvothermal synthesis conditions, as well as participating in characterization, evaluation of photocatalytic activity of the samples, and interpretation of the obtained data.
- Tulebekov, Y., Orazov, Z., Satybaldiyev, B., Snow, D. D., Schneider, R., & Uralbekov, B. Reaction steps in heterogeneous photocatalytic oxidation of toluene in gas phase—A review. Molecules, 28(18), 6451 (2023). https://doi.org/10.3390/molecules28186451(WoS — Q1, Impact Factor 4.6; Scopus — Percentile 81%, CiteScore 8.6 according to 2024). Contribution of the doctoral candidate:

literature analysis followed by writing sections based on the general principles of photocatalysis.

- Orazov, Z. K., Tulebekov, Y., Bakhadur, A. M., Uralbekov, B. M. Kinetic model of photocatalytic oxidation of the dye (Orange II) by superoxide radicals. Chemical Bulletin of Kazakh National University, 110(4), 4–10. (2023). https://doi.org/10.3390/molecules28186451 (WoS — Q4, Impact Factor 0.3 according to 2024). Personal contribution of the doctoral candidate: carrying out experimental work to assess photocatalytic activity, identifying the proposed decomposition mechanism and proposing a kinetic model of decomposition, as well as interpreting the results and writing the article.
- In 2 abstracts of reports presented at international conferences and symposia. Contribution of the doctoral candidate in preparing publications: conducting experimental studies on obtaining doped TiO_2 nanoparticles from NH_2-MIL-125 metal-organic frameworks, as well as participation in physicochemical analyses.

The following conclusions were made based on the results of the dissertation research:

1. By varying the conditions (precursor ratio, synthesis duration, calcination temperature), porous nanosized TiO_2 particles were obtained. By the solvothermal synthesis method, NH_2-MIL-125 metal-organic frameworks were obtained (S_{BET} = 415.5 m^2/g) and highly crystalline NH_2-MIL-125 (S_{BET} = 1076 m^2/g), followed by their calcination and obtaining N-TiO_2 with inherited porosity (S_{BET} = 107.8 m^2/g) and N-TiO_2 obtained from crystalline metal-organic framework structures (S_{BET} = 72.5 m^2/g); all obtained materials were characterized by XRD and FT-IR spectroscopy methods.
2. Evaluation of optical properties by diffuse reflectance spectroscopy and photocatalytic activity of the obtained N-TiO_2 nanoparticles showed that nanoparticles obtained after calcination of NH_2-MIL-125 (I) metal-organic framework structures exhibit higher photocatalytic activity under visible light ($(13.3 \pm 0.3) \times 10^{-3}$ min^{-1} vs $(4.5 \pm 0.21) \times 10^{-3}$ min^{-1}).
3. Impregnation with Fe^{3+} ions (0.3; 0.7; 1 mol.%) leads to an increase in photocatalytic activity, while 0.7 mol.% is the optimal concentration above which a decrease in the photocatalytic activity of the material begins. Investigation of optical properties determined the effect of Fe^{3+} ions by decreasing the band gap and shifting absorption into the visible region. FT-IR spectroscopy characterization did not show structural changes.
4. Calcination of the NH_2-MIL-125/GO composite at 450 °C yields N-TiO_2/GO heterostructures, where titanium dioxide consists of anatase phase (XRD), N-TiO_2 particles with a size of 13 ± 3 nm are located on GO sheets (TEM/EDS), with a specific surface area up to 131 m^2/g and mesopores of 9 nm (N_2 adsorption). The shift of the low-frequency peak position in Raman spectroscopy showed the formation of oxygen vacancies, and according to XPS data, from the deconvolution of the N 1s spectrum, two nitrogen states were identified: the peak at ~398.3 eV is assigned to substitutional N (N–Ti–O bonds) and the peak at ~400.9 eV to interstitial N (Ti–O–N bonds). The nanocomposites absorb in the visible region and have a band gap of 3.12 eV.
5. The optimal composition is N-TiO_2/GO with 30 wt.% GO. Complete decolorization of Orange II in 4 h and Eosin Y in 30 min, and carbamazepine in 210 min under visible light; the photodegradation rate is described by pseudo-first-order kinetics. After 5 sequential repeated cycles, the photoactivity of the nanocomposites is retained at 93 % without noticeable phase changes and agglomeration.
6. The PL spectroscopy and photoresponse results show a decrease in recombination

upon the addition of GO, which acts as an electron acceptor and reduces recombination. The addition of scavengers such as DMSO, AO, NaN_3, t-BuOH, and TEMPOL showed that the active species $\bullet O_2^-$ (dominant), h^+, $^1O_2$, and •OH play an important role in photodecomposition reactions, since the addition of the corresponding scavengers leads to a decrease in photodegradation efficiency down to 0, 28, 35, and 51%, respectively.

Assessment of the completeness of the tasks performed. All tasks formulated to achieve the goals of this dissertation were successfully completed. TiO_2 materials doped with Fe^{3+} ions and heterostructured with graphene oxide were synthesized using solvothermal synthesis and impregnation, followed by calcination at 450 ℃. The optimal temperature and time parameters for MOF synthesis and its calcination were determined, all samples were calcined at 450 ℃ with a heating rate of 10 ℃ min^{-1} for 2 h, which ensured maximum product yield and high photocatalytic activity. Evaluation of the photocatalytic activity of N-TiO_2-x%Fe and N-TiO_2/x%GO showed the possibility of shifting the band gap toward the visible region and influencing electron-hole recombination, depending on MOF synthesis conditions, dopant concentration, and heterostructuring components. Thus, the aims of the dissertation were achieved, as evidenced by the obtained photocatalytic materials that are active under visible light.

Assessment of the technical and economic efficiency of the solutions proposed in the dissertation work. All tasks formulated to achieve the goals of this dissertation work have been successfully solved. TiO_2 compounds doped with Fe^{3+} ions, as well as heterostructures with graphene oxide, were synthesized using solvothermal synthesis and impregnation methods followed by calcination at 450 °C. The optimal conditions for MOF synthesis and its calcination were determined. All samples were calcined at 450 °C at a heating rate of 10 °C/min for 2 hours, which ensured acceptable phase purity and its photocatalytic activity in the visible-light region. Evaluation of the photocatalytic activity of N-TiO_2-x %Fe and N-TiO_2/x %GO materials showed the possibility of shifting the band gap into the visible region and influencing the recombination process of electron–hole pairs depending on the synthesis conditions of the MOF, the concentration of introduced elements and compounds.

Compliance with scientific development directions or state programs. The dissertation work was carried out within the framework of grant funding projects and "Zhas Galym 2025–2027" of the Committee of Science of the Ministry of Science and Higher Education of the Republic of Kazakhstan: GF "Improved photocatalytic air treatment technology for removal of volatile organic compounds" (IRN AP09057924-OT-23), GF "Development of visible-driven heterostructured TiO_2-based photocatalysts for air treatment" (IRN AP19679298), and ZG 2025–2027 "Development of TiO_2-based semiconductor nanopowders for photocatalytic degradation of organic pollutants under visible light" (IRN AP25796519).