ABSTRACT

of the thesis performed in the form of a series of articles

«**Development and study of Al-doped photocatalyst based on $SrTiO_3$ with dual co-catalysts for efficient water purification and hydrogen production**»

submitted for the degree of

Doctor of Philosophy (PhD) in the educational program

8D07103 – «Materials Science and Engineering»

KUSPANOV ZHENGISBEK BORANBAYULY

The purpose of the thesis is the development and investigation of an Al-doped $SrTiO_3$-based photocatalyst with dual photodeposited cocatalysts to enhance the efficiency of photocatalytic water purification and hydrogen production.

Research objectives and their role within the implementation of the scientific study:

1. To synthesize high-purity and highly crystalline $SrTiO_3$ using the chemical precipitation method, followed by thermal treatment and optimization of synthesis conditions.
2. To investigate aluminum doping of the synthesized $SrTiO_3$ via the molten flux method and to study its physicochemical and electronic properties using the DFT approach.
3. To deposit dual co-catalysts based on Rh/Cr_2O_3 and CoOOH onto the surface of $SrTiO_3$@Al through the photodeposition method, followed by examination of their morphology, structure, and optical characteristics.
4. To evaluate the influence of modification degree and synthesis parameters on the photocatalytic activity of the samples during the degradation of an organic dye under visible light and during photocatalytic water splitting for hydrogen generation.
5. To conduct large-scale field experiments on hydrogen production using the developed panel-type photocatalytic reactor with an effective light absorption area of 1 m^2.

Research methods

To achieve the stated goal, a comprehensive set of theoretical and experimental methods was employed. A critical analysis of scientific and technical literature was conducted to assess the current state and development prospects of photocatalysts based on nanostructured semiconductor materials. The experimental part of the study included the design, synthesis, and development of composite photocatalysts. For a comprehensive investigation of the structure and properties of the obtained materials, a wide range of modern physicochemical analytical techniques was utilized, including X-ray diffraction (XRD), scanning electron microscopy (SEM), transmission electron microscopy (TEM), X-ray photoelectron spectroscopy (XPS), and UV–Vis diffuse reflectance spectroscopy (UV–Vis DRS). Additionally, the density functional theory (DFT) method was applied to interpret experimental data and model the electronic properties of the photocatalysts.

Main provisions (proven scientific hypotheses and other conclusions that are new knowledge) to be defended:

1. Increasing the calcination temperature from 800 to 1100 °C during the chemical precipitation synthesis of $SrTiO_3$ promotes the growth of particle size, crystallinity, and phase purity due to the complete decomposition of the intermediate $SrCO_3$ phase. Subsequent Al doping significantly suppresses undesirable Ti^{3+} recombination centers in $SrTiO_3$ and enhances the concentration of oxygen vacancies, thereby improving charge carrier transport;

2. The photodeposition of dual co-catalysts (Rh/Cr_2O_3 and CoOOH) on the surface of $SrTiO_3$@Al substantially enhances the photocatalytic activity of the samples through more efficient charge separation. The synthesized composite exhibited the highest photocatalytic efficiency (89%) in degrading an organic contaminant under visible light within 60 minutes, with a reaction rate constant of 0.0312 min^{-1};

3. The modified composite $Rh/Cr_2O_3/SrTiO_3$@Al/CoOOH demonstrated significantly improved photocatalytic hydrogen evolution performance, reaching 11.04 $mmol \cdot g^{-1} \cdot h^{-1}$ — 2300 and 3067 times higher than those of $SrTiO_3$@Al and pristine $SrTiO_3$, respectively. Furthermore, the use of a panel-type photocatalytic reactor for water splitting proved promising for large-scale, low-cost renewable hydrogen production, with the synthesized composite generating 106 mL of hydrogen per hour under natural sunlight using a 1 m^2 photocatalytic panel.

Description of the main research results

The thesis was carried out in the form of a series of scientific publications and is devoted to the development and validation of approaches aimed at improving the efficiency of $SrTiO_3$-based photocatalysts for water purification and hydrogen production. The key findings are as follows:

1. A comprehensive literature review revealed that $SrTiO_3$ and its analogs are widely studied as photocatalysts; however, their low efficiency under visible light and high charge recombination rates significantly limit practical application. This emphasizes the need for further research focused on enhancing the activity and stability of $SrTiO_3$ through doping and cocatalyst modification.

2. It was shown that increasing the calcination temperature (800–1100 °C) after chemical precipitation from TiO_2 and $Sr(NO_3)_2$ precursors leads to larger particle sizes, higher crystallinity, and improved phase purity due to the complete decomposition of the intermediate $SrCO_3$ phase. According to SEM and TEM data, $SrTiO_3$ particles calcined at 800 °C have sizes of about 30–50 nm, while at 1100 °C the sizes increase to 150–250 nm and acquire a well-defined cubic morphology. Calcination at 1100 °C was found to be optimal, providing phase-pure and highly crystalline $SrTiO_3$.

3. It was established that the molten flux method enables the incorporation of aluminum into the $SrTiO_3$ lattice without disrupting its crystal structure. Aluminum doping suppresses Ti^{3+} recombination centers and increases the concentration of oxygen vacancies, collectively improving charge transport and photocatalytic efficiency (as confirmed by structural, spectral, and DFT analyses).

4. Photodeposition of Rh/Cr_2O_3 (core–shell) and CoOOH co-catalysts onto

the $SrTiO_3$@Al surface was found to accelerate charge separation and reduce recombination of photogenerated carriers. The synthesized composite exhibited high activity in the photodegradation of a model organic pollutant (methylene blue): 89% removal within 60 minutes, with a pseudo-first-order rate constant of k = 0.0312 min^{-1} — significantly exceeding the activity of $SrTiO_3$@Al and pristine $SrTiO_3$.

5. The modified Rh/Cr_2O_3/$SrTiO_3$@Al/CoOOH composite demonstrated a photocatalytic hydrogen evolution rate of 11.04 $mmol \cdot g^{-1} \cdot h^{-1}$, which is 2300 and 3067 times higher than that of $SrTiO_3$@Al and $SrTiO_3$, respectively.

6. A panel-type photocatalytic reactor with an active area of 1 m^2 (16 sub-reactors, powder deposition by drop-casting) was designed and tested. Under natural sunlight, the composite achieved a hydrogen evolution rate of up to 106 $mL \cdot h^{-1} \cdot m^{-2}$, confirming its technological feasibility and scalability potential for large-scale green hydrogen production.

Substantiation of the novelty and importance of the obtained results

The necessity of this research arises from the urgent demand for modified photocatalysts capable of efficient water purification and solar-driven hydrogen generation with an extended absorption range and reduced charge recombination.

Scientific novelty:

- It was established that, in the chemical precipitation synthesis of $SrTiO_3$, the calcination temperature strongly affects particle size, purity, and crystallinity; the optimal temperature of 1100 °C allows the formation of highly crystalline and phase-pure $SrTiO_3$;

- It was shown that the molten flux method enables aluminum incorporation into $SrTiO_3$ without altering its lattice structure. Aluminum doping suppresses Ti^{3+} recombination centers and promotes the formation of oxygen vacancies, enhancing photocatalytic activity;

- It was discovered that photodeposition of dual co-catalysts (Rh/Cr_2O_3 and CoOOH) on $SrTiO_3$@Al accelerates charge separation and reduces electron–hole recombination. The synthesized composite exhibited enhanced photocatalytic activity in methylene blue degradation (87% in 60 minutes), surpassing $SrTiO_3$@Al and $SrTiO_3$ by factors of 4.9 and 6.6, respectively;

- It was demonstrated that the concept of a panel-type photocatalytic reactor for water splitting is an effective and scalable approach for cost-efficient renewable hydrogen production. The Rh/Cr_2O_3/$SrTiO_3$@Al/CoOOH composite produced 106 mL of hydrogen per hour under real outdoor conditions using a 1 m^2 photocatalytic panel.

Practical significance. In the course of this research, optimal conditions were developed for the synthesis of $SrTiO_3$ with high crystallinity and particle sizes ranging from 150 to 250 nm. The effectiveness of aluminum doping and the separate photodeposition of dual cocatalysts was confirmed as a means to enhance the photocatalytic activity of the composite. The developed Rh/Cr_2O_3/$SrTiO_3$@Al/CoOOH composite demonstrated the ability to degrade an organic dye (10 mg/L concentration) by 89% within 60 minutes. Furthermore, a pilot-scale setup with an effective area of 1 m^2 was assembled, showing efficient

hydrogen generation and potential for practical implementation. Using this composite, the photocatalytic system produced an average of 106 mL of hydrogen per hour under natural sunlight, demonstrating its scalability and strong potential for commercialization.

Compliance with scientific development directions or government programs

This work was carried out within the framework of the following scientific projects:

- The grant funding competition of the Committee of Science of the Ministry of Science and Higher Education of the Republic of Kazakhstan (2022–2024), Project No. AP14869381, "Development of a composite photocatalyst $SrTiO_3$@Al/Graphene Oxide for efficient hydrogen generation via water splitting."
- The program-targeted funding project "Development and advancement of innovative devices, materials, and high-tech solutions for the implementation and utilization of hydrogen energy in Kazakhstan," Project No. BR18574073, Ministry of Science and Higher Education of the Republic of Kazakhstan (2022–2024).

The contribution of the doctoral student to the preparation of each publication

The author's personal contribution includes direct participation in experimental work, formulation of research objectives, analysis and interpretation of the obtained results, and preparation of manuscripts and reports.

A total of 10 scientific papers have been published based on the dissertation research, including 1 article in a scientific journal recommended by the Committee for Quality Assurance in Science and Higher Education (CQASE) of the Ministry of Science and Higher Education of the Republic of Kazakhstan for obtaining the PhD degree, and 9 articles in peer-reviewed journals indexed in international databases such as Web of Science (Clarivate Analytics, USA) and Scopus (Elsevier, Netherlands).

Articles published in journals indexed in international scientific databases (Web of Science and Scopus):

1. **Kuspanov Z**. et al. Efficient photocatalytic degradation of methylene blue via synergistic dual co-catalyst on SrTiO3@Al under visible light: Experimental and DFT study // Journal of the Taiwan Institute of Chemical Engineers. – 2024. – V. 165. – P. 105806. (Q1, percentile 85%, IF 5.5, CiteScore 9.1) https://doi.org/10.1016/j.jtice.2024.105806;
2. **Kuspanov Z**. et al. Investigating and correlating the photocatalytic activity of synthesised strontium titanate nanopowder with calcination temperature // Environmental Technology & Innovation. – 2024. – V. 36. – P. 103852. (Q1, percentile 96%, IF 6.7, CiteScore 14.0) https://doi.org/10.1016/j.eti.2024.103852;
3. **Kuspanov Z**. et al. Photocatalysts for a sustainable future: Innovations in large-scale environmental and energy applications // Science of The Total Environment. – 2023. – V. 885. – P. 163914. (Q1, percentile 95%, IF 8.2, CiteScore 17.6) https://doi.org/10.1016/j.scitotenv.2023.163914;
4. **Kuspanov Z**. et al. Multifunctional strontium titanate perovskite-based

composite photocatalysts for energy conversion and other applications // International Journal of Hydrogen Energy. – 2023. – V. 48. – P. 38634–54. (Q1, percentile 86%, IF 7.2, CiteScore 13.5) https://doi.org/10.1016/j.ijhydene.2023.06.168;

5. Kudaibergen, A., **Kuspanov Z**. et al. Synthesis, Structure, and Energetic Characteristics of Perovskite Photocatalyst SrTiO3: an Experimental and DFT Study // Eurasian Chemico-Technological Journal. – 2023. – V. 25. – P. 139–46. (Q4, percentile 32%, CiteScore 1.1) https://doi.org/10.18321/ectj1516;

6. **Kuspanov Z**. et al. Efficient Photocatalytic Hydrogen Evolution via Cocatalyst Loaded Al-doped SrTiO3 // Eurasian Chemico-Technological Journal. – 2024. – V. 26. – P. 133–40. (Q1, percentile 32%, CiteScore 1.1) https://doi.org/10.18321/ectj1636;

7. A. Serik, N. Idrissov, A. Baratov, A. Dikov, S. Kislitsin, Ch. Daulbayev, **Zh. Kuspanov**. Recent Progress in Photocatalytic Applications of Electrospun Nanofibers: A Review // Molecules. – 2024. – Vol. 29(20). – P. 4824. (Q1, percentile 83%, IF- 4,2, CiteScore 7,4) https://doi.org/10.3390/molecules29204824;

8. M. Bissenova, Arman Umirzakov, Konstantin Mit, Almaz Mereke, Yerlan Yerubayev, A. Serik, **Zh. Kuspanov.** Synthesis and Study of SrTiO3/TiO2 Hybrid Perovskite Nanotubes by Electrochemical Anodization // Molecules. – 2024. – V. 29(5). – P. 1101. (percentile 83%, IF- 4,2, CiteScore 7,4). https://doi.org/10.3390/molecules29051101;

9. Yergaziyeva, G., **Kuspanov Z**. et al. Advancements in catalytic, photocatalytic, and electrocatalytic CO2 conversion processes: Current trends and future outlook // Journal of CO2 Utilization. – 2024. – V. 80. – P. 102682. (Q1, percentile 91%, IF 7.2, CiteScore 13.9) https://doi.org/10.1016/j.jcou.2024.102682.

1 article published in a scientific journal recommended by the CQASE MSE RK.

1. **Kuspanov Zh.,** Daulbayev Ch., Yeleuov M., Mansurov Z. Multilayer Graphene/$SrTiO_3$ Derived from Bio-Waste as an Efficient Photocatalytic System // Combustion and Plasma Chemistry. – Almaty, 2023. – V.21. №2 – P. 71–80. https://doi.org/10.18321/cpc21(2)71-80. (in russian).