ANNOTATION
to the dissertation for the degree of doctor of Philosophy (PhD) in the educational program
"6D074000 – Nanomaterials and nanotechnologies."
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on the topic "Synthesis of photocatalytic materials for splitting of water with generation of H_2"

General description of work. The dissertation is dedicated to the synthesis and investigation of materials based on $SrTiO_3$ with enhanced photocatalytic properties for hydrogen production via photocatalytic water splitting.

Relevance of the research topic. Non-renewable energy sources such as oil, coal, and natural gas have been forming in the Earth's crust for millions of years, and their intensive exploitation leads to their rapid depletion within a short period of time. Thus, it becomes evident that for sustainable development, the utilization of alternative energy sources based on renewable resources is necessary, such as solar, wind, and hydro energy. Furthermore, the use of non-renewable energy sources leads to environmental pollution, greenhouse gas emissions, and global climate change.

As an inexhaustible and the most extensive renewable energy source, natural solar radiation delivers a tremendous amount of radiant energy to the Earth's surface. However, the challenge of efficiently harvesting and converting intermittent solar energy, with relatively low density, into energy that can be stored in chemical bonds and used on demand for various practical purposes, remains unresolved. In turn, hydrogen bonds have been meticulously studied as a potential energy carrier in the cycle of clean energy conversion. Emulating natural photosynthesis through photocatalytic water splitting using photo-generated electrons and holes can facilitate the utilization of solar energy in hydrogen production with relatively lower production and system costs.

To address these issues, the dissertation demonstrates the potential of using perovskite compound based on $SrTiO_3$ as a photocatalyst. Utilizing $SrTiO_3$ in the process of photocatalytic hydrogen production offers several advantages. Firstly, this material exhibits high activity, enabling efficient water splitting into hydrogen and oxygen under ultraviolet light irradiation. Secondly, $SrTiO_3$ is a cost-effective and readily available material, making it attractive for industrial applications. Additionally, this material possesses stability and durability, allowing for prolonged use in hydrogen production processes. Thus, the application of $SrTiO_3$ in photocatalytic hydrogen production represents an effective and promising direction in the development of new hydrogen production technologies.

The process of obtaining composite photocatalysts involves adding specific amounts of other components to the material used for photocatalytic hydrogen production. This process can significantly enhance the efficiency and rate of water decomposition into hydrogen and oxygen. One of the advantages of composite photocatalysts is the increased light sensitivity of the material, allowing for the utilization of a broader spectrum of light for the photocatalytic reaction. This increases the amount of energy available for water splitting, thereby greatly

accelerating the reaction kinetics. Additionally, the addition of various compounds can alter the chemical and physical properties of the material, thereby enhancing its stability and durability, making it more efficiently and economically viable for hydrogen production processes. Thus, the modification of photocatalysts is one of the most promising directions in the development of new hydrogen production technologies.

The goal of the work is to develop new one-dimensional photocatalysts based on $SrTiO_3$/C with improved optical properties, investigate their photocatalytic properties, and determine the effectiveness of their application in hydrogen production.

Work objectives. To achieve the goal of dissertation work, the following tasks were set:

1. Fabrication of fibers based on $SrTiO_3$/C via electrospinning followed by the examination of their chemical composition, properties, and photocatalytic activity for hydrogen generation.
2. Development of $SrTiO_3$/C-based composites with the addition of metal oxide particles (Fe_2O_3, Cr_2O_3, and CuO) and subsequent investigation of their chemical composition, physicochemical properties, and photocatalytic activity for hydrogen production.
3. Synthesis of composite fibers based on $SrTiO_3$/C with the addition of graphene-like porous carbon and study of the influence of porous carbon on the physicochemical properties and photocatalytic activity of the composite.
4. Evaluation of the efficiency of the obtained materials by determining the amount of generated hydrogen during the photocatalytic decomposition of a water mixture under UV irradiation.

Basic provisions for defense:

1. The addition of transition metal oxide particles (Fe_2O_3, Cr_2O_3 and CuO) can enhance the optical properties and decrease the bandgap width of the one-dimensional $SrTiO_3$/C photocatalyst from 3.12 eV to 3.11, 2.89, and 2.84 eV, respectively.
2. Reducing the bandgap width of the $SrTiO_3$/C photocatalyst by adding metal oxide particles enhances its photocatalytic activity and hydrogen production by splitting the water mixture to 833±25.2, 845±24.6, and 996±27.4 μmol g^{-1} h^{-1} with the addition of Fe_2O_3, Cr_2O_3 and CuO particles, respectively.
3. Modification of the one-dimensional $SrTiO_3$/C photocatalyst with graphene-like porous carbon reduces the bandgap width of $SrTiO_3$/C to 2.72 eV.
4. Modifying the $SrTiO_3$/C photocatalyst with graphene-like porous carbon positively affects its optical properties and photocatalytic activity for hydrogen evolution up to 129±3.6 mmol g^{-1} h^{-1} during photocatalytic water splitting.

The object of the study is photocatalysts based on $SrTiO_3$/C modified with metal oxide particles (Fe_2O_3, Cr_2O_3 and CuO) and graphene-like porous carbon.

The subject of the research is the influence of various additives (metal oxide particles and graphene-like porous carbon) on the photocatalytic activity of $SrTiO_3$/C followed by studying the effectiveness of their application for hydrogen production through photocatalytic water splitting.

Research methods

The following research methods were employed in the study: X-ray diffraction analysis (XRD), scanning electron microscopy (SEM), spectrophotometry based on light transmission and absorption measurements, Raman spectroscopy, transmission electron microscopy (TEM), and thermogravimetric analysis (TGA). Quantitative and qualitative analysis of the gas mixture generated during the photocatalytic reaction was conducted using gas chromatography.

Scientific novelty of the work

In this work, the following results of scientific novelty were obtained:

1. Composite photocatalysts based on $SrTiO_3$/C were obtained via electrospinning with optimized optical properties achieved through the addition of transition metal oxide particles. The addition of metal oxides (Fe_2O_3, Cr_2O_3 and CuO) positively impacted the reduction of the bandgap width of the $SrTiO_3$/C photocatalyst from 3.12 eV to 3.11, 2.89 and 2.84 eV, respectively.

2. Composite one-dimensional photocatalysts based on $SrTiO_3$/C with the addition of Fe_2O_3, Cr_2O_3 and CuO showed increased hydrogen production via photocatalytic splitting of the "water/methanol" mixture: 833±25.2, 845±24.6, and 996±27.4 μmol g^{-1} h^{-1} with the addition of Fe_2O_3, Cr_2O_3 and CuO particles, respectively.

3. It was found that the addition of graphene-like porous carbon to the one-dimensional $SrTiO_3$/C photocatalyst enhances the efficient separation of photo-induced charge carriers in $SrTiO_3$/C/x-GPC composite photocatalysts, thereby reducing the probability of their recombination. Moreover, the introduction of graphene-containing porous carbon leads to a reduction in the bandgap width from 3.12 eV ($SrTiO_3$/C) to 2.7 eV.

4. Composite one-dimensional photocatalysts based on $SrTiO_3$/C/x-GPC demonstrated high hydrogen generation efficiency during the photocatalytic splitting of the water-methanol mixture, with an average hydrogen output of up to 129±3.6 mmol g^{-1} h^{-1}.

Theoretical significance.

The theoretical significance of this study lies in investigating the influence of various additives (metal oxides, graphene-like carbon) on the optical characteristics of the perovskite one-dimensional photocatalyst based on $SrTiO_3$/C. Specifically, the research examines how narrowing the bandgap width of the $SrTiO_3$/C photocatalyst through the formation of a composite with metal oxide nanoparticles and carbon affects its activity in hydrogen production via photocatalytic water splitting.

Practical significance

The results obtained within the framework of the dissertation research can be applied in the field of producing "green" hydrogen from renewable sources, particularly through the efficient splitting of water mixtures using solar light. These developments can intensify the process of developing hydrogen energy in the Republic of Kazakhstan.

Connection with scientific research and government programs

The research was conducted within the framework of the scientific and technical program BR05236795 "Development of Hydrogen Energy Technology in the

Republic of Kazakhstan," funded by the Ministry of Science and Higher Education of the Republic of Kazakhstan (2018-2020).

Publications. As a result of the research on the dissertation topic, 18 scientific papers were co-authored, including 1 article in the international journal Chemical Physics Letters (Q2, percentile 67%), 2 articles in the international journal Nanomaterials (Q1, percentile 81%), 1 article in the international journal International Journal of Hydrogen Energy (Q1, percentile 95%), 1 article in the International journal Applied Surface Science (Q1, percentile 95%), 1 article in the international journal Science of The Total Environment (Q1, percentile 95%), 2 articles in the journal Combustion and Plasma Chemistry included in the list of journals recommended by the Committee for Control in the Field of Education and Science of the Ministry of Education and Science of the Republic of Kazakhstan, as well as 10 materials and abstracts at international scientific conferences.

Description of the doctoral candidate's contribution to the preparation of each publication

In the article "Aligned composite $SrTiO_3$/PAN fibers as 1D photocatalyst obtained by electrospinning method," the author participated in conducting experimental work, interpreting results, and writing the article.

In the article "Influence of metal oxide particles on the bandgap of 1D photocatalysts based on $SrTiO_3$/PAN fibers," the author carried out experimental data collection, interpreted results, and contributed to writing the article.

In the article "Bio-waste-derived few-layered graphene/$SrTiO_3$/PAN as an efficient photocatalytic system for water splitting," the author participated in obtaining and discussing experimental data, as well as writing the article.

In the articles "Recent developments of TiO_2-based photocatalysis in hydrogen evolution and photodegradation: A review," "0D, 1D, and 2D nanomaterials for visible photoelectrochemical water splitting: A review," and "Photocatalysts for a sustainable future: Innovations in large-scale environmental and energy applications," the author participated in writing the review sections of the articles and formatting the articles according to the journal's requirements.

In the articles "Obtaining nano-sized fibers based on $SrTiO_3$ by the electrospinning method for photocatalytic coatings" and "Thermodynamics and kinetics of photocatalysis for hydrogen production during water splitting," the author contributed to writing the initial draft of the articles.

Scope of work structure. The dissertation work is completed on 98 pages (excluding appendices) and includes 40 figures and 1 table. It consists of an introduction, literature review, experimental section, results and discussions, conclusion, and a list of references, encompassing 223 sources.