ANNOTATION

Dissertations for the degree of Doctor of Philosophy (PhD)
6D060400-Physics

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Impurity influence of graphene oxide on photoelectric and photocatalytic properties of the TiO_2 films

Relevance of the topic. The ecological purity of energy technologies is an extremely important issue, which leads to increased attention to renewable energy sources, in particular, to hydrogen energy. The use of hydrogen energy has many advantages, which include accessibility, inexhaustibility, and complete safety for the environment. However, despite the huge potential and broad prospects, only a small part of this energy is used by humanity. This is due to a number of unresolved issues. The production of hydrogen fuel H_2 by converting solar energy is considered one of the main strategies for solving the global energy problem.

Photoelectrochemical splitting of water on the TiO_2 electrode was initiated by Fujishima and Honda. Since then, the question of the possibility of producing photocatalytic H_2 has attracted close attention. Various semiconductor photocatalysts, such as TiO_2, ZnO, CdS, C_3N_4, WO_3 and $BiVO_4$ have been investigated for this purpose. It should be noted that titanium dioxide occupies a special place because of its physical and optical properties, such as high melting point, chemical inertness, high phototransformation efficiency and photostability, and fast electron recombination.

Most of these materials have a wide band gap, photo-corrosion, and low efficiency of electron-hole pair separation. To solve these problems, the semiconductor is doped with metals and non-metals, composites are created on its basis, noble metals are applied to the surface of the semiconductor, heterojunctions, quantum dots are made, and dye sensitization is carried out.

Among these approaches, the creation of composite materials is the most promising method for improving the characteristics of a semiconductor. The formation of composites based on other semiconductors, metals, and carbon materials reduces the recombination rate, increases the charge separation ability, and increases the transport capacity of TiO_2.

Graphene and its sp^2 hybridization modifications are widely used in energy and environmental materials, such as solar energy conservation, photovoltaics, photoelectrochemical and photocatalytic generation of hydrogen / hydrocarbon fuels, and photocatalysis of organic pollutants. In recent years, composites based on TiO_2 and graphene with its modifications have attracted much attention for improving charge separation and electron transport.

However, it is quite difficult to use graphene as a precursor for the synthesis of a nanocomposite with TiO_2 due to the lack of functional reaction groups. To solve this problem, graphene oxide (GO) and reduced graphene oxide (rGO) are more suitable.

Many synthesis strategies are mainly focused on creating TiO_2 nanocrystals with the desired size and morphology, with their subsequent modification and application to the surface of graphene sheets. However, these hybrid materials have disadvantages. Their size is too small to be easily agglomerated. At the same time, during the process of photodegradation of organic compounds, the effective surface area of TiO_2 and graphene of such a hybrid material can significantly decrease.

Therefore, the method of hydrothermal synthesis of nanocomposites based on modifications of graphene and TiO_2 seems to be the simplest and most technologically advanced for practical use. A detailed description of this method is described in the works. The literature data show that nanocomposite materials obtained by the hydrothermal method are the most effective photocatalyst for H_2 isolation.

The aim of the thesis is to study the influence of graphene derivatives on the electrophysical and photocatalytic properties of TiO_2 films.

The objects of research are nanocomposite films based on titanium dioxide, graphene oxide, reduced graphene oxide and silver nanoparticles.

The scientific novelty consists of the following:

1) for the first time, a nanocomposite material based on reduced graphene oxide and TiO_2 was synthesized by the hydrothermal method;

2) it is found that the generated photoinduced current is much greater in nanocomposite materials than in films based on TiO_2 nanoparticles;

3) for the first time, a triple nanocomposite material based on graphene derivatives, TiO_2 and Ag/ TiO_2 nanostructure with improved photocatalytic and charge-transport properties was obtained;

4) a technologically optimal configuration of a photodetector based on nanocomposite materials and a method for increasing their optoelectronic characteristics under the action of the silver nanoparticles plasmon effect are proposed.

Structure and **scope** of the dissertation. The structure of the dissertation work is determined by the tasks set and consists of an introduction, five sections, a conclusion, and a bibliography. It is presented on 102 pages of typewritten text, illustrated with 42 figures, 12 tables, and contains a list of cited literature from 222 titles.

The main results include the following:

1. The addition of graphene derivatives to TiO_2 films increases the generated photoinduced current and increases the photocatalytic activity of the semiconductor.

2. Doping of the nanocomposite material with «core–shell» nanostructures of the Ag/TiO_2 composition makes it possible to obtain a highly efficient photocatalyst under the action of localized plasmon resonance.

3. The use of 3D nanocomposites in combination with plasmon nanoparticles increases the photoelectric characteristics of detectors due to the high mobility of charge carriers.

Scientific and practical significance of the work:

The resulting nanocomposite materials can be used as the main element as photocatalysts in electrochemical and photovoltaic cells and gas analyzers. The results on the influence of graphene derivatives on the photocatalytic activity and electrophysical properties, as well as the results of the study of the electric transport properties of nanocomposite films, can become the basis for the development of photodetectors.

Approbation of the work and publications. The main results of the work were reported and discussed at the following conferences: international scientific and technical conference "Russian-Japanese Conference Chemical Physics of Molecules and Polyfunctional Materials" (2018, Orenburg); international scientific symposium "Modern problems of Condensed Matter Physics, Nanotechnologies and Nanomaterials" (2018, Almaty); XIV International scientific conference dedicated to the 80th anniversary of the founder of the conference, Professor T. A. Kuketaev – "Solid State Physics, Functional Materials and New Technologies (FTT-2018)" (2018, Bishkek-Karaganda), Journal open press conference series "Materials Science and Engineering" (2018); Proceedings of the X International Conference "Fundamental Problems of Optics – 2018" (2018, St. Petersburg); "VIII International Conference on Photonics and Information Optics" (2019, Moscow); "International Symposium Fundamentals of Laser Assisted Micro- & Nanotechnologies" (2019, Saint - Petersburg); Proceedings of the V International Scientific and Practical Conference "V Global science and Innovations 2019: Central Asia" (2019, Nur-Sultan), The 7th International Conference on nanomaterials and advanced energy storage systems (INESS-2019) (2019, Almaty); The 11th International Conference "Chaos and structures in nonlinear systems. Theory and Experiment" (2019, Karaganda); Al-Farabi in the modern Kazakh context. "International scientific and practical conference dedicated to the 1150th anniversary of Abu Nasr ibn al-Farabi" (2020, Karaganda).

Publications. According to the results of the dissertation work, 22 printed works were published: 4 articles in journals included in the Thomson Reuters and Scopus database (1 article in the Russian Journal of Physical Chemistry A, IF–0.72, 1 article in Theoretical and Experimental Chemistry IF-0.48, 1 article in Materials Research Express IF-1.93 and 1 article in Optics and Spestroscopy, IF–0.84); 4 articles in journals recommended by the Committee for Control in the Sphere of Education and Science MES RK, and 14 publications in the materials of international conferences, including 1 article in foreign countries.