ABSTRACT

Development of a targeted method for producing photoactive inorganic coatings based on copper modified titanium dioxide

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Relevance of the research topic

Currently, titanium dioxide (TiO_2) based inorganic photoactive materials are widely used in photocatalytic processes, which correspond to the concept of sustainable development of natural resources and closed-loop economy. This interest in TiO_2 is due to its high chemical stability and lack of toxicity, which makes it possible to use it in photocatalytic systems for the deep water purification from organic pollutants. Highly dispersed TiO_2 powders produced by the chemical industry are unsuitable for these purposes, since upon completion of the purification process, it becomes necessary to separate them from the treated medium. Therefore, it is more appropriate to use immobilized TiO_2 in the form of highly porous coatings.

The low quantum efficiency due to the high degree of recombination of photogenerated charge carriers is a significant disadvantage of TiO_2. This drawback requires the development of new TiO_2 based photoactive coatings. Increase in the quantum efficiency of TiO_2 is achieved by synthesizing nanosized materials and modifying them with elements of various nature. Increase in the external surface area to volume ratio contributes to the photogenerated charge carriers direct migration into the reaction zone. The use of highly ordered TiO_2 nanotubes (NTs) coatings is an example of efficient photocatalysis. An even greater effect can be achieved by considering both morphology of the coatings and their ability to create electron-hole pairs under the action of light. Heterovalent doping of TiO_2 crystal lattice and the creation of TiO_2 based heterostructural systems promotes a decrease in the charge carriers recombination degree and a broadening of the spectral sensitivity of TiO_2. According to the literature data, copper is one of the most accessible and promising TiO_2 modifiers.

Degree of development of the topic

A large number of works have been devoted to the creation of TiO_2 based photoactive materials. A significant contribution to the development of this field was made by Parmon V.N., Ryabchuk V.K., Rempel A.A., Artemiev Y.M., Kozlov D.V., Vorontsov A.V., Schmuki P., Grimes C.A. and many others. Despite the increased interest in the TiO_2 photoactive properties by scientists around the world, it has not yet been possible to develop an effective photocatalytic water treatment system, which necessitates further research in this area.

The aim of this work was to develop a methodology for highly ordered TiO_2 NTs coatings targeted modification with copper and to study the physicochemical correlations of the phenol and azorubine photocatalytic oxidation on the surface of the obtained photoactive materials in aqueous solutions in the presence/absence of hydrogen peroxide.

In order to achieve this goal, the following **tasks** had to be solved:

1. To develop a solvothermal method for controlled copper doping of TiO_2 NTs obtained by anodization of metallic titanium; to establish the effect of the process temperature and duration on the material copper content and by varying them, to obtain samples of Cu-TiO_2 NTs photoactive coatings with different copper contents.

2. To study the effect of the copper content on Cu-TiO_2 NTs physicochemical characteristics; to establish a correlation between the copper content and photoactivity of the obtained coatings.

3. To study the influence of the heterogeneous photocatalytic process conditions (pH, initial concentration of phenol and azorubine, process duration, and hydrogen peroxide concentration) on the phenol and azorubine oxidation degree for the original and copper-modified coatings.

4. To conduct resource tests of the developed photoactive coatings photocatalytic properties.

Scientific novelty

1. A method for producing highly ordered Cu-TiO_2 NTs coatings with a controlled copper content of (0 - 3.9) ± 0.2% wt. was scientifically grounded and developed.

2. The modifying effect of copper introduced into the TiO_2 NTs amorphous matrix with subsequent crystallization at 450°C was found to be manifested in a fundamental change in the crystal structure of TiO_2: the appearance of a rutile phase, an increase in the light absorption degree in the UV-Vis region of the solar spectrum, and an increase in photocatalytic activity in a wide pH range (3-10) regardless of the presence/absence of H_2O_2.

3. It was found that the photocatalytic activity as a function of the obtained coatings copper content has a maximum at 2.0-2.5% wt.

4. The influence of initial concentrations of phenol (1-50 mg/l) and azorubin (1-50 mg/l), temperature (25 - 80°C) and process duration (15 - 120 min), pH of aqueous solutions (3 - 10) and H_2O_2 concentration (0.5 - 20 mmol/l) on phenol and azorubin photocatalytic oxidation on the surface of obtained photoactive materials was determined.

Theoretical and practical significance

The author's technique for obtaining inorganic photoactive coatings was developed, enabling control of the crystal structure, optical and photocatalytic properties of the obtained materials. The developed coatings have high photocatalytic activity and sufficient operational stability, which makes it possible to use them as photocatalysts in water purification and disinfection devices. The obtained correlations of phenol and azorubin photocatalytic degradation under different conditions (pH, τ, $C_{init.}$, $C_{H_2O_2}$) form the basis for designing effective deep photocatalytic water purification systems.