Synthesis of nanostructured materials based on titanium dioxide and copper for catalytic processes

Andrei Denisenko

Abstract

Relevance of work. To date, one of the most under review objects are semiconductor nanomaterials. Among them, materials based on titanium dioxide are distinguished. Interest in TiO_2 is due to its properties, as well as prospects for application. The range of possible applications of the material is quite wide: from use in the field of photocatalytic (FC) processes to integration of the material into modern microelectronics. Depending on the application, there are some limiting properties of the material, especially the particle size, which affect the efficiency of the application. Among existing methods for obtaining nanomaterials based on TiO_2 with controlled properties, the most promising is the method of electrochemical oxidation of titanium (anodizing method). This method makes it possible to control the characteristics and properties of the obtained anode nanotubular materials in a wide range by varying the anodizing conditions. In this regard, establishing the relationship between the conditions of obtaining and the characteristics of nanotubes is an important aspect to be studied when looking for practical applications of this material. Of the wide range of applications for nanotubes, the researchers pay the most attention to photocatalysis. The FC processes allow achieving complete oxidation of organic pollutants, including hard-to-oxidize ones, to harmless substances. In this case, in comparison with traditional methods of purification for their implementation does not require the preparation and processing of additional reagents and materials. According to the World Health Organization, phenol is the most dangerous and widespread pollutant of industrial effluents. Thus, the creation of a photocatalytic system that allows effective purification of the water environment from phenol is an urgent task. Previously, nanotube coating TiO_2 demonstrated high photocatalytic activity (FA) in the process of oxidation of organic dyes (compared to commercial catalyst

Degussa P-25). It was found that the limiting stage of the process is the internal diffusion of molecules. One of the ways to level out the diffusion limits of the process is to produce nanotubes (NT) with a large diameter. This can be done by extending the range of anodizing parameters. The use of NT TiO_2 films as a photocatalyst has a number of advantages due to the unique geometry of the material, and the genesis of such coatings with nanoparticles of different nature (metals, metal oxides, semiconductors) opens up an opportunity to improve the efficiency of the catalyst.

The purpose of this work was to develop a method for obtaining composite materials based on an ordered matrix of titanium dioxide nanotubes and copper nanoparticles for photocatalytic systems of liquid phase destruction of phenol.

The following tasks had to be solved in order to achieve the set **goals:**

1. To study the relationship between the anodizing parameters and the characteristics of the resulting TiO_2 nanotubes (NT) under conditions of maintaining a constant temperature of the anodizing solution with an accuracy of 0.5 °C. To carry out comparative FA tests of the obtained materials, to determine geometrical characteristics and chemical composition of NT TiO_2, providing their maximum FA.
2. To develop methods for obtaining composite copper photocatalysts of NT Cu/TiO_2 and NT Cu_2O/TiO_2 composition using ion layering and deposition approaches from the gas phase (PVD) of copper precursor II with subsequent reduction.
3. Study the activity of created composite materials in heterogeneous photocatalytic systems of liquid phase destruction of phenol.
4. To develop a method for obtaining a nanotubular array of titanium dioxide on an elastic polymeric substrate, as well as a method for evaluating the optical properties of films based on NT TiO_2.

Scientific novelty of the work:

1. For the first time the data on the influence of anodizing parameters on the characteristics of NT TiO_2 under conditions of rigid maintenance of a constant temperature in the reaction zone have been obtained, which allowed to formulate specific conditions for the synthesis of NT intended for various applications.
2. The influence of the synthesis method and conditions on the structure and properties of the obtained composite materials of Cu/NT TiO_2 and Cu_2O/NT TiO_2 composition has been established.
3. Photocatalytic properties of new composite materials of Cu/NT TiO_2 and Cu_2O/NT TiO_2 composition in the reaction of phenol destruction in aqueous media have been studied.
4. Destruction of phenol in Cu/NT TiO_2-phenol-H_2O_2-water and Cu_2O/NT TiO_2-phenol-H_2O_2-water systems was studied for the first time. It was found that addition of hydrogen peroxide in the FC system increases the reaction rate of phenol destruction by many times. The process of phenol oxidation in Cu/NT TiO_2-phenol-H_2O_2-water and Cu_2O/NT TiO_2-phenol-H_2O_2-water systems is described by the first order kinetic equation.

Practical significance of the work:

1. An array of experimental data on the influence of anodizing conditions on the characteristics of the resulting TiO_2 nanotubes has been obtained, on the basis of which it is possible to predict the geometric characteristics and properties of the material. Threshold values of nanotubes characteristics providing achievement of the maximum FA of the catalyst based on TiO_2 nanotube coating have been established.
2. The method of obtaining composite photo catalysts of Cu/NT TiO_2 and Cu_2O/NT TiO_2 composition showing high activity in the reaction of phenol oxidation in water under the influence of light has been developed.
3. An effective heterogeneous photocatalytic system for destruction of phenol in aqueous medium with the use of composite catalyst and hydrogen

peroxide addition has been developed, which allows achieving complete destruction of phenol in 1 hour.

4. The method of obtaining an elastic composite from titanium dioxide nanotubes and polymeric substrate has been developed. The method of estimation of optical properties of films from TiO_2 nanotubes and composites based on them is developed by transfer of coatings from metal base to transparent polymeric substrate and measurement of their optical properties by means of spectrophotometer without diffuse reflection attachment. The developed approach allows to quickly assess optical properties without using expensive equipment and complex mathematical models.