Section 2. Materials science

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INFLUENCE OF THE SURFACE CONDITIONS ON THE PROPERTIES OF THE OXIDE PHOTOCATALYSTS

Abstract. Optical studies of micro- and nano-sized powders of titanium dioxide of various modifications and nano-sized powders of zinc oxide have been conducted in the paper. It is established that in the optical transmission spectra of nano-sized powders there is a drop in the visible light region in the wavelength interval betveen of 550–750 nm. This indicates an enhancement of light absorption in this area, an increase in the use of visible light energy for photocatalysis, and an improvement in the efficiency of photocatalysis. Oxide vacancies are suggested to be the cause of the observed effect. EPR studies confirm this opinion.

Keywords: TiO_2 photocatalysts, magnetic cocatalysts, oxide vacancies, improvement of the photocatalyst efficiency, EPR spectra of photocatalysts.

Introduction

Photocatalysis is a phenomenon when the action of light activates the redox chemical reactions. Special substances called photocatalysts are used in the process of photocatalysis. Photocatalysts are substances that cause the activation of oxidation-reduction responses in the environment by the action of light. They can split water into oxygen and hydrogen under the influence of sunlight, which can be used as an environmentally friendly fuel [1]. Photocatalysts can also destroy harmful substances which exist in the environment, including bacteria and viruses [2]. Thus, creating efficient photocatalysts is connected to solving the most important energy and environmental problems. The main problem that prevents the widespread practical use of photocatalysts is their low efficiency [3; 4]. Photocatalysis proceeds as follows: under the influence of light, pairs of electrons and holes are formed in the semiconductor. They move to the surface, interact with water molecules and cause their decomposition into oxygen and hydrogen through oxidation-reduction reactions. The low efficiency of photocatalysts is mainly caused by two reasons: 1) Electrons and holes created by light participate in small amounts in the reaction due to their recombination [4] and; 2) Visible rays participate weakly in the reaction; Since the existing stable photocatalysts have a large value of the energy gap, only high-frequency rays can induce charges in these substances; Although, theoretically, the energy of the charges, which are induced by low-frequency rays (e.g. red light), is sufficient to split water molecules [5]. Different strategies are used to solve these problems, e.g. various impurities are used for modifying the energy gap of photocatalysts as they reduce its size and improve the inclusion of visible light in the reaction [4; 5]. To reduce the recombination of electrons and holes, a method of deposition of smaller clusters on the surface of photocatalytic nanopowder grains is used, which captures electrons or holes and reduces their recombination [6–8]. Some progress has been made in improving the efficiency of photocatalytic reactions, but the desired results are not achieved yet. Therefore, it is essential to look for and use new strategies. The presented study serves this purpose.

Materials

Studies of certain photocatalytic properties of titanium dioxide (TiO2) and zinc oxide (ZnO) powders have been done. Photocatalytic powders of anatase and rutile modification of TiO_2 and ZnO of different sizes were selected for the research, as well as the so-called P25 – which is a mixture of these two modifications and is characterized by higher photocatalytic activity than pure modifications. The materials were purchased from Us-nano and were used without any further purification.

The morphology and elemental composition of the powders were determined by ESM, EDS and XRD studies. ESM studies determined the particle sizes of the investigated powders, and EDS studies investigated the elemental composition of the powders. It was determined that the purchased powders were of high purity, and the total content of impurities was less than 1%. XRD analysis determined that the anatase-modified titanium dioxide was crystallographically pure, as it consisted of 100% anatase modification, and the rutile-modified sample was not pure, as it consisted of 95% rutile and 5% anatase modification. As for P25, it has been found that P25 consists of 86% anatase and 14% rutile modifications.

Results and discussions

As a result of the study of the optical spectra of the photocatalytic powders, it was found that in the transmission spectra of the nanosized powders, the drop in the visible light region in the wavelength interval of 550–750 nm is noticed. Figure 1 shows the optical transmission spectrum of P25 in the wavelength range of 240–800 nm. The picture shows a drop in the wavelength range between 550 and 750 nm. This indicates an enhancement of light absorption in this area and thus improves the use of visible light for photocatalysis, causing an increase in photocatalysis efficiency.

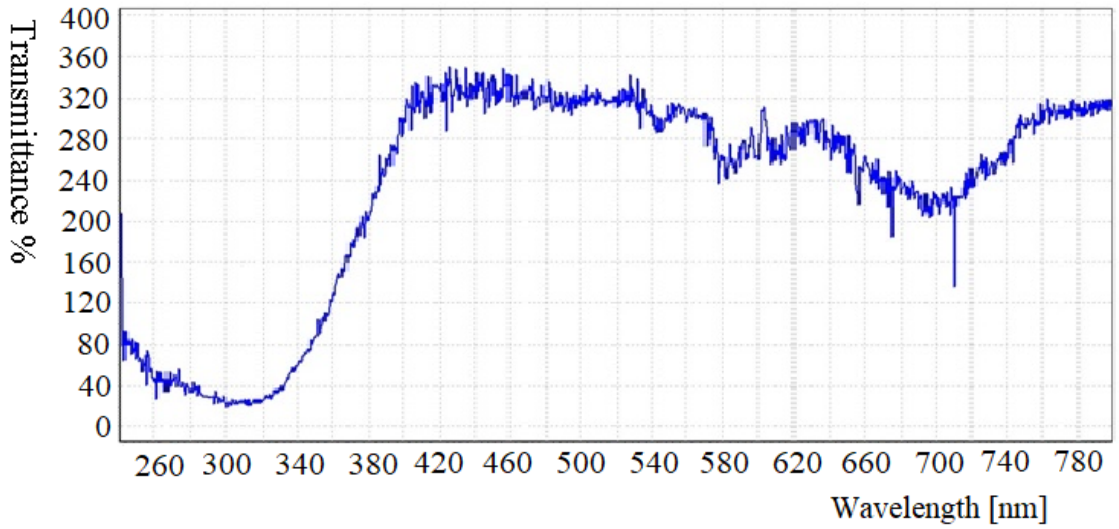

Figure 1. Optical transmission spectrum of P25

Said drop is invisible in the optical transmission spectra of the micro-sized powders. The results of the experiments indicate that the observed phenomenon can be connected to surface effects since the main difference between micro- and nano-sized powders lies in the differences in the amounts of the surface areas of these powders.

Research has also established that the said drop in the visible region of the transmission spectrum disappears even in spectra of nano-sized powders when the surface of their grains is decorated with cobalt or nickel clusters. The clusters were layered with the simple and inexpensive non-electrical technology developed at the E. Andronikashvili Institute of Physics [9]. Figure 2 shows the optical transmission spectrum in the wavelength range between 240 and 800 nm for P25 nanopowder. The surfaces of P25 nanopowder nanograins are decorated with cobalt clusters. The image shows the disappearance of the drop in the transmission spectrum in the visible region, which is the result of decoration.

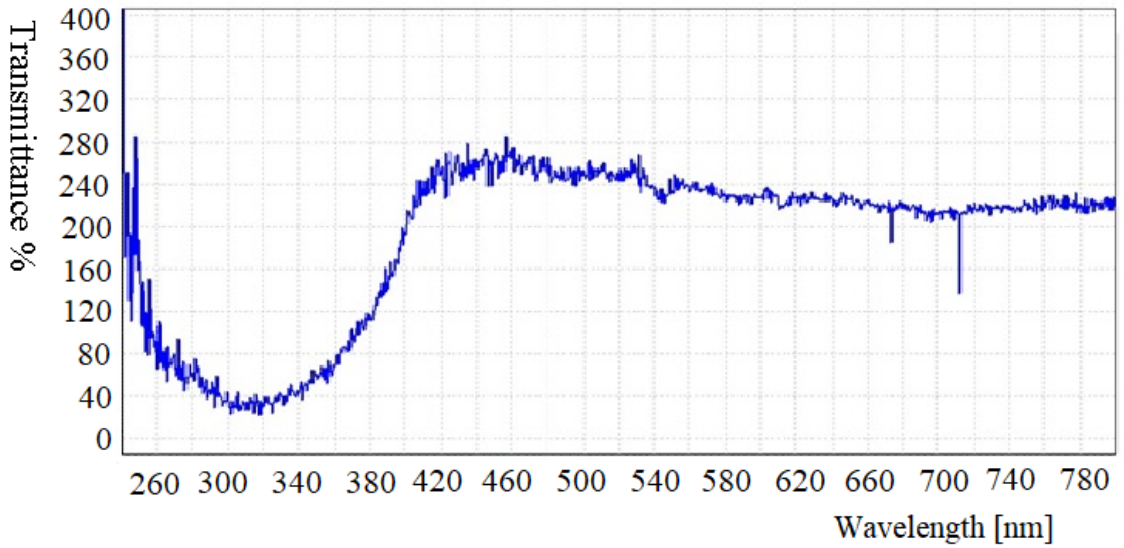

Figure 2. Optical transmission spectrum of nanopowders P25 with nanograins decorated with Co clusters

This confirms that the observed phenomenon is related to surface effects. It must be noted that the disappearance of the drop in the spectrum is not caused by the deterioration of light penetration into the powder grains, which could seem to be a result of the deposition of clusters but it is not. As (Figure 1) and (Figure 2) show, another drop in the ultraviolet region of the transmission spectrum, associated with the gap in the main energy spectrum of this substance, does not change after the deposition of clusters.

Experiments conducted on ZnO nanopowders showed that the transmission spectra of ZnO nanopowders also show a drop in the wavelength interval between 550 and 750 nm. This indicates that the observed phenomenon is connected not to metal but to oxygen atoms, most likely, to the vacancies of these atoms.

EPR studies have shown that titanium dioxide micro-powders do not have an EPR signal. The EPR signal appears in the free radical region of the spectrum only if the grain size is nano-sized. (Figure 3) shows the EPR spectrum of titanium dioxide nano-size powder P25 with an average grain size of 25 nm. The spectrum represents a narrow singlet (g = 2.0017 and ΔH = 0.705 mTL) placed between the 3rd and 4th components of the Mn^{2+} standard; this narrow singlet is usually attributed to electrons trapped by oxygen vacancies [10]. Numbers 1,2,3,4,5 indicate Mn^{2+} (standard) components.

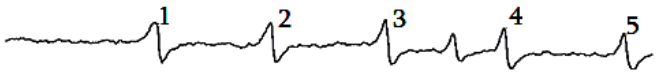

Figure 3. EPR spectrum of P25 (g = 2.0017, ΔH = 0.705mTl); Numbers 1,2,3,4,5 indicate Mn^{2+} (standard) components

The EPR spectra of photocatalytic nanopowders were also studied after their grain surfaces have been decorated with metallic clusters. Figure 4 shows the EPR spectrum of titanium dioxide P25/Co decorated with cobalt clusters. It is a broad asymmetric singlet (g = 2.2023 mTl and ΔH = 78.2 mTl), which most likely appears as a result of the interaction of cobalt atoms with oxygen atoms and also with oxygen vacancies, since the signal of oxygen vacancies, which was observed before deposition, disappears at this time. This indicates that, as a result of depositing clusters on the surface of photocatalyst nanoparticles, isolated oxygen vacancies pass into other complexes, which leads to the disappearance of the effect of oxygen vacancies in the EPR spectrum and probably also the disappearance of the drop in the light transmission spectrum, which is associated with oxygen vacancies.

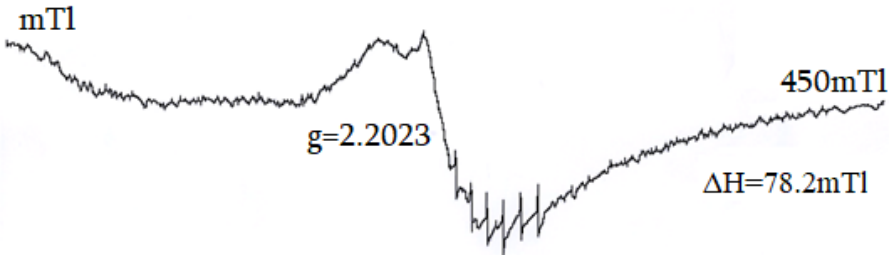

Figure 4. EPR spectrum of P25 decorated with cobalt clusters (g=2.2023, ΔH=78.2mTl); Similar results were obtained for other photocatalytic nanopowders as well

Conclusion

In the presence of oxygen vacancies on the surface of titanium dioxide nanopowder grains, these vacancies can enhance light absorption in the visible region in the wavelength interval between 550 and 750 nm. Therefore, oxygen vacancies increase the efficiency of oxide photocatalysts from the point of view of solar energy conversion.

As a result of decorating the surfaces of oxide photocatalysts with metallic co-catalytic clusters, the absorption of light in the visible wavelength range between 550 and 750 nm disappears, since the surface vacancies interact with the atoms of the

clusters and form complexes that do not absorb in this region.

According to EPR spectra, before the deposition of clusters, electrons are in oxygen vacancies and give a signal with a factor of g=2.0017, and after the deposition of clusters, new complexes are formed and electrons give a signal with a factor of g = 2.2023.

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