

Photocatalytic Properties of Nanocrystalline TiO₂ Modified with CuO and WO₃

V. A. Lebedev^a, V. V. Sudin^b, D. A. Kozlov^a, and A. V. Garshev^{a, b}

^a*Faculty of Materials Science, Lomonosov Moscow State University, Moscow, 119991 Russia*

^b*Baykov Metallurgy and Materials Institute, Russian Academy of Sciences, Leninskii pr. 49, Moscow, 119991 Russia*
e-mail: vasya_lebedev@mail.ru

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Abstract—Much attention is paid to studies of the processes occurring in heterogeneous catalysis with the use of nanomaterials, in particular, photocatalysis. Titanium dioxide and zinc oxide are among the most widespread photocatalysts due to their high chemical stability, suitable band gap, and rather high lifetime of non-equilibrium electron–hole pairs. In order to increase the photocatalytic activity (PCA) of these materials, including the case of a visible light action, various approaches are applied, in particular, the development of a composition material with a metal–semiconductor or semiconductor–semiconductor contact. We have chosen semiconductors of *n*-type (WO₃) and *p*-type (CuO) as components of such composites because of their potential positive influence on the PCA of titanium dioxide at the expense of spatial separation of non-equilibrium charge carriers and, respectively, increase in their lifetime. In order for the obtained composites to be commercially valuable, we have chosen a method of synthesis by modifying the ready TiO₂ preparations, including those that are commercially available (Degussa P25). It has been shown that the modification with CuO lowers PCA of titanium dioxide, while the modification with WO₃ enhances it by 25%. It has been demonstrated that WO₃/TiO₂ composite manifests PCA under visible light illumination.

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INTRODUCTION

Titanium dioxide (titania) in a nanocrystalline state is one of the most perfectly studied materials used for photocatalysis [1, 2]. The chemical stability of nanoparticles of this material makes it a highly attractive object for application under very different conditions of chemical processes. The synthesis of such materials, which manifest photocatalytic properties under a visible light illumination, makes it even more useful. For this purpose, it is necessary to develop composites of TiO₂ with semiconductors, which absorb the light in a visible spectral region and whose band structure in the contact region would promote the generation of nonequilibrium charge carriers under visible light illumination and increase the lifetime of these carriers. Theoretically, such a mutual interaction could be expected for a number of TiO₂/semiconductor composition materials; however, the possibility of the practical implementation of such processes in the contact region between TiO₂ and semiconductor has not been proven certainly as yet. Indirect proof for the presence of such an interaction may be the registration of changes in the material functional properties, e.g., changes in the photocatalytic properties by keeping other equal conditions by measuring the photocatalytic activity of various samples.

Taking into account the necessity of comparing the properties of the composition material with unmodified titania and the fact that the used method of synthesis should allow us to obtain a nanocomposite with a good contact between crystalline nanoparticles of its components, we have chosen the method of impregnation from a whole variety of nanocomposite synthesis methods.

For modifying titania we have chosen copper oxide and tungsten oxide as the semiconductor materials absorbing the light both in UV and visual spectrum regions. The choice was also determined by the suitable band gap structure of these substances and the possibility of practically comparing the dependence of the modified titania functional properties on the semiconductor type. Due to the fact that the conduction band of tungsten oxide is lower than the corresponding band of TiO₂ [3] (Fig. 1), a transfer of the electrons from a titania particle onto WO₃ particle becomes possible. Such a process results in an effective separation of nonequilibrium charge carriers and an increase in their lifetime. On the other hand, due to the lower position of the WO₃ valence band relative to that of TiO₂, a transfer of the holes generated at WO₃ [4, 5] becomes possible. These charge carriers will be key participants of the process of photocatalysis under a visible light illumination. The possibility of such trans-

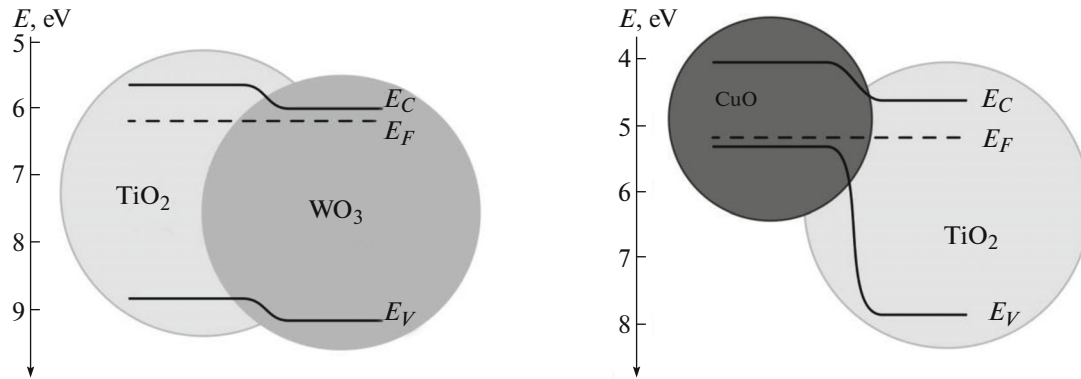


Fig. 1. Scheme of the band structure of CuO/TiO₂ and WO₃/TiO₂ contacts according to the data of [3].

fers implies the high photocatalytic activity both in UV and visible regions. In the case of CuO, the transport of nonequilibrium charge carriers through CuO/TiO₂ contact will proceed in the opposite direction: the photogenerated holes from TiO₂ should be transported onto CuO [6], while nonequilibrium electrons should be transported from CuO onto TiO₂ (Fig. 1). Thus, oxidative processes will proceed predominantly at copper oxide surface.

It is also necessary to pay attention to a correct comparison of the material functional properties. It is possible by account for a number of factors affecting the rate of photocatalytic reactions, such as the amount of the catalyst, the dye concentration, impurities, intensity of irradiation, oxygen concentration, temperature, rate of stirring, and pH of aqueous solutions.

An account for these factors by the determination of the rate of photocatalytic decomposition of methyl orange in an aqueous solution and studying the obtained samples by transmission and scanning electron microscopy, X-ray phase analysis, and spectroscopy of diffuse reflectance allow us to characterize in detail TiO₂/semiconductor composition material.

EXPERIMENTAL

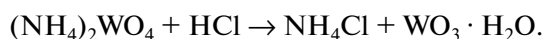
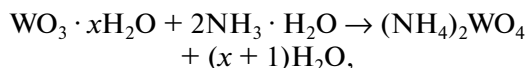
A mesoporous titania was synthesized by the template method: a hydrolysis of titanium butylate Ti(OⁿBu)₄ was carried out in an aqueous solution in the presence of a nonionic surface active substance (SAS) Pluronic P123, representing a triblock copolymer of polyethylene–polypropylene. A batch of triblock copolymer was dissolved in distilled water, HCl was added to achieve pH 2, and 1% mol NH₄F was added to increase the efficiency of polycondensation [7]. Then the solution was cooled to 0°C and Ti(OⁿBu)₄ (Aldrich, 97%) was added under stirring, which led to the formation of a white suspension. Upon the beginning of hydrolysis, the suspension was

treated in an ultrasonic bath and then stirred at room temperature for 72 h, centrifugated, rinsed with distilled water to a neutral pH, and air-dried. In order to remove the template residuals, the sample was annealed in an oxygen flux for 3 h at a temperature of 350°C.

In order to obtain titania samples coated with copper(II) oxide nanoparticles, we used the method of impregnation of both a commercially available preparation of TiO₂ (P25 Degussa) and preliminarily synthesized mesoporous titania with salts of Cu²⁺ and the subsequent thermal decomposition of the latter. For an impregnating solution, we have chosen Cu(NO₃)₂ and copper formate. The deposition was carried out in the following way: a powder of titanium dioxide in a ratio 1 g on 2 ml was added to solutions of copper nitrate and formate. The obtained suspension was intensively stirred for 20 min; then it was centrifugated, the solution was decanted, and the obtained sediment was rinsed with water and repeatedly centrifugated under the same conditions. After this, titanium dioxide was again transferred into a suspension and frozen in liquid nitrogen to carry out a freeze-drying. The dried samples were annealed in a muffle furnace for 2 h at a temperature of 550°C in air to the formation of copper(II) oxide.

In order to obtain TiO₂ nanoparticles modified by the deposition of WO₃, we used the method of tungsten oxide deposition onto the surface of TiO₂ particles from the solution. The batches of sodium tungstate with a mass estimated for the preparation of the samples contained 1, 5, 10, and 15 mol% of WO₃, respectively, were taken. After this, a fresh sediment of tungstic acid WO₃ · xH₂O was obtained from each batch by the hydrolysis of sodium tungstate in muriatic acid, which then was centrifugated and rinsed several times. The sediments of tungstic acid were dissolved in concentrated ammonia. One gram of titanium dioxide powder was added to the ammonia solution and the suspension was intensively stirred for 20 min. Then the

suspension was brought to pH 2 by adding muriatic acid, in order to deposit tungstic acid onto the titanium dioxide surface.



The suspension was centrifugated, rinsed, frozen in a liquid nitrogen, and subjected to sublimational drying.

In order to study the intrinsic photocatalytic activity of a nanocrystalline tungsten oxide, which is obtained by a modification of TiO_2 , a reference sample was synthesized by depositing WO_3 onto a neutral mesoporous matrix (SiO_2) according to the method described above by designing WO_3 content of 5 mol%. A mesoporous SiO_2 was synthesized for this purpose according to the method mentioned in [7].

METHODS OF STUDIES

The absorption spectra were registered on a Lambda 950 spectrophotometer (PerkinElmer, United States) in a wavelength range from 250 to 1000 nm in a diffuse reflectance mode. The measured spectra were recalculated according to the Kubelka–Munk formula:

$$\frac{K}{S} = \frac{(1 - R_\infty)^2}{2R_\infty} \equiv F(R_\infty),$$

where K and S are the coefficients corresponding to the absorption and reflection from the sample and R is the reflected signal intensity; it is important to note that $F(R_\infty) \sim \alpha$, which makes it possible to determine the band gap by rearranging the spectra in the Tauc plot [8] with the use of $(F(R_\infty)h\nu)^{1/2}$ instead of $(\alpha h\nu)^{1/2}$ [9]. The 1/2 degree is used in the case of semiconductors with an indirect allowed transfer, to which titanium dioxide belongs.

The X-ray diffraction experiments were carried out on a Rigaku D/MAX 2500 powder diffractometer with a rotating anode in a reflectance mode (the Bragg–Brentano geometry) with the use of $\text{Cu K}\alpha_{1,2}$ radiation and a graphite monochromator. The X-ray generator had the following parameters: the accelerating voltage was 45 kV and the power of the X-ray tube was 11.25 kW. Acquiring of diffraction patterns for the phase analysis was performed in quartz and oriented silicon cuvettes using a standard holder designed for six samples. A collection of X-ray diffraction patterns for the phase analysis was carried out in a mode of a continuous θ -2 θ scanning at a rate of detector movement of 3°/min and an averaging parameter of 0.02° on a 2 θ scale. The identification of the diffraction maxima was carried out using JCPDS database.

Analyses by scanning electron microscopy (SEM) and X-ray spectral microanalysis (EDX) were carried

out on a LEO SUPRA 50VP device (Germany) with the use of an X-MAX 80 energy dispersive analyzer (Oxford Inst.) at an accelerating voltage of 20 kV and an aperture of 60 μm . An acquisition of the characteristic X-ray radiation spectra was carried out with a spectrometer resolution of 10 eV per a channel and a rate of counts from 2000 to 20000 cps. The analysis was carried out using a total X-ray radiation from the whole chosen area. The calculation of the elemental composition was carried out with the use of the Oxford INCA software package.

An analysis by transmission electron microscopy (TEM) was carried out using a Zeiss Libra 200 microscope with a field emission cathode at an accelerating voltage of 200 kV.

In order to measure the photocatalytic activity of the samples, we used an original measuring setup based on a commercially available quartz reactor of the firm AceGlass Inc. The scheme of the setup is shown in Fig. 2. This setup is composed of a quartz reactor in whose working zone (1) a sample suspension and a dye are placed. During the experiment, it is possible to pass gas through a membrane (2) through a reaction mixture. The reactor working zone is illuminated by a cylindrical high-pressure mercury bulb (3); its power is 5.5 W. The lamp is cooled and, simultaneously, the suspension is thermostatically controlled by a flux of cooling liquid (water or a liquid color filter) through a cooling system (4). In order to study the photocatalytic activity in a visible region, a standard liquid color filter with a transmission band from 500 to 600 nm was used. The aqueous solution of CuCl_2 (10 wt %), NaNO_3 (15 wt %), CaCl_2 (13.4 wt %) was used as liquid color filter [10].

The use of methyl orange as one of the most widespread diazo dyes as a photodecomposing agent, is, in our opinion, the most reasonable, because in this case the first stage of degradation takes place with a destruction of a diazo group being a coloration center [11]. The measurements were carried out in a medium of a phosphate buffer solution (pH 6.9), which excludes possible changes in the position of the dye absorption peak and this peak intensity. In order to take into account possible temperature dependences of the photocatalytic oxidation rate and the rates of the adsorption/desorption processes, all the measurements of PCA of oxidation were carried out in a thermostatically controlled mode at a temperature of 40°C.

During an experiment, a continuous sampling is carried out from the reactor using a peristaltic pump (5). A flow of the reaction mixture passes through a U-shaped cell (6), where its absorption spectrum is measured. In order to measure the absorption spectra of suspensions, we used an HRX-2000 xenon lamp, an OceanOptics QE65000 spectrophotometer, an OceanOptics system of light guiding fibers, and an original cuvette section which allows

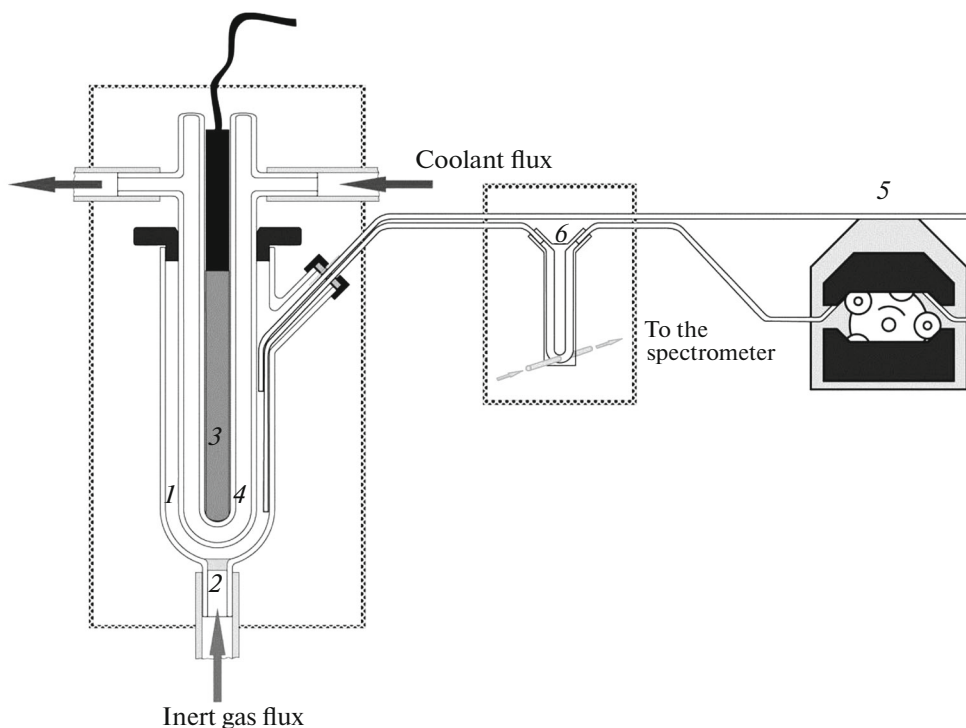


Fig. 2. Scheme of the setup for measuring the photocatalytic activity; the designations are given in the text.

one to work with absorption values from 0.1 to 3. The absorption spectra were collected digitally in an automatic mode with an interval of 5 s. Each spectrum was obtained as a result of averaging of at least ten single measurements.

The measurements of PCA were carried out by the implementation of the following operations: a sample batch of 2.5–3.5 mg was placed into 8 mL of a phosphate buffer solution (pH 6.9), treated in an ultrasonic bath for 5 min to remove coarse aggregates, and then placed into the working zone of the quartz reactor. The suspension stabilized and its absorption spectrum stopped noticeably changing in 15–20 min, after that 7 mL of a methyl orange solution was added (with a concentration of 100 mg/L). Then, also in 15–20 min, after the dye absorption process was completed, a UV lamp was switched on and the measurement of PCA was carried out for 5–6 h. The processing of obtained spectra was carried out in an automatic mode using a program written in the Python 2.7 programming language. The program works according to the following algorithm: first, in each obtained spectrum the intensity of an absorption maximum is calculated; then, a dependence of the intensity maximum on time is plot. A spectrum corresponding to the stabilized TiO_2 suspension is manually indicated on this dependence, after that the program in an automatic mode subtracts the absorption spectrum of the stabilized suspension from all the subsequent spectra. In the obtained set of optical absorption spectra of methyl orange, a search

for maxima is carried out and the dependence of the absorption intensity maximum for methyl orange on time is plot.

DISCUSSION OF RESULTS

An X-ray analysis of the obtained preparation of mesoporous titania, hereafter called mTiO_2 , has shown that it consists of anatase with a small amount of brookite (Fig. 3a). The powders of the composites obtained by impregnation with a solution of copper nitrate possessed a yellow-green color and the coloration intensity increased with the impregnating solution concentration. The preparations obtained using copper formate did not differ from those obtained using copper nitrate. Similar data were obtained using electron microscopy, X-ray spectral microanalysis, X-ray phase analysis, and optical spectroscopy. A deposition of tungsten oxide brought to the samples a pale yellow coloration whose intensity increased with the content of the modifying oxide (WO_3).

The spectra of diffuse reflectance from the CuO/TiO_2 samples obtained by impregnating with copper nitrate and WO_3/TiO_2 are presented in Figs. 4a and 4b. By recalculation of these spectra in the Tauc plot, we have determined that the absorption edge for the initial titanium oxide corresponds to the band gap of 3.0–3.1 eV. A shift in the absorption edge of TiO_2 is observed in the absorption spectra for the composites

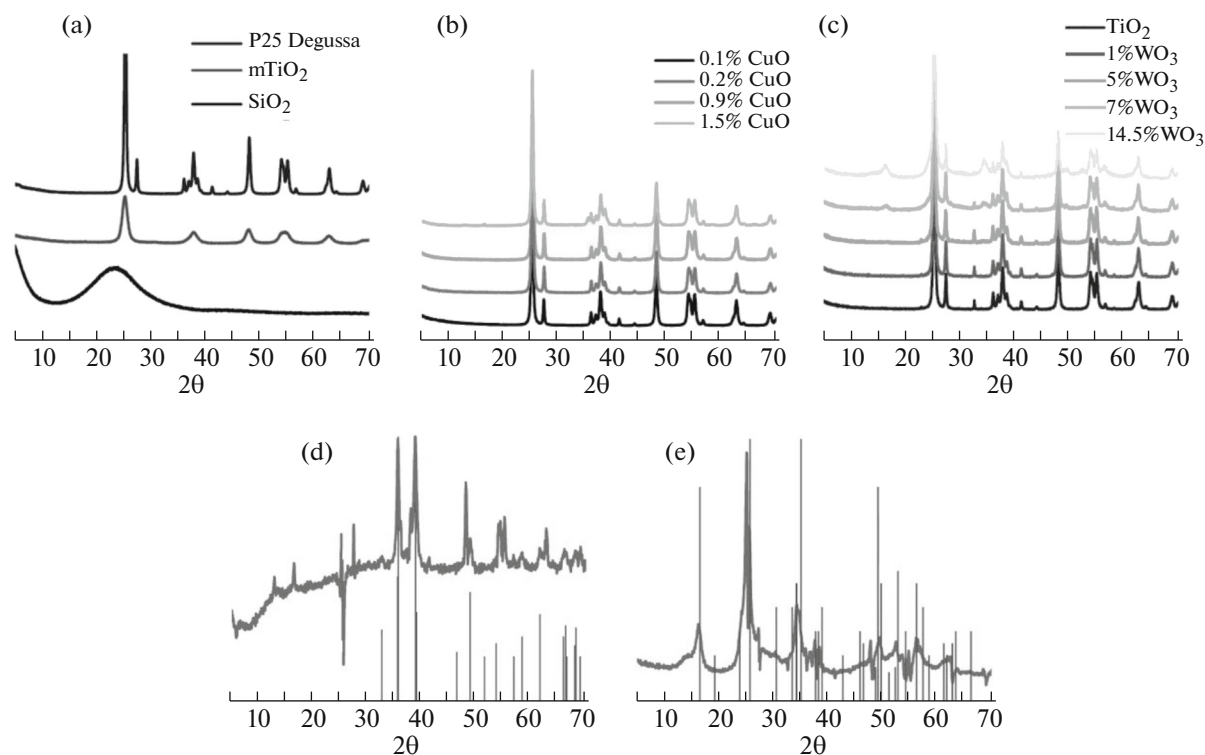


Fig. 3. (a) Diffractogram of mesoporous titanium dioxide and Degussa P25 preparation, (b) diffractograms of the samples CuO/TiO₂ obtained using copper nitrate, (c) diffractograms of the WO₃/TiO₂ samples, (d) difference diffractogram of the CuO/TiO₂ sample and the initial titanium dioxide (the diffraction maxima of the CuO phase (tenorite, [48-1548]) are marked), (e) difference diffractogram of the WO₃/TiO₂ sample and the initial titanium dioxide (the diffraction maxima of the phase WO₃ · H₂O [43-679] are marked).

with copper oxide, which is most probably associated with the formation of defect levels in an energy range of 2.2–2.7 eV in TiO₂ as a result of annealing. An absorption band is observed in these composites with an edge at ~1 eV, which corresponds to copper(II) oxide. An absorption edge in an energy range of 2.4–2.5 eV is observed in the absorption spectra for the composites with WO₃, and corresponds to tungsten(VI) oxide. Additional peaks, except for a small shift in the absorption edge of TiO₂, are not observed in the spectra of these composites; this is expected for the case of the applied synthesis of WO₃/TiO₂ composites without a high-temperature annealing.

The diffractograms obtained for the CuO/TiO₂ and WO₃/TiO₂ samples are presented in Figs. 3b and 3c, respectively. In order to separate the peaks corresponding to CuO phase, we have built a difference diffractogram for a composite with a maximum estimated mass content of CuO and the initial sample of titanium dioxide P25, which is presented in Fig. 3d. In order to separate the peaks corresponding to WO₃, we have also built a difference diffractogram. The result is presented in Fig. 3e. The position of the diffraction

maxima corresponds to the basic phases of the composition of CuO (tenorite, [48-1548]) and WO₃ · H₂O (hydrated tungsten oxide [43-679]).

In order to obtain information about the microstructure of nanoparticles of modifying oxides located on the TiO₂ surface, we have carried out an analysis using transmission electron microscopy. The microphotographs of the obtained nanocomposites are presented in Fig. 5. As follows from this data, samples do not contain coarse inclusions of modifying semiconductors, and titanium dioxide is not changed in the process of modification with semiconductors.

The microphotographs of a CuO/TiO₂ sample reveal the formation of nanoparticles with a size of 5–7 nm on TiO₂ surface. These particles are composed of copper oxide, which is proven by the electron diffraction data. The particles can be seen in the images obtained from WO₃/TiO₂ samples (Fig. 5c), which possess a long shape that is not typical for titania. In the electron diffraction patterns the intensity maxima are registered, which do not correspond to any of titania modifications, but are close to the maxima for

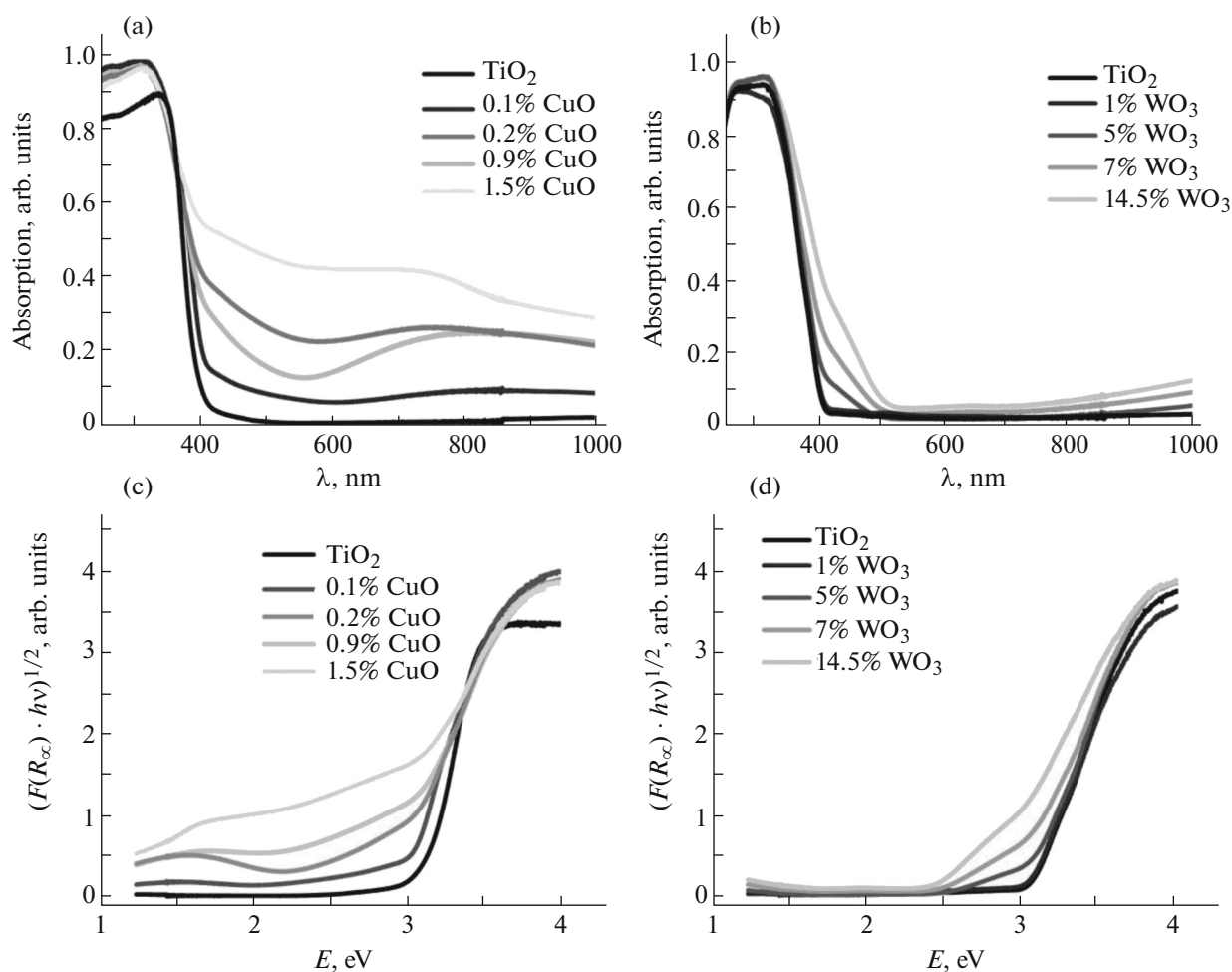


Fig. 4. (a, b) Spectra of diffuse reflectance of CuO/TiO₂ and WO₃/TiO₂ composites; (c, d) the same spectra in the Tauc plot.

WO₃ · H₂O. The ability of tungsten oxide to form rod-shaped structures is proven by the literature data [12]. In order to study the morphology of tungsten oxide structures, which are present in a sample, we have obtained SEM images, including those in backscattered electrons (a chemical contrast mode) (Fig. 5f). Bright rod-shaped particles are seen in the image; they are composed of heavier atoms than surroundings, which can be a proof of the presence of tungsten in them. The content of copper and tungsten oxides in the composites was determined using EDX method; homogeneity of CuO and WO₃ distribution over the samples was checked by EDX mapping.

After an analysis of the chemical composition and microstructure, we measured the photocatalytic activity for each of the samples. The kinetic curves for all the samples were plotted in the semilogarithmic scale and fitted by a linear law, where the slope coefficient corresponded to the reaction rate constant. In order to compare PCAs for various samples, their rate con-

stants of were normalized to the sample weight and, as a result, the constants measured in 1/(s g) units were obtained. To avoid the influence of possible inessential changes in the parameters of PCA measurements on the measured value of the reaction rate constant, the PCA of the initial titanium dioxide P25 was measured for every series of the samples. The data of the photocatalytic activity of the samples under the UV light illumination are presented in Fig. 6, where PCA of the composites are normalized to PCA of the initial TiO₂ preparations. An error of measurements amounted to no more than 20%, which was verified by repeated experiments.

PCA of the mesoporous titania is about 30–40% of the measured photocatalytic activity of P25 Degussa. It may be caused by a high weight amount of X-ray amorphous phases in the resulting preparation.

It has been shown that WO₃/TiO₂ composites manifest higher PCA in a UV range in comparison with the initial titania preparations, as expected for a

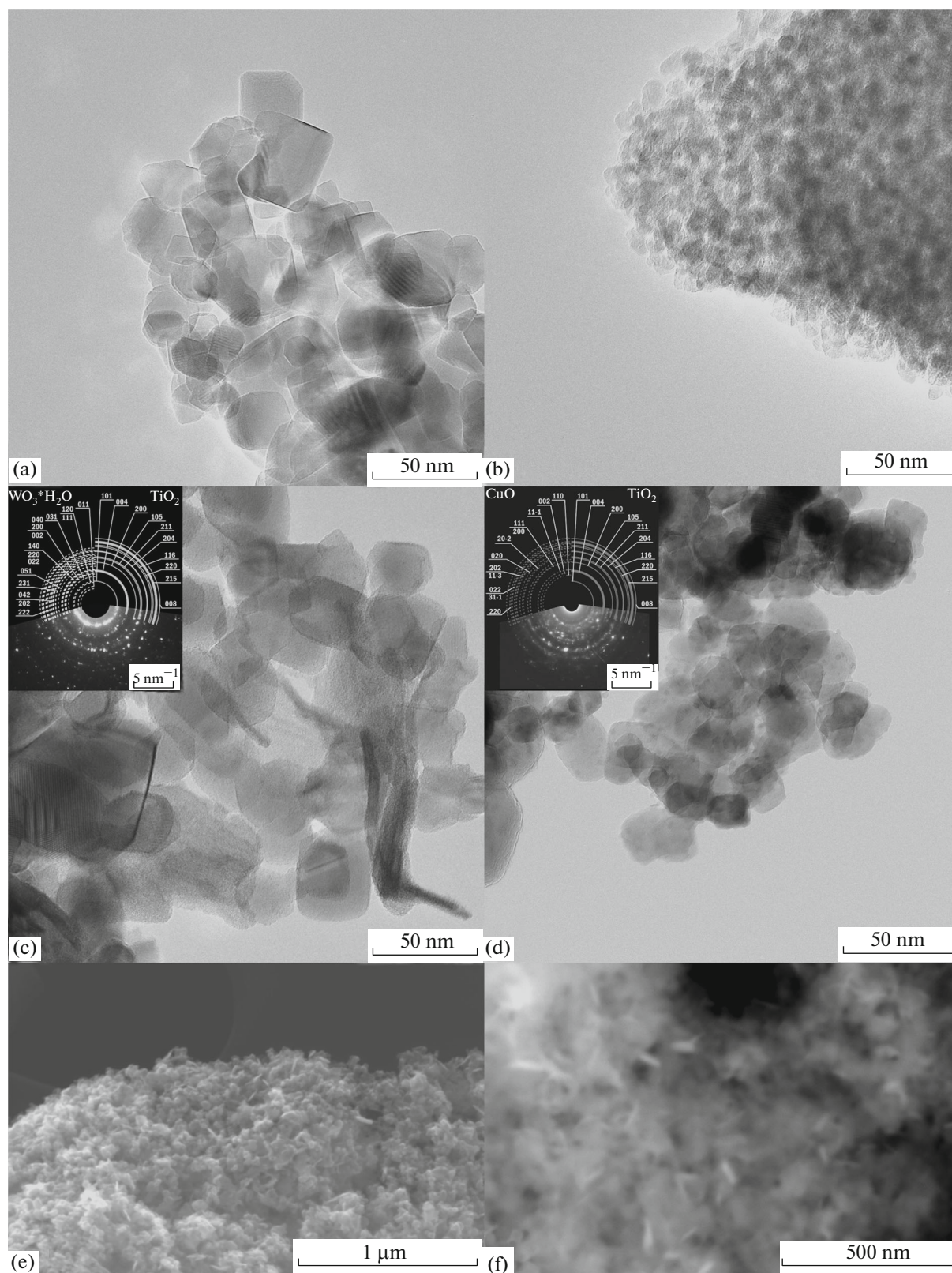


Fig. 5. (a) TEM microphotograph of the initial commercial P25 Degussa TiO₂ preparation, (b) TEM microphotograph of the initial mesoporous TiO₂, (c) TEM microphotograph of WO₃/TiO₂ nanocomposite, (d) TEM microphotograph of CuO/TiO₂ nanocomposite, (e) SEM microphotograph of WO₃/TiO₂ nanocomposite, (f) SEM microphotograph of WO₃/TiO₂ nanocomposite obtained in backscattered electrons (chemical contrast).

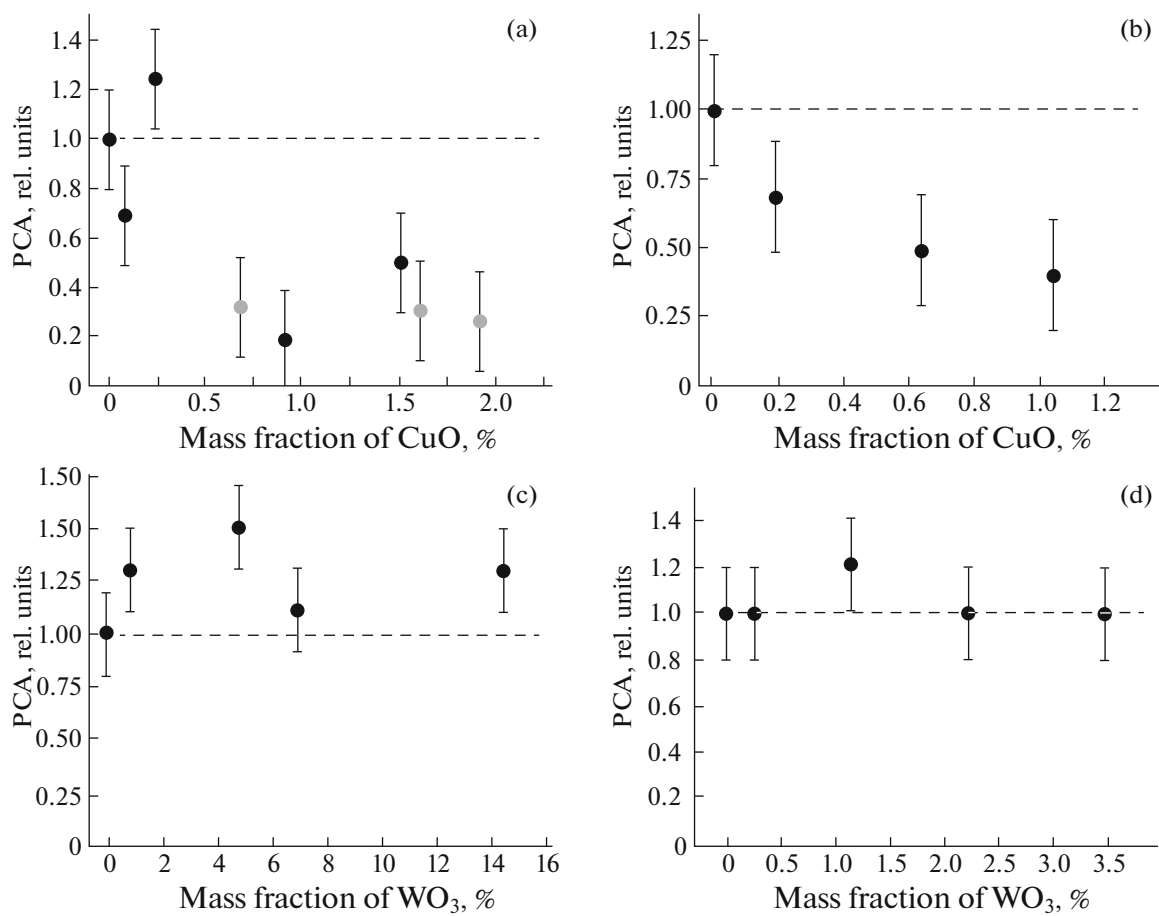


Fig. 6. Photocatalytic activity of the composites normalized to PCA of the initial TiO_2 : (a) CuO on the Degussa P25 preparation (the samples obtained using copper formate are marked in light), (b) CuO on mesoporous TiO_2 , (c) WO_3 on the Degussa P25 preparation, and (d) WO_3 on mesoporous TiO_2 .

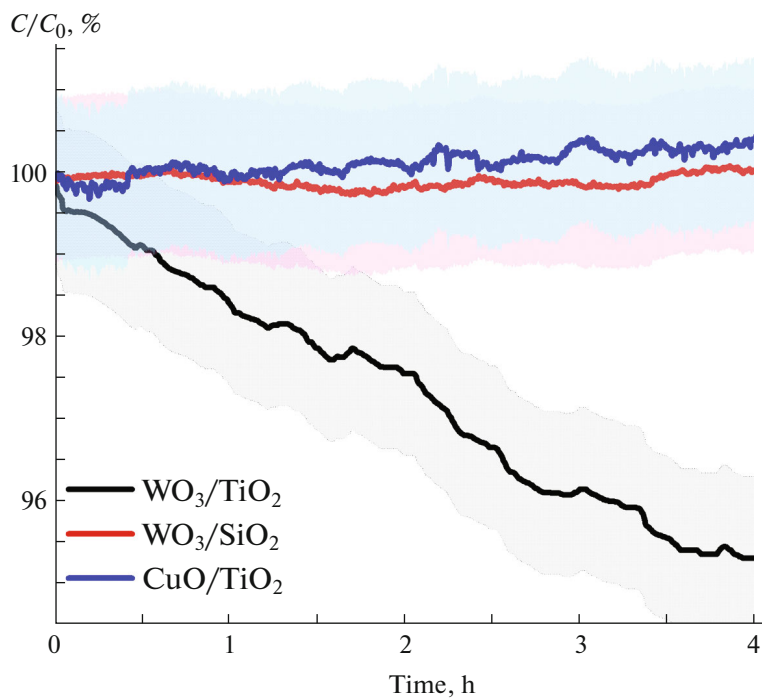


Fig. 7. Kinetic curves of photodecomposition under a visible light illumination in the presence of various photocatalysts.

composite promoting an increase in the lifetime of photogenerated holes in titania nanoparticles. A modification of TiO_2 with copper oxide leads to lowering in PCA both in the case of a commercial TiO_2 and in the case of mesoporous titania, which can be explained either by the low efficiency of separation of nonequilibrium charge carriers in a system, where a transfer of holes onto a modifier particle is required, or by a lower rate of decomposition of organic substances on CuO surface.

An experiment where WO_3 was deposited onto a carrier of mesoporous silicon dioxide has shown that such a catalyst manifests photocatalytic activity about 30% of Degussa P25; in this case, mesoporous silicon dioxide does not possess photocatalytic activity, which was proven by the corresponding measurements of PCA.

The photocatalytic activity in a visible spectral region was measured for CuO/TiO_2 , WO_3/TiO_2 , and WO_3/SiO_2 preparations. The kinetic curves obtained in the course of the experiment are presented in Fig. 7. As follows from this data, WO_3/TiO_2 nanocomposite manifests an observable PCA under the visible light illumination, while CuO/TiO_2 and even WO_3/TiO_3 does not change the dye concentration during the experiment. It should be noted that neither P25 Degussa preparation nor mesoporous SiO_2 possess photocatalytic activity by measuring under these conditions.

It was shown, that the modification of TiO_2 with tungsten oxide allows not only to increase the photocatalytic activity in UV region, but also to obtain a composite WO_3/TiO_2 material with an observable PCA under the illumination of a visible light in a range from 500 to 600 nm.

CONCLUSIONS

The modification of TiO_2 with copper oxide leads to a deterioration of the photocatalytic properties in a UV range compared with a nonmodified material. A noticeable PCA in a visible region is not observed for these materials. This can be accounted for by both a hampered separation of charge carriers at CuO/TiO_2 interface and a relatively inefficient oxidation of organic substances by photogenerated holes on CuO surface.

The modification of TiO_2 with tungsten oxide leads to an increase in PCA in UV region of the spectrum by more than 25% when compared to the initial TiO_2 ; in this case, the modified materials manifest PCA in a visible region, which is probably a consequence of an efficient separation of charge carriers at WO_3/TiO_2 interface both in the case of generation of nonequilibrium charge carriers in TiO_2 bulk and in WO_3 .

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REFERENCES

1. K. Hashimoto, H. Irie, and A. Fujishima, "TiO₂ photocatalysis: a historical overview and future prospects," *Jpn. J. Appl. Phys.* **44**, 8269 (2005).
2. M. Kaneko and I. Okura, *Photocatalysis: Science and Technology* (Kodansha, Springer, New York, 2002).
3. M. T. Greiner, M. G. Helander, W.-M. Tang, Zh.-B. Wang, J. Qiu, and Zh.-H. Lu, "Universal energy-level alignment of molecules on metal oxides," *Nature Mater.*, No. 11, 76–81 (2012).
4. D. Tomova, V. Iliev, S. Rakovsky, M. Anachkov, A. Eliyas, and G. Li Puma, "Photocatalytic oxidation of 2,4,6-trinitrotoluene in the presence of ozone under irradiation with UV and visible light," *J. Photochem. Photobiol. A: Chem.* **231**, 1–8 (2012).
5. D. Zhao, Ch. Chen, C. Yu, W. Ma, and J. Zhao, "Photoinduced electron storage in WO_3/TiO_2 nanohybrid material in the presence of oxygen and postirradiated reduction of heavy metal ions," *J. Phys. Chem. C* **113**, 13160–13165 (2009).
6. G. Li, N. M. Dimitrijevic, L. Chen, T. Rajh, and K. A. Gray, "Role of surface/interfacial Cu^{2+} sites in the photocatalytic activity of coupled $\text{CuO}-\text{TiO}_2$ nanocomposites," *J. Phys. Chem. C* **112**, 19040–19044 (2008).
7. J. M. Kim, Y.-J. Han, B. F. Chmelka, and G. D. Stucky, "One-step synthesis of ordered mesocomposites with non-ionic amphiphilic block copolymers: implications of isoelectric point, hydrolysis rate and fluoride," *Chem. Commun.*, 2437–2438 (2000).
8. E. A. Davis and N. F. Mott, "Conduction in non-crystalline systems V. Conductivity, optical absorption and photoconductivity in amorphous semiconductors," *Philos. Mag.* **22** (179), 0903–0922 (1970).
9. A. E. Morales, E. S. Mora, and U. Pal, "Use of diffuse reflectance spectroscopy for optical characterization of un-supported nanostructures," *Rev. Mex. Fis.* **53** (5), 18–22 (2007).
10. M. Ya. Mel'nikov and V. L. Ivanov, *Experimental Methods of Chemical Kinetics. Photochemistry* (Mosk. Gos. Univ., Moscow, 2004) [in Russian].
11. I. K. Konstantinou and T. A. Albanis, "TiO₂-assisted photocatalytic degradation of azo dyes in aqueous solution: kinetic and mechanistic investigations. A review," *Appl. Catal. B: Environ.* **49**, 1–14 (2004).
12. D. Rajagopal, D. Nataraj, Y. Mangalaraj, and R. Djaoued, "Controlled growth of WO_3 nanostructures with three different morphologies and their structural, optical, and photodecomposition studies," *Nanoscale Res. Lett.* **4**, 1335–1342 (2009).

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