

A Novel Titania-based Photocatalyst for Water Purification

Elena Savinkina, Galina Kuzmicheva, and Lyubov Obolenskaya

Abstract—The recently reported nanosize η -modification of titanium dioxide was studied as a photocatalyst for water purification. Its synthesis was modified to increase the yield up to 95% and prepare the particles with variable parameters. The photocatalytic activity of η -TiO₂, which was studied in the model reactions of dye degradation under UV radiation, strongly depends on crystallite size, pre-treatment of the samples, and pH. It increases with the increase of pH and retains on multiply usage.

Keywords—Hydrolysis, Nanosize particles, Photocatalysis, Titanium dioxide, Metastable titania.

I. INTRODUCTION

WATER and air pollution has been a problem throughout history. Efficient water use is an environmental priority in all countries of the world [1]. Water quality is directly influenced by the surrounding environment's features [2]. Air pollutants are responsible for the acidification of water ecosystems and eutrophication of waters [3]. The methods used for water purification include physical, biological and chemical processes. Among various water purification and recycling technologies, adsorption is a fast, inexpensive and universal method [4, 5]. In recent years, semiconductor photocatalytic process has shown a great potential as a low-cost, environmental friendly and sustainable treatment technology to align with the "zero" waste scheme in the water/wastewater industry [6]. During the last decade, titanium dioxide (titania, TiO₂) nanoparticles have emerged as promising photocatalysts for water purification, water treatment, air cleaning, etc. [7, 8].

Titanium dioxide is known to form 12 modifications (including high pressure forms and metastable forms produced synthetically). The stable rutile and brookite and metastable anatase occur in nature as well-known minerals and can be prepared in both bulk and nanosize forms. Rutile, anatase and

brookite all contain six coordinated titanium (Fig. 1). Titania is the most widely used white pigment. In recent years, preparation, modification, and applications (Fig. 2) of TiO₂ nanosize modifications attract interest of many researchers [10, 11]. Titanium dioxide is the promising photocatalyst due to the most efficient photoactivity, highest stability, lowest cost, and absence of toxicity [12].

A considerable technique and academic interest in the photocatalytic properties of nanosize TiO₂ has led to many detailed studies of photodegradation of dyes and the related kinetics and mechanism study [13]–[19]. The release of colored waste waters containing dyes lost in the dyeing processes in textile industry is a considerable source of pollution. Traditional physic-chemical techniques just transfer organic compounds from water to another phase, causing a secondary pollution. The most suitable solution of the problem is the complete destruction of the contaminants with heterogeneous photocatalysis (using TiO₂ as a photocatalyst) which can be carried under ambient conditions (atmospheric oxygen) and may lead to complete mineralization of organic carbon into CO₂ [13].

In many works, commercial photocatalysts Hombikat UV 100 (pure anatase crystalline form) and Degussa P-25 (anatase and rutile mixture in 3–4 : 1 ratio) were studied. Numerous attempts to create more efficient photocatalysts resulted in maximally twofold accelerating the degradation of organic dyes as compared to Degussa P-25 showing the highest photocatalytic activity [13]–[19].

Several factors were found to accelerate the reactions catalyzed by TiO₂ [13]–[19]: the increase of the temperature of annealing the samples (higher degree of crystallinity); optimal sizes of particles varying in the 7–10 nm range (the best ratio of the rates for the bulk and surface recombination of the electron–hole pair); decrease of pH (protonation of the surface Ti–OH groups influencing the dye adsorption).

Recently, the new metastable η -modification of titanium dioxide was first synthesized (with yield <30%) as a nanosize powder with high adsorption properties [20]. Further study of η -TiO₂ [21]–[24] showed availability of good (photo)catalytic activity for this modification.

Therefore, the purpose of the work was to modify the synthesis of η -TiO₂ for increasing its yield and quality and to study its photocatalytic activity in relation to various factors.

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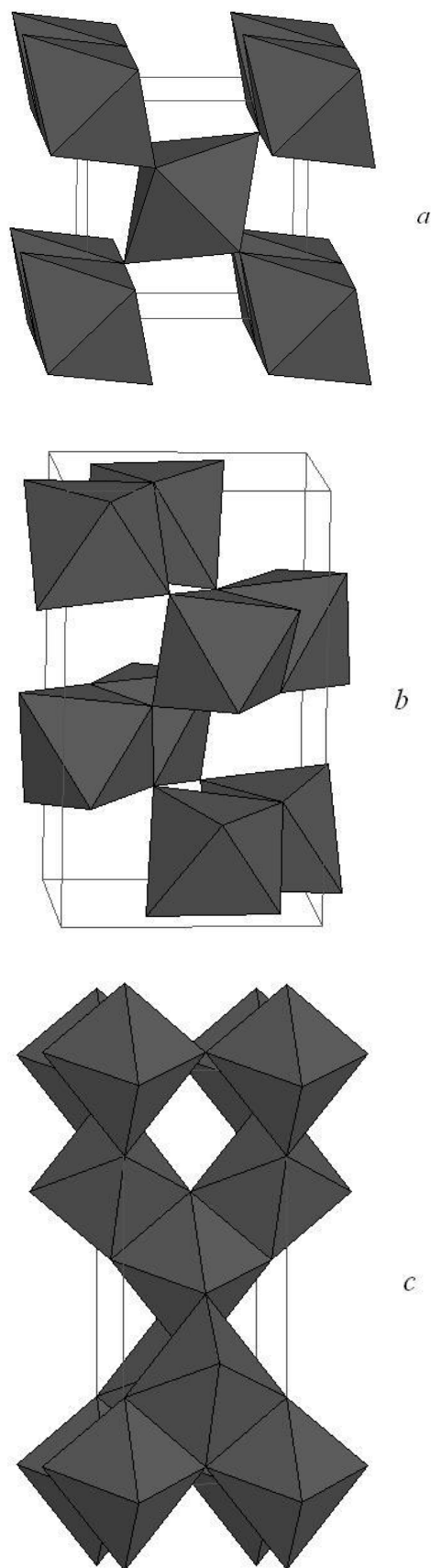


Fig. 1. The crystal structures of rutile (a), brookite (b), and anatase (c). [9]

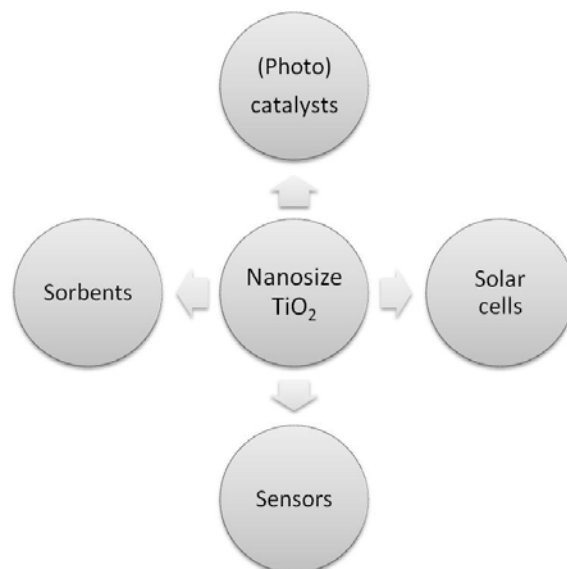


Fig. 2. Applications of nanosize TiO₂.

II. EXPERIMENTAL

A. Synthesis

Commercial titanium oxysulfate–sulfuric acid complex hydrate (Aldrich) was used as an initial reagent without further purification. The reported technique of preparing η -TiO₂ by TiOSO₄ hydrolysis [20] could not assure high yield and appropriate morphology of the product; therefore we varied initial concentration of the reagent and synthesis conditions: temperature, heating rate and duration, stirring rate, nature and quantity of a coagulant, and final treatment of the solid (for more details, see Results and Discussion). In a typical experiment, the initial reagent was stirred in water (mass ratio TiOSO₄·xH₂SO₄·yH₂O : H₂O = 1 : 6) under heating up to 90°C until complete dissolution; the reaction mixture was allowed to stay at this temperature for several minutes till light coagulation; then the KCl solution was added (8.5 mole per one mole Ti^{IV}); the resulting solid was filtered off, washed with water and acetone and dried at 90°C for 1 h. Yield 95%.

B. Characterization

All the samples were characterized by X-ray diffraction (XRD) patterns, which were collected on HZG-4 (Ni filter) and DRON-3 (diffracted-beam flat graphite monochromator) powder diffractometers (CuK_α radiation, sample rotation, angular range 2θ = 2°–80°, step scan mode with a counting time of 10 s per data point and a scan step of 0.02°). The intensity data set was reduced using the PROFILE FITTING V 4.0 software package. Qualitative XRD phase analyses were carried out using JCPDS PDF-2, RETRIEVE, and earlier data.

Electron micrographs and electron diffraction patterns were obtained on a JEOL JEM 2100 high-resolution transmission electron microscope (TEM) (LaB6 cathode as an electron source; accelerating voltage, 200 kV; minimum electron beam diameter in transmission mode, 20 nm; specimen tilts of ±60° about the *x* axis and ±25° about the *y* axis; point and line

resolutions of 2.3 and 1.4 E, respectively; maximum accelerating voltage, 200 kV; direct magnification up to $1.5 \times 106\times$).

Thermal analysis was carried out with a DTAS-1300 DSC instrument.

The particle (crystallite) size L was evaluated using the Scherrer formula: $L = 0.9\lambda/\beta\cos\theta$, where λ is the X-ray wavelength, $2\theta \approx 25^\circ$, $\beta = \sqrt{B^2 - b^2}$ is the physical width of the diffraction peak from the phase of interest (diffraction line profiles were fitted with Gaussians), B is the measured integral breadth of the peak, and $b \approx 0.14^\circ$ is the instrumental correction obtained with an $\alpha\text{-Al}_2\text{O}_3$ standard. The standard deviation was $\pm 5\%$.

The free specific surface area of the samples S was determined by the Brunauer–Emmett–Teller (BET) method from low-temperature nitrogen adsorption.

Aggregation kinetics was studied by the dynamic light-scattering method with the use of laser analyzer with high-sensitive photomultiplier (DelsaNano, $\lambda = 658$ nm). The ζ potential was measured with the same instrument.

IR spectra were recorded with an Infracum FT-02 spectrometer in nujol.

Electronic absorption spectra were recorded with an Aquilon CF 103 UV/vis spectrophotometer.

C. Photocatalysis

Properties of the $\eta\text{-TiO}_2$ samples was studied in the model reactions of photocatalytic degradation for color removal from aqueous solution containing organic dyes methyl orange (4-dimethylaminoazobenzene-4'-sulfonic acid sodium salt), xylenol orange (3,3'-bis[N,N-bis(carboxymethyl)-aminomethyl]-o-cresolsulfonephthalein tetrasodium salt), and methylene blue (3,7-bis(dimethylamino)phenothiazin-5-ium chloride) under illumination of UV light (UFO-V-4, DRT-125 mercury lamp, $\lambda = 250\text{--}400$ nm, $E = 3.11\text{--}4.97$ eV) in a photoreactor system with continuous stirring. The depth and surface of the solution were 0.04 m and 0.09 m², respectively. In a typical experiment, the $\eta\text{-TiO}_2$ powder was added into aqueous solution of a dye; the initial dye concentration and the amount of $\eta\text{-TiO}_2$ concentrations were set at 0.33–1.04 M and 2.5–5.0 M, respectively; pH varied in the 1–9 range. The dye degradation was monitored by absorbance at $\lambda = 490\text{--}510$ and 450–470 nm for methyl orange and xylenol orange in acidic and neutral solutions, respectively, and at $\lambda = 550\text{--}590$ nm for methylene blue.

III. RESULTS AND DISCUSSION

A. Characterization of $\eta\text{-TiO}_2$

The X-ray diffraction data for the samples are indicative of nanoscale modification of titanium dioxide with $\eta\text{-TiO}_2$ structure. The specific X-ray feature of $\eta\text{-TiO}_2$ is a strong diffraction reflection at $2\theta \sim 4.7^\circ\text{--}5.2^\circ$ with an interplanar distance of $d \sim 20(5)$ Å and the presence of peaks at $2\theta \sim 25^\circ$, 33° , and 48° [20] (Fig. 3).

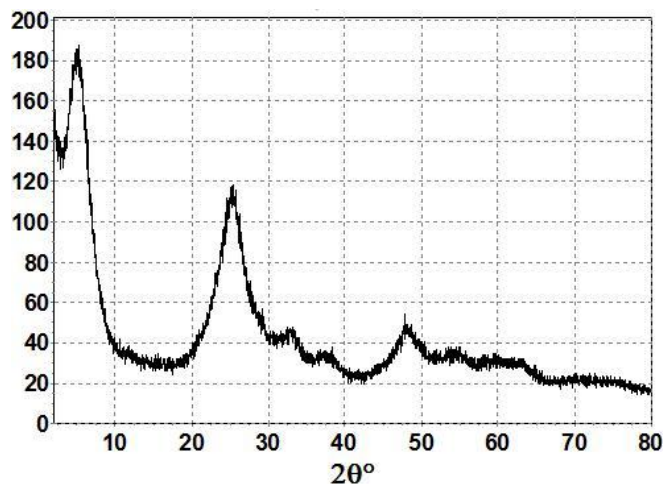


Fig. 3. X-Ray powder diffraction pattern of $\eta\text{-TiO}_2$.

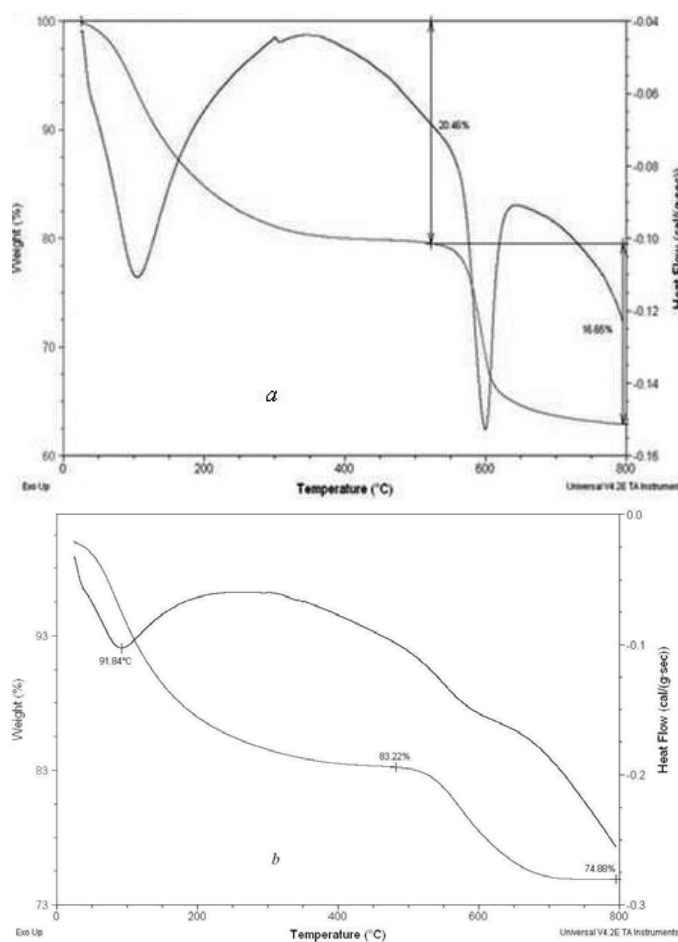


Fig. 4. Thermal curves for $\eta\text{-TiO}_2$ (a) and anatase (b).

The $\eta\text{-TiO}_2$ phase seems to be metastable, and its structure can be derivative from the anatase structure; small changes in conditions of the $\eta\text{-TiO}_2$ preparation lead to the formation of a metastable phase with the anatase structure, and the $\eta\text{-TiO}_2$ phase precedes the formation of this phase [23]. Thermal curves for $\eta\text{-TiO}_2$ and anatase (Fig. 4) differ by an endothermal effect at $\sim 650^\circ\text{C}$ which can be assigned to a phase transfer from the $\eta\text{-TiO}_2$ to anatase modification.

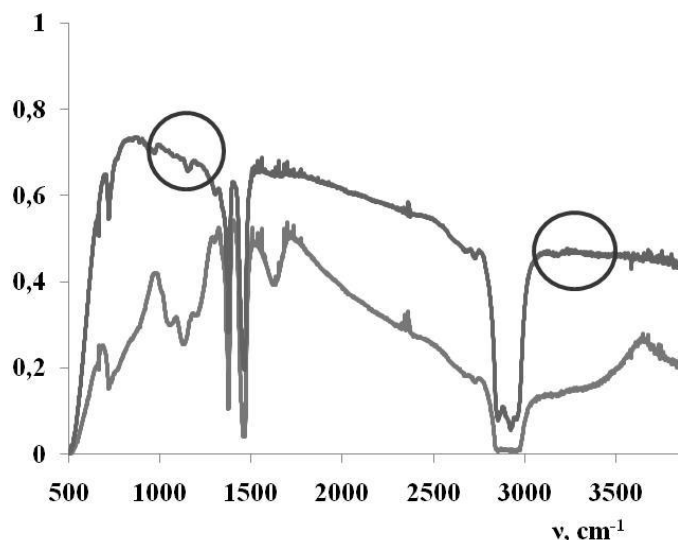


Fig. 5. IR spectra of η -TiO₂ before (1) and after (2) heating at 800°C. Circles show disappearance of the δ (TiOH) and ν (OH) modes at ~ 1100 cm⁻¹ and ~ 3300 cm⁻¹, respectively.

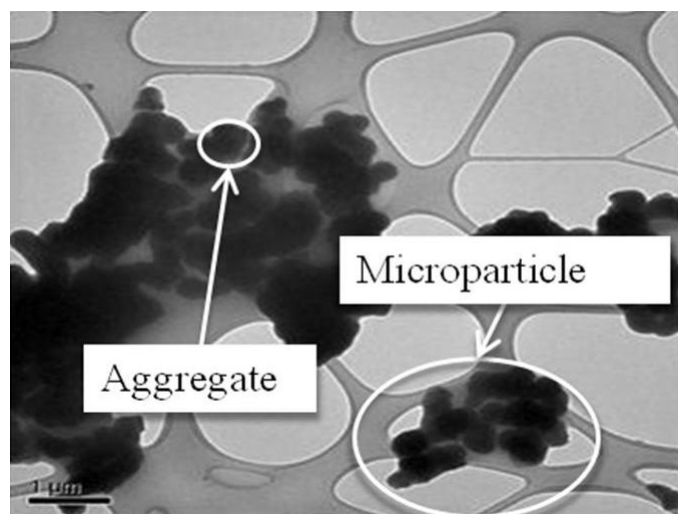


Fig. 6. TEM micrograph of the η -TiO₂ aggregates.

Two-stage mass loss is caused by removal of water molecules, which are weakly (the first stage) and strongly (the second stage) bonded to the titania surface. The water removal is supported by IR spectroscopy (Fig. 5). Bands assigned to vibrations of the surface hydroxyl groups disappear under heating.

However, a prolonged storage in air (for at least half a year) of samples with η -TiO₂ does not cause changes in the diffraction picture, which is evidence of its relative stability.

The crystallite size (L) for η -TiO₂ is varied in the 3–6 nm range by changing reagent concentration, temperature, and synthesis duration. Nanoparticles of η -TiO₂ (8–14 nm in size [24]) tend to form agglomerates covered with an amorphous shell (Fig. 6). According to BET data, the free specific surface area is 4–18.0 m²/g, and ultrapour size is 0.002–0.004 cm³/g. The IR spectra show that the surface of the η -TiO₂ samples is hydrated and hydroxylated [23].

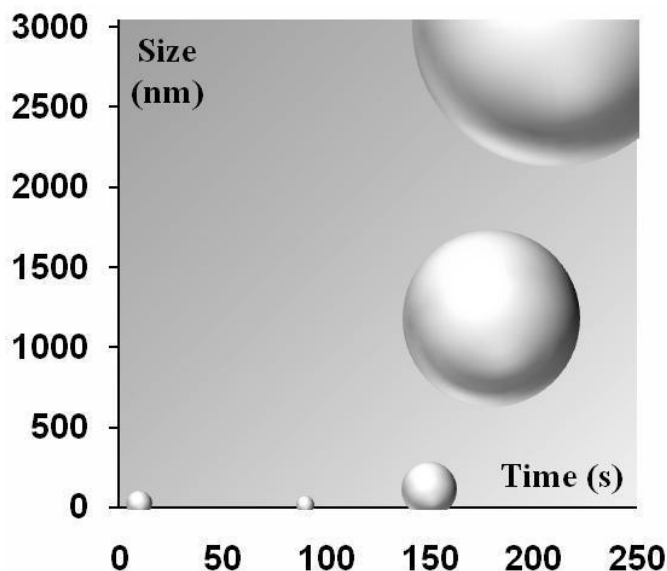


Fig. 7. Aggregation kinetics in the reaction mixture: 0.54 M Ti(IV), 298 K, index of refraction 1.3328, dynamic viscosity 0.8878 cp.

An important characteristic of titanium dioxide is the bandgap. For nanosize particles, it increases by ~ 0.05 – 0.2 eV relative to bulk rutile and anatase (3.03 and 3.18 eV, respectively); photocatalytic activity of both rutile and anatase increases with increase in BET surface area and with the magnitude of the blue shift in the bandgap [25]. The bandgap for the η -TiO₂ nanoparticles was calculated from the UV spectra of sols prepared by re-dispersion of synthesized powders as described in [27], [28]. Plots of $(\alpha E)^{1/2}$ vs. E , where E is an energy of the UV absorption band and α is calculated as $\alpha = 2.303 \cdot I \cdot \rho \cdot (l \cdot c)^{-1}$, where I is absorbance intensity, ρ is TiO₂ density, c is the loading of the colloid, and l is the path length) gave straight lines; their intercepts are ascribed to the bandgap absorption edge of titania. Its value (3.65–3.77 eV) is higher than for bulk anatase.

B. Synthesis Conditions

The titanyl sulfate hydrolysis in dilute solutions begins just after its contact with water (Fig. 7).

To record the UV spectrum of non-hydrolyzed TiOSO₄, we used icy water (Fig. 8, curve 1). The spectrum changed immediately at room temperature indicating disappearance of titanyl and formation of a TiO₂ sol (Fig. 8, curves 2–9). Rapid spectral changes occurred during the first 30 min of the hydrolysis, after which minor absorption spectral changes were noted. Heating led to the noticeable decrease of the absorption (Fig. 8, curves 10–12), indicating further hydrolysis.

A shift of the UV absorption edge correlates with the particle size [28]. Therefore, we can conclude that the growth of the TiO₂ nanoparticles stops in first 30 min of the TiOSO₄ hydrolysis at room temperature resulting in formation of stable sols, which can be destroyed under heating or by adding coagulants. In [20], the coagulation of η -TiO₂ was caused by addition of HCl. However, the yield of the product prepared by the technique reported in [20] is not high.

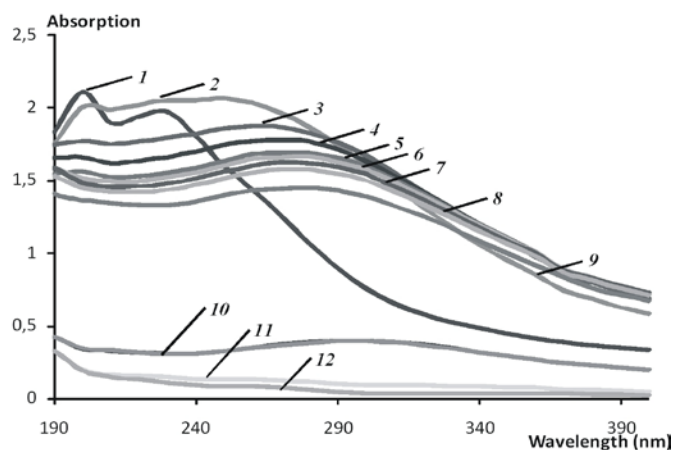


Fig. 8. UV spectra of TiOSO₄ ($6.8 \cdot 10^{-4}$ M): unhydrolyzed (1); hydrolyzed at 20–25°C for 0 (2), 10 (3), 20 (4), 34 (5), 40 (6), 50 (7), 60 (8), 87 (9) min; hydrolyzed at 20–25°C for 80 min with one-fold (10), two-fold (11), and three-fold (12) heating up to 75°C.

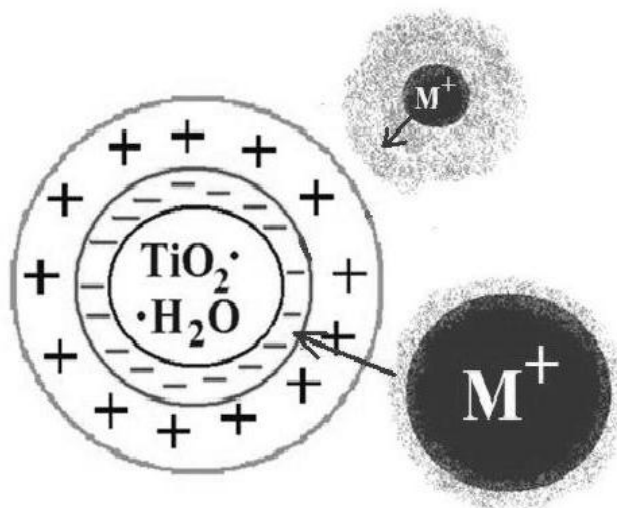


Fig. 9. Scheme of titania coagulation.

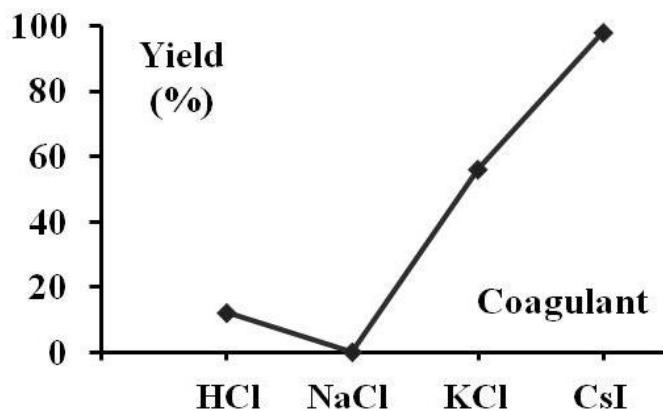


Fig. 10. Dependence of the yield on the coagulant nature.

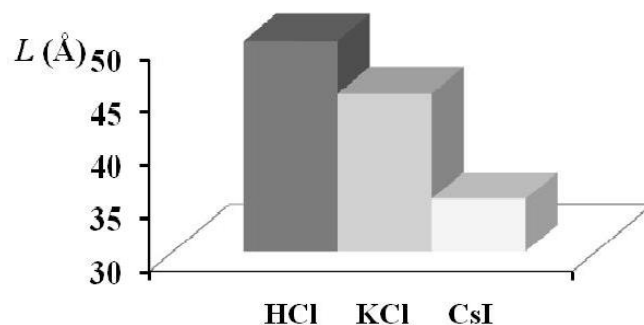


Fig. 11. Dependence of the crystallite size on the coagulant nature.

Increasing the η -TiO₂ yield is a difficult task since an enhancement of the TiOSO₄ hydrolysis leads to formation of the more stable anatase phase. Therefore, the main way for ruling the η -TiO₂ yield is affecting its coagulation (Fig. 9).

We tested a number of coagulants and found the best results for alkali-metal halides, namely KCl and CsI (Fig. 10).

Slight variations of other conditions (higher temperature or the coagulant : Ti^{IV} ratio and lower TiOSO₄ concentration) can also increase the product yield; the yield is independent of hydrolysis duration, stirring, volume of a coagulant solution, and anion nature.

Since the yield is strongly dependent on the cation nature of the coagulant, the counterion layer in the coagulated particles must carry a negative charge. The ζ potential (–50.2 mV) fits the ζ potential range permitting coagulation (–30–70 mV).

Such factors as the heating rate, hydrolysis duration, maximal temperature and the coagulant nature have a strong effect on the crystallite size of the product. It is noteworthy that varying the coagulant in the HCl–KCl–CsI row simultaneously increases the yield of the product and decreases the crystallite size (Fig. 11). The additional coagulant quantity enlarges the yield but has no effect on the crystallite size. All other parameters increasing the yield lead to the increase of the crystallite size.

The samples with the optimal crystallite size of 4 nm (see below) can be prepared under the following conditions: initial concentration of TiOSO₄, 0.67 M; heating rate, 8 deg/min; hydrolysis duration, 6–10 min; KCl : Ti(IV) ratio, 8.5 : 1.

C. Photocatalytic Properties of η -TiO₂

The photocatalytic decolorization of the dyes (Fig. 12) can be described by the first order kinetic model, $\ln(c_0/c) = kt$, where c_0 is the initial concentration and c is the concentration at time t ; the correlation constant for the fitted line was calculated to be $R^2 = 0.91$ – 0.99 (Fig 13). This is supported by independence of the reaction rate of the η -TiO₂ content and its increase with the increase of the dye concentration. After mixing the initial components, the dye decolorization begins after an induction period (15–30 min). The induction period disappears on pre-stirring the η -TiO₂ suspension for 30 min followed by addition of a dye or by ultrasonic pre-treatment of the reaction mixture. Pre-dispersion of the sample with either ultrasound or stirring increases the reaction rate (Fig. 14).

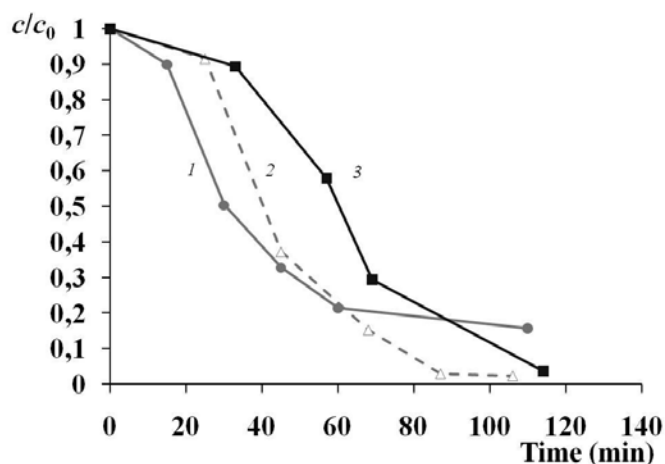


Fig. 12. Kinetic curves for decolorization of xlenol orange (1), methyl orange (2) and methylene blue (3).

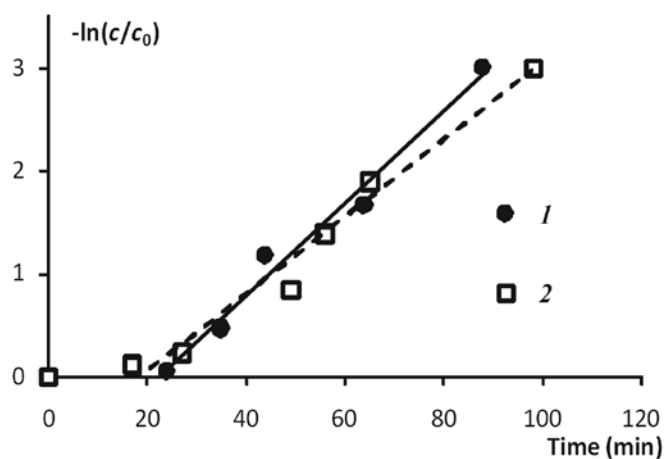


Fig. 13. Photocatalytic decomposition first order kinetics profiles of methyl orange, $c_0 = 1.04$ M, pH 2 (1) and methylene blue, $c_0 = 0.33$ M, pH 5 (2).

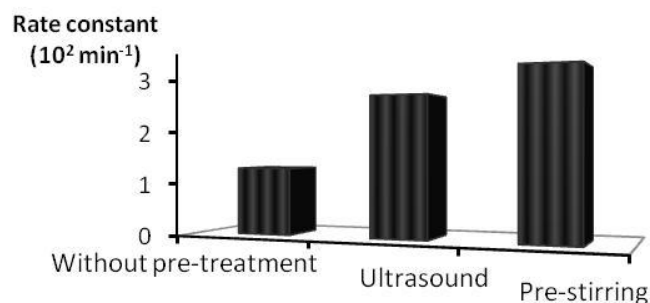


Fig. 14. Dependence of rate constant on pre-treatment of η -TiO₂ for photocatalytic decolorization of methylene blue.

In contrast to nanosize anatase and its mixtures with rutile [13]–[17], photocatalytic activity of the η -TiO₂ samples noticeably increases with the increase of pH (Fig. 15), especially for methylene blue. It is noteworthy that decomposition of methylene blue proceeds only in neutral and alkaline solutions.

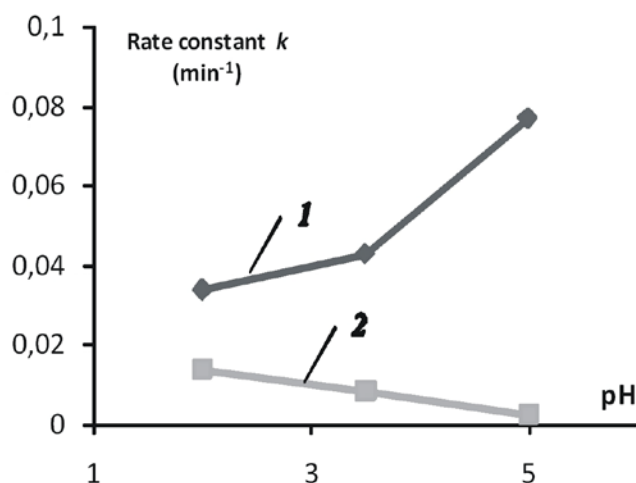


Fig. 15. First-order kinetics rate constant (k) of methyl orange decomposition vs. pH for η -TiO₂ (1) and Degussa P25 [13] (2).

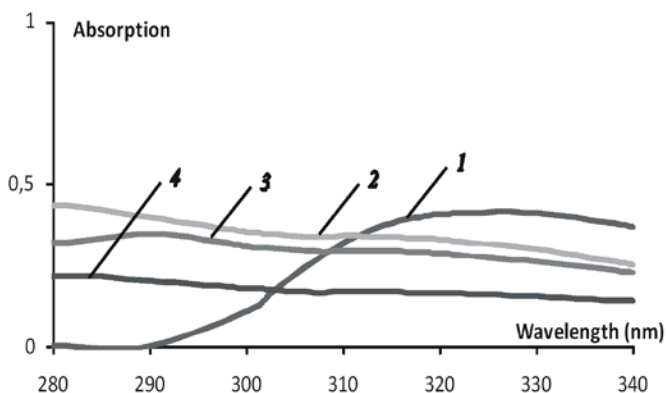


Fig. 16. UV spectra of η -TiO₂ sols sampled from the reaction mixture in 0 (1), 30 (2), 64 (3), and 94 min (4), pH 3.

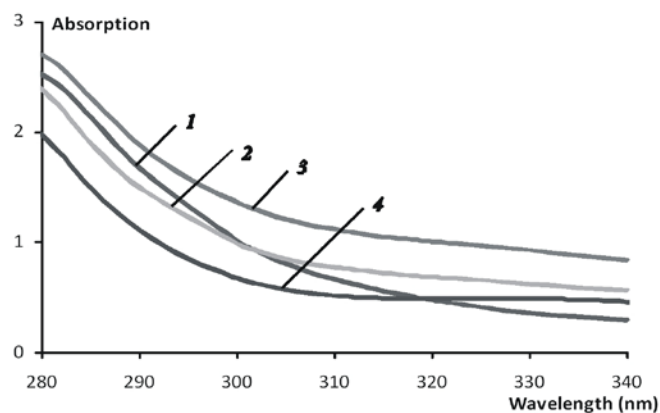


Fig. 17. UV spectra of η -TiO₂ sols sampled from the reaction mixture in 0 (1), 25 (2), 55 (3), and 85 min (4), pH 11.

Occurrence of the induction period and high photocatalytic activity at pH > 3 may be caused by destruction of agglomerates where crystallites are joined with an amorphous interlayer. It seems that pre-dispersion and/or alkalization of the reaction mixture facilitate dissolution of the amorphous interlayer resulting in formation of smaller η -TiO₂ particles.

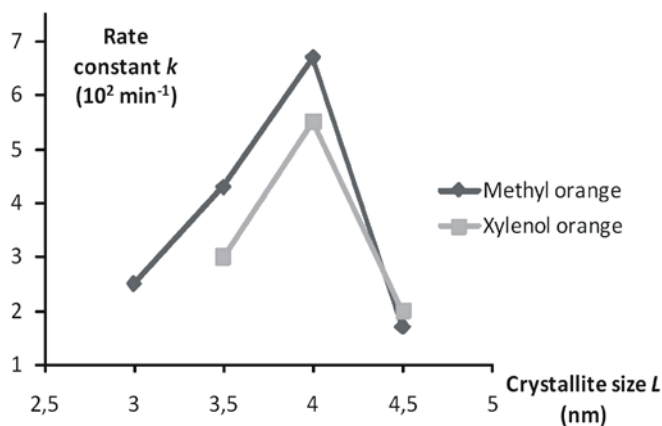


Fig. 18. First-order kinetics rate constant (k) of dye decomposition vs. crystallite size (L) for η -TiO₂.

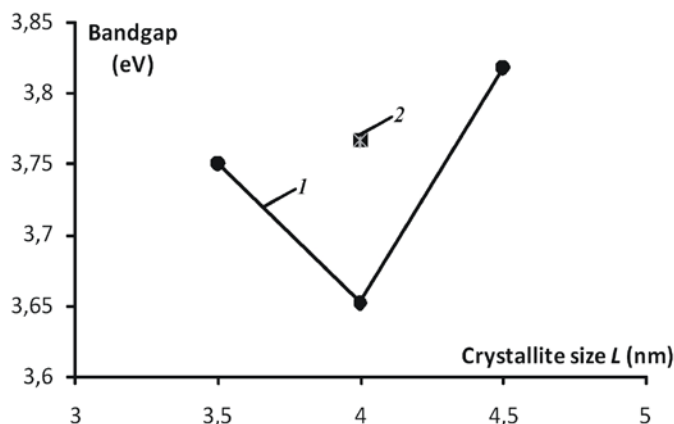


Fig. 19. Bandgap for re-dispersed particles vs. crystallite size (L) for η -TiO₂, coagulated with an alkali-metal halide (1) and HCl (2).

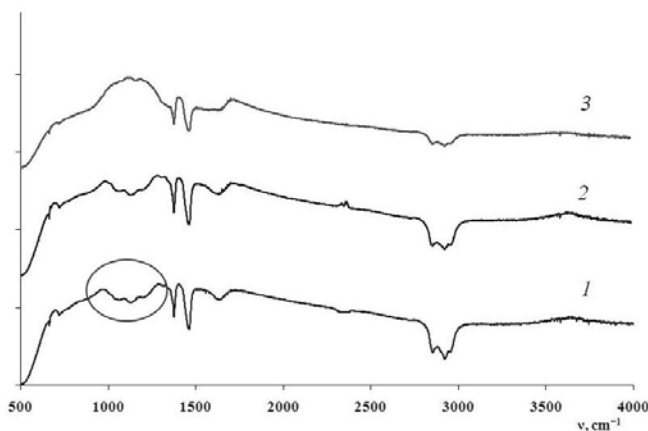


Fig. 20. IR spectra of η -TiO₂ before photoreaction (1) and after photoreaction at pH < 7 (2) and > 7 (3). The circle shows the band of δ (TiOH) at ~ 1100 cm⁻¹

It leads to enlargement of the catalyst surface contacting with the dye solution. This fact is supported by UV spectra of the acidic and alkaline reaction solutions (Figs. 16, 17). Absorption by nanosize particles is noticeably higher at pH 11 than at pH 3.

The rate of the dye decolorization is maximal for the

samples where the η -TiO₂ crystallites are 4 nm in size (Fig. 18). The same crystallite size corresponds to the minimal bandgap (Fig. 19) for the η -TiO₂ particles.

Frequencies and intensities of the bands assigned to the active -OH groups on the η -TiO₂ surface (~ 1100 cm⁻¹, δ TiOH; ~ 3300 cm⁻¹, ν OH) in the IR spectra of the samples do not change after their use in the reaction of the dye photodestruction (Fig. 20).

This indicates regeneration of the active groups on the surface and therefore possibility of multiple utilization of the photocatalyst. Direct measurements showed no decrease of the rate constant after the two-fold use of a sample.

IV. CONCLUSION

We were able to synthesize the recently reported nanosize η -modification of titanium dioxide with yields up to 95% and to examine its photocatalytic activity.

In addition to higher yield (as compared to the earlier reported synthesis of η -TiO₂ [20]), the number of stages is diminished (5 instead of 7), duration of energy-losing stages is shortened (80 min instead of 170 min), use of the HCl and NaOH concentrated solutions is excluded.

Depending on conditions, the sizes of η -TiO₂ crystallites, nanoparticles, spherical particles and agglomerates vary in the 3–6, 8–14, 200–300 and 900–1000 nm ranges, respectively. The photocatalytic activity of η -TiO₂ depends on crystallite sizes, pre-treatment of the samples, and pH. The unique properties of η -TiO₂ can be caused by its formation under mild synthetic conditions; the small uniform crystallites are combined in aggregates by amorphous layers protecting them from contact with environment and destroying under prolonged stirring, ultrasound and/or high pH.

The η -modification of titanium dioxide can be combined with SiO₂, Pt, Cu, etc. for better (photo)catalytic properties.

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