Efficiency of sensitizing nano-titania with organic dyes and peroxo complexes

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Abstract A new method of sensitizing titania by treatment of the reaction mixture with Methylene Blue, Methyl Red or hydrogen peroxide is developed; the sensitizer was introduced into the reaction mixture while synthesizing nanosize TiO_2 from titanyl sulfate. The samples prepared by this method are compared to the samples prepared by cold impregnation of Methylene Blue, Methyl Red or hydrogen peroxide on titania, pre-synthesized by sulfate method, or commercial Degussa P25 and Hombikat UV100. The samples were characterized by X-ray diffraction; their photocatalytic activity was studied in the model reaction of Methyl Orange decomposition in aqueous solution under UV and visible light. The highest photocatalytic activity under visible light was found for titania, sensitized with titanium peroxo complexes by the new method. It is also active for photodegradation of salicylic acid under visible light.

Keywords Nanoparticles · Titania · Sensitization · Dyes · Titanium peroxo complexes

Introduction

Nanosize titania is the most promising photocatalyst due to efficient photoactivity, high stability, and low toxicity. Titania has been used for energy conversion and photodegradation of many contaminants under UV radiation; its photocatalytic properties in this region are well studied (Hashimoto et al. 2007). To utilize visible light, various

methods were used to modify TiO_2 , including doping and photosensitization (Carp et al. 2004; Banerjee 2011; Viswanathan and Krishnamurthy 2012).

Inorganic sensitizers, organic dyes, and coordination metal complexes are very effective sensitizers that were studied mostly (Fujishima and Rao 1998; Sauvé et al. 2000; Pei and Luan 2012; Zhou et al. 2012). Epling and Lin (2002) investigated photo-assisted bleaching of 15 dyes utilizing TiO_2 and visible light; good rate for Methylene Blue (MeB) decomposition can be explained by titania sensitization; the MeB photobleaching rates were: anatase > amorphous titania > rutile. Hussein and Alkhateeb (2007) sensitized titanium dioxide by impregnation of organic dyes on the commercial photocatalyst Degussa P25. The photo-oxidation of benzyl alcohol was found to be in the sequence: riboflavin > Safranin O > naked TiO_2 > Methyl Red (MeR) > Eosin B > Methylene Blue. Dye sensitization is usually accompanied by such problems as dye desorption and backward transfer (recombination) during the photoreaction (Zhang et al. 2012). Houas et al. (2001) presented a detailed reaction mechanism from the initial step of adsorption involving the cationic functional group of MeB molecule, which is probably adsorbed perpendicularly to the surface down, to the final products (CO_2 , SO_4^{2-} , NH_4^+ , and NO_3^-).

Titanium is known to form yellow-colored peroxo complexes. Zou et al. (2009) prepared H_2O_2 -sensitized sulfated titania nanoparticles with a response to visible light by introduction of hydrogen peroxide into a photo-reactor containing titania and Methyl Orange (MeO); degradation of MeO was completed in 4 h. A sol–gel technique using the peroxo titanic acid sol as a precursor for fabrication of the TiO_2 photocatalytic films is reported; the peroxo titanic acid sol was synthesized from titanyl sulfate (Ge and Xu 2007) or titanium(IV) tetrabutoxide

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(Sonawane et al. 2003) and H_2O_2 solution. The films showed high photocatalytic activity under UV light; however, no experiments using visible light were carried out in these works. Karuppuhachamy and Jeong (2006) prepared amorphous powder of titanium peroxo complex from TiOSO_4 and H_2O_2 at room temperature, which was then converted to anatase by heat treating at 300 °C; photocatalytic activity of the product was not studied.

The purpose of the work was to prepare sensitized photocatalysts on the basis of titanium dioxide (using organic and inorganic compounds) by various methods and studying their photocatalytic activity in the model reactions of MeO and salicylic acid degradation.

Materials and methods

Synthesis

Nano-anatase (A) was prepared by hydrolysis of TiOSO_4 by the reported method (Obolenskaya et al. 2012a, b) with the use of solvated titanyl sulfate (Aldrich) as an initial reagent.

Sensitization of titanium dioxide with Methylene Blue (3,7-bis(dimethylamino)phenothiazin-5-ium chloride), Methyl Red (2-(N,N-dimethyl-4-aminophenyl)azobenzenecarboxylic acid), or hydrogen peroxide was performed by two different methods (Table 1).

Method 1 (samples 1–9) is based on the cold impregnation of a sensitizer on TiO_2 in a similar manner as described by Carp et al. (2004). Titania powder (0.25 g) was dispersed in 50 ml of 7×10^{-5} M solution of Methylene Blue (TiO_2 : MeB = 250:1), 7×10^{-5} M solution of Methyl Red (TiO_2 : MeR = 250:1), or 10 M solution of H_2O_2 (TiO_2 : H_2O_2 = 1:160), stirred for 40 min with a magnetic stirrer at room temperature, filtered off, washed with water and acetone, dried at room temperature and ground.

The method was used for sensitizing anatase (A), prepared by hydrolysis of titanyl sulfate, commercial Aeroxide Degussa (Evonik) P25, prepared by pyrolysis of titanium tetrachloride, and Hombikat UV100, prepared by pyrolysis of titanyl sulfate, with MeB, MeR, and H_2O_2 (see Table 1 for sample numbering).

Method 2 (samples 10–12) is based on adding a sensitizing agent into the reaction solution while synthesizing

TiO_2 from TiOSO_4 (Obolenskaya et al. 2012a, b). Solvated titanyl sulfate (Aldrich) was mixed with water (1:5.44) and heated up to 87 °C till complete dissolution. The reaction mixture was stirred at 88–90 °C for 1.5 min and quickly cooled down to 0 °C. Then aqueous solutions of KCl (final concentration 3.3 mol/L) and MeB, MeR, or H_2O_2 were added, the precipitate was filtered off, washed with water, aqueous solution of Na_2SO_3 (to remove unreacted H_2O_2) and acetone, and dried at 90–98 °C.

It is noteworthy that sensitization by method 2 is inapplicable to Degussa P25 and Hombikat UV100, since they cannot be synthesized in solution.

Titania sensitized with H_2O_2 , MeB, and MeR is stable at least for 2 months (6 months in a refrigerator), 1 year, and 6 months, respectively.

Characterization

All the samples were characterized by X-ray diffraction (XRD) patterns, which were recorded with sample rotation on an HZG-4 (Ni filter) diffractometer: CuK_α radiation in the diffracted beam, stepwise mode (counting time 10 s, a step of 0.02°). Qualitative XRD phase analyses were carried out using JCPDS PDF-2 and literature data. The sizes of coherent scattering regions (L , Å) were evaluated using the Scherrer formula:

$$L = 0.9\lambda / \beta \cos \theta,$$

where β is the measured integral breadth of the peak ($2\theta \sim 25^\circ$).

The microstructure of the samples was studied by scanning electron microscopy with the use of a JSM 7500F electron microscope in the secondary electron mode.

The nitrogen sorption capacity at -196°C for the samples was measured volumetrically within the range of equilibrium relative nitrogen pressures of 0.01–0.99 with a Micromeritics ASAP 2020 gas analyzer (GSI no. 46147-10). The specific surface area and pore volume of samples were determined by the Brunauer–Emmett–Teller (BET) method and by comparative method from the adsorption isotherm in the region of equilibrium relative pressure of nitrogen 0.05–0.35 and 0.4–0.8, respectively.

The average sizes of particles were calculated according to formula:

$$N = Kp(\rho A),$$

Table 1 Sample numbering/rate constants (k , min^{-1}) for MeO decomposition under visible light

Sensitizer	Method 1 anatase (A)	Method 1 Degussa P25	Method 1 Hombikat UV100	Method 2
MeB	Sample 1 (A-MeB)/0.0022	Sample 4 (P25-MeB)/0.0019	Sample 7 (UV100-MeB)/0.0014	Sample 10 (MeB- TiO_2)/0.0082
MeR	Sample 2 (A-MeR)/0.0014	Sample 5 (P25-MeR)/0.0006	Sample 8 (UV100-MeR)/0.0009	Sample 11 (MeR- TiO_2)/0.0064
H_2O_2	Sample 3 (A- H_2O_2)/0.0047	Sample 6 (P25- H_2O_2)/0.0012	Sample 9 (UV100- H_2O_2)/0.0035	Sample 12 (H_2O_2 - TiO_2)/0.0470

where N is the average size of the particles; K_p is the shape factor of the particles (6 for cubes and spheres, 4 for prisms and round rods, 2 for plates); ρ is the density of the material ($\rho = 3.84 \text{ g/cm}^3$); and A is the specific surface area of the material.

Microphotos were made with a Levenhuk camera installed on a Levenhuk D2L microscope. The average sizes of aggregates were estimated by measuring ten randomly chosen aggregates and calculating simple mean value.

Electronic absorption spectra were recorded with an Aquilon CF 103 UV/vis spectrophotometer. IR spectra were recorded with an Infracum FT-02 (Nujol mulls) spectrometer at room temperature.

Photocatalysis

Properties of the samples were studied in the model reactions of photocatalytic degradation of organic dye Methyl Orange (4-dimethylaminoazobenzene-4'-sulfonic acid sodium salt) or salicylic acid under UV (DRT-125 mercury lamp, $\lambda = 250\text{--}400 \text{ nm}$) and visible irradiation (OSRAM halogen lamp with a filter, $\lambda > 450 \text{ nm}$, nominal power 40–250 W) 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, a sample was put into aqueous solution of the MeO dye or salicylic acid; the initial MeO dye or salicylic acid concentration and the amount of TiO₂ were set at 0.05, 0.4 mmol/L and 0.4 g/L, respectively; pH ~ 5 for all samples excluding non-treated anatase (A) (pH ~ 3). Degradation was monitored by measuring intensity of the peak at $\lambda = 450\text{--}470 \text{ nm}$ at pH ~ 3 or 495–515 nm at pH ~ 5 for the MeO dye (MeO is an acid–base indicator, and the position of the absorption band depends on pH) and at $\lambda = 280 \text{ nm}$ for salicylic acid.

The photocatalytic destruction of the MeO dye and salicylic acid 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 (Brown and Darwent 1984). Uncertainties in determining rate constants were $\sim 10 \%$.

Results

Characterization of samples

Figures 1 and 2 show the X-ray diffraction patterns of the samples, containing initial titania, which were used for preparing photocatalysts by method 1, and samples 10–12, prepared by method 2, respectively.

Fig. 1 XRD patterns: 1—self-made anatase (A), 2—Hombikat UV100 (UV100), 3—Aeroxide Degussa (Evonik) P25 (P25)

Fig. 2 XRD patterns of titania, sensitized by method 2 with MeB (1), MeR (2), and H₂O₂ (3)

Samples of TiO₂, prepared by the sulfate method, contain only one phase, anatase (Fig. 1; Table 2). Degussa P25 contains nano-anatase and nano-rutile in the $\sim 85:15$ ratio (Fig. 1; Table 2). Hombikat UV100 (Fig. 1) contains, along with nano-anatase, a phase with a characteristic diffraction reflection at $2\theta \sim 12^\circ$. According to Dadachov (2006), this peak belongs to hydrous titania TiO_{2-x}(OH)_{2x}yH₂O, where y is about 1. Therefore, Hombikat UV100 contains $\sim 9 \%$ of hydrous titania (Table 2). According to technical information, Degussa P25 and Hombikat UV100 consist of nanoparticle ~ 20 and $<10 \text{ nm}$ in size, respectively. Our measurements with the use of SEM and comparative method based on nitrogen

Table 2 Composition (%) and coherent scattering regions (L , Å) for titania samples

Sample	Anatase/ L	Rutile/ L	η -TiO ₂ / L	Hydrous titania
Anatase (A)	100/75(4)	—	—	—
Degussa P25	85/178(9)	15/255(13)	—	—
Hombikat UV100	91/82(4)	—	—	9
1 (A-MeB)	99/70(3)	—	—	1
2 (A-MeR)	58/80(4)	—	—	42
3 (A-H ₂ O ₂)	87/70(3)	—	—	13
4 (P25-MeB)	85/170(8)	13/170(13)	—	2
5 (P25-MeR)	53/185(9)	9/320(16)	—	38
6 (P25-H ₂ O ₂)	54/180(9)	8/245(12)	—	38
7 (UV100-MeB)	54/90(5)	—	—	46
8 (UV100-MeR)	99/80(4)	—	—	1
9 (UV100-H ₂ O ₂)	69/85(4)	—	—	31
10 (MeB-TiO ₂)	—	—	85/50(2)	15
11 (MeR-TiO ₂)	—	—	83/40(2)	17
12 (H ₂ O ₂ -TiO ₂)	81/50(2)	—	—	19

Fig. 3 Degree of decolorization of Methyl Orange under visible light in the presence of MeB-sensitized titania: 1—sample 1 (A-MeB), 2—sample 7 (UV100-MeB), 3—sample 10 (MeB-TiO₂)

sorption capacity showed the sizes of the particles 28–30 nm for Degussa P25 and 12 nm for Hombikat UV100. Specific surface area measured by the comparative method was 53–54 m²/g for Degussa P25 and >123 m²/g for Hombikat UV100; volume of micro pores (<300 nm) was 0.163 and 0.344 cm³/g, respectively.

Impregnation with organic dyes and H₂O₂ by method 1 changes titania composition. Since modification of the titania samples was carried out in aqueous media, all modified samples contain hydrous titania (Table 2). Its quantity is small (1–2 %), when self-made anatase (A) and Degussa P25 are modified with MeB and large (up to

Fig. 4 Degree of decolorization of Methyl Orange under visible light in the presence of MeR-sensitized titania: 1—sample 2 (A-MeR), 2—sample 5 (P25-MeR), 3—sample 8 (UV100-MeR), 4—sample 11 (MeR-TiO₂)

42 %), when the same initial titania samples are treated with MeR and H₂O₂. Content of hydrous titania in Hombikat UV100 decreases down to 1 % on treatment with MeR and increases up to 46 and 31 % on treatment with MeB and H₂O₂, respectively (Table 2). The anatase:rutile ratio in the samples based on Degussa P25 and sizes of coherent scattering regions in all samples prepared by method 1 do not vary significantly (Table 2).

Preparing sensitized titania by the new method for sensitizing titania—method 2—resulted in formation of the samples containing η -TiO₂ (83–85 %) and hydrous anatase (15–17 %) when using organic dyes, and containing anatase (81 %) and hydrous anatase (19 %) when using H₂O₂ (Fig. 2; Table 2).

Photocatalytic properties of sensitized titania under visible light

The MeB- and MeR-sensitized titania (A) samples, prepared by method 1 (samples 1 and 2, respectively), show no significant preference as compared to the commercial photocatalysts Degussa P25 (samples 4 and 5, respectively) and Hombikat UV100 (samples 7 and 8, respectively) (Table 1; Figs. 3, 4). The degree of MeO decolorization in the presence of P25-MeB sample is nonmonotonous; an increase of the dye concentration at 130–170 min can be caused by washing the pre-adsorbed dye off the surface of Degussa P25.

Sensitization of titania by method 2, developed in this work, with MeB (sample 10) and MeR (sample 11) results in higher photocatalytic activity (Table 1; Figs. 3, 4, curves 4); see “Discussion”. The best result for dye sensitizing was achieved with the use of MeB (sample 10).

Fig. 5 Degree of decolorization of Methyl Orange under visible light in the presence of H_2O_2 -sensitized titania: 1—sample 3 (A- H_2O_2), 2—sample 6 (P25- H_2O_2), 3—sample 9 (UV100- H_2O_2), 4—sample 12 (H_2O_2 - TiO_2)

After treatment with hydrogen peroxide (method 1), Degussa P25 turned pale yellow; the yellow color for A- H_2O_2 and UV100- H_2O_2 was more intensive. However, the samples on the basis of Hombikat UV100 decolorize on storage (even in darkness). The rate of the photoreaction was higher for A- H_2O_2 (sample 3) and UV100- H_2O_2 (sample 9) and lower for P25- H_2O_2 (sample 6) than for the corresponding dye-sensitized samples (Table 1; Fig. 5, curves 1–3). However, it was much lower than for samples 10 and 11, prepared by sensitizing titania with dyes by the new method, developed in this work (method 2).

The best visible light photocatalyst, H_2O_2 - TiO_2 (sample 12) was prepared by treatment of the reaction mixture with H_2O_2 while synthesizing titanium dioxide from titanyl sulfate (method 2). As shown in Fig. 5 (curve 4) complete decomposition of MeO in the presence of H_2O_2 - TiO_2 under visible light takes 60–80 min, which is better than for the samples sensitized with organic dyes (Figs. 3, 4). It is noteworthy that the sample contains no free or adsorbed H_2O_2 since it was completely removed during preparing sensitized TiO_2 . All peroxy groups are strongly coordinated by titanium atoms. Therefore, in contrast to Zou et al. (2009), the effect of destruction MeO with H_2O_2 is excluded.

The results of studying photocatalytic activity of sensitized titania under visible light and dependence of the rate constants on the lamp power are summarized in Figs. 6 and 7. For all the samples, increase of the lamp power first leads to increase of the reaction rate. However, for the samples prepared by method 2, the reaction rate is almost independent of the lamp power >60 W; this may be caused by stronger electron–hole pair recombination as compared to the samples prepared by method 1.

The H_2O_2 - TiO_2 (sample 12) photocatalytic activity exceeds the activity of the earlier reported visible light-responsive

Fig. 6 First-order kinetics rate constant (k) of Methyl Orange decomposition under visible light in the presence of titania sensitized by method 2 (1) and anatase (A) (2), Hombikat UV100 (3), and Degussa (Evonik) P25 (4) sensitized by method 1

Fig. 7 Rate constant vs. halogen lamp power for sensitized titania: A-MeB, A-MeR, A- H_2O_2 (samples 1–3, respectively) and MeB- TiO_2 , MeR- TiO_2 , H_2O_2 - TiO_2 (samples 10–12, respectively)

photocatalysts. The best previous results were the following: complete decomposition of MeO catalyzed by N/Ag- and S/Ag-doped titania took 1.5 and 4 h, respectively (Varma et al. 2011). Our photocatalyst (H_2O_2 - TiO_2) decreases the degradation time down to 1 h, although we used less powerful lamp along with lower catalyst content and MeO concentration.

Photocatalytic properties of sensitized titania under UV light

Sensitization should not affect photocatalytic properties of titania under UV radiation; however, they can be changed due to modification of the surface. That is why we compared photocatalytic activity of pure titania (self-made titania, Degussa P25, and Hombikat UV100) and the samples treated with MeB, MeR, and H_2O_2 . In addition, photocatalytic activity of initial titania, pre-dispersed in water by stirring for 40 min, was also examined.

The results are summarized in Table 3 and Fig. 8.

Discussion

The samples of self-made titania, sensitized by treatment with organic dyes and hydrogen peroxide, are inferior to commercial titania in photocatalytic activity under UV radiation (Fig. 8). However under visible light, their

Table 3 Rate constants (k , min^{-1}) for MeO decomposition under UV light in the presence of pure and modified titania (samples 1–9)

Treatment with	Anatase (A)	Degussa P25	Hombikat UV100
–	0.039	0.068	0.084
H ₂ O	0.036	0.052	0.084
MeB	1/0.040	4/0.065	7/0.079
MeR	2/0.001	5/0.074	8/0.043
H ₂ O ₂	3/0.088	6/0.069	9/0.090

Fig. 8 First-order kinetics rate constant (k) of Methyl Orange decomposition under UV light in the presence of titania sensitized by method 1: 1—anatase (A), 2—Hombikat UV100, 3—Degussa P25

photocatalytic activity is comparable (for self-made titania sensitized by method 1) to Degussa P25 and Hombikat UV100 or much higher (for titania sensitized by method 2) (Fig. 6). Therefore, we can conclude that sensitization with MeB, MeR, and H₂O₂ is more effective for anatase, prepared by hydrolysis, than for anatase and/or rutile, prepared by pyrolysis.

The best results were achieved for the samples, prepared by the novel method 2, since sensitizers can incorporate into the surface of forming nano-titania. When nano-titania is already formed (method 1), the incorporation becomes more difficult. This is supported by IR spectroscopy. IR spectra of all the samples contain bands of titania (Table 4). However, the bands of sensitizers are observable only in the spectra of the samples prepared by method 2.

Earlier, it was suggested that photocatalytic destruction of organic matter on TiO₂ films proceeds partly through formation of hydroxyl radicals which are formed from surface hydroxyl groups created by interactions between adsorbed water and vacancies on the TiO₂ surface; a correlation between the amount of OH groups on the surface of the different TiO₂ films and the photocatalytic activity was found (Simonsen et al. 2008). It was shown that formation of more hydroxyl groups in the surface of TiO₂ results in higher photocatalytic activity when treating hydrothermally the TiO₂ powder (P25) in pure water at 150 °C for different times (Jianguo et al. 2006).

Although activity for Degussa P25 photocatalyst is often higher than for Hombikat UV 100 (Colón et al. 2001), in this work, Degussa P25 is more active only when it is sensitized with MeR under UV radiation and with MeB under visible light. The efficiency of various sensitizers in the photoreaction under visible light increases in the sequence MeR–MeB–H₂O₂ for self-made titania (A).

The mechanisms of sorption for H₂O₂ and organic dyes are fundamentally different. Hydrogen peroxide reacts chemically with titania surface producing colored peroxo titanium complexes (Kubota et al. 1995), while MeR

Table 4 IR spectra of the samples

Assignment	Method 1			Method 2		
	A–MeB sample 1	A–MeR sample 2	A–H ₂ O ₂ sample 3	MeB–TiO ₂ sample 10	MeR–TiO ₂ sample 11	H ₂ O ₂ –TiO ₂ sample 12
$\delta(\text{Ti–O–Ti})$, $\delta(\text{Ti–O–O})$	721	722	721; 882, 986	721	721	727; 798, 892, 996
$\delta(\text{Ti–O–H})$	1,062, 1,168	1,065, 1,122–1,139	1,041 + 1,074, 1,136	1,116, 1,147	1,050, 1,121	1,065, 1,119
$\delta(\text{H–O–H})$	1,599, 1,622	1,618–1,643	1,640	1,627–1,634	1,616–1,655	1,633
$\nu(\text{H–OH})$	3,141–3,263	3,101–3,349	3,178–3,219, 3,328–3,420	3,131–3,403	3,210–3,391	3,109–3,456
$\delta(\text{Ti–O–Ti})$, $\delta(\text{Ti–O–O})$	721	722	721; 882, 986	721	721	727; 798, 892, 996
$\delta(\text{Ti–O–H})$	1,062, 1,168	1,065, 1,122–1,139	1,041 + 1,074, 1,136	1,116, 1,147	1,050, 1,121	1,065, 1,119

Fig. 9 Microphotos of anatase (A) dispersed in water (a), 6.6×10^{-4} M MeR (b), 6.6×10^{-4} M MeB (c), and 10 M H_2O_2 (d). Circles in photo (d) are oxygen bubbles eliminating from concentrated H_2O_2

Fig. 10 Microphotos of TiO_2 sol mixed with 10 M KCl and 6.6×10^{-4} M MeR (a), 6.6×10^{-4} M MeB (b) and 10 M H_2O_2 (c)

anchors through carboxylic groups (Anselmi et al. 2012) and MeB is adsorbed physically (Chang et al. 2004).

Since Degussa P25 has more developed, but non-hydroxylated surface, it shows almost no difference in photocatalytic activity on sensitization with H_2O_2 and dyes. Slightly higher activity of MeB-sensitized Degussa

Table 5 Average sizes (μm) of microparticles formed during treatment of anatase (A) (method 1, samples 1–3) and TiO_2 sol (method 2, samples 10–12) with dyes and H_2O_2

Sample	After 1–2 min	After 15 min
1 (A–MeB)	~ 4	~ 40
2 (A–MeR)	~ 8	~ 8
3 (A– H_2O_2)	~ 2	~ 2
10 (MeB– TiO_2)	~ 4	~ 10
11 (MeR– TiO_2)	~ 6	~ 9
12 (H_2O_2 – TiO_2)	~ 2	~ 1

P25 can be explained by good sorption of the dye on its surface. We can propose that lower photocatalytic activity for MeR-sensitized titania in all cases, excluding Hombikat UV 100, is caused by competition between sensitizer (MeR) and substrate (MeO) with similar structures for titania surface. Hombikat UV100 differs from other titania samples by significantly higher specific surface area. Therefore, Hombikat UV100 has enough working surface to level competition between MeR and MeO.

Microphotos allow analyzing processes of formation of microparticles in the reaction mixtures on preparing samples by the two methods (Figs. 9, 10; Table 5). The average size of anatase (A) microparticles dispersed in water is $\sim 3 \mu\text{m}$; they form elongated aggregates ($\sim 15 \mu\text{m}$). When using method 1, microparticle size increases on treatment with organic dyes and decreases on treatment with H_2O_2 . Chemical sorption of MeR and H_2O_2 on titania causes destruction of aggregates, while physical sorption of MeB initiates further aggregation. Treatment of titania sol with dyes and H_2O_2 along with a coagulant (method 2) produces microparticles united in growing aggregates. It is noteworthy that the use of H_2O_2 results in formation of smaller microparticles and needle-like aggregates with developed surface. Therefore, formation of peroxo chelate complexes with surface titanium atoms decreases the size of the particles and increases their photocatalytic activity.

To confirm the visible light photocatalytic properties of the best catalyst, H_2O_2 – TiO_2 , we tested its photocatalytic activity in the reaction of degradation of molecules without absorbing visible light. The rate of destruction of salicylic acid with H_2O_2 – TiO_2 ($k = 0.017 \text{ min}^{-1}$) was higher than with the commercial visible light-responsive photocatalyst $\text{TiO}_2(\text{Mn})$ -Aldrich (Obolenskaya et al. 2013) ($k = 0.008 \text{ min}^{-1}$) (Fig. 11). Salicylic acid decomposes in 2 h. In comparison, films of titanium oxide prepared with the use titanium peroxide (air dried and further heated at 400°C) were found to decompose salicylic acid under UV light in 4 h (Sonawane et al. 2003). Ma et al. (2012) found that 1.0 % Eu/N– TiO_2 catalyst showed photocatalytic performance with k of 0.0064 min^{-1} and the degradation of 88 % salicylic acid in 5 h; Liu et al. (2012) achieved 72.62 % degradation of

Fig. 11 Degree of destruction of salicylic acid under visible light in the presence of H_2O_2 – TiO_2 (1) and $\text{TiO}_2(\text{Mn})$ -Aldrich (2)

salicylic acid in 120 min of visible light irradiation with the use of B-doped TiO_2 .

Conclusion

Sensitization of TiO_2 samples with the organic dyes and peroxo complexes is a promising tool in expanding the effective absorption wavelength of TiO_2 from ultraviolet to visible region.

The reaction rate constant of the MeO degradation under visible light depends on the catalyst type, the sensitizer, and the sensitization method.

In this work, we used traditional method of cold impregnation (method 1) and the new method of sensitizing titania during the process of its synthesizing (method 2).

The best results were obtained for peroxide-sensitized TiO_2 (H_2O_2 – TiO_2 , sample 12) prepared by method 2. The active sites in this photocatalyst are the colored titanium peroxocomplexes on the surface of titania nanoparticles.

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