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PREPARATION AND CHARACTERIZATION OF TITANIUM DIOXIDE MODIFIED WITH CARBON WITH ENHANCED PHOTOCATALYTIC ACTIVITY

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The aim of our work was to prepare nanoscale composites based on TiO_2 and carbon photocatalytically active under UV and visible irradiation in the destruction of safranin T. The samples were characterized by XRD, BET, SEM, UV-Vis and IR spectroscopy. X-ray analysis revealed photocatalytically active phase of anatase in all the composites. The powders consist of roundish agglomerates, crystallite size in agglomerates is 15 nm. Analysis of nitrogen sorption–desorption isotherms for the samples show the presence of a hysteresis loop which is the evidence for mesoporous structure.

Vibrational spectra of the composites reveal the following bands: near $700\,cm^{-1}$ corresponding to the Ti–O stretching vibration; around $3407\,cm^{-1}$ attributed to the surface-adsorbed H_2O; at $1628\,cm^{-1}$ which is referred to deformational vibrations in adsorbed water, and around $1300–1500\,cm^{-1}$ corresponding to carbon–oxygen bonds.

Absorption spectra of nanocomposites show a bathochromic shift as compared with those of TiO_2. Modification of TiO_2 with carbon leads to band gap narrowing of composites, as well as to emerging of additional energy levels in the band gap of TiO_2 with energies of 3.12–3.14 eV under valence band; that leads to sensitizing of C/TiO_2 composites to visible irradiation. Nanocomposites show higher photocatalytic activity compared to pure TiO_2. It may be connected with the participation of carbon in the inhibition of electron–hole recombination, prolongation of charge lifetime, increasing of efficiency of interfacial charge separation from TiO_2 to carbon and formation of doping electronic states inside the TiO_2 band gap.

Keywords: titanium dioxide, carbon, safranin T, photocatalysis

INTRODUCTION

Photocatalysis has proven to be a promising technique for the degradation of hazardous compounds in aqueous solutions. Titanium dioxide is the widely used photocatalyst for water purification, however, it has several serious disadvantages: the low quantum yield of the reaction, wide band gap (3.2 eV), high rate of electron-hole recombination, and peculiarity of light adsorption by TiO_2 resulting in its photochemical activity only in the UV region of spectrum. But ultraviolet light occupies only 4 % of sunlight; on the other hand, visible light accounts about 43 %. Thus, it seems more practical and favorable to use visible light rather than ultraviolet light for the degradation of water pollutions. So, an urgent problem in photocatalysis is a search for photocatalytic systems active under visible light irradiation which gives an opportunity of their widespread practical application.

Researchers are trying to shift the optical sensitivity of TiO_2 from UV to the visible-light region by many methods, such as metal loading, doping and coupling of composite semiconductors. Nanocomposites composed of TiO_2 and carbon materials (C) are widely popular photocatalysts because they combine the advantages of TiO_2 (good UV photocatalytic activity, low cost, and stability) to the enhanced charge carrier separation and lower charge transfer resistance brought by carbon. Many different C/TiO_2 photocatalysts have been studied, including C-doped TiO_2, TiO_2 supported on carbon materials, carbon nanostructures embedded in TiO_2 and C-coated TiO_2 [1–6].

So, the aim of our work was to prepare the samples of carbon/TiO_2 by an economical pathway and to test them under UV and visible light irradiation. We chose cationic dye safranin T (*ST*) as the model of pollutants to evaluate the degradation activity of composites.

EXPERIMENTAL

Preparation of composites. The samples of titanium dioxide modified with carbon were

obtained through calcination of mixtures of titanium(IV) tetrabutoxide (Aldrich), citric acid, glycerol [7], and different samples of carbon: C1 (0.05, 0.07, 1 and 1.3 g) and C2 (0.05, 0.07, 1 and 1.3 g). The carbon samples were obtained according to technique developed in this laboratory and have different textural characteristics (Table 1). So, the samples designated as $1C1/TiO_2$, $2C1/TiO_2$, $3C1/TiO_2$, $4C1/TiO_2$ and $1C2/TiO_2$, $2C2/TiO_2$, $3C2/TiO_2$, $4C2/TiO_2$, respectively. The powders were prepared at stepwise heating (200, 300, 400 and 500 °C) in the presence of air oxygen. Before annealing, mixture was carefully stirred up to yield uniform mass. For pure titanium dioxide, the same mixture was used, but without addition of activated carbon.

Characterization of photocatalysts. To analyze samples morphology a scanning electron microscope (SEM JSM 6490 LV, JEOL, Japan) was used.

X-ray phase analysis was performed using a diffractometer Dron-4-07 (Russia) at CuK_α radiation (with copper anode and nickel filter) in reflection beam and the Bragg–Brentano registration geometry ($2\theta = 10$–70 °). Average crystallite size was determined using broadening of the most intensive band by means of the Debye–Scherrer equation [8]: $D = 0.9\lambda/B\cos\theta$, where 0.9 is a constant, λ is a wavelength, nm. Crystalline sizes were determined through characteristics of the most intensive peaks. Interplanar distance (d, nm) was calculated using Wulff–Bragg's equation: $n\lambda = 2d\sin\theta$, where $n = 1$ is the order of reflection, $\lambda = 0.154$ nm is the wavelength, θ is the scattering angle, degrees. Thereby, $d = n\lambda/2\sin\theta$.

The values of specific surface area (S_{sp}) of the samples as well as distribution of pores by volume were determined using a Quantachrom NovaWin2 device. The specific surface of the samples was obtained from the isotherms of nitrogen sorption-desorption using the Brunauer–Emmet–Teller (BET) approach [9]. The pore radius (R) and the pore volume (V_{tot}) were calculated from the desorption branches of the isotherms using the Barret–Joiner–Halenda method [10].

Optical spectra of powders were measured using a Perkin-Elmer Lambda Bio 35 spectrophotometer in the range between 200 and 1000 nm which allows one to convert data of corresponding spectra by the help of the Kubelka–Munk equation.

IR spectra of the powders were registered using a single-ray FT IR spectrometer Thermo Nicolet Nexus FT-IR (Germany) in the region 500 to 4000 cm^{-1}. Synthesized samples under study were mixed with freshly calcined KBr in 1:4 ratio.

Photocatalytical experiment. Photocatalytic activity of the samples was evaluated by rate constants of destruction (k_d) of cationic dye ST ($C = 0.03$ g/l). Before irradiation, catalyst suspension in aqueous substrate solution was left in dark up to achieve adsorption equilibrium. In order to determine the optimal quantity of photocatalyst in the reactions under study, its concentration was increased at the constant substrate concentration. The dependence of safranin destruction rate constant (k_d) on the catalyst concentration shows that at low dye concentrations (≤ 2 g/l) an increase of the safranin destruction rate constant with the increase of photocatalyst amount in the reaction millieu is observed while it achieves a plateau consequently when photocatalyst concentration approaches roughly 2 g/l. All the rest photocatalytic reactions were carried out at the photocatalyst concentration equal to 2 g/l. Analagous dependences were obtained in the works [11, 12].

Irradiation of aqueous solutions (pH 6.5) of dye was performed at room temperature in quartz reactor in the presence of air oxygen. The light source was a high-intensity Na discharge lamp GE Lucalox (Hungary) with power of 70 W, the latter emitting in the visible region with maxima at 568, 590, and 600 nm and an UV lamp BUV-30 (Russia) with the power of 30 W and radiation maximum at 254 nm.

Concentrations of the substrate were measured spectrophometrically using a Shimadzu UV-2450 spectrophotometer at $\lambda = 520$ nm for ST. Photocatalytic rate constants for the model compound were calculated using the first order kinetic equation.

RESULTS AND DISCUSSION

Analysis of SEM-images of the samples shows that they consist of roundish agglomerates (Fig. 1 *a*). Diffractograms of all powders show intensive peaks which belong to anatase phase (Fig. 1 *b*) as in works [1, 3, 4]. No signal of brookite or rutile is detected by XRD. So, insertion of carbon into the binary composites does not induce new crystalline forms different from anatase. The peaks are quite broad, indicating small

crystallite sizes. Crystallite size in agglomerates of samples as calculated through Debye–Scherrer equation equals to 15 nm.

The samples show the presence of a hysteresis loop which is the evidence for mesoporous structure of the powders (Fig. 2 *a*). The isotherms correspond to type IV of IUPAC classification for mesoporous materials with H1 type of hysteresis loop.
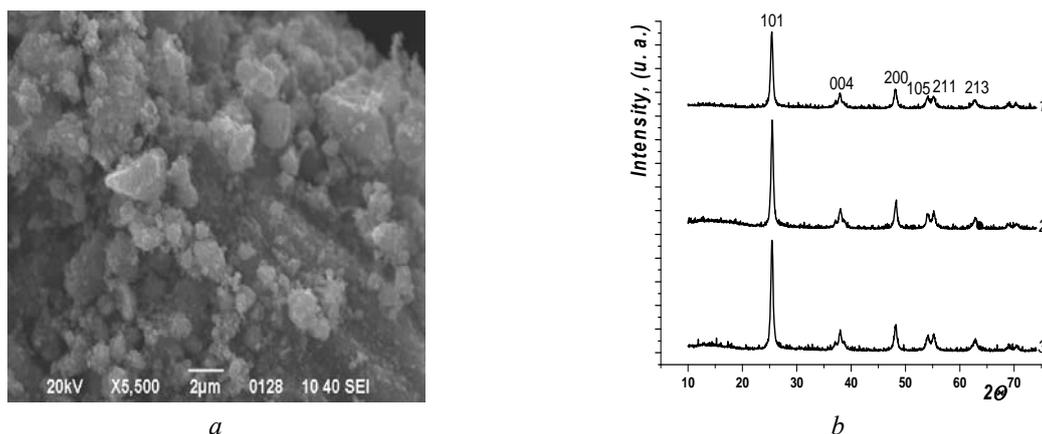
Predominance of pores up to 35 nm is characteristic of pure titanium dioxide, whereas for composite samples this value is of 5–35 nm (Fig. 2 *b*).

The texture characteristics of the samples are presented in Table 1. Compared with titanium dioxide, specific surface of binary system C/TiO_2 samples decreases with C1 addition and increases with C2 (≥ 0.07 g) addition, pore volume and radius decreasing.

Fig. 1. SEM-image of the $1C1/TiO_2$ sample (*a*) and XRD patterns (*b*) for: *1* – TiO_2, *2* – $3C2/TiO_2$, *3* – $3C1/TiO_2$
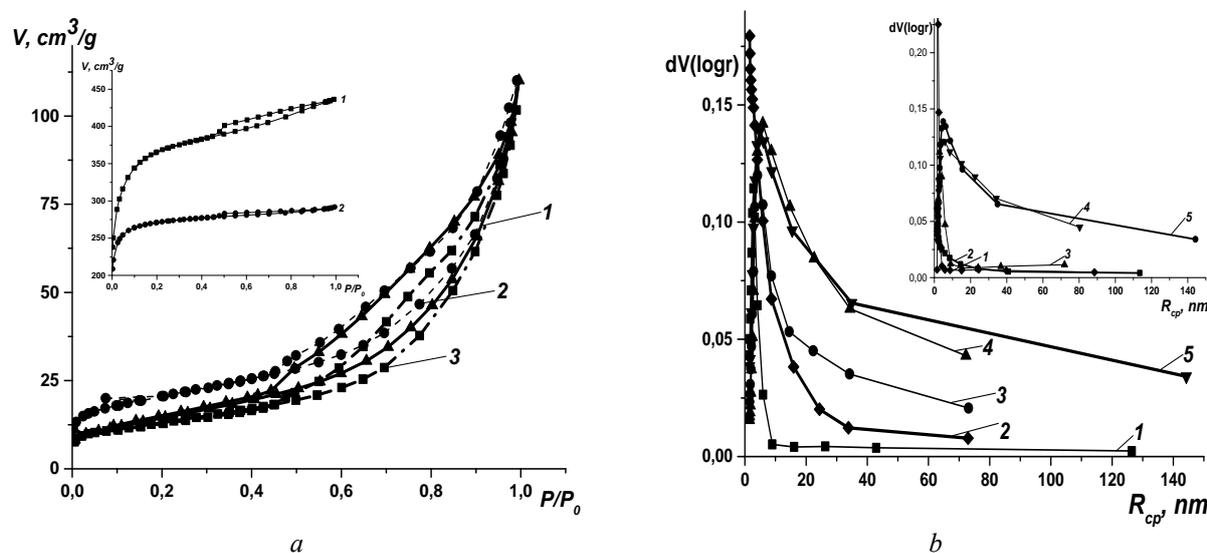

Fig. 2. Isotherms of nitrogen sorption–desorption obtained at 20 °C for the studied samples (*a*): *1* – TiO_2, *2* – $4C2/TiO_2$, *3* – $4C1/TiO_2$ (insets: *1* – C1, *2* – C2) and pore size distribution for the samples (*b*): *1* – $2C1/TiO_2$, *2* – C1, *3* – $3C1/TiO_2$, *4* – $4C1/TiO_2$, *5* – TiO_2 (insets: *1* – $3C2/TiO_2$, *2* – 2C2, *3* – $2C2/TiO_2$, *4* – $4C2/TiO_2$, *5* – TiO_2)

The functional groups of the TiO_2 and C/TiO_2 materials were characterized by FTIR transmittance, as shown in Fig. 3.

The band near 700 cm^{-1} corresponds to the Ti-O stretching vibration, and is present in all samples. The broad band around 3407 cm^{-1}

attributed to the surface-adsorbed H_2O and the absorption band at 1628 cm^{-1} refers to deformational vibrations in adsorbed water [13]. Broad band around 3407 cm^{-1} remains in spectra of modified samples, but the band at 1628 cm^{-1} almost vanishes and intensive peaks in the region

of 1300–1500 cm^{-1} appear. They correspond to carbon–oxygen bonds [14].

Absorption spectra of nanocomposites (Fig. 4) show a bathochromic shift as compared to the absorption band of pure TiO_2. The UV–Vis spectra reveal that the pure TiO_2 exhibit an absorption edge around 380 nm, the composite samples extended the absorption to the visible range (around 420 nm). This may indicate that carbon and TiO_2 nanoparticles are integrated to form C/TiO_2 nanocomposites [4].

Table 1. Structural characteristics of the samples

Sample	S_{sp}, m²/g	V_{tot}, cm³/g	R, nm
C1	1386.0	0.68	9.8
C2	1064.0	0.45	8.5
TiO_2	53.2	0.17	6.4
1C1/TiO_2	34.8	0.06	3.6
2C1/TiO_2	51.9	0.06	2.3
3C1/TiO_2	43.3	0.11	5.1
4C1/TiO_2	47.2	0.16	6.7
1C2/TiO_2	35.5	0.09	5.5
2C2/TiO_2	77.5	0.08	2.1
3C2/TiO_2	55.1	0.07	2.5
4C2/TiO_2	73.5	0.17	4.6
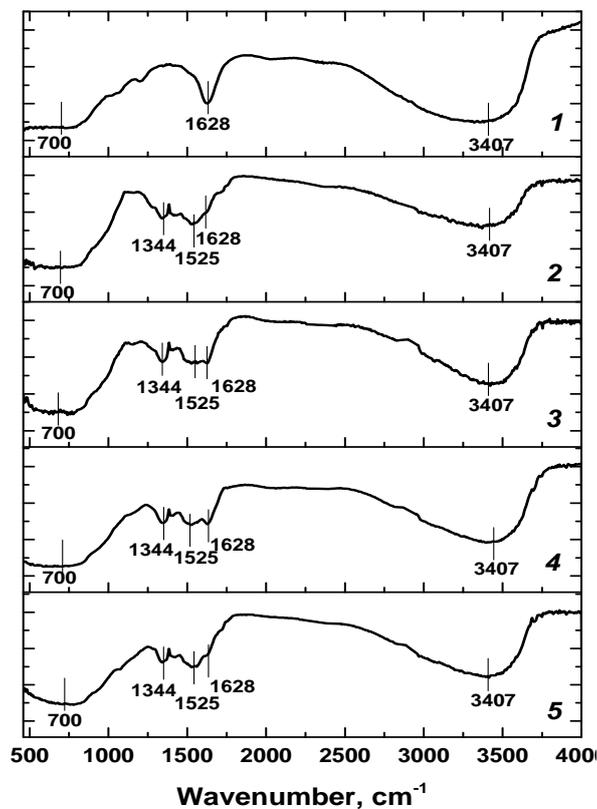
Fig. 3. IR spectra of: *1 – TiO_2, 2 – 4C2/TiO_2, 3 – 2C2/TiO_2, 4 – 4C1/TiO_2, 5 – 2C1/TiO_2*
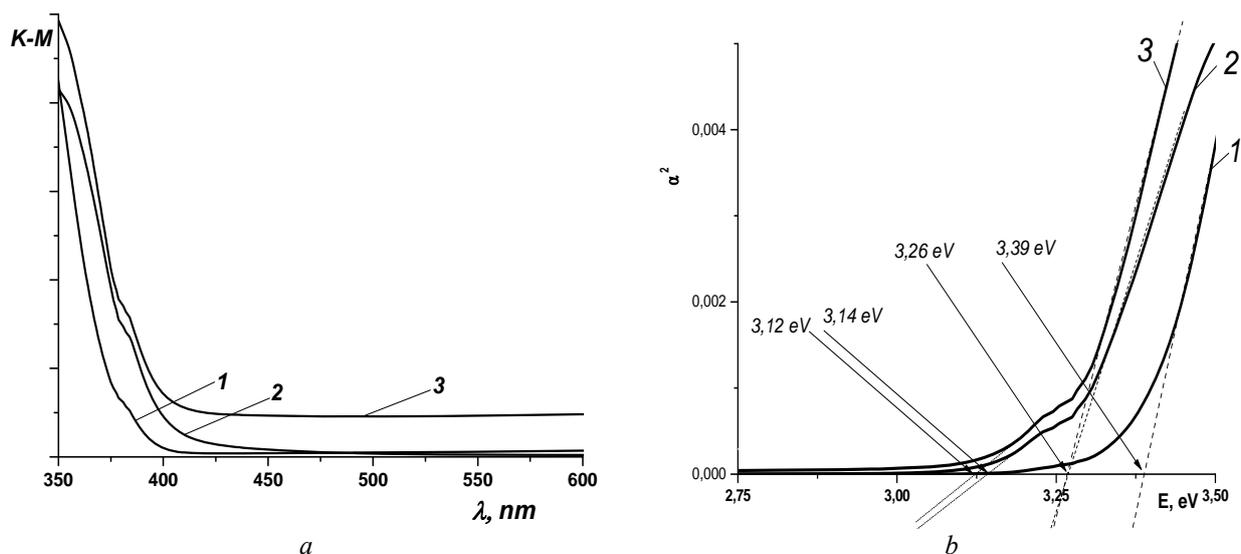
Fig. 4. *a*: UV-Vis diffuse reflectance spectra of samples: *1* – TiO_2, *2* – $2C2/TiO_2$, *3* – $3C2/TiO_2$; *b*: Square of extinction coefficient as dependent of incident irradiation energy for powders: *1* –TiO_2, *2* – $2C2/TiO_2$, *3* – $3C2/TiO_2$

Modification of titanium with carbon leads to band gap narrowing of composites (Fig. 4 *b*), as well as to emerging of additional energy levels in the band gap of TiO_2 with energies of 3.12–3.14 eV under valence band; that leads to sensitizing of C/TiO_2 composites to irradiation in the visible region of spectrum.

The photocatalytic activity of all the materials was tested for the decomposition of safranin T in aqueous solution. Previous to irradiation,

photocatalyst–dye systems were kept in the dark to achieve sorption equilibrium for 24 h. Irradiation of dye solution in water in the presence of photocatalyst leads to a decrease in dye concentration in solution, process rate depending on photocatalyst composition (Table 2). Thus, rate of catalytic destruction of dye at UV irradiation in presence of titanium dioxide powder increases more than by a factor of ten (Table 2).

Table 2. Photocatalytic activity of investigated samples in the destruction of safranin T

Sample	UV ($k_d \times 10^{-4}$, s^{-1})	Vis ($k_d \times 10^{-4}$, s^{-1})
	SF	
–	0.2	–
TiO_2	2.9	–
$1C1/TiO_2$	3.9	0.3
$2C1/TiO_2$	7.7	0.4
$3C1/TiO_2$	4.9	0.4
$4C1/TiO_2$	2.5	0.2
$1C2/TiO_2$	3.7	0.9
$2C2/TiO_2$	5.8	1.1
$3C2/TiO_2$	4.5	0.8
$4C2/TiO_2$	2.8	0.8

C/TiO_2 samples manifested a higher photocatalytic activity as compared to that of pure titanium dioxide at UV irradiation (Table 2). According to [15], the effect of carbon content is different for different pollutants or different light sources. In our case, the greatest activity was detected for the samples $2C1/TiO_2$ and $2C2/TiO_2$.

Enhancement of photocatalytic activity of the modified samples may be connected with the participation of carbon in the inhibition of electron–hole recombination and prolongation of lifetime of charges which take part of the destruction processes and with the increasing of efficiency of interfacial charge separation from

TiO_2 to carbon. The authors [4] suggested that partial charge transfer occurred from carbon nanoparticles to TiO_2 by the interfacial Ti–O–C linkages and the electron-accepting sites on the carbon nanoparticles facilitate interfacial charge separation.

Dye in aqueous solution, as being exposed to visible light either without any catalyst, or in the presence of pure titanium oxide shows no concentration change. Composite samples were photocatalytically active in destruction of ST under visible light irradiation, in contrast with pure titanium dioxide which acts as a photocatalyst only under UV irradiation. The greatest activity was detected for 2C2/TiO_2 sample. According to the literature [16], carbon in the composites acts as a doping agent, and some C-Ti bonds are formed.

The mechanism of the C/TiO_2 photocatalytic activity improvement under visible light can be explained by the formation of doping electronic states inside the TiO_2 band gap [17]. In our case, addition of carbon narrows the band gap of the composites as compared to that of pure TiO_2 (3.39 eV); it also leads to emerging of additional energy levels in the band gap of TiO_2 with energies of 3.12–3.14 eV under valence band; that leads to sensitizing of C/TiO_2 composites to irradiation in visible region of spectrum; so it is possible to obtain photoactivity at visible irradiation.

Thus, composite materials proved to be perspective photocatalysts. They might be used in photocatalysis for industrial waste purification of various organic impurities, in particular, dyes that are stable in the environment.

Отримання та характеризація діоксиду титану, модифікованого вуглецем, з підвищеною фотокаталітичною активністю

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Одержано нанорозмірні композиційні матеріали на основі діоксиду титану і вуглецю. Зразки характеризували методами РФА, БЕТ, СЕМ, УФ і видимої спектроскопії та ІЧ-спектроскопії. За допомогою рентгенофазового аналізу в усіх композитах виявлено фотокаталітично активну фазу анатазу. Дослідження ізотерм сорбції-десорбції азоту для синтезованих зразків показало наявність петлі гістерезису, що свідчить про мезопоривату структуру порошків. Встановлено, що композити складаються з круглястих агломератів, розмір кристалітів в яких становить 15 нм. Нанокомпозитні зразки виявили підвищену фотокаталітичну активність в деструкції органічного барвника сафраніну Т при УФ та видимому опроміненні в порівнянні з чистим діоксидом титану. Це може бути пов'язано з участю вуглецю в інгібуванні процесу рекомбінації електронів та дірок, подовженні життя зарядів, збільшенні ефективності міжфазового розділу зарядів на межі фаз TiO_2 та вуглецю, а також формуванні додаткових електронних рівнів.

Ключові слова: діоксид титану, вуглець, сафранін Т, фотокаталіз

Получение и характеризация диоксида титана, модифицированного углеродом, с повышенной фотокаталитической активностью

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Получены наноразмерные композиционные материалы на основе диоксида титана и углерода. Образцы характеризовали методами РФА, БЭТ, СЭМ, УФ и видимой спектроскопии, а также ИК-спектроскопии.

Рентгенофазовый анализ показал наличие фотокаталитически активной фазы анатаза во всех композитах. Исследование изотерм сорбции-десорбции азота для синтезированных образцов показало наличие петли гистерезиса, что свидетельствует о мезопористой структуре порошков. Установлено, что композиты состоят из округлых агломератов, размер кристаллитов в которых составляет 15 нм. Нанокомпозитные образцы проявили более высокую фотокаталитическую активность в деструкции органического красителя сафранина Т при УФ и видимом облучении по сравнению с чистым диоксидом титана. Это может быть связано с участием углерода в ингибировании процесса рекомбинации электронов и дырок, продлении жизни зарядов, увеличении эффективности межфазового разделения зарядов на границе фаз TiO_2 и углерод, а также формировании дополнительных электронных уровней.

Ключевые слова: диоксид титана, углерод, сафранин Т, фотокатализ

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