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Effect of Heat Treatment on Titanium Dioxide Co-Doped with Tin and Sulfur

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Abstract

Titanium dioxide nanoparticles co-doped with tin and sulfur were studied in the concentrations of 1, 2, 3, 4, and 5 at.% of Sn. The processes of thermal effects on samples and the colorimetric characteristics of thin films obtained from the samples are considered. A color change is noted upon doping, with a transition from white to pale yellow. There is also a noticeable decrease in the mass of the samples during annealing until a temperature of 517 °C is reached, then the mass remains unchanged. The differential thermal analysis curve in this temperature range shows exothermic and endothermic peaks associated with the doping process. The color characteristics are determined and the influence of doping elements on them and the connection with photocatalytic activity are shown.

Keywords: Titanium dioxide; Nanoparticles; Doping; Thermophysical processes; Optical properties

1. INTRODUCTION

Nanomaterials based on titanium dioxide are considered promising semiconductor photocatalysts for a number of reasons, primarily high stability, high photocatalytic activity, and lack of toxicity. However, it is sensitive only to UV radiation due to the band gap, which for the anatase phase is 3.2 eV [1,2]. Photocatalysis is considered as a way to solve current environmental problems and the energy crisis, since the process is carried out only by solar energy. Much attention has been paid to obtaining visible light sensitive TiO_2 [3–5]. To date, many ionic dopants have been studied [6] in various valence states, including metal ions (e.g., Cu^{2+}, Co^{3+}, Mo^{5+}) and nonmetallic ions (e.g., B^{3+}, N^{3+}, F^{-}). The optical and electronic properties of solid materials strongly depend on the structure, including the type of bonding and arrangement of atoms, phases and their distribution, as well as defects [7,8].

Various approaches to obtaining TiO_2 photocatalyst material have also been proposed, such as engineering the shape and facets of nanocrystals, forming heterojunctions with other semiconductors, and adding noble metal (Au or Pt) co-catalysts to improve charge separation by forming an interfacial Schottky barrier [9]. It is known that TiO_2 nanomaterials can change color when doped. In Ref. [10] this effect is explained by changing the electronic structure of the material due to the introduction of suitable "intraband" electronic states that change the light absorption and optical properties of TiO_2. For example, nitrogen doping results in "yellow" TiO_2 powders exhibiting a red shift in the onset of optical absorption to ~ 500 nm [11].

Hydrogenation treatment under various conditions (pressure, temperature, etc.) produced gray to black colored forms of TiO_2 that exhibit strong absorption of visible and near-infrared light [12]. It is observed that the darker the color, the higher the ability to absorb light, so "black TiO_2" shows the highest intensity of visible light absorption. Nanomaterials based on TiO_2 and especially "black" are of great interest for photocatalytic hydrogen production using solar energy [13]. It is noted that "gray" titanium leads to the formation of peculiar defective catalytic centers, which make it possible to generate hydrogen without co-catalysts (usually Pt and other noble metals). The precise understanding of the structural and electronic nature of these catalytically active sites still remains unclear, as do the fundamental structure-activity relationships that

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determine the formation of crystal defects, enhanced light absorption, charge separation, and photocatalytic activity.

In this work, the thermophysical processes of co-doping titanium dioxide with tin and sulfur were studied. The influence of doping elements on the optical characteristics of thin films of doped titanium dioxide and its photocatalytic activity is shown.

2. EXPERIMENTAL DETAILS

Co-doped titanium dioxide samples were obtained using commercial titanium dioxide nanopowder Degussa P25 with particle sizes less than 50 nm with mechanical mixing with a source of S and Sn ions of tin sulfate with concentrations of 1, 2, 3, 4, 5 at.%, followed by annealing at 400 °C. The experiment is described in more detail in Ref. [14].

A paste was prepared by mixing co-doped TiO_2 powder with distilled water (1:3 by weight) in an agate mortar. TiO_2 paste was scraped onto a transparent indium tin oxide (ITO) glass by the doctor blade method to form titanium dioxide film with a thickness of ~ 100 μm. The TiO_2 thin film then was annealed in air at 300 °C for 120 min in an electric muffle (EKPS-5).

A Shimadzu DTG-60H was used for thermogravimetry (TG) and differential thermal analysis (DTA). Samples of mixtures of TiO_2 and $SnSO_4$ were heated in platinum pans over a range of 25–1000 °C at a constant rate of 10 °C/min under air flow 35 ml/min. The results of TG analysis are interpreted more accurately by processing TG curves. In particular, the derivative of the TG signal (rate of mass change), represented by the DTG curve, allows us to establish the point in time or temperature at which the weight change occurs most rapidly. The results of DTA analysis are processed similarly, and the resulting curves are designated DDTA.

The chemical composition of doped TiO_2 nanopowders was determined by the energy-dispersive X-ray analysis (EDX-8000, Shimadzu). The morphology of doped TiO_2 nanoparticles was studied using the field emission scanning electron microscopy (MIRA-3, Tescan). In addition, the colorimetric parameters of the TiO_2 thin film on ITO including L^* (lightness), a^* (red–green) and b^* (yellow–blue), the yellowness index (YI) and the whiteness index (WI) were measured using a spectrophotometer (LAMBDA 1050, PerkinElmer) equipped with a 150 mm integrating sphere accessory. The colorimetric data based on CIE 1931 (2 degree observer angle and Illuminant C).

3. RESULTS AND DISCUSSION

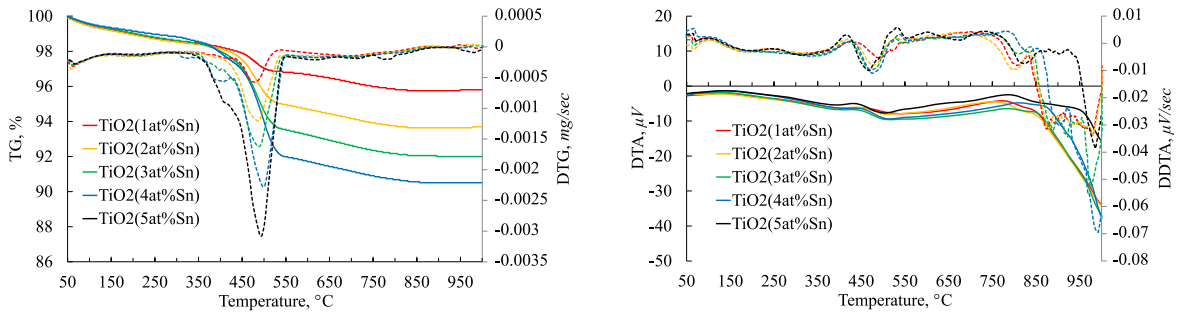
To study the processes occurring during titanium dioxide co-doping, samples were taken at the stage of mechanical mixing of titanium dioxide powder and tin sulfate. As can be seen from the data shown in Fig. 1, with increasing temperature, the mass of samples doped with tin and sulfur decreases, accompanied by thermal effects. During heat treatment in air, a significant loss of sample mass is observed in the temperature range of 360–517 °C and a peak in the DTG curve at 440 °C. DTA shows two peaks in this interval: an endothermic peak at about 440 °C and a subsequent exothermic peak at about 500 °C. The observed phenomenon can be attributed to the thermal process of decomposition of $SnSO_4$ accompanied by the release of a gaseous component, as evidenced by a decrease in mass on the TG curve and the endothermic nature of the peak of the DTA curve.

When thermally unstable $SnSO_4$ is heated above 360 °C the following reaction is possible:

$$SnO_4 \xrightarrow{t^\circ} SnO_2 + SO_2 \uparrow.$$

The subsequent second DTA peak correlates with the crystallization of tin oxide from the amorphous state. The third DTA peak lies in the region of ~ 800 °C and is associated with the exothermic anatase rutile transformation (ART).

Characteristics of the TG curves are presented in Table 1. According to Table 1, it is clear that the mass loss of the sample increases with increasing dopant content, which corresponds to an increase in losses associated with the thermal decomposition of $SnSO_4$.



(a) (b)

Fig. 1. TG (solid), DTG (dashed) curves (a) and DTA (solid), DDTA (dashed) curves (b) of the studied samples, characterizing mass loss and thermal information respectively.

Table 1. Sample weight loss according to TG data.

Sample	Weight loss, mg	Weight loss, %
TiO_2-P25D	0.05	0.3
TiO_2-1at.%Sn	0.3	1.6
TiO_2-2at.%Sn	0.56	3.2
TiO_2-3at.%Sn	0.81	4.6
TiO_2-4at.%Sn	1.11	6.3
TiO_2-5at.%Sn	1.52	8.5

Table 2. Mass percentages of elements in the samples before heat treatment (in wt.%).

Element	TiO_2 samples with different dopant contents				
	TiO_2-1at.%Sn	TiO_2-2at.%Sn	TiO_2-3at.%Sn	TiO_2-4at.%Sn	TiO_2-5at.%Sn
Ti	53.87	56.191	52.309	49.116	48.118
O	40.441	36.037	36.091	37.676	35.354
Sn	5.133	6.959	10.350	11.774	14.649
S	0.556	0.813	1.250	1.434	1.779

Table 3. Mass percentages of elements in the samples after heat treatment (in wt.%).

Element	TiO_2 samples with different dopant contents				
	TiO_2-1at.%Sn	TiO_2-2at.%Sn	TiO_2-3at.%Sn	TiO_2-4at.%Sn	TiO_2-5at.%Sn
Ti	49.93	51.18	51.3	53.89	53.36
O	45.07	42.12	39.7	35.33	33.64
Sn	4.63	6.26	8.49	10.19	12.32
S	0.37	0.44	0.51	0.59	0.68

Table 4. Estimated *Lab* values and *YI*, *WI*.

Sample	*L**	*a**	*b**	*WI*	*YI*
TiO_2-1at.%Sn	85.03	–2.294	–5.228	92.96	–13.38
TiO_2-2at.%Sn	77.56	–2.544	–9.408	104.01	–25.38
TiO_2-3at.%Sn	86.31	–2.529	–4.472	91.33	–11.71
TiO_2-4at.%Sn	72.24	–2.298	–8.157	93.49	–22.77
TiO_2-5at.%Sn	50.96	–3.359	5.986	–26.69	14.37

Table 2 presents the results of determining the chemical composition of samples before heat treatment using the EDX method. The content of Sn and S elements increases in proportion to the dopant content in the sample.

After heat treating and washing the sample, we observe a slight decrease in the amount of tin and a significant decrease in sulfur in the samples (see Table 3). This decrease in the amount of sulfur indicates the fact that most of the sulfur, during the thermal decomposition of tin sulfate, volatilized in the form of gaseous SO_2 and did not participate in the doping of titanium dioxide. Scanning electron microscopy shows that all studied samples are powders of spherical titanium dioxide nanoparticles; the size of the nanoparticles does not change much during doping and the final diameter does not exceed 100 nm.

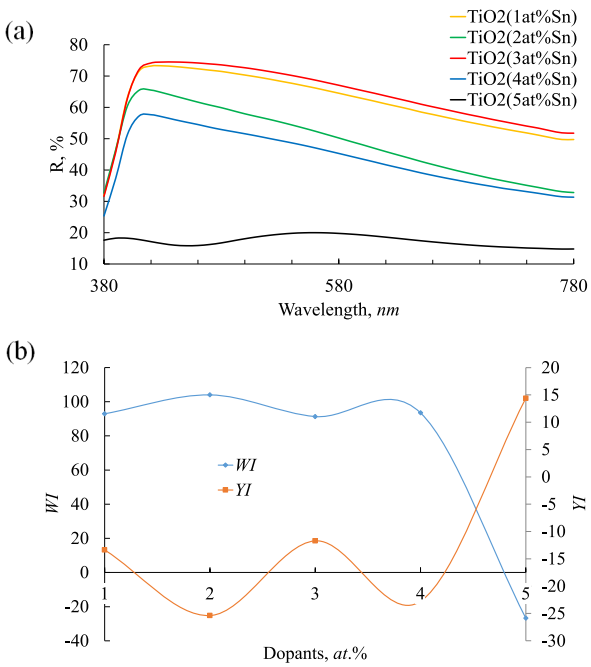


Fig. 2. (a) Spectrum of the samples in visible range and (b) estimated yellowness index (*YI*) and whiteness index (*WI*).

The impurity of titanium dioxide and degree of particle interaction have significant influence on TiO_2 whiteness. The standardized CIE values are used to characterize colorimetric parameters. Figure 2 displays recorded spectrum in visible region (379–779 nm) from thin films doped with titanium dioxide on ITO. Estimated *Lab* values and *YI*, *WI* are given in Table 4. The higher the *L** value, the higher the brightness, the lower the *b** value, the less yellow the appearance.

The whiteness of titanium dioxide is sensitive to the presence of impurities, especially heavy metals. This is due both to the color effect of the impurities themselves, as well as due to the distortion of the crystal lattice and the violation of symmetry. We observe this effect most strongly when titanium dioxide is doped with 5% of tin (Fig. 2b), it is clearly seen that the whiteness index is greatly reduced to –26.69 and the yellowness index increases up to 14.37.

Previously, in Ref. [14], we studied similar samples for photocatalytic activity; it should be noted titanium dioxide samples co-doped with sulfur and tin (5 at.% Sn) exhibit the highest photocatalytic activity during the decomposition of the organic pollutant (methylene blue)

under visible light. It has been established that when titanium dioxide is co-doped with Sn and S at a Sn content of 5 at.%. band gap decreases by 0.3 eV to 2.98 eV.

4. CONCLUSION

The thermophysical processes occurring when titanium dioxide is doped with tin and sulfur have been studied, and the influence of doping elements on the color characteristics of photocatalytically active titanium dioxide nanoparticles co-doped with tin and sulfur has been determined.

During annealing when doping process, thermochemical reactions can be distinguished, accompanied by mass loss when heated in the temperature range 360–517 °C with two peaks associated with the decomposition of $SnSO_4$ to tin oxide and subsequent crystallization of tin oxide from the amorphous state. In the high temperature region around 800 °C, peak associated with ART is observed.

As the concentration of the dopant increases, the color of the samples changes from white to pale yellow (*WI* decreases, *YI* increases), which may indicate structural changes in the sample and the formation of defects. The photocatalytic test showed that materials with the highest yellowness index exhibit the greatest activity.

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Влияние термообработки на содопированный оловом и серой диоксид титана

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Аннотация. Исследованы допированные оловом и серой наночастицы диоксида титана в соответствующих концентрациях 1, 2, 3, 4, 5 ат.% Sn. Рассмотрены процессы термического воздействия на образцы и колориметрические характеристики тонких пленок, полученных из наночастиц допированного диоксида титана. Отмечается изменение цвета при допировании с переходом от белого к бледно-желтому. А также заметное снижение массы образцов при отжиге до достижения температуры 517 °C, далее масса остается неизменной. На ДТА-кривой в этом интервале температур отмечаются экзотермические и эндотермические пики, связанные с процессом допирования. Определены цветовые характеристики допированного диоксида титана, показано влияние на них допирующих элементов и связь с фотокаталитической активностью.

Ключевые слова: диоксид титана; наночастицы; допирование; теплофизические свойства; оптические свойства