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Synthesis of Titanium Dioxide Nanotubes and Their Use in Photocatalytic Processes for Removal of Sulphur Compounds from Oil Products

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Abstract

Titanium dioxide nanotubes were synthesised using industrial rutile pigments under the optimum conditions selected. Physicochemical properties and the catalytic activity of the former were examined. As shown, oxidation of sulphur compounds of diesel fraction in the presence of titanium dioxide nanotube-based catalysts allows simple and efficient treatment of oil products.

Key words: photocatalysis, titanium dioxide nanotubes, synthesis, oxidation of sulfur compounds, diesel fraction

INTRODUCTION

Lately, great attention has been paid to photocatalysis processes to remove toxic chemicals from water and air [1]. Oxide and sulphide semiconductor materials, deposited metal oxides, and deposited oxide dispersions are used as catalysts [2 and 3]. Titanium dioxide (TiO_2) is one of the widely used materials for photocatalysis processes due to its relatively low cost, non-toxicity, and efficiency. The catalytic activity of the former is linked to the relatively large lifetime of photogenerated charge carriers (about 250 ns) [4]. The major restrictions for the practical use of TiO_2 in photochemical processes is a low quantum efficiency of the process because of the weak separation of photogenerated charge carriers and the requirement to use UV radiation only because of the high energy gap width of TiO_2 (3.2, 3.3, and 3.0 eV) [5–8]. Because of this property, the use of the solar radiation, in the range of which about 7 % falls on the UV portion, is low-efficient. At the same time, 45 % is accounted for the visible range [9].

Titanium dioxide is a wide-band-gap semiconductor that exists in nature as several crystal modifications (anatase, rutile, and brookite). Most

works on photocatalysis explore rutile and anatase. Upon UV radiation of titanium dioxide, adsorption of the photon with the energy higher than the energy gap width leads to the formation of electron-hole pairs. If there no recombination of free charges, they may migrate along the surface where electrons are captured by titanium atoms, whereas holes – by surface OH^- groups. The captured holes yield the OH^\bullet radical interacting with hydroxyl groups, whereas electrons interact with O_2 and H_2O to form active radicals, such as O_2^- , HOO^\bullet , and HO^\bullet . It is these free radicals that are able to oxidize C–H bonds, which leads to the destruction of organic molecules.

Photocatalytic oxidation processes mainly proceed on titanium dioxide surface; therefore, it has been suggested to use of TiO_2 nanoparticles for these purposes. Using these nano-species that have a large specific surface area appears to be the most logical approach [10].

In order to decrease losses and prevent likely recombination processes appearing upon a transition from transitions from one particle to another one, it was suggested to use TiO_2 -based nanostructures with monodimensional (1D) electron

transport. These structures include nanotubes [11–13], nanorods [14], and nanowires [15]. Owing to structure peculiarities, all of them have increased electron acceptor properties, which facilitates a fast transfer of electrons and a slow recombination process. As reported in [16], recombination processes in TiO₂ nanotubes (NT) proceed 10 times slower than those in nanoparticles.

Production rates of high sulphur oil grow every year. In this regard, there is an increased use relevance of photocatalytic processes to oxidise sulphur compounds of oil and its fraction, as their elevated content leads to equipment corrosion, the poisoning of catalysts for manufacturing processes the deterioration of the quality of finished products, and aggravation of the environmental situation [17].

There are quite a few methods to remove sulphur compounds from oil and oil products. The former include extraction, adsorption, oxidation, hydrotreatment, *etc.* The major drawbacks of the listed methods are expensive reagents, large covered amounts, and significant energy costs. Photocatalytic purification methods are deprived of the specified drawbacks and allow reaching a relatively high degree of removal of sulphur compounds from oil fractions. For example, the desulphurization process of diesel fuel using photooxidation over a nanodispersed titanium dioxide was considered in [18]. As demonstrated, the degree of removal of total sulphur is 61.9 %. The use of TiO₂ catalyst (Degussa P25) [19] enables to remove 46.6 % of sulphur from diesel fuel.

The objective of the research work was to obtain monomeric titanium dioxide particles (nanotubes) from industrially used titanium rutile pigment, explore physicochemical properties of the resulting compounds, and to consider an opportunity to use rutile pigments and TiO₂ nanotubes in photocatalysis processes when sulphur compounds are removed from diesel fraction.

EXPERIMENTAL

The research used two titanium pigments. One of them contained 98.5 % of the rutile phase (TiO₂-1) and the other one was comprised of rutile (95.0 %), anatase (4.5 %), and CaCO₃ (TiO₂-2) (0.5 %). Diesel fuel was investigated having been boiled out within 180–360 °C; the total sulphur content was 0.22 %.

In order to determine physicochemical properties of rutile pigments and NT based thereon, X-ray phase analysis (XPA), high-resolution trans-

mission electron microscopy (HRTEM), and also IR and Raman spectroscopy (RS), were used.

The Shimadzu XRD 7000 diffractometer (Japan) with copper CuK_α radiation according to Bragg-Bretano scheme with a step of 0.03 and exposure time at the point of 6 s was used to carry out XPA in an angular range of 10–80°. The calculation of the X-ray amorphous fraction was performed with standard software made available on the device. The IR spectra were recorded using a Nicolet 5700 FT-IR spectrometer with a Raman modulus. The particle size and shape of the nanomaterial were determined according to micrographs acquired using a JEM-100 CX II JEOL electron microscope.

Catalytic photooxidation processes of organosulphur compounds of diesel fraction were conducted in the presence of TiO₂. The UV spectra were irradiated with the UV photodiode lamp with a power of 10 WT (China). The radiation wavelength was varied between 370 and 400 nm. The oxidized sulfur compounds were extracted with CH₃CN at a 1 : 2 volume ratio of diesel fraction/acetoneitrile. Sulphur content in the initial and purified fractions was determined by combustion in the lamp according to GOST 19121–73.

RESULTS AND DISCUSSION

Figure 1 reports the Raman spectrum of a sample of TiO₂-1 rutile pigment.

The resulting spectrum is typical for the rutile structure. The former has 4 vibrational modes described in [20]. The sample displays high-intensity bands at 227, 441, and 609 cm⁻¹ and a low intensity-band at a frequency of 147 cm⁻¹.

The Raman spectrum of the TiO₂-2 sample is identical to that of the TiO₂-1 specimen, except for the additional band near 1065 cm⁻¹ that is referred to symmetrical stretching vibrations of the O–C–O bond. And then, the higher intensity of the band at 145 cm⁻¹ may indicate the presence of the anatase phase.

As can be seen in XRD patterns, the TiO₂-1 sample contains the rutile phase only (a crystallinity of 75.7 %) and the TiO₂-2 specimen is comprised of three phases, such as rutile, anatase, and calcite (in a 88 : 10 : 2 % ratio, correspondingly).

According to a micrograph of the rutile pigment sample (Fig. 2), as exemplified by TiO₂-1, the crystals are parallelepiped-shaped with sizes within 250–300 nm *per* 400–500 nm.

In order to obtain NT, there was used the method proposed by Tomoko Kasuga *et al.* [21

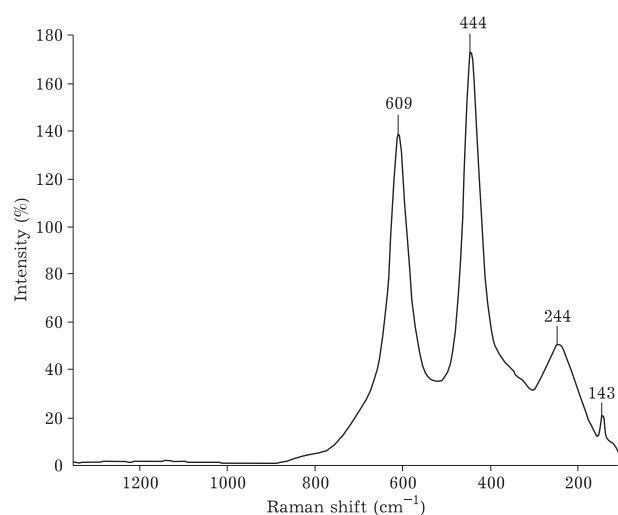


Fig. 1. Raman spectrum of TiO₂-1 rutile pigment.

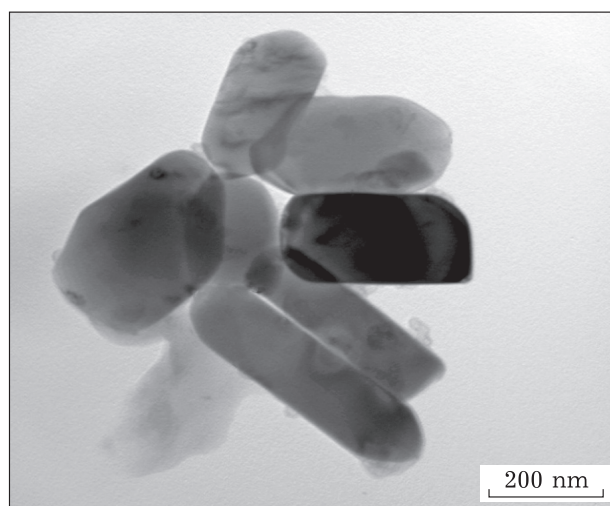


Fig. 2. Micrograph of TiO₂ rutile pigment.

and 22]. According to the technique specified, TiO₂ is exposed to hydrothermal treatment in a concentrated solution of alkali (NaOH). Table 1 reports the data for the effect of the temperature, alkali concentration and reaction time on the formation process of NT.

Following the end of the reaction, the resulting product was rinsed with a 0.1 M solution of nitric acid (HNO₃) and distilled water till a neutral reaction.

According to literature data [23], TiO₂ NT may be characterised through XPA, RS, and TEM. XRD patterns should have three blurred low-intensity peaks in the small-angle region 2θ (10.535, 24.608, and 28.299), according to RS – a peak in the region of 270 cm⁻¹. Our results prove the literature data.

Figure 3 reports the Raman spectrum of the TiO₂ NT sample derived upon synthesis No. 7. According to a relatively intense peak near 276 cm⁻¹, TiO₂ nanotubes are formed.

The XRD patterns of the samples produced in syntheses No. 4, 5, and 7 contain low-intense reflec-

tions with maxima in the range of angles 2θ 10.594, 25.185, and 28.415. The reflections correspond to TiO₂ NT, which is demonstrated in Fig. 4 as exemplified by a sample derived in synthesis No. 7.

Figure 5 demonstrates a micrograph of TiO₂ NT on an example of a sample derived in synthesis No. 7. The NT diameter, *d* is 10–12 nm.

Papers 24 and 25 proposed for the first time the mechanism that explained the formation of TiO₂ particles with nanotube morphology. As suggested, large crystal TiO₂ particles are transformed into sodium titanate with a layered structure in the presence of alkali (NaOH) at a temperature not over 120 °C. Sodium titanate is then delaminated onto separate crystal layers that lose stability upon an increase in temperature and is folded into scrolls (tubes). A sodium cation is removed from their framework after product treatment with solutions of mineral acids and separate crystal nanotubes are generated.

According to the data acquired, the formation conditions of TiO₂ NT are as follows: an alkali concentration of not over 8 M, a reaction tem-

TABLE 1

Preparation conditions of TiO₂ nanotubes (NT)

Synthesis number	Starting material	<i>T</i> , °C	<i>t</i> , h	<i>C</i> _{NaOH} , g/L	XPA, 2θ	<i>v</i> , cm ⁻¹ (RS)	HRTEM <i>d</i> , nm
1	TiO ₂ -1	190	16	12.5	No crystal phase	607 : 445; 249 weak.; 200	Round shaped aggregates 80–100
2	TiO ₂ -1	190	6	12.5	Same	607 : 445; 249 weak; 200	Same
3	TiO ₂ -1	160	16	10	Same	607 : 445; 249 weak; 200	Same
4	TiO ₂ -1	120; 150	4; 8	8	10.535; 24.608; 28.299	607 : 445; 270; 193	NT 10–16
5	TiO ₂ -1	120; 150	4; 4	8	10.535; 24.608; 28.299	1085; 608; 445; 248; 200	NT 10–16
6	TiO ₂ -2	180	8	12.5	No crystal phase	1085; 608;	Aggregates 80–100
7	TiO ₂ -2	120; 150	4; 4	8	10.535; 24.608; 28.299	445; 270; 200	NT 10–16

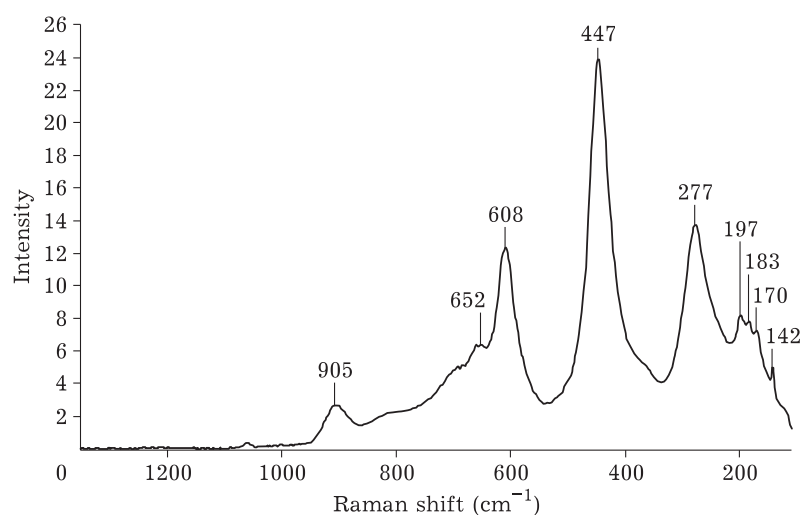


Fig. 3. Raman spectrum of a sample of TiO_2 nanotubes (NT) obtained in synthesis No. 7.

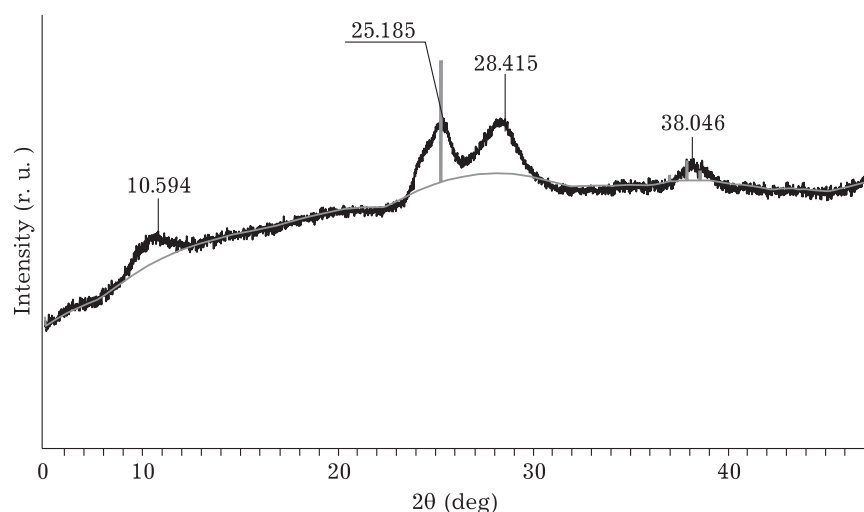


Fig. 4. XRD pattern of a sample of TiO_2 nanotubes (NT).

perature of below 120–150 °C; a reaction time of not less than 4 h.

Catalytic photooxidation of oil diesel fraction was carried out in the presence of TiO_2 -1 and TiO_2 -2 pigments, and also TiO_2 NT. Table 2 lists the results of this research.

When diesel fraction was exposed to UV radiation with a wavelength of 380 nm in the presence of TiO_2 , sulphur content was reduced from 0.22 and 0.09 mass % to 0.12 mass % for TiO_2 -1 and TiO_2 -2 catalysts, respectively. When titanium dioxide nanotubes were used as catalyst in a similar experiment, there was the highest reduction of sulphur content in diesel fraction, as high as 0.03 mass %. Thus, titanium dioxide nanotubes display the highest activity when sulphur compounds are photocatalytically removed from diesel fraction. That is linked to their ability to transfer electrons quickly and slow down recombination processes.

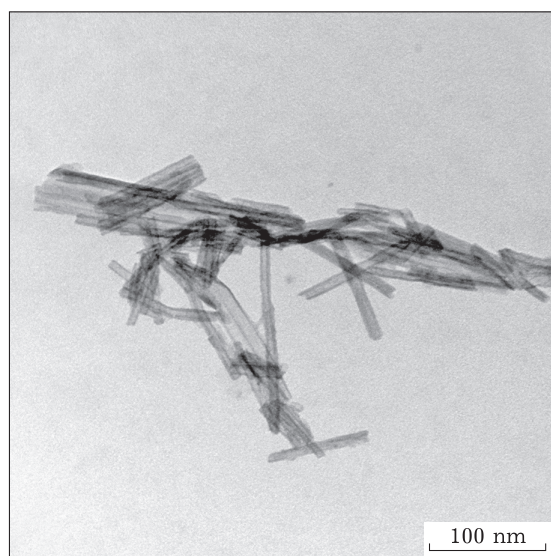


Fig. 5. Micrograph of TiO_2 nanotubes (NT).

TABLE 2

Results of diesel fraction purification by catalytic photooxidation

Catalyst	λ , nm	Residual sulphur content, %	SC removal degree, %
TiO ₂ -1	370	0.17	23.0
	380	0.09	59.0
TiO ₂ -2	370	0.19	14.0
	380	0.12	45.0
NT TiO ₂	370	0.12	45.0
	380	0.03	86.0

Note. SC stands for sulphur compounds. Process temperature is 20 ± 2 °C, raw material volume of 100 mL, catalyst and sulphur contents of 1 % and 0.22 %, respectively, in the initial DF.

CONCLUSION

The formation conditions of TiO₂ nanotubes have been determined when performing the research. The former are as follows: an alkali concentration of not more than 8 M, a reaction temperature of not above 120–150 °C, and a reaction time of at least 4 h.

Physicochemical methods have proven nanotube formation upon synthesis. According to XPA, there are low-intense reflections with maxima in the range of angles 2θ 10.535, 24.608, and 28.299 referred to titanium dioxide. A relatively intense peak near 276 nm in the IR spectrum indicates that TiO₂ nanotubes are formed. Their morphology has been examined by HRTEM; they have a diameter $d = 10\text{--}12$ nm.

Catalytic photooxidation processes of oil diesel fraction have been investigated using rutile titanium dioxide pigments and nanotubes. As determined, the latter are the most efficient catalyst.

Thus, undesirable components may be removed from oil quite efficiently when rutile titanium dioxide pigments and nanotubes are used upon catalytic photooxidation of sulphur compounds.

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