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V. D. Samokhina, V. V. Avdin,  
S. A. Khainakov, D. A. Uchaev &  
J. R. Garcia**

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# Synthesis of silica–titania composite oxide via “green” aqueous peroxy-route

I. V. Krivtsov · M. V. Ilkaeva · V. D. Samokhina ·  
V. V. Avdin · S. A. Khainakov · D. A. Uchaev ·  
J. R. Garcia

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**Abstract** The preparation procedure of silica–titania composite oxide using novel solution/sol single precursor containing titanium peroxocomplex and silicic acid has been described. Pechini-type sol–gel process has been used to prepare oxides from the aqueous precursor. Some structural, morphological and textural characteristics of the prepared material have been presented. Composite SiO<sub>2</sub>/TiO<sub>2</sub> has high surface area (*c.a.* 300 m<sup>2</sup>/g), and it is composed of anatase nanoparticles with the mean diameter of 5 nm embedded in amorphous silica, then TiO<sub>2</sub> prepared via similar method is presented as a mixture of anatase and rutile phases. The proposed synthetic procedure meets the requirements of “green chemistry”.

**Keywords** Silica–titania · Peroxotitanic acid · Aqueous peroxocomplex · Anatase nanocrystals · Si–O–Ti bonds

## 1 Introduction

Titanium dioxide, mainly in anatase phase, is a widely-known photocatalyst, efficiently oxidizing organic compounds under UV-irradiation or (more rarely) under visible

light. Since the interest in photocatalysis appeared, the study of the ways of TiO<sub>2</sub> modification for various purposes got under way. There are a number of studies reporting the modification of TiO<sub>2</sub>-based catalysts in order to enhance their catalytic activity under visible light by means of nitrogen-doping [1], iodine-doping [2] and doping with nanoparticles of noble metals. The other way of titania modification is doping or making composites with other metal oxide semiconductors [3–6]. Silica–titania materials attracted a great deal of attention due to high hydroxylation of the mixed oxide surface and generation of the acid sites of the different strength [7]. The alkoxide sol–gel route is found to be the most frequently used for the preparation of the silica–titania materials. It allows taking control over hydrolysis rate of the precursors, by means of prehydrolysis of the less reactive precursor or by usage of complexing agents, and preparing materials of high purity, homogeneity and highly-developed surface area. However, alkoxides are unstable, because of their sensitivity to air humidity, they are expensive and toxic substances, moreover, it is necessary to use significant amount of organic solvents during alkoxide-based sol–gel procedures. On the other hand, application of inorganic salts for mixed SiO<sub>2</sub>/TiO<sub>2</sub> synthesis leads to the formation of low purity oxides, due to the presence of significant amount of adsorbed cations or anions on the oxide surfaces that could affect structure formation processes and decrease catalytic activity. Besides, the high hydrolysis rate and nuclearity of inorganic precursors allow no control of aggregation, phase formation and morphology.

At the present time economic and environmental issues demand the synthesis of functional materials to be accomplished via inexpensive techniques, meeting the requirements of “green chemistry”, which implies the design of the materials and processes that minimize the use

I. V. Krivtsov (✉) · D. A. Uchaev  
Scientific-Educational Center for Nanotechnology, South Ural  
State University, Lenina Prospekt 76/1a, 303, 454080  
Chelyabinsk, Russia  
e-mail: zapasoul@gmail.com

M. V. Ilkaeva · V. D. Samokhina · V. V. Avdin  
Department of Chemistry, South Ural State University,  
Chelyabinsk, Russia

S. A. Khainakov · J. R. Garcia  
Department of Organic and Inorganic Chemistry, University of  
Oviedo, 33006 Oviedo, Spain

and generation of hazardous substances. The significant progress in this direction has been made by utilizing aqueous peroxocomplexes of titanium in the synthesis of  $\text{TiO}_2$  particles [8–10], barium titanate [11] and lead titanate powders [12], but, as it appeared to us from the analyzed literature, the synthesis of the composite silica–titania material from the single aqueous solution containing titanium peroxocomplex and silicic acid has not been reported yet. No toxic substances, such as alkoxides or volatile organic solvents, have been used during the preparation procedures, thus making the proposed technique produce less impact on the environment. This communication reports the peroxocomplex-mediated synthesis of silica–titania via Pechini-type sol–gel method [13] and some morphological, textural and structural features of the prepared composite oxide.

## 2 Materials and methods

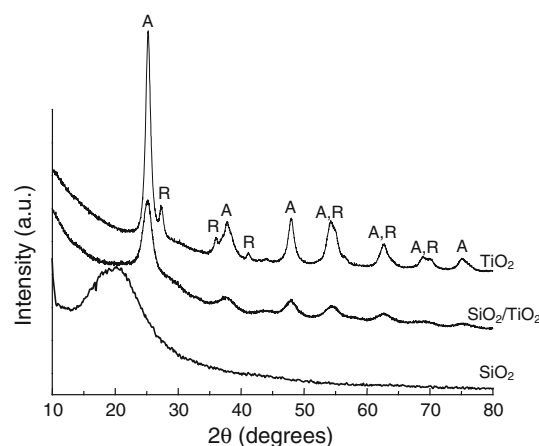
All reagents used in the present study were of analytical grade. Titanium oxysulfate hydrate ( $\text{TiOSO}_4 \cdot n\text{H}_2\text{O}$ ), containing not more than 17 % of  $\text{H}_2\text{SO}_4$ , was purchased from Aldrich, sodium metasilicate water solution ( $\text{Na}_2\text{SiO}_3$ ) was obtained from Cotarcas S.A. Titanium content in the titanium oxysulfate hydrate was determined gravimetrically. Titration method was applied in order to determine silica concentration in  $\text{Na}_2\text{SiO}_3$  solution. Required amount of titanium oxysulfate hydrate powder was dissolved in deionized water at 50 °C in excess of sulfuric acid and  $\text{Na}_2\text{SiO}_3$  was diluted in order to reach its 0.1 M concentration. The first stage of the synthesis was a preparation of the silica–titania hydrogel by co-precipitation of sodium metasilicate and titanium oxysulfate equimolar solutions with 0.1 M concentrations, the final concentration of the precursors was 0.05 M in 100 mL of the reaction mixture. The pH value of the reaction mixture was adjusted by the addition of 1.5 M sodium hydroxide solution until it reached the value of 4.6. This condition was chosen because of its closeness to the value of pH of the isoelectric point of titanium oxide [14], thus the presence of adsorbed cations or anions could be minimized. The prepared hydrogel was centrifuged at 7,000 rpm and washed out six times with deionized water. Then the hydrogel was dissolved in 10 mL of 30 wt%  $\text{H}_2\text{O}_2$  (Aldrich) in the presence of 6-fold excess of L(+)-tartaric acid (Prolabo) (in relation to  $\text{Ti}^{4+}$  ions), which was introduced into the precursor solution in order to increase the stability and solubility of titanium peroxo-species [8]. Dissolution went on for approximately 15 min, as a result the non-opalescent clear solution/sol acquired bright orange color, indicating the formation of titanium peroxocomplex [8]. At the next stage the precursor solution/sol was gradually evaporated in the

water bath until the formation of polymeric tartaric gel, dried under vacuum at 100 °C for 24 h and annealed in the air at 470 °C for 4 h. Pure  $\text{TiO}_2$  was prepared using the same procedure, but in the absence of silica source. It worth mentioning that the  $\text{SiO}_2/\text{TiO}_2$  ratio remained 1/1 after the composite oxide was obtained, as it was checked by EDS-attachment to scanning electron microscope Jeol JSM 7001F.

Powder XRD analysis was carried out using X'Pert Philips X-ray diffractometer, operating at  $\text{Cu K}\alpha$  radiation. The crystallite sizes were determined by Scherrer equation using (011) reflection for anatase phase and (110) for rutile. The lattice parameters were calculated by means of GSAS software. FTIR-spectra were registered by means of Bruker Tensor 27 spectrometer from the samples in KBr pellets. TEM investigation was carried out with help of Jeol JEM-2100 microscope. Specific surface area was calculated by the BET equation from the data obtained by low-temperature nitrogen adsorption determined by Sorbi-MS analyzer (Meta, Novosibirsk, Russia). Diffusive-reflectance UV–vis spectra were collected from the samples supported on barium sulfate pellets by Shimadzu UV-2700 instrument with integrated sphere attachment. The band gap energy was calculated using Kubelka–Munk method, providing by UVProbe software.

## 3 Results and discussion

The method of  $\text{TiO}_2$  preparation from titanium peroxocomplexes via Pechini-like sol–gel process is widely known [15], as well as formation of  $\text{TiO}_2$  particles in hydrothermal conditions [16]. However this route is rarely applied to composite oxide synthesis, such as silica–titania. Mostly, the preparation of materials of this kind is limited to dispersing titanium peroxocomplexes of low nuclearity



**Fig. 1** XRD patterns of the  $\text{SiO}_2$ ,  $\text{TiO}_2$  and  $\text{SiO}_2/\text{TiO}_2$  samples, where A stands for anatase phase and R is for rutile

**Table 1** The lattice parameters and crystallite sizes obtained from XRD data for TiO<sub>2</sub> and SiO<sub>2</sub>/TiO<sub>2</sub> samples

Sample	Lattice parameters			Crystallite size, nm
	a	b	c	
TiO <sub>2</sub> anatase	3.785 ± 0.001	3.785 ± 0.001	9.454 ± 0.001	9.5
TiO <sub>2</sub> rutile	4.581 ± 0.002	4.581 ± 0.002	2.932 ± 0.001	17.0
SiO <sub>2</sub> /TiO <sub>2</sub> anatase	3.771 ± 0.001	3.771 ± 0.001	9.431 ± 0.003	5.1

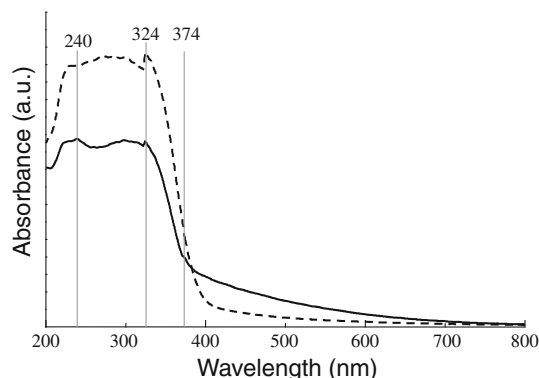
onto preformed silica particles [17], but this excludes the possibility of formation of homogeneous material. At the same time, formation of Si–O–Ti linkages might lead to the formation of acid-sites more readily generating free radicals under UV-excitation, than pure TiO<sub>2</sub> [7].

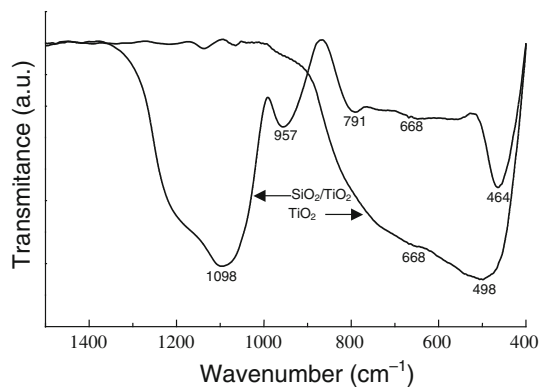
We have found that silica–titania hydrogel can be dissolved in hydrogen peroxide 30 wt% water solution. There are two plausible explanations to the fact: first, Ti<sup>4+</sup> ions in the hydrogel form soluble peroxocomplexes and transit to the liquid phase causing cleavage of Si–O–Ti linkages, which in turn leads to the formation of monomeric silicic acid, without tendency to polymerization due to low pH values. Second, the hydrogel can be dispersed in hydrogen peroxide leading to the formation of the non-opalescent solution of the small nanoclusters composed of silica units and titania peroxo-species. Despite the fact that determination of the exact mechanism is the topic for further investigation, now we can state that the proposed method allows preparation of a novel precursor for the composite silica–titania materials. It is worth mentioning that other common ways of preparing silica–titania from inorganic sources would not lead to the same result as the method proposed in the present study. For instance, using conventional co-precipitation technique, it is impossible to control nuclearity and polymerization rate of the titania hydroxo-species, because even in the low pH region they are never present in the monomeric forms. The other imaginable method is to introduce complexing agent into the solution of oxytitanium sulfate, before its mixing with silica salt, in order to slow down the hydrolysis rate of Ti<sup>4+</sup> ions. In this method the oxides would form under the influence of sulfate and sodium ions, which in turn, after the annealing, might lead to the formation of titania with high sodium content.

The presence of silica has great influence on the formation of titania phase. From XRD data (Fig. 1) it is seen that TiO<sub>2</sub> is present in the form of a pure anatase (ICDD PDF2 99-101-0957) phase in the silica–titania sample, and no presence of titanium silicate (ICDD PDF2 00-043-0055) phases are detected. In the absence of silica source, the mixture of anatase and rutile (ICDD PDF2 99-101-0954) phase oxide is formed at the same experimental conditions. Silica prepared at such conditions has amorphous nature and shows no diffraction peaks; that is why the general crystallinity of the SiO<sub>2</sub>/TiO<sub>2</sub> sample is lower than it is

observed for TiO<sub>2</sub>. The data obtained for TiO<sub>2</sub> and SiO<sub>2</sub>/TiO<sub>2</sub> samples from XRD analysis are summarized in Table 1. According to XRD analysis the crystallite size of anatase phase is significantly reduced in the composite oxide. The lattice parameters calculated for both investigated samples reveal another difference in their structures, the unit cell of anatase crystal in SiO<sub>2</sub>/TiO<sub>2</sub> sample is found to be somewhat smaller than it is for pure titanium oxide.

DR UV–vis spectrophotometry is one of most frequently used techniques for characterization of the materials based on TiO<sub>2</sub>. As it was found for titanium silicalite (known as TS-1) [18], the absorption in the regions of 200–212 nm and 260–280 nm corresponds to charge transfer process in isolated internal [TiO<sub>4</sub>] and [HOTiO<sub>3</sub>] units. The peak at 240 nm is clearly seen only in the spectrum of SiO<sub>2</sub>/TiO<sub>2</sub> sample, showing the presence of isolated titania tetrahedral units on the silica surface. The band at 312–328 nm and the absorption area at 370–380 nm are attributed to Ti(IV) species in large titania particles (Fig. 2). The other interesting feature of the DR UV–vis spectra is the absorbance of visible irradiation. Etacheri et. al. [19] studied the formation of TiO<sub>2</sub> in the presence of excess hydrogen peroxide, and they found that titania prepared from the gel containing 16-fold excess of H<sub>2</sub>O<sub>2</sub> absorbed light in the visible range of the spectrum and had a narrow band gap, while the reference sample showed no absorption in that region. The band gap energy for pure TiO<sub>2</sub>, calculated with the use of Kubelka–Munk method, equaled 3.25 eV, then the addition of silica caused broadening of the band gap

**Fig. 2** DR UV–vis spectra of the TiO<sub>2</sub> (dashed line) and SiO<sub>2</sub>/TiO<sub>2</sub> (straight line) samples



**Fig. 3** FTIR spectra of the TiO<sub>2</sub> and SiO<sub>2</sub>/TiO<sub>2</sub> samples

and that parameter for SiO<sub>2</sub>/TiO<sub>2</sub> sample was found to be 3.39 eV.

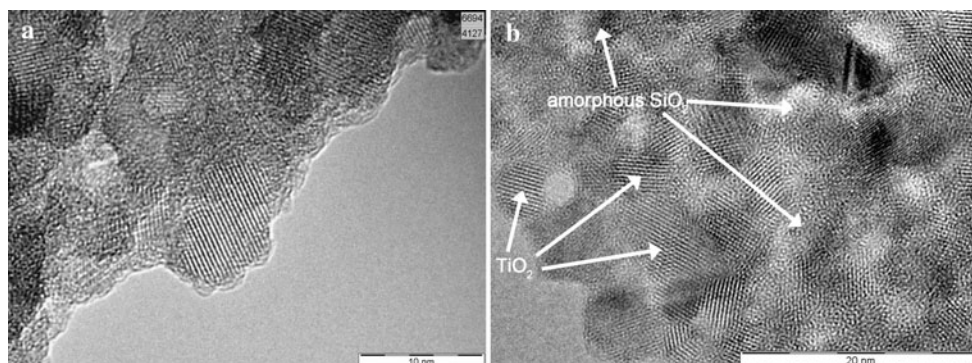
FTIR spectroscopy is one of the informative techniques allowing characterization of materials containing amorphous phase. Moreover, it is found to be of great use in studying of the composite oxide, as we have shown earlier examining silica–zirconia xerogels [20]. On the FTIR spectrum (Fig. 3) of pure titania only the broad absorption in the region from 900 to 400 cm<sup>-1</sup> is present, corresponding to Ti–O–Ti various modes vibration. The most intensive absorption on the spectrum of the composite oxide with the maximum at 1,098 cm<sup>-1</sup> corresponds to TO<sub>3</sub> mode of SiO<sub>2</sub> with the shoulder at 1,200 cm<sup>-1</sup> (LO<sub>3</sub> mode) [21]. Presence of the silica TO<sub>2</sub> mode at 791 cm<sup>-1</sup> indicates that the samples contain SiO<sub>2</sub> fragments which are not bonded to the titania units [21]. The intensive band at 957 cm<sup>-1</sup> can be attributed to surface silanols, as well as to Si–O–Ti linkages. Taking into account that the intensity of surface silanol vibrations is usually low [7], it is more probable that this peak corresponds to Si–O–Ti bond vibrations.

Transmission electron microscopy (Fig. 4a) shows crystals of pure TiO<sub>2</sub> and the presence of very small titania nanocrystals with the mean size about 5 nm embedded in the amorphous silica matrix for SiO<sub>2</sub>/TiO<sub>2</sub> material

(Fig. 4b). Crystal sizes determined by TEM are found to be in good agreement with the results of XRD analysis. From both methods the reduced size of anatase crystals in the composite is obvious. Formation of TiO<sub>2</sub> particles during the composite oxide synthesis is hindered, because of the inhibited diffusion of the formed crystalline nuclei due to the presence of amorphous polymerized silica. The SiO<sub>2</sub>/TiO<sub>2</sub> sample seems more porous on the TEM image (Fig. 4) than it should be in the accordance with the results obtained from the low-temperature nitrogen adsorption. The specific surface area for pure TiO<sub>2</sub> is found to be 95 m<sup>2</sup>/g, then the composite oxide has much more developed surface with a value of 300 m<sup>2</sup>/g. It is likely that the enhanced surface area of the silica–titania sample is the consequence of formation of the separated amorphous SiO<sub>2</sub> phase during the annealing stage.

#### 4 Conclusion

The prepared composite has several interesting properties making this material promising for the application in photocatalysis, such as presence of Si–O–Ti linkages, detected by FTIR spectroscopy, in its structure, high surface area, 100 % pure anatase phase of TiO<sub>2</sub> contained in the composite. Anatase has very small crystallite size (approximately 5 nm) in the composite, because silica suppresses the growth and aggregation of TiO<sub>2</sub> crystals in the larger domains, thus contributing to the particle size reducing and the surface area enhancing of the composite oxide. As it seems for us these properties can be the result of formation of SiO<sub>2</sub>/TiO<sub>2</sub> from the precursor composed of silicic acid and titanium peroxocomplex having low-nuclearity, high stability and no tendency to hydrolyze and form inorganic gel in the water solution. However, the mechanisms of the precursor formation and evolution of oxide phases from it are not clear and demand special attention. Thus the detailed study of structure formation, morphological, textural properties and catalytic activity of



**Fig. 4** HRTEM images of the TiO<sub>2</sub> **a** and SiO<sub>2</sub>/TiO<sub>2</sub> **b** samples

the silica–titania composite oxides prepared via proposed route in comparison with the  $\text{SiO}_2/\text{TiO}_2$  prepared via conventional inorganic sol–gel method is the subject of the further investigation and discussion. Beside, the precursor composed of silicic acid and titania peroxocomplex might be a suitable in the preparation of thin films, which is also going to be discussed in the next studies.

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