

ИНСТИТУТ ТЕХНИЧКИХ НАУКА САНУ

Кнез Михаилова 35/IV

Београд

Предмет: Захтев за покретање поступка за избор дипл. инж. Ивана Дуганџића,
истраживача приправника у звање истраживач сарадник

НАУЧНОМ ВЕЋУ ИНСТИТУТА ТЕХНИЧКИХ НАУКА САНУ

Молим Вас да, у складу са Правилником о поступку и начину вредновања, и квантитавном исказивању научноистраживачких резултата истраживача (Сл. Гласник РС, бр. 38/08), и Правилником о стицању звања истраживач сарадник, Научно веће Института техничких наука САНУ покрене поступак за избор у звање истраживач сарадник.

За чланове комисије за припрему извештаја научном већу предлажем:

- др Оливеру Милошевић, научног саветника Института техничких наука САНУ
- др Лидију Манчић, вишег научног сарадника Института техничких наука САНУ
- др Миодрага Здујића, научног саветника Института техничких наука САНУ

У прилогу достављам:

1. биографију
2. диплому завршених основних студија
3. доказ о уписаним докторским студијама
4. библиографију са копијом рада

У Београду

13.09.2012

Подносилац захтева:

Иван Дуганџић, дипл. инж.

Иван Дуганџић
истраживач приправник ИТН САНУ

Биографија Иван М. Дуганџић

Иван Дуганџић рођен је 16.08.1981. године у Београду, Република Србија. Основне студије уписао је школске 2000/2001 године на Технолошко-металуршком факултету Универзитета у Београду и завршио их 2009. са просечном оценом 8.14 и 10 на дипломском раду “Експериментално одређивање и моделовање вискозности бинарних система алкохола са алканима, ацетоном и п-бутил ацетатом”. У периоду од јуна 2006. до јануара 2007. боравио је на студијској пракси и усавршавању у Антверпену, Белгија. Постдипломске студије уписао је 2009. године на Технолошко-металуршком факултету Универзитета у Београду на катедри за Хемијско инжењерство. Тренутно је на трећој години студија.

У Институту техничких наука САНУ запослен је од 2009. године као истраживач приправник. Ангажован је на пројекту основних истраживања ОИ 172035 “Рационални дизајн и синтеза биолошких активних и координационих једињења и функционалних материјала, релевантних у (био) нанотехнологији” и на пројекту интегралних и мултидисциплинарних истраживања ИИИ 45020 “Материјали редуковане димензионалности за ефикасну апсорпцију светлости и конверзију енергије”.

Области интересовања: развој и оптимизација процеса синтезе оптички активних наноструктурних материјала методама спреј пиролизе и хидротермалне синтезе, савремене методе карактеризације, фотокаталитички материјали и површинска модификација.

Библиографија Иван Дуганчић

М 21 Рад у врхунском међународном часопису:

1. Dugandžić I M, Jovanović D J, Mančić L T, Zheng N, Ahrenkiel S P, Milošević O B, Šaponjić Z V, Nedeljković J M Surface modification of submicronic TiO₂ particles prepared by ultrasonic spray pyrolysis for visible light absorption 2012 *Journal of Nanoparticle Research* **14** (10) 1157 (DOI 10.1007/s11051-012-1157-1)

М 34 Саопштење са међународног скупа штампаног у изводу:

1. **Ivan Dugandžić**, Vesna Lojpur, Lidija Mančić, Maria Eugenia Rabanal, Olivera Milošević, Dense spherical rare oxide particles synthesis *via* spray pyrolysis of polymeric precursor solution, YUCOMAT 2010, The Twelfth Annual Conference, Herceg Novi, Montenegro, *September 6-10*, The Book of Abstracts, **p92**
2. **Ivan Dugandžić**, Vesna Lojpur, Katarina Marinković, Lidija Mančić, Maria Eugenia Rabanal, Olivera Milošević, Nanophosphors synthesis through solvothermal route, ModTech 2011, International Conference in Modern Manufacturing Technologies, Chisinau, Republic of Moldavia, *May 25-27, 2010*, The Book of Abstracts, **p.369**
3. Lidija Mančić, Katarina Marinković, **Ivan Dugandžić**, Vesna Lojpur, Olivera Milošević, Soft chemistry routes for synthesis of 3D and 1D nanostructures, 1st Conference of the Serbian Ceramic Society, Belgrade, Serbia, *March 17-18, 2011*, Program and the Book of Abstracts, **p.45**
4. **Ivan Dugandžić**, Dragana Jovanović, Lidija Mančić, Zoran Šaponjić, Jovan Nedeljković, Olivera Milošević, Assembling and spheroidization of colloidal TiO₂ nanoparticles *via* aerosol route, SM-2011, The Ninth Students' Meeting, Novi Sad, Serbia, *November 16-18, 2011*, Programme and the Book of Abstracts, **p29**
5. **Ivan Dugandžić**, Dragana Jovanović, Lidija Mančić, Zoran Šaponjić, Olivera Milošević, Jovan Nedeljković, Aerosol-assisted low-temperature processing of colloidal TiO₂ nanoparticles: Two different manners for improving the optical properties, Tenth young researchers' conference materials science and engineering, Belgrade, Serbia, *December 21-23, 2011*, Program and the Book of Abstracts, **p29**
6. **Ivan Dugandžić**, Dragana Jovanović, Lidija Mančić, Zoran Šaponjić, Olivera Milošević, Jovan Nedeljković, Aerosol-assisted processing of dopamine-TiO₂ colloidal solution, Advanced Ceramic and Application I, Belgrade, Serbia, *May 10-11, 2012*, Program and the Book of Abstracts, **p27**
7. Lidija Mančić, **Ivan Dugandžić**, Dragana Jovanović, Zoran Šaponjić, Jovan Nedeljković, Olivera Milošević, Surface modified TiO₂ particles obtained through aerosol processing of

colloid, NANO 2012, XI International Conference on Nanostructured Materials, *August 26-31, 2012*, Program and the Book of Abstracts CD, **P-116**

8. **Ivan Dugandžić**, Dragana Jovanović, Lidija Mančić, Zoran Šaponjić, Jovan Nedeljković, Olivera Milošević, The optical properties of dopamine-TiO₂ submicronic sized particles, ICOM 2012, The 3rd International conference of the Physics of optical Materials and Devices, *September 3-6, 2012*, Program and the Book of Abstracts, **p23**

РЕПУБЛИКА СРБИЈА



УНИВЕРЗИТЕТ У БЕОГРАДУ
ТЕХНОЛОШКО - МЕТАЛУРШКИ ФАКУЛТЕТ

ДИПЛОМА

О СТЕЧЕНОМ ВИСОКОМ ОБРАЗОВАЊУ

ИВАН (Милош) ДУГАНЦИЋ

РОЂЕН 16. АВГУСТА 1981. ГОДИНЕ У БЕОГРАДУ, САВСКИ ВЕНАЦ, РЕПУБЛИКА СРБИЈА, УПИСАН ЈЕ 2000/01. ШКОЛСКЕ ГОДИНЕ, А ДАНА 25. ЈУНА 2009. ГОДИНЕ ЗАВРШИО ЈЕ СТУДИЈЕ НА ТЕХНОЛОШКО-МЕТАЛУРШКОМ ФАКУЛТЕТУ, ОДСЕК - **ХЕМИЈСКО ИНЖЕЊЕРСТВО** СА ОПШТИМ УСПЕХОМ 8,14 (ОСАМ И 14/100) У ТОКУ СТУДИЈА И ОЦЕНОМ 10 (ДЕСЕТ) НА ДИПЛОМСКОМ ИСПИТУ.

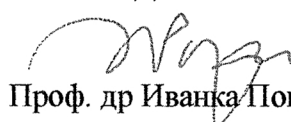
НА ОСНОВУ ТОГА ИЗДАЈЕ МУ СЕ ОВА ДИПЛОМА О СТЕЧЕНОМ ВИСОКОМ ОБРАЗОВАЊУ И СТРУЧНОМ НАЗИВУ

ДИПЛОМИРАНИ ИНЖЕЊЕР ТЕХНОЛОГИЈЕ

Редни број из евиденције о издатим дипломама 9758

У Београду, 25. јуна 2009. године

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Проф. др Иванка Поповић

РЕКТОР


Проф. др Бранко Ковачевић



Република Србија
Универзитет у Београду
Технолошко-металуршки факултет
Д.Бр.2009/4045
Датум: 20.12.2011. године

На основу члана 161 Закона о општем управном поступку и службене евиденције издаје се

УВЕРЕЊЕ

Дуганџић (Милош) Иван, бр. индекса 2009/4045, рођен 16.08.1981. године, Београд, Савски венац, Република Србија, уписан школске 2011/2012. године, у статусу: самофинансирајући; тип студија: Докторске академске студије; студијски програм: Хемијско инжењерство 08.

Према Статуту факултета студије трају (број година): три године.
Рок за завршетак студија: у двоструком трајању студија.

Ово се уверење може употребити за регулисање војне обавезе, издавање визе, права на дечији додатак, породичне пензије, инвалидског додатка, добијања здравствене књижице, легитимације за повлашћену возњу и стипендије.



Овлашћено лице факултета



Република Србија
Универзитет у Београду
Технолошко-металуршки факултет
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Овлашћено лице факултета

Surface modification of submicronic TiO₂ particles prepared by ultrasonic spray pyrolysis for visible light absorption

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Abstract Spherical, submicronic TiO₂ assemblage with high specific surface area and controllable phase composition was prepared in the process of ultrasonic spray drying/pyrolysis in a wide temperature range (150–800 °C) by using as a precursor aqueous colloidal solution consisting of TiO₂ nanoparticles (4.5 nm). Submicronic, soft and grained spherical TiO₂ particles ($d = 370\text{--}500$ nm) comprising clustered nanocrystals (<10 nm) were obtained at low processing temperature, while particle densification, intensive growth of the clustered primary units and anatase-to-rutile transformation (~30 wt%) were observed at the higher temperatures. Detailed structural and morphological characterisation were performed by X-ray powder diffraction, scanning and field emission electron microscopy, transmission electron microscopy, and laser

particle size analysis. Moreover, the surface modification of TiO₂ particles through the formation of charge-transfer (CT) complex was achieved with different ligands: ascorbic acid, dopamine, catechol, 2,3-dihydroxynaphthalene, and anthrarobin. Optical properties of the surface-modified TiO₂ particles were studied by using diffuse reflection spectroscopy. The binding structure between the surface titanium atoms and different ligands was determined by using Fourier transform infrared spectroscopy. The formation of CT complexes induced significant red shift of optical absorption in comparison to unmodified TiO₂ particles.

Keywords TiO₂ nanoparticles · Spray drying/pyrolysis · Surface modification · Charge-transfer complex · Optical properties

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Introduction

Titanium dioxide (TiO₂) is one of the most studied semiconductors suitable for use in heterogeneous catalysis (López-Muñoz et al. 2011), photocatalysis (Hashimoto et al. 2005), solar cells (Grätzel 2003), production of hydrogen, ceramics, electric devices, as well as white pigment, corrosion-protective coatings, gas sensors (Diebold 2003), etc. Also, TiO₂ nanoparticles deposited on textile fibers show antibacterial and self-cleaning activities (Mihailović et al. 2010). It is well known that the bulk TiO₂ material appears in three major crystal phases: rutile (tetragonal), anatase

(tetragonal), and brookite (rhombohedral). Rutile is a high temperature stable phase and has band gap energy of 3.0 eV (415 nm), while the anatase formed at a lower temperature with band gap energy of 3.2 eV (380 nm), and refractive index of 2.3, is common in fine-grained (nanoscale) natural and synthetic samples (Kim et al. 2005). Due to its large band gap ($E_g = 3.2$ eV), TiO_2 absorbs less than 5 % of the available solar photons. Dye-sensitization is one of the most promising pathways for increasing the TiO_2 photoactivity through intensive utilization of visible light in solar cells (Pan et al. 2011). Depending on the mechanism for electron injection from the dye to the semiconductor, dye-sensitized TiO_2 solar cells (DSSC) can be classified into two types: indirect and direct. In indirect DSSCs, photoexcitation by absorption in the dyes is followed by electron injection from the excited dyes to TiO_2 . In direct DSSCs, electrons are additionally injected by direct electron injection from the dyes to TiO_2 by photoexcitation of the dye-to- TiO_2 charge-transfer (CT) bands (Tae et al. 2005). Many benzene derivatives with phenolic or carboxylic groups are able to make very stable complexes with the TiO_2 surface involving replacement of TiO_2 surface hydroxyl groups by deprotonated ligands (Ye et al. 2011). The catechol molecule, one of the simplest and smallest sensitizers, adsorbs dissociatively at the TiO_2 surface through the deprotonated hydroxyl groups (Duncan and Prezhdo 2007). Several relevant reports have proposed direct photoinjection of electrons from the catechol ground state to the conduction band of TiO_2 (Persson et al. 2000; Syres et al. 2010). The related compounds such as ascorbic acid and salicylic acid also give strong bands in the visible region upon binding to TiO_2 (Hines and Boltz 1952; Hultquist 1964).

So far, the surface modification of commercial TiO_2 nanoparticles with benzene derivatives (mainly catechol and salicylic acid) have been studied (Liu et al. 1999; Li et al. 2006). Over the last several years, more attention was focused on the formation of a CT complex of colloidal TiO_2 with bidentate benzene derivatives (Janković et al. 2009) and enediol ligands (Janković et al. 2010; Savić et al. 2012). The origin of the significant band gap changes observed in colloidal TiO_2 after modification lies in the fact that surface Ti atoms, owing to the large curvature of nanoparticles, adjust their coordination environment to form under-coordinated sites (Chen et al. 1999). These five-

coordinated defect sites are the source of novel enhanced and selective reactivity of nanoparticles toward bidentate ligand binding. It should be pointed out that the formation of bidentate surface complexes is possible only if the ligand possesses at least two donor groups, or one group containing two donor atoms (Macyk et al. 2010). Binding photosensitizers onto TiO_2 surfaces via catechol group is a very promising method for creating stable interfaces for use in solar cell applications, namely catechol and its derivatives, can act as an effective anchor for binding dye sensitizer onto inorganic surfaces in high density and binding strength (Ye et al. 2011). Grätzel et al. reported a ruthenium-polypyridine complex containing catechol that could adhere effectively onto TiO_2 semiconductor nanoparticles as effective photosensitizers for photovoltaic cells (Rice et al. 2000). This material might find interesting application in physiological environments because of potential long-term stability in wet conditions and resistance to oxidation (Ye et al. 2011).

This article presents for the first time aerosol-assisted processing of spherical submicronic particles from colloidal TiO_2 solution that can be successfully modified with different ligands: ascorbic acid, dopamine, catechol, 2,3-dihydroxynaphthalene, and anthrarobin.

Aerosol or spray drying/pyrolysis process is basically a soft chemistry route employing the “bottom-up” approach for powder processing. Its diversity is a consequence of the combinatorial tuning of the independent processing parameter, e.g., nature of precursor solution, type of atomisation, manner of aerosol decomposition energy transfer to the system, processing temperature and time, as extensively reported in the literature (Okuyama and Lenggoro 2003; Milosevic et al. 2009; Boissiere et al. 2011).

The ultrasonic spray pyrolysis of colloidal TiO_2 precursor solution was already reported in the literature (Nedeljković et al. 1997; Saponjić et al. 1998; Lee et al. 1999). Here, for the first time, aerosol processing conditions were optimized towards obtaining highly spherical submicronic TiO_2 particles with tailored crystallinity, phase composition, and surface structure. It is known that the submicron-sized anatase TiO_2 particles ($d = 0.2\text{--}0.3\ \mu\text{m}$) can be used as light scattering centers in dye-sensitized solar cells (Lan et al. 2010). Due to the nanostructured nature, it is shown that surface-modified soft assemblage of TiO_2

nanoparticles synthesized at lower temperatures keep their unique ability to absorb light through direct CT by photoexcitation of the ligand-to-TiO₂ bands, conventionally associated with colloidal systems.

Experimental

Synthesis and characterisation of TiO₂ colloid

Colloidal solution of TiO₂ nanoparticles was prepared in a manner analogous to a previously proposed procedure (Rajh et al. 1996). All the chemicals were of the highest purity available and were used without further purification (Aldrich, Fluka). Milli-Q deionized water with resistivity of 18.2 MΩ cm⁻¹ was used as a solvent. Briefly, 8 ml of TiCl₄ cooled to -20 °C was added drop-wise to water held at 4 °C under vigorous stirring and then kept at this temperature for 30 min. Initially, the pH of the solution was about 0. Slow growth of the particles was achieved by using dialysis at 4 °C against water until the pH value of 3.5 was reached. The concentration of the TiO₂ colloids was determined using spectrophotometric measurements of the Ti(IV)-peroxide complex obtained after complete dissolution of TiO₂ in concentrated H₂SO₄ (Thompson 1984; Jeffery et al. 1989). The sizes of the colloidal particles and their phase composition were estimated from transmission electron microscopy (TEM) and selected electron diffraction data (SAED).

Synthesis of submicronic TiO₂ particles

Synthesis of submicronic TiO₂ particles was performed using a laboratory setup for ultrasonic spray pyrolysis, as previously explained (Milosevic et al. 2009). It consists of an ultrasonic atomizer for aerosol droplets generation (RBI, France) with three transducers operating at a frequency of 1.3 MHz, tubular flow reactor with three independently controlled temperature zone, diffusion dryer (Model 3062, TSI), and electrostatic precipitator. Aerosol, generated from a 0.05 M TiO₂ colloid precursor was introduced into a tubular flow reactor using a nitrogen flow of 0.0333 dm³ s⁻¹ corresponding to the residence time of 33 s in the reactor. The processing temperatures were varied in a wide temperature range from 150 to 800 °C. Based on the precursor physico-chemical

characteristics and applied atomisation frequency, the aerosol droplet was calculated to be 3.46 μm (Lang 1962; Liu et al. 1986).

Surface modification of TiO₂ particles

The synthesized powders were modified by the following procedure: 30 mg of bare TiO₂ particles were dispersed in 20 ml H₂O in ultrasonic bath; pH was adjusted to 3 by adding a few drops of 0.1 M HCl solution; at the end, 0.1 mmol of ligand is added. Various ligands were used: ascorbic acid, dopamine (3,4-dihydroxyphenethylamine), catechol (1,2-dihydroxybenzene), 2,3-dihydroxynaphthalene, and anthra-robin (3,4-dihydroxyanthranol). The obtained suspensions were dried in vacuum for 10 h at 40 °C. Surface modification, indicated by powder coloration, was the most intensive for the TiO₂ powder obtained at 150 °C, smaller for samples obtained at 300 °C, and non-existing for the samples obtained at higher processing temperatures. Because of that the optical properties of surface-modified TiO₂ powders were presented only for the samples obtained at 150 °C.

Characterization of TiO₂ particles

The morphology of TiO₂ particles was determined using scanning electron microscopy (Philips XL30 SEM) equipped with secondary, backscattered and an energy dispersive X-ray detector, as well as TEM (JEOL-JEM 2100 LaB₆ operated at 200 kV). Images were acquired with a Gatan Orius camera and analyzed using Gatan Digital Micrograph software.

Samples were embedded in araldite resin (Ted Pella, Inc.) and sectioned at room temperature to 80–100 nm thickness using a RMC PowerTome XL ultramicrotome with a Diatome diamond blade or glass knife.

Particle size distributions were determined by the laser particle sizer (Mastersizer 2000, Malvern Instruments Ltd., UK). For each run, the powder was de-agglomerated in an ultrasonic bath for 30 min.

Powder phase composition was analyzed using X'Pert Philips powder diffractometer with Cu Kα radiation at 40 kV and 40 mA. The 2θ range was from 10° to 100° with a step scan of 0.02 and a counting time of 10 s per step. Unit cell parameters and crystallite size (CS) were determined using Topas Academic software (Coelho 2004).

Optical properties of surface-modified TiO₂ particles were studied in details using diffuse reflection measurements in UV–Vis spectral range (Labsphere RSA-PE-19), while structure of surface CT complexes was investigated using FTIR spectroscopy (Termo Nicolet 380).

Results and discussion

Conventional TEM imaging at high magnification of precursor colloidal TiO₂ nanoparticles, shown in Fig. 1, reveals that nearly spherical nanoparticles have low degree of crystallinity and average size of 4.5 nm. The inset in Fig. 1 shows a fast Fourier transform of the image, revealing that observed lattice fringe is close to the (101) anatase value (0.36 nm).

Aerosol processing of TiO₂ nanoparticles is based on the formation of aerosols of precursor solutions followed by controlled aerosol decomposition at high temperature. During decomposition, in dependence of temperature and time, the aerosol droplets undergo evaporation/drying, precipitation, and thermolysis in a continuous online process. Consequently, spherical, solid, agglomerate-free, either submicronic nanostructured, or nanoscaled particles could be obtained through the mechanism of primary nanoparticle coalescence, collision, and sintering (Milosevic et al. 2009). Because the heterogeneous gas/liquid–solid reaction occurs at the level of droplets with sizes of only a few micrometers, compositional segregation is prevented, while high heating/cooling rates additionally enable generation of metastable materials (Wang

et al. 2006). In general, the advantages of aerosol processing are recognized in possibility to design the particle morphology and to control the particle size, chemical composition, and crystallinity.

The SEM images of TiO₂ particles obtained through aerosol processing of colloids consisting of 4.5 nm TiO₂ nanoparticles at different temperatures are shown in Fig. 2. It can be noticed that spherical, non-agglomerated TiO₂ particles are obtained at all processing temperatures. Closer inspection indicates rough particle surfaces due to the presence of small primary building units.

Roughness/porosity of TiO₂ particles decreases with the increase of processing temperature. Fairly narrow particle size distributions were found for all TiO₂ samples (Supporting Information, Fig. A1). Also, the average particle size, d , decreases (499, 433, 376, and 373 nm) with the increase of the processing temperatures (150, 300, 500, and 800 °C, respectively) due to closer packing of the primary units.

Low magnification TEM measurements of TiO₂ particles obtained at 150 °C (Fig. 3a) confirmed SEM observations regarding the particle size and morphology (Fig. 2a). Moreover, the high magnification TEM image (Fig. 3b) indicated polycrystalline nature of the synthesized particles, with grain size that corresponds well to the size of precursor TiO₂ nanoparticles. Additional TEM measurements of the submicronic TiO₂ sample synthesized at 150 °C and sectioned by ultramicrotome showed absence of any cavity within particles (Fig. 3c). Also, the submicronic TiO₂ particles processed at higher temperature (800 °C) have spherical filled morphology with apparent substructure (Fig. 3d). The size of the substructural units varies from 20 to 80 nm.

XRPD patterns of the TiO₂ powders obtained through aerosol-assisted processing of TiO₂ colloids are shown in Fig. 4. Due to different processing temperatures, the appearance of different crystalline phases, as well as their conversion, was noticed (see Table 1).

As expected, the TiO₂ submicronic particles obtained at lower processing temperatures are mainly composed from anatase crystal phase. Presence of diffraction lines around $2\theta \sim 10^\circ$ implicates appearance of monoclinic protonated titanates with different content of interlayer water (H₂Ti₅O₁₁·3H₂O at 150 °C and H₂Ti₃O₇ at 300 °C). Both phases have similar

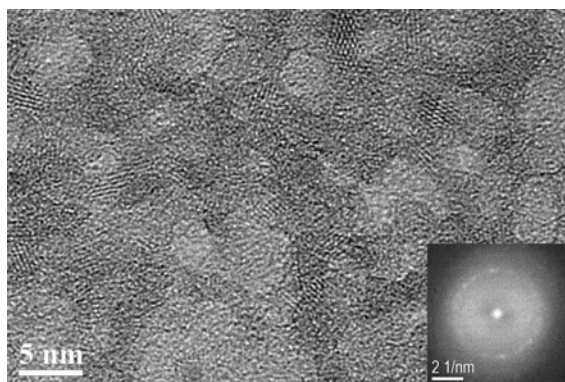


Fig. 1 Typical TEM image of colloidal TiO₂ nanoparticles used as a precursor in the process of ultrasonic spray drying/pyrolysis. *Inset* shows SAED image

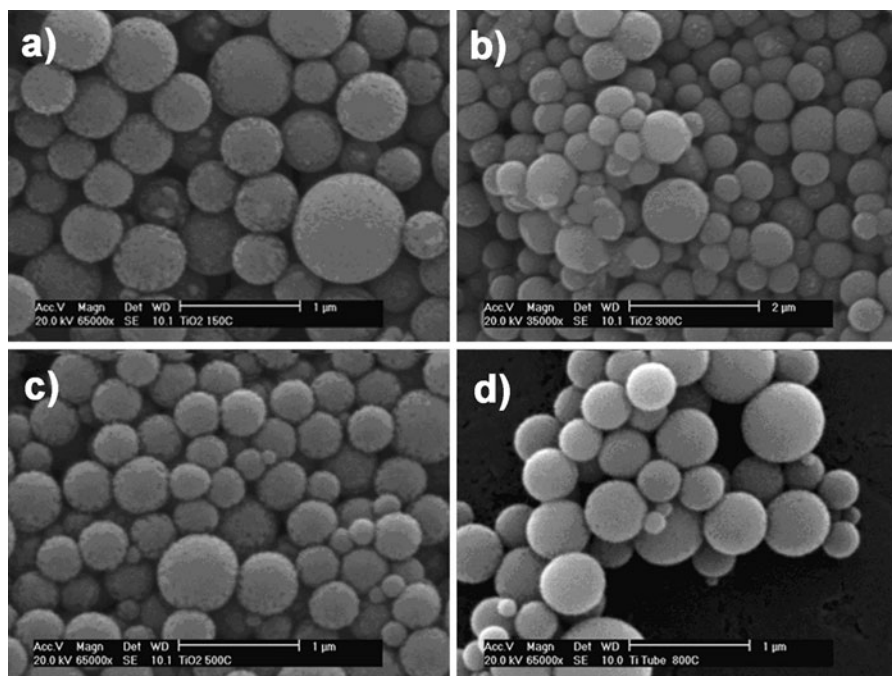


Fig. 2 Typical SEM images of TiO_2 particles obtained at different temperatures **a** 150 °C, **b** 300 °C, **c** 500 °C, and **d** 800 °C

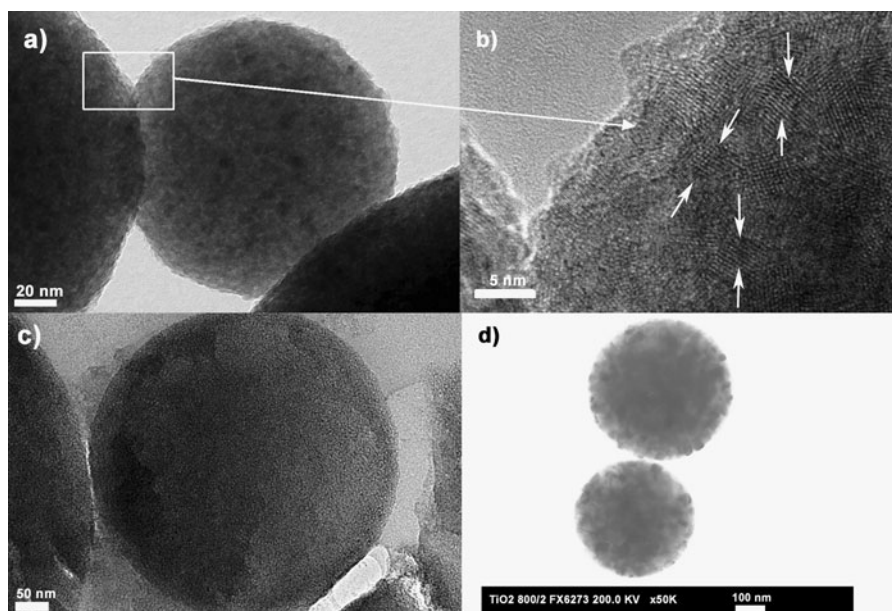


Fig. 3 TEM images of **a** TiO_2 particles obtained at 150 °C, **b** marked region at a higher magnification, **c** cross section of the particle obtained at 150 °C, and **d** TiO_2 particles obtained at 800 °C

structural features as anatase due to the existence of the four-edge sharing TiO_6 octahedra and their zigzag configuration (Ishiguro et al. 1978; Sasaki et al. 1992).

The presence of the metastable $\text{TiO}_2(\text{B})$ phase, characterized by the Freudenbergite type structure is also noticeable in all samples. This monoclinic TiO_2

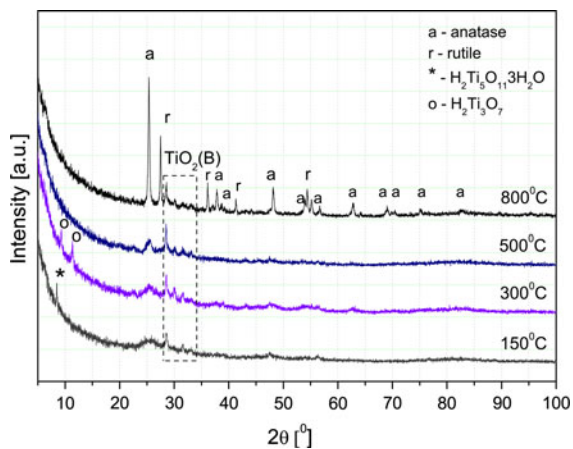


Fig. 4 XRPD patterns of TiO_2 powders synthesized through aerosol-assisted processing of colloids consisting of 4.5 nm TiO_2 nanoparticles at different temperatures

modification poses lower density and a structure characterized by a combination of the edge- and corner-sharing TiO_6 octahedra forming the channels. In powder obtained through aerosol-assisted processing of TiO_2 colloids at 500 °C, $\text{TiO}_2(\text{B})$ is the only additional phase beside anatase, whereas a further increase of processing temperature results in rutile appearance.

As it already pointed out in the literature, appearance of the $\text{TiO}_2(\text{B})$ phase during thermal treatment represents an intermediate step towards to the more stable TiO_2 rutile phase (Morgadojr et al. 2007). Approximately 30 wt% of anatase is converted to the rutile phase in powder processed at 800 °C. Dimensions of anatase CS (Table 1) are in good agreement with those estimated by observation in HRTEM images (Fig. 3b).

Table 1 Powder phase composition and XRPD based microstructural data

T (°C)	Powder phase composition		
150	Anatase, TiO_2	TiO_2 (B)	$\text{H}_2\text{Ti}_5\text{O}_{11} \cdot 3\text{H}_2\text{O}$
	Tetragonal, I41/amdS	Monoclinic, C2/m	Monoclinic, C2/m
	$a = 3.859$ [8] Å	$a = 12.25$ [1] Å	$a = 23.46$ [2] Å
	$c = 9.73$ [3] Å	$b = 3.769$ [5] Å	$b = 3.848$ [4] Å
300	Anatase, TiO_2	TiO_2 (B)	$\text{H}_2\text{Ti}_3\text{O}_7$
	Tetragonal, I41/amdS	Monoclinic, C2/m	Monoclinic, C2/m
	$a = 3.766$ [6] Å	$a = 12.112$ [6] Å	$a = 15.79$ [1] Å
	$c = 9.55$ [3] Å	$b = 3.735$ [2] Å	$b = 3.774$ [4] Å
500	Anatase, TiO_2	TiO_2 (B)	
	Tetragonal, I41/amdS	Monoclinic, C2/m	
	$a = 3.891$ [5] Å	$a = 12.15$ [1] Å	
	$c = 9.67$ [2] Å	$b = 3.736$ [5] Å	
800	Anatase, TiO_2	TiO_2 (B)	Rutile, TiO_2
	Tetragonal, I41/amdS	Monoclinic, C2/m	Tetragonal, P42/mnm
	$a = 3.784$ [1] Å	$a = 12.51$ [1] Å	$a = 4.595$ [1] Å
	$c = 9.525$ [1] Å	$b = 3.695$ [6] Å	$c = 2.96$ [1] Å
	CS = 53 [2] nm	$c = 6.561$ [6] Å	CS = 113 [16] nm
		$\beta = 107.67$ [7]°	

TiO_2 anatase, PDF 89-4921: $a = 3.777$, $c = 9.501$; TiO_2 (B), PDF 74-1940: $a = 12.17$, $b = 3.741$, $c = 6.524$, $\beta = 107.05$; TiO_2 rutile, PDF 89-4920: $a = 4.584$, $c = 2.953$; $\text{H}_2\text{Ti}_5\text{O}_{11} \cdot 3\text{H}_2\text{O}$, PDF 44-0130: $a = 23.43$, $b = 3.749$, $c = 15.029$, $\beta = 117.16$; $\text{H}_2\text{Ti}_3\text{O}_7$, PDF 47-0561: $a = 16.02$, $b = 3.749$, $c = 9.191$, $\beta = 101.45$

Reflection spectra of TiO₂ powder modified with different ligands such as ascorbic acid (AA), dopamine (DOP), catechol (CAT), 2,3-dihydroxynaphthalene (2,3 DHN), and anthrarobine (ANT) were compared to the reflection spectrum of the unmodified TiO₂ powder obtained under the same experimental conditions (Fig. 5). The effective band gap energies of modified TiO₂ powder with AA, DOP, CAT, 2,3DHN, and ANT were calculated using Kubelka–Munk spectra obtained by transformation of the diffuse reflectance R to the Kubelka–Munk function $F_{KM}(R)$ according to the following relation:

$$F_{KM}(R) = (1 - R)^2 / 2R.$$

By plotting the function $f_{KM} = (F_{KM} \cdot E_{\text{phot}})^{1/2}$ versus E_{phot} , the linear part of the curve was extrapolated to $f_{KM} = 0$ to get band gap energy of the samples (Murphy 2007). The effective band gaps of AA, DOP, CAT, 2,3DHN, and ANT modified TiO₂ powders were found to be 1.85, 1.82, 1.86, 1.77, and 1.73 eV, respectively.

Surface-modified TiO₂ particles exhibit significant red shift of the optical absorption compared to unmodified ones. These results are presented in Table 2 along with the structural formulae of ligands, proposed binding structures, and photo images of TiO₂ powders.

It is clear that surface modification with different ligands and consequent formation of CT complexes induced a decrease of the effective band gap in the

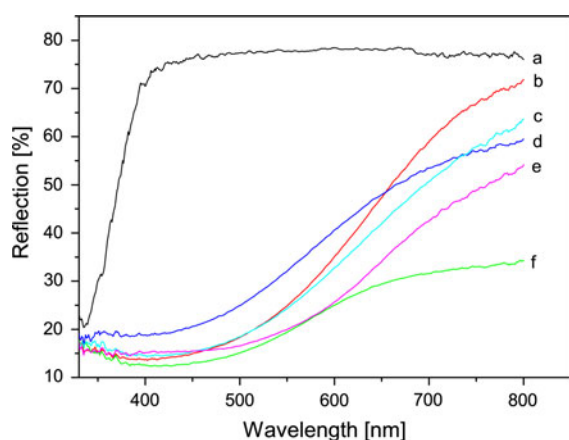
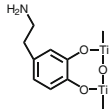
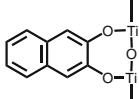
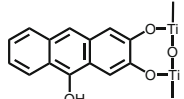
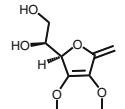


Fig. 5 Diffuse reflection spectra of surface-modified submicronic bare TiO₂ particles with different ligands **a** no ligand, **b** ascorbic acid, **c** 2,3-dihydroxynaphthalene, **d** dopamine, **e** anthrarobin, and **f** catechol

Table 2 Proposed binding structure of different ligands to TiO₂, photos of surface-modified TiO₂ powders and their effective band gap

Binding structures of ligand-to-TiO ₂	Photos of surface modified TiO ₂ powders and their effective band gap (E_g)/eV	
TiO ₂		3.2
TiO ₂ /DOP 		1.82
TiO ₂ /CAT 		1.86
TiO ₂ /2,3DHN 		1.77
TiO ₂ /ANT 		1.73
TiO ₂ /AA 		1.85

range of 1.3–1.5 eV in comparison to the bare TiO₂ particles ($E_g = 3.2$ eV). Obtained values of the effective band gap energies of surface-modified TiO₂ particles are quite comparable with values that we have previously reported after surface modification of colloidal precursor (4.5 nm TiO₂ nanoparticles) (Rajh et al. 1999; Janković et al. 2009, 2010; Savić et al. 2012). To the best of our knowledge, coloration of surface-modified commercial TiO₂ powders with the same/similar ligands has not been previously reported in the literature, i.e., the optical changes were observed only for small (less than 20 nm) TiO₂ nanospheres. The significant change of effective band gap energy of

small TiO_2 nanoparticles was assigned to the formation of CT complexes between electron-donating ligands and coordinately unsaturated Ti atoms at the surface. It is well known that, in the nanosize regime ($d < 20$ nm), due to the large curvature of TiO_2 particles, the coordination of surface Ti atoms changes from octahedral (six-coordinate) to square-pyramidal (penta-coordinate). Binding of electron-donating ligands to coordinately unsaturated Ti atoms simultaneously restores their coordination to octahedral geometry and changes the electronic properties of a TiO_2 semiconductor. As a consequence, absorption of light by the CT complex promotes electrons from the chelating ligand directly into the conduction band of TiO_2 nanocrystallites, resulting in the red shift of the semiconductor absorption compared to unmodified nanocrystallites (Xagas et al. 2000; Garza et al. 2006). As in the case of individual colloidal TiO_2 nanoparticles ($d < 20$ nm), the appearance of CT complexes between surface Ti atoms of submicronic TiO_2 particles obtained at 150 °C and electron-donating ligands most likely lies in the unsaturated nature of surface Ti atoms. The TEM and XRPD microstructural data support this conclusion, because it clearly revealed that submicronic TiO_2 particles processed at 150 °C are composed of the primary crystallites with sizes of just a few nanometers (Fig. 3b; Table 1). On the other hand, the formation of CT complexes was not observed for TiO_2 submicronic particles processed at higher temperatures (500 and 800 °C), which have substructural units with sizes larger than 20 nm (Table 1), and consequently surface Ti atoms with octahedral coordination. The coloration of submicronic TiO_2 particles opens up the possibility for additional improvement of light harvesting by sensitizer (CT complex) due to light scattering by large titania particles. As pointed out by Grätzel (2009) the scattered photons are contained in the solar cell film by multiple reflections, increasing their optical path length substantially beyond the film thickness. It has been shown that the enhanced absorption of solar light using 200–400 nm sized anatase particles as scattering centers increases the photo-current in dye-sensitized solar cells (Rothenberger et al. 1999). FTIR spectroscopy measurements were performed to elucidate the mechanism for binding of ligands to the surface of TiO_2 . Because the infrared spectrum of TiO_2 powder has only the characteristic broadband in 3700–2000 cm^{-1} spectral region (Janković et al. 2010), we were

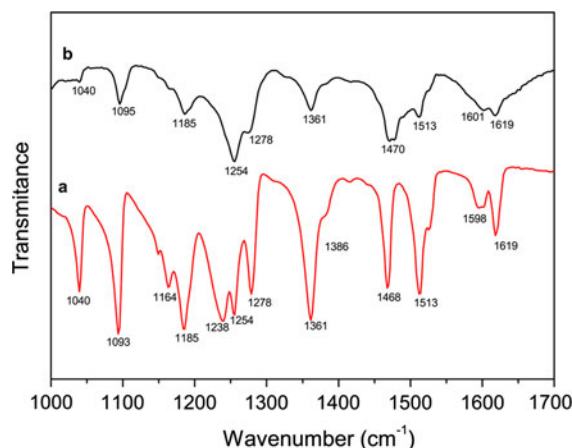


Fig. 6 FTIR spectra of **a** catechol and **b** catechol adsorbed on submicronic TiO_2 particles

able to measure surface-modified TiO_2 powders in 1700–1000 cm^{-1} spectral region, where the characteristic bands of ligands exist.

The FTIR spectra of catechol, free and bound to the surface of submicronic TiO_2 particles, were presented in Fig. 6. The main bands and their assignment (Connor et al. 1995; Araujo et al. 2005a, b) in free catechol (Fig. 6, curve a) are as follows: stretching vibrations of aromatic ring $\nu(\text{C}-\text{C})/\nu(\text{C}=\text{C})$ at 1619, 1598, 1513, and 1468 cm^{-1} , stretching vibrations of the phenolic group $\nu(\text{C}-\text{OH})$ at 1278, 1254, and 1238 cm^{-1} , bending vibrations of the phenolic group $\delta(\text{C}-\text{OH})$ at 1361, 1185, 1164, and 1149 cm^{-1} , and bending vibrations of $\delta(\text{C}-\text{H})$ at 1093 and 1040 cm^{-1} . Upon adsorption of catechol onto submicronic TiO_2 particles (Fig. 6, curve b), the difference between FTIR spectra of free and adsorbed ligands appears, indicating surface complexation with catechol bound to the oxide surface in bidentate form. Bending $\delta(\text{C}-\text{OH})$ vibrations in the region below 1200 cm^{-1} lose their hyperfine structure, while the pronounced band at 1361 cm^{-1} nearly disappears. The prominent stretching vibration of the phenolic group $\nu(\text{C}-\text{OH})$ at 1238 cm^{-1} a completely disappears, while the bands at 1254 and 1278 cm^{-1} become very weak.

The binding of catechol to TiO_2 via two adjacent phenolic groups even affects the stretching of the aromatic ring (bands above 1400 cm^{-1}). It should be pointed out that those almost identical changes in FTIR spectra were observed upon binding of catechol onto colloidal 4.5 nm TiO_2 nanoparticles (Janković et al. 2009). Catecholate type of binding, with two

adjacent phenolic OH groups taking part in complexation, was reported to result in the formation of bidentate binuclear bridging complexes (Janković et al. 2009, 2010). In the case of colloidal 4.5 nm TiO₂ nanoparticles, we have recently found that the molar ratio between surface Ti atoms and catechol in the complex is 2:1, supporting bridging coordination structure of the CT complex (Janković et al. 2009). Having in mind that primary building units of submicronic TiO₂ particles correspond in size to the precursor TiO₂ nanoparticles, we believe that identical optical behavior for both kinds of particles are the consequence of the identical coordination structure of the CT complex. (A proposed coordination structure is presented in Table 2.)

For the sake of clarity, FTIR spectra of free and adsorbed ascorbic acid, dopamine, 2,3-dihydroxynaphthalene, and anthrarobin onto submicronic TiO₂ particles are given in Supporting Information, Figs. A2–A5, respectively. It is important to point out that observed changes in FTIR spectra of ligands, which occur upon their adsorption onto the surface of submicronic TiO₂ particles, are essentially the same as described in the literature upon adsorption of ligands onto TiO₂ particles in the nanometer size domain, whose surface Ti atoms are coordinately unsaturated (AA (Rajh et al. 1999), DOP (Dimitrijevic et al. 2009), 2,3DHN and ANT (Janković et al. 2009). Of course, for all above mentioned ligands, catecholate type of binding with two adjacent OH groups takes place in complexation with surface Ti atoms.

Conclusion

In summary, submicronic soft TiO₂ assemblages with high specific surface area and controllable phase composition were prepared using colloidal TiO₂ ($d = 4.5$ nm) solution as a precursor in the process of ultrasonic spray drying/pyrolysis on different temperatures (150, 300, 500, and 800 °C). Fine tuning of the TiO₂ phase composition and particle size distribution is achieved as a function of temperature. The submicronic TiO₂ particles obtained at lower processing temperatures (150, 300, and 500 °C) are mainly composed of the anatase crystal phase, whereas ~30 wt% of anatase is converted to the rutile phase in powder processed at 800 °C. All investigated

surface ligands (dopamine, catechol, 2,3-dihydroxynaphthalene, anthrarobin, and ascorbic acid) form CT complex with undercoordinated surface Ti atoms of submicronic TiO₂ particles consisting of 4.5 nm TiO₂ substructural units. The formation of ligand-to-TiO₂ CT band, previously exclusively assigned to the colloidal nanoparticles ($d < 20$ nm), was confirmed by significant red shift of optical absorption and changing of the effective band gap of submicronic TiO₂ particles in comparison to unmodified ones. Catecholate type of binding in CT complex was confirmed by FTIR measurements.

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