ИНСТИТУТ ТЕХНИЧКИХ НАУКА САНУ

Кнез Михаилова 35/IV Београд

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

НАУЧНОМ ВЕЋУ ИНСТИТУТА ТЕХНИЧКИХ НАУКА САНУ

Молим Вас да, у складу са Правилником о поступку и начину вредновања и квантитавином 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 реизбор 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, научног саветника 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 радова
- 5. Одлука о стицању истраживачког звања

У Београду 24.07.2015.

Подносилац захтева:

Lyranyuh Mbart

дипл. инж. Иван Дуганџић истраживач сарадник ИТН САНУ

Биографија Иван М. Дуганџић

Иван М. Дуганџић рођен је 16.08.1981. године у Београду, Република Србија. Дипломирао је 2009. године на Технолошко-металуршком факултету Универзитета у Београду, Одсек Хемијско инжењерство, са просечном оценом 8,14 и 10 на дипломском раду са темом "Експериментално одређивање и моделовање вискозности бинарних система алкохола са алканима, ацетоном и н-бутил ацетатом". У периоду од јуна 2006. до јануара 2007. боравио је на студијској пракси у Антверпену, Белгија (АГФА-Геваерт Гроуп). Члан је Српског хемијског друштва и Српског керамичког друштва. Докторске студије уписао је 2009. године на Технолошко-металуршком факултету, Универзитета у Београду, на одсеку Хемијско инжењерство, под руководством ментора проф. др Жељка Грбавчића.

У Институту техничких наука САНУ запослен је од 2009. године као истраживач приправник. Ангажован је 12 месеци на пројектима Министарства просвете, науке и технолошког развоја Републике Србије и то на пројекту основних истраживања ОИ 172035 "Рационални дизајн и синтеза биолошки активних и координационих једињења и функционалних материјала, релевантних у (био) нанотехнологији" и на пројекту мултидисциплинарних истраживања ИИИ 45020 "Материјали редуковане димензионалности за ефикасну апсорпцију светлости и конверзију енергије".

Такође, током рада био је ангажован и на истраживачко развојном пројекту који се реализује између Института техничких наука САНУ и Народне банке Србије – Завода за израду новчаница и кованог новца, Топчидер. У звање истраживач сарадник изабран је 02.11.2012. Израду докторске тезе реализује у Институту техничких наука САНУ под непосредним руководством др Оливере Милошевић, научног саветника, а у сарадњи са Институтом "Винча", као и универзитетима: Карлос ИИИ-Мадрид, Шпанија и Осака, Јапан.

Области интересовања су му: Нанотехнологије, наноструктурни материјали, синтеза наноструктурних материјала у дисперзном систему – аеросолу, хидротермална метода, савремене методе карактеризације наноструктурних материјала, површинска модификација, хетерогена фотокатализа.

Библиографија Иван М. Дуганџић

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РЕПУБЛИКА СРБИЈА



УНИВЕРЗИТЕТ У БЕОГРАДУ ТЕХНОЛОШКО - МЕТАЛУРШКИ ФАКУЛТЕТ

ДИПЛОМА

О СТЕЧЕНОМ ВИСОКОМ ОБРАЗОВАЊУ

ИВАН (Милош) ДУГАНЦИЋ

РОЪЕН 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

ЛЕКАН Проф. др Иванка Поповић

PEKTOF др Бранко Ковачевић



Република Србија Универзитет у Београду Технолошко-металуршки факултет Д.Бр.2009/4045 Датум: 24.06.2015. 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, Београд-Савски Венац, Република Србија, уписан школске 2014/2015. године, у статусу: самофинансирајући; тип студија: Докторске академске студије; студијски програм: Хемијско инжењерство.

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 вожњу и стипендије.

Овлашћено лице факултета en



Република Србија Универзитет у Београду Технолошко-металуршки факултет Д.Бр.2009/4045 Датум: 24.06.2015. године

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Овлашћено лице факултета lan

ИНСТИТУТ ТЕХНИЧКИХ НАУКА САНУ

Научно веће ИТН САНУ

Деловодни број 433/1 Датум 02.11.2012.

На основу чланова 59, 70 и 82 Закона о научноистраживачкој делатности (Службени гласник Републике Србије бр. 110/05, 50/06 – исправка и 18/2010 – исправка), чланом 22 Статута Института техничких наука САНУ, чланом 45 Пословника о раду Научног већа ИТН САНУ и Правилником о утврђивању услова и предлога за стицање звања истраживач сарадник и избор у звање истраживач сарадник ИТН САНУ, на седници Научног већа одржаној 01.11.2012. године, донета је

ОДЛУКА О СТИЦАЊУ ИСТРАЖИВАЧКОГ ЗВАЊА Иван Дуганџић, дипл. инж. технологије

стиче истраживачко звање

истраживач сарадник

Образложење

Иван Дуганџић, дипл. инж. технологије, запослен на радном месту истраживача приправника у Институту техничких наука САНУ, покренуо је 13.09.2012. године поступак за избор у истраживачко звање истраживач сарадник. На седници Научног већа од 13.09.2012. године је формирана Комисија за избор именованог у истраживачко звање, која је 01.10.2012. године поднела извештај о избору и који је стављен на увид јавности у електронском облику на вебстраници Научног већа и у принтаном облику у Секретаријату Института.

На основу овог извештаја Комисије и приложеног изборног материјала, утврђено је да Иван Дуганџић испуњава све услове из члана 70 Закона о научноистраживачкој делатности за стицање истраживачког звања истраживач сарадник, те је Научно веће већином гласова одлучило као у диспозитиву одлуке.

редседник Научног већа основан 1947 г Сорон Куриб Проф. др Зоран Ђурић

Кнез Михаилова 35/IV, П.Ф. 377, 11000 Београд, Србија

Тел.: 011 21 85 437, 26 36 994; Факс: 21 85 263, мејл: its@itn.sanu.ac.rs, http://www.itn.sanu.ac.rs Текући рачун: 840-1613660-30, 840-1613666-12, ПИБ: 100039438, матични бр. 07011016 **RESEARCH PAPER**

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

Ivan M. Dugandžić · Dragana J. Jovanović · Lidija T. Mančić · Nan Zheng · Scott P. Ahrenkiel · Olivera B. Milošević · Zoran V. Šaponjić · Jovan M. Nedeljković

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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 = 370-500 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 ($\sim 30 \text{ wt\%}$) 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

Electronic supplementary material The online version of this article (doi:10.1007/s11051-012-1157-1) contains supplementary material, which is available to authorized users.

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N. Zheng · S. P. Ahrenkiel South Dakota School of Mines and Technology, 501 E. Saint Joseph Street, Rapid City, SD 57701, USA particle size analysis. Moreover, the surface modification of TiO₂ particles through the formation of chargetransfer (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

Introduction

Titanium dioxide (TiO_2) 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 $(E_{\rm g} = 3.2 \text{ eV})$, TiO₂ absorbs less than 5 % of the available solar photons. Dye-sensitization is one of the most promising pathways for increasing the TiO₂ 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 TiO2 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 TiO₂. In direct DSSCs, electrons are additionally injected by direct electron injection from the dyes to TiO₂ by photoexcitation of the dyeto-TiO₂ 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 TiO₂ surface involving replacement of TiO₂ 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 TiO₂ (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 TiO₂ (Hines and Boltz 1952; Hultquist 1964).

So far, the surface modification of commercial TiO₂ 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 TiO₂ 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 TiO₂ after modification lies in the fact that surface Ti atoms, owing to the large curvature of nanoparticles, adjust their coordination environment to form undercoordinated sites (Chen et al. 1999). These fivecoordinated 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 TiO₂ 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-polypyrodine complex containing catechol that could adhere effectively onto TiO₂ 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 contitions and resistance to oxidation (Ye et al. 2011).

This article presents for the first time aerosolassisted 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 "bottomup" 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 TiO₂ 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 TiO₂ particles with tailored crystallinity, phase composition, and surface structure. It is known that the submicron-sized anatase TiO₂ particles ($d = 0.2-0.3 \mu m$) can be used as light scattering centers in dye-senzitized sollar cells (Lan et al. 2010). Due to the nanostructured nature, it is shown that surface-modified soft assemblage of TiO₂

nanoparticles synthesized at lower temperatures keep their unique ability to absorb light through direct CT by photoexcitation of the ligand-to- TiO_2 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 M Ω 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 $3.46 \ \mu m$ (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 anthrarobin (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 TiO_2 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 K α radiation at 40 kV and 40 mA. The 2 θ 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 TiO_2 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 TiO_2 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 nanostuctured, 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



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

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 TiO_2 particles obtained through aerosol processing of colloids consisting of 4.5 nm TiO_2 nanoparticles at different temperatures are shown in Fig. 2. It can be noticed that spherical, non-agglomerated TiO_2 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 TiO_2 powders obtained through aerosol-assisted processing of TiO_2 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. 2 Typical SEM images of TiO₂ particles obtained at different temperatures a 150 °C, b 300 °C, c 500 °C, and d 800 °C



Fig. 3 TEM images of a TiO₂ particles obtained at 150 °C, b marked region at a higher magnification, c cross section of the particle obtained at 150 °C, and d TiO₂ 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 $TiO_2(B)$ 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, $TiO_2(B)$ 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 $TiO_2(B)$ 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

<i>T</i> (°C)	Powder phase composition		
150	Anatase, TiO ₂	TiO ₂ (B)	$H_2Ti_5O_{11}\cdot 3H_2O$
	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
	CS = 2.5[2] nm	c = 6.544 [5] Å	c = 15.01 [1] Å
		$\beta = 107.05 \ [5]^{\circ}$	$\beta = 117.31 \ [6]^{\circ}$
300	Anatase, TiO ₂	TiO_2 (B)	H ₂ Ti ₃ O ₇
	Tetragonal, I41/amdS	Monoclinic, C2/m	Monoclinic, C2/m
	a = 3.766 [6] Å	a = 12.112 [6] Å	<i>a</i> = 15.79 [1] Å Å
	c = 9.55 [3] Å	b = 3.735 [2] Å	<i>b</i> = 3.774 [4] Å
	CS = 9[1] nm	c = 6.535 [2] Å	c = 9.55 [1] Å
		$\beta = 107.23 \ [4]^{\circ}$	$\beta = 100.54 \ [7]^{\circ}$
500	Anatase, TiO ₂	TiO_2 (B)	
500 500 500	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	
	CS = 21 [4]	c = 6.426 [7] Å	
		$\beta = 108.24 \ [7]^{\circ}$	
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	<i>a</i> = 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
		$\beta = 107.67 \ [7]^{\circ}$	

TiO₂ anatase, PDF 89-4921: a = 3.777, c = 9.501; TiO₂ (B), PDF 74-1940: a = 12.17, b = 3.741, c = 6.524, $\beta = 107.05$; TiO₂ r utile, PDF 89-4920: a = 4.584, c = 2.953; H₂Ti₅O₁₁·3H₂O, PDF 44-0130: a = 23.43, b = 3.749, c = 15.029, $\beta = 117.16$; H₂Ti₃O₇, 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), cathechol (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:

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

By plotting the function $f_{\rm KM} = (F_{\rm KM} \cdot E_{\rm phot})^{1/2}$ versus $E_{\rm phot}$, the linear part of the curve was extrapolated to $f_{\rm KM} = 0$ 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 TiO_2 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 TiO_2 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 TiO_2 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 TiO_2 , photos of surface-modified TiO_2 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 (<i>Eg</i>)/eV			
TiO ₂		3.2		
		1.82		
TiO ₂ /CAT	2	1.86		
TiO ₂ /2,3DHN		1.77		
		1.73		
		1.85		

range of 1.3–1.5 eV in comparison to the bare TiO₂ particles ($E_g = 3.2 \text{ eV}$). 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 TiO₂ 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 TiO₂ 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 TiO₂ semiconductor. As a consequence, absorption of light by the CT complex promotes electrons from the chelating ligand directly into the conduction band of TiO₂ 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 TiO₂ nanoparticles (d < 20 nm), the appearance of CT complexes between surface Ti atoms of submicronic TiO₂ 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 TiO₂ 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 TiO2 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 TiO₂ 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 TiO₂. Because the infrared spectrum of TiO₂ 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 TiO₂ 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 TiO₂ 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 v(C-C)/v(C=C) at 1619, 1598, 1513, and 1468 cm⁻¹, stretching vibrations of the phenolic group v(C-OH) at 1278, 1254, and 1238 cm^{-1} , bending vibrations of the phenolic group δ (C–OH) at 1361, 1185, 1164, and 1149 cm⁻¹, and bending vibrations of δ (C–H) at 1093 and 1040 cm⁻¹. Upon adsorption of catechol onto submicronic TiO₂ 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 $\delta(C-$ 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 v(C-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 TiO₂ 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 TiO_2 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-dihydrohynapthalene, 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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Ultrasonic spray pyrolysis of surface modified TiO₂ nanoparticles with dopamine

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HIGHLIGHTS

- The surface-modified TiO₂ nanoparticles with dopamine were used as a precursor.
- Colored submicronic TiO₂ particles were obtained after ultrasonic spray pyrolysis.
- CT complex was formed between electron donating ligands and surface Ti atoms.
- The effective band-gap of surface modified TiO₂ powders decreases to 1.3 eV.

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G R A P H I C A L A B S T R A C T

ABSTRACT

Spherical, submicronic TiO₂ powder particles were prepared in the low temperature process of ultrasonic spray pyrolysis (150 °C) by using as a precursor aqueous colloidal solutions consisting of surface modified 45 Å TiO₂ nanoparticles with dopamine. Detailed structural and morphological characterization of colored submicronic TiO₂ spheres was performed by X-ray powder diffraction (XRPD), scanning electron microscopy (SEM), transmission electron microscopy (TEM), laser particle size analysis and FTIR techniques. Also, optical characterization of both dopamine-modified TiO₂ precursor nanoparticles and submicronic TiO₂ powder particles was performed using absorption and diffuse reflectance spectroscopy, respectively. A significant decrease of the effective band gap (1.9 eV) in dopamine-modified TiO₂ nanoparticles in the process of ultrasonic spray pyrolysis under mild experimental conditions. Due to the nanostructured nature, surface-modified assemblage of TiO₂ nanoparticles preserved unique ability to absorb light through charge transfer complex by photoexcitation of the ligand-to-TiO₂ band, conventionally associated with extremely small TiO₂ nanoparticles (d < 20 nm) whose surface Ti atoms, owing to the large curvature, have penta-coordinate geometry.

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1. Introduction

Titanium dioxide (TiO₂) is one of the most studied semiconductors, with a variety of applications in heterogeneous catalysis [1], photocatalysis [2], solar cells [3], production of hydrogen, ceramics, electric devices, corrosion-protective coatings,

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gas sensors [4], and smart textile materials with antibacterial and self-cleaning activity [5]. 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, while the anatase formed at a lower temperature with band gap energy of 3.2 eV and refractive index of 2.3, is common in fine-grained (nanoscale) natural and synthetic samples [6]. Due to its large band gap, TiO₂ absorbs less than 5% of the available solar photons. Dye-sensitization is one of the most promising pathways for increasing the TiO₂ photoactivity through intensive utilization of visible light in solar cells [7].

Depending on the mechanism for electron injection from the dye to the semiconductor, dye-sensitized TiO_2 solar cells (DSSCs) 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 directly injected from ground state of the dye to-TiO₂ charge-transfer (CT) complex to conduction band of TiO₂ [8]. Many benzene derivatives with phenolic or carboxylic groups are able to make very stable complexes with the TiO₂ surface involving replacement of TiO₂ surface hydroxyl groups by deprotonated ligands [9].

Over the last several years, more attention was focused on the formation of a CT complex between surface Ti atoms from extremely small colloidal TiO₂ nanoparticles and bidentate benzene derivatives [10], as well as enediol ligands [11,12]. The origin of the significant red shift of optical absorption observed in colloidal TiO₂ nanoparticles after surface 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 [13]. 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 that contains two donor atoms [14].

Additional improvement of the efficiency of light absorption in DSSCs can be achieved by using submicronic TiO₂ powder particles $(d = 0.2-0.3 \ \mu\text{m})$ as light scattering centers [15]. In our previous paper [16], we showed that it is possible to perform surface modification of submicronic TiO₂ spheres, prepared in the process of ultrasonic spray pyrolysis by using colloids consisting of extremely small TiO₂ nanoparticles $(d = 45 \ \text{Å})$ as a precursor, and to extend optical absorption in the visible spectral range with variety of ligands: ascorbic acid, dopamine, catechol, 2,3-dihydroxynaph-thalene and anthrarobin.

In this paper, instead of using bare TiO₂ nanoparticles, for the first time, surface-modified TiO₂ nanoparticles with dopamine were used as a precursor in the process of ultrasonic spray pyrolysis at low temperature (150 °C) in order to obtain colored submicronic TiO₂ powder particles. Due to larger specific surface area modification of TiO₂ nanoparticles is more efficient compared to submicronic ones, and their processing by ultrasonic spray pyrolysis can provide TiO₂ powder particles with desired size and better absorption properties. Ultrasonic spray pyrolysis 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 parameters, including the nature of precursor solution, type of atomization, manner of aerosol decomposition energy transfer to the system, processing temperature and time [17–19]. Structural and optical properties of both dopamine-modified TiO₂ precursor nanoparticles and colored submicronic TiO₂ spheres were thoroughly studied and compared using high-resolution TEM, SEM, XRPD, FTIR, as well as absorption and diffuse reflectance spectroscopy, respectively. Significant red shift of optical absorption of dopamine modified colloidal TiO_2 precursor nanoparticles (about 1.3 eV) was preserved after formation of submicronic TiO_2 powder particles under mild experimental conditions due to their nanostructured nature, i.e., preserved square pyramidal coordination of surface Ti atoms, typical for extremely small TiO_2 nanoparticles (d < 20 nm).

2. Experimental details

2.1. Synthesis of colloidal 45 Å TiO₂ nanoparticles

All the chemicals used were of the highest purity available and were used without further purification (Aldrich, Fluka). Milli-Q deionized water (resistivity 18.2 $M\Omega$ cm⁻¹) was used as solvent. The colloids consisting of 45 Å TiO₂ nanoparticles were synthesized according to the method described in literature [20]. Typically, the TiO₂ colloids were prepared by the drop-wise addition of titanium(IV) chloride to cooled water. The pH of the solution was between 0 and 1, depending on the TiCl₄ concentration. Slow growth of the particles was achieved by using dialysis at 4 °C against water until the pH 3.5 was reached. The concentration of TiO₂ was determined from the concentration of the peroxide complex obtained after dissolving 0.1 ml of TiO₂ colloid in solution consisting of 2 ml of 30% H_2O_2 , 2 ml of concentrated H_2SO_4 and 20.9 ml of water [21,22]. The concentration of peroxide complex was determined spectrophotometrically measuring absorbance at 408 nm ($\epsilon_{408} = 710 \text{ M}^{-1} \text{ cm}^{-1}$).

2.2. Surface modification of colloidal 45 Å TiO_2 nanoparticles with dopamine

Surface modification of colloidal TiO₂ nanoparticles resulting in the formation of a charge transfer (CT) complex was achieved by the addition of surface-active ligand (dopamine) up to concentrations required to cover all surface sites (($[Ti_{surf}] = [TiO_2]12.5/D$) [23], where [Ti_{surf}] is the molar concentration of surface Ti sites, $[TiO_2]$ is the molar concentration of TiO₂ in molecular units, and D is the diameter of the particle in angstroms). Surface modification of colloidal TiO₂ nanoparticles with dopamine was performed by adding dopamine hydrochloride whose concentrations corresponded to 3, 33, 67 and 100% of the concentration of Ti_{surf} atoms. In the application of continual variations method (Job's method) [24] for the spectrophotometric determination of the complex composition, the solutions were prepared by mixing some different volumes of equimolar solutions of 2 mM Tisurf (7.2 mM TiO2) and 2 mM dopamine. A series of solutions is prepared in which the sum of the total concentration of Ti_{surf} and dopamine is constant (2 mM), but their proportions are continuously varied: volumes of TiO₂ solution used varied from 1 to 9 ml and those of modifiers' solutions from 9 to 1 ml with the total volume being always 10 ml. In order to prepare samples for XRPD and FTIR measurements, the dispersions containing surface modified TiO₂ nanoparticles were dried under argon at room temperature, and powders obtained were placed into the vacuum oven for 8 h to get to complete dryness.

2.3. Synthesis of dopamine modified submicronic TiO₂ powder particles

In order to synthesize submicronic TiO_2 powder particles, colloidal solutions consisting of bare 45 Å TiO_2 nanoparticles, as well as dopamine modified 45 Å TiO_2 nanoparticles (concentration of dopamine corresponding to 3, 33, 67 and 100% of Ti_{surf} atoms) were used as a precursor in the process of low temperature

Fig. 1. Typical TEM image of colloidal TiO_2 nanoparticles used as a precursor in the process of ultrasonic spray pyrolysis.

ultrasonic spray pyrolysis (150 °C). The ultrasonic spray pyrolysis was performed using a laboratory setup already described in the literature [18]. It consists from an ultrasonic atomizer for the generation of aerosol droplets operating at 1.3 MHz (RBI, France), a tubular flow reactor with the three independently controlled temperature zones, a diffusion dryer (Model 3062, TSI) and an electrostatic precipitator. Aerosol, generated from the colloidal solutions, was introduced into a tubular flow reactor using nitrogen as a carrier gas with flow rate of 0.033 dm³ s⁻¹ and corresponding residence time of droplets in the reactor zone of 33 s. Based on the properties of colloidal TiO₂ solutions and applied atomization frequency, the average droplet and the average particle size of TiO₂ powder particles were estimated to be about 3.5 μ m and 380 nm, respectively [25,26].

2.4. Instruments and measurements

The size distribution of colloidal 45 Å TiO₂ nanoparticles was determined by using transmission electron microscopy (JEOL JEM-2100 LaB₆ operated at 200 kV). The morphology of surfacemodified submicronic TiO₂ powder particles was determined by scanning electron microscopy (JEOL JSM-6610 LV operated at 20 kV). The particle size distribution of surface modified submicronic TiO₂ spheres was determined by laser particle sizer (Mastersizer 2000, Malvern Instruments Ltd). For each run, the powder was de-agglomerated in an ultrasonic bath for at least 15 min. The X-ray powder diffraction (XRPD) analysis was performed by using PW 1050 (Philips) diffractometer with CuK_{α} radiation. The investigated 2θ range was from 10 to 80° with a step scan of 0.05° and scanning time of 10 s per step. Optical properties of dopamine-modified 45 Å TiO₂ nanoparticles, as well as dopamine modified submicronic TiO₂ powder particles, were studied in details in UV-Vis spectral range by using absorption spectroscopy (Thermo Scientific Evolution 600 UV/Vis spectrophotometer) and diffuse reflectance measurements (Labsphere RSA-PE-19), respectively. The structures of charge transfer (CT) complexes were investigated using FTIR spectroscopy (Nicolet 380 FTIR spectrophotometer, Thermo Scientific).

3. Results and discussion

High-resolution TEM imaging of colloidal TiO_2 nanoparticles (Fig.1) revealed nearly spherical TiO_2 precursor nanoparticles with a low level of crystallinity and average size of about 4.5 nm.

Typical X-ray powder diffraction (XRPD) pattern of the dried colloidal TiO₂ precursor nanoparticles is presented in Fig. 2a. All

Fig. 2. The XRPD patterns of the: (a) colloidal TiO_2 nanoparticles, and (b) TiO_2 powder synthesized at 150 °C in the process of ultrasonic spray pyrolysis by using surface modified TiO_2 nanoparticles by dopamine as a precursor with standard data for anatase structure (JCPDS, card No. 21-1272).

diffraction peaks match well to the anatase crystal structure (JCPDS #21-1272) without indication of the presence of any other phases. The grain size was determined from diffraction peak broadening by using Scherrer's equation, and it was found to be 2.5 nm. It can be noticed that the grain size calculated from XRPD data corresponds well to the average diameter of TiO₂ nanoparticles determined by TEM measurements. Typical XRPD pattern of submicronic TiO₂ powder particles is shown in Fig. 2b. It should be noticed that this diffraction pattern is almost identical to the diffraction pattern of precursor TiO₂ nanoparticles indicating the presence of pure anatase phase. Also, the grain size of about 2.5 nm, determined using Scherrer's diffraction formula, is in excellent agreement with grain size observed in high-magnification TEM measurements.

It is well known that, in the nanosize regime (d < 20 nm), due to the large curvature of TiO₂ particles, coordination of surface Ti (Ti_{surf}) atoms changes from octahedral (six-coordinate) to square pyramidal (penta-coordinate) [13]. Binding of electron-donating ligands to coordinately unsaturated Ti atoms restores their octahedral geometry and leads to the formation of charge transfer (CT) complexes. As a consequence of changes in electronic structure of TiO₂ upon surface modification, a red shift of semiconductor absorption has been observed compared to unmodified nanocrystallites [27].

The absorption spectra of colloids consisting from unmodified Fig. 3a and surface-modified TiO₂ nanoparticles with dopamine

Fig. 3. (a) Absorption spectra of colloids consisting from unmodified TiO₂ nanoparticles, (b–e) and surface modified TiO₂ nanoparticles with different dopamine concentrations (3, 33, 66 and 100% of Ti_{surf} atoms, respectively). Photographs of colloidal solutions consisting of bare TiO₂ nanoparticles and dopamine modified TiO₂ nanoparticles with concentration corresponding to 3 and 100% of Ti_{surf} atoms are also included.

with different surface coverage are shown in Fig. 3b-e. Significant red shift of absorption was noticed even when dopamine concentration was as low as 3% of the concentration of Tisurf atoms (Fig. 3b). At the concentration level of dopamine higher than 33% of Tisurf atoms, maximal red shift of absorption was achieved and further increase of dopamine concentration had no effect on the optical properties of TiO_2 nanoparticles (Fig. 3c-e). It is clear that surface modification of TiO₂ nanoparticles with dopamine induced a significant decrease of the effective band gap (1.9 eV) compared to unmodified semiconductor (3.2 eV). These results are in agreement with experimental data concerning surface modification of TiO₂ nanoparticles with dopamine reported in literature [28]. The catecholate type of binding to metal-oxide surfaces inherent to the adsorption of molecules having two adjacent OH groups, was reported to result in the formation of both bidentate mononuclear chelating and bidentate binuclear bridging complexes.

Some authors [27,29,30] claim that five-membered ring coordination complexes predominate, while others [31–35] find bridging complexes energetically more favorable. Recently, we have shown that a simple Job's method of continuous variation [10], developed for determination of composition of complexes in homogeneous media, can also be used for determination of the complex composition in heterogeneous colloidal systems consisting of highly uniform and sufficiently small particles that do not scatter light [11].

According to Job's method, the stoichiometric ratio is determined from the plot of the absorbance as a function of the mole fraction of metal or ligand. The ratio $x_{max}/1 - x_{max}$, where x_{max} corresponds to the mole fraction in the absorbance maximum, equals the stoichiometric ratio. The stoichiometric ratio Ti_{surf}/L is obtained by plotting the absorbance of the CT complex vs. $x = [Ti_{surf}]/[Ti_{surf}] + [L]$. Characteristic Job's curve for surface modified TiO₂ nanoparticles by dopamine is presented in Fig. 4. Job's plot reached a maximum value at a mole fraction [Tisurf]/[Tisurf] + [L] \approx 0.67, confirming that the molar ratio between Ti_{surf} atoms and dopamine in the complex is 2:1. Based on this result, we concluded that catecholate type of binding between dopamine and surface Ti atoms takes place through the formation of bidentate binuclear bridging complexes.

Fig. 4. Job's curve of equimolar solutions for ligand– Ti_{surf} complexes ($[Ti_{surf}] + [L] = const.$) with proposed binding structure between dopamine and surface Ti atoms.

This result is in agreement with literature data concerning binding geometry of bidentate benzene derivatives and colloidal TiO₂ nanoparticles [10]. The process of ultrasonic spray pyrolysis has been already applied in order to prepare uniform submicronic spheres using colloidal TiO₂ nanoparticles as a precursor [16]. In this case, novelty is usage of surface modified TiO₂ nanoparticles instead of bare ones. The processing temperature was chosen to be as low as 150 °C in order to avoid thermal decomposition of dopamine (241 °C) [36] and to preserve square pyramidal coordination of surface Ti atoms that is typical only for extremely small TiO₂ particles (d < 20 nm) [28].

Typical SEM image of submicronic TiO_2 particles obtained in the process of ultrasonic spray pyrolysis using colloids consisting of surface-modified TiO_2 nanoparticles with dopamine is shown in Fig. 5a. Corresponding particle size distribution determined using laser particle sizer is presented in Fig. 5b. It can be noticed that the process of ultrasonic spray pyrolysis led to the formation of fairly uniform, non-agglomerated TiO_2 powder particles.

The average particle size of TiO₂ powder particles was found to be around 440 nm. Slight variations of the average size of TiO₂ particles (size range from 420 to 470 nm) were observed for different dopamine concentration (SEM images are not shown). The processing of surface modified TiO₂ nanoparticles with dopamine led to the formation of submicronic TiO₂ particles with smooth surface.

For comparison, SEM image and particle size distribution of TiO_2 powder particles obtained under the same experimental conditions, but using bare TiO_2 nanoparticles as a precursor, are shown in Fig. 5c and d, respectively. Basically, similar TiO_2 powder particles were obtained in both cases, except that processing of bare TiO_2 nanoparticles led to the formation of slightly larger TiO_2 powder particles (average diameter around 500 nm). Low-magnification TEM measurements of TiO_2 powder particles obtained using surface modified TiO_2 nanoparticles with dopamine (Fig. 6a) confirmed SEM observations regarding the particle size distribution. High magnification TEM image (Fig. 6b) indicated polycrystalline nature of the synthesized TiO_2 powder particles with grain size around 2.5 nm that corresponds well to the size of colloidal TiO_2 nanoparticles used as a precursor.

Diffuse reflection spectra of submicronic TiO_2 powders obtained in the process of ultrasonic spray pyrolysis using as a precursor of TiO_2 nanoparticles with different surface coverage with dopamine

Fig. 5. (a) Typical SEM image of submicronic TiO₂ powder particles obtained in the process of ultrasonic spray pyrolysis at 150 °C by using dopamine modified TiO₂ nanoparticles as a precursor (dopamine concentration is 33% of Ti_{surf} atoms), and (b) corresponding size distribution. (c) Typical SEM image of submicronic TiO₂ powder particles obtained in the process of ultrasonic spray pyrolysis at 150 °C by using bare TiO₂ nanoparticles as a precursor, and (d) corresponding size distribution.

(Fig. 7b–e) were compared to the diffuse reflection spectrum of bare TiO_2 powder obtained under the same experimental conditions (Fig. 7a).

Photographs of modified TiO₂ powders with different surface coverage of dopamine (concentrations correspond to 3 and 33% of the concentration of Ti_{surf} atoms), and of bare TiO₂ powder, are shown as insets to Fig. 7. Modified TiO₂ powders with higher concentration of dopamine have the same color as a sample synthesized with dopamine concentration corresponding to 33% of Ti_{surf} atoms. It should be pointed out that the same behavior was observed for corresponding precursor TiO₂ colloids. The effective band-gap energies of surface modified TiO₂ powders with dopamine were calculated using Kubelka–Munk spectra obtained by the transformation of the diffuse reflectance to the Kubelka–Munk function [37]. The largest decrease of the effective band-gap energy (1.3 eV) was observed for dopamine concentrations higher than 33% of Ti_{surf} atoms. Most likely, due to steric hindrance surface of TiO_2 powder is saturated with dopamine molecules at concentration lower than the concentration of Ti_{surf} atoms. Basically, the band-gap energies of dopamine modified TiO_2 powders (around 1.9 eV) are identical to the band-gap energies of corresponding precursors.

FTIR spectroscopy measurements were performed in order to clarify whether or not ultrasonic spray pyrolysis induced any changes in binding efficiency and geometry of dopamine modified TiO₂ nanoparticles during formation of submicronic TiO₂ powder particles. Since the infrared spectrum of TiO₂ powder has characteristic bands in the following regions: 1000–400 cm⁻¹ due to Ti–O and Ti–O–Ti stretching vibrations and in 3700–2000 cm⁻¹ due to hydrogen-bonded OH stretching vibrations [11,38,39], we were able to measure dopamine modified TiO₂ nanoparticles, as well as dopamine modified TiO₂ powders in 1700–1000 cm⁻¹ spectral region, where the characteristic bands of dopamine exist.

Fig. 6. (a) TEM images of submicronic TiO₂ particles obtained in the process of ultrasonic spray pyrolysis at 150 °C by using dopamine modified TiO₂ nanoparticles as a precursor (dopamine concentration is 33% of Ti_{surf} atoms), and (b) marked region at a higher magnification.

Fig. 7. Diffusive reflection spectra of (a) bare submicronic TiO_2 particles and surface modified submicronic TiO_2 particles with various dopamine concentrations: (b) 3, (c) 33, (d) 66 and (e) 100% of Ti_{surf} atoms. Photographs of bare submicronic TiO_2 particles and submicronic TiO_2 particles modified with dopamine (3 and 100% of Ti_{surf}) atoms are also included.

The FTIR spectra of free dopamine, bound to the surface of precursor TiO₂ nanoparticles and surface of submicronic TiO₂ powders particles are shown in Fig. 8a-c, respectively. It should be noticed that FTIR spectra of dopamine bound to the surface of precursor TiO₂ nanoparticles and dopamine bound to the surface of submicronic TiO₂ powder particles are almost identical, but on the other hand, there are differences in comparison to FTIR spectrum of free dopamine indicating formation of charge-transfer complex between dopamine and TiO₂. The main bands and their assignments in free dopamine are as follows: stretching vibrations of $\sigma[(-C=C-)/(C-C)]$ in benzene ring at 1471, 1497 and 1615 cm⁻¹. in plane asymmetric banding vibrations of β (NH³⁺) at 1600 cm⁻¹, in plane symmetric bending vibration of β (CH₂) group at 1340 cm⁻¹, stretching vibrations of $\sigma(CO)$ at 1283 cm⁻¹, in plane bending vibrations of phenolic group and CH/CH₂ groups in the region bellow 1200 cm⁻¹. The binding of dopamine to TiO₂ via two adjacent phenolic groups affects the in-plane bending vibrations of the

Fig. 8. FTIR spectra of: (a) free dopamine, (b) dopamine bound to the surface of precursor TiO_2 nanoparticles, and (c) dopamine bound to the surface of submicronic TiO_2 powder particles (dopamine concentration corresponded to the 100% of Ti_{surf} atoms).

phenolic group β (C–OH) at 1320 cm⁻¹, inducing a decrease in intensity of this band [40]. The structural changes induced by protonation of dopamine amino group after binding to the surface of colloidal TiO₂ nanoparticles at pH = 3 influence its vibrational properties and consequently corresponding IR spectrum. As can be seen in Fig. 8, a new band at 1428 cm⁻¹ appears in the FTIR spectra of dopamine-modified precursor TiO₂ nanoparticles (Fig. 8b) and dopamine modified submicronic TiO₂ powder particles (Fig. 8c). This band is assigned a symmetric N–H umbrella mode that is characteristic for the protonated NH³⁺ group of dopamine molecules [40].

Having in mind the similarity of FTIR spectra in Fig. 8b and c, we also concluded that under mild conditions in the process of ultrasonic spray pyrolysis there is no existence of unbound dopamine molecules and their undesired oxidation, which for the result could have colored quinones derivatives [41]. Efficiency of binding and surface geometry of dopamine remained the same.

4. Conclusions

To conclude, the process of ultrasonic spray pyrolysis led to the formation of colored submicronic TiO₂ powder particles using dopamine modified TiO₂ nanoparticles as a precursor. Significant red shift of optical absorption of dopamine-modified colloidal TiO₂ precursor nanoparticles (about 1.3 eV), compared to bare ones, was preserved after formation of submicronic TiO₂ powder particles under mild experimental conditions (150 °C). The process of ultrasonic spray pyrolysis extended formation of charge transfer complexes between electron donating ligands and surface Ti atoms, has so far been achieved only for extremely small TiO₂ nanoparticles (d < 20 nm), in submicronic size range. The main reason is preserved square pyramidal coordination of surface Ti atoms in soft submicronic TiO₂ assemblages. It should be emphasized that process of ultrasonic spray pyrolysis opens up possibility to design TiO₂ powder particles with desired optical, size and morphology characteristics by proper choice of ligand, frequency of aerosol generator and pre- or post ligand treatment.

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Aerosol route as a feasible bottom-up chemical approach for up-converting phosphor particles processing

Advanced Powder Technology

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1. Introduction

Rare-earth based up-converting phosphor (UCP) nanocrystalline particles represent the new, sophisticated generation in materials science and engineering with the potential use in modern display and labeling technologies, sensors, optical data storage, telecommunications, etc. [1–5]. They exhibit the unique property of emitting visible light following photoexcitation in near infrared region. The most efficient up-converting host materials belong to the group of the yttrium based- inorganic compounds like fluorides, oxides and oxysulfides codoped with the trivalent rare earths (Yb³⁺, Er³⁺, Tm³⁺, Pr³⁺, Ho³⁺, etc.). Among other yttrium compounds, yttrium oxide represents an efficient UCP phosphor host material for the substitution of rare earth ions because of its low phonon energy, <600 cm⁻¹, broad optical transparency range 0.2– 8 μm, high refractive index, >1.9 and large energy band-gap, 5.8 eV [6]. Yttrium oxide posses a cubic crystal structure with a space group, S.G. $Ia3-(T_h^7)$ in which there are two crystallographically different rare-earth sites, C2 (75%) and S6 (25%); by that, a unit cell is composed of four atom positions, three having a point symmetry C2 and one position with a point symmetry S6 [7].

ABSTRACT

The opportunities of the hot wall aerosol synthesis, i.e. conventional spray pyrolysis (CSP) method are demonstrated for the generation of highly spherical three-dimensional (3D) nanostructured phosphor particles with uniformly distributed components, phases and nano-clustered inner structure. With the presumption that certain particle morphology is formed during the evaporation/drying stage, the aerosol transport properties and powder generation are correlated with the particles structural and morpholog-ical features. With the help of various analyzing techniques like Field Emission Scanning Electron Microscopy (FE-SEM), Transmission Electron Microscopy (TEM) coupled with energy dispersive X-ray Analysis and STEM mode (TEM/EDS), X-ray Powder Diffraction (XRPD) and fluorescence measurements the feasible processing of up-conversion rare-earth Y₂O₃:Er, Yb phosphors powders are discussed.

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High luminescence efficiency is basically associated with high radiative transition rates which can be achieved with optimum doping concentration, uniform distribution of the luminescent centers in the host matrix and the overall particle structure and morphology control, which altogether signify the importance of innovative and controllable UCP phosphor processing route in the current research efforts [7-9]. Moreover, of particular importance is the controlled synthesis of the host lattice having targeting crystal structure which determines the distance between the dopant ions, their relative spatial position, their coordination numbers, and the type of anions surrounding the dopant. In addition, the low symmetry and low phonon energies of the host lattice are essential for reducing the multiphonon relaxation and increasing the lifetime of the intermediate states involved in upconversion [10]. Most of research are concerned with halide host matrix processing and particularly with the hexagonal sodium yttrium fluoride which has been regarded as one of the most efficient up conversion host matrix having the phonon energies below 500 cm^{-1} [11–13]. Of the medium phonon energies host matrices, cubic yttria posses high chemical and thermal stability and is one of the most efficient non-halide host material [11].

Among the diversity of the "bottom-up" chemical approaches for nanomaterials processing, synthesis through dispersion phase (aerosol) enables generation of ultrafine, either single or complex powders with controlled stoichiometry, chemical and phase con-

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Nomenclature

C _i d _d d _p D L	initial precursor solution concentration (mol dm ⁻³⁾ droplet diameter (m) particle diameter (m) tube diameter (m) tube length (m)	Dimensi Bi Nu Re Re _t	ionless number Biote number [1] Nusselt number [1] flow Reynolds number [1] particle Reynolds number [1]
F _a b	flow rate of gas phase (carrier gas, air) (m ² s ⁻¹)	Cubacrin	a ta
11 _t 1.	thermal conductivity ($M m^{-1} K^{-1}$)	Subscrip	nis air
К _W М	molecular weight (g mol ^{-1})	u d	dlf dromlata
T	tomporeture (K)	и :	
1	temperature (K)	1	initial precursor solution
t	time (s)	р	particles
ua	mean velocity of gas phase (carrier gas, air) (m s ⁻¹)	w	water
Greek let	tters	Equation	ns 1/2
γ	surface tension of precursor (N m^{-1})	d_d	$0.34 \cdot \left(\frac{8 \cdot \pi \cdot \gamma_i}{2 \cdot \pi^2}\right)^{1/3}$
μ	shear viscosity of gas/liquid phase (m Pas)		$\left(\rho_{i} \gamma^{2} \right)$
ρ	density of gas/liquid phase (kg m^{-3})	dn	$d_{\rm d} \cdot \left(\frac{c_i M_{\rm Y_2O_3}}{c_i M_{\rm Y_2O_3}}\right)^{1/3}$
τ	residence time of droplets/particles (s)	чp	$\mu \left(\rho_{Y_2 o_3} \right)$
φ	volume fraction of solute [1]	(2)	$c_i: M_{Y_2O_3}$
φ^*	critical volume fraction of solute [1]	φ	$\Psi = \overline{1000 \cdot \rho_i}$
•			

tent provided by high heating and cooling rates, short residence time and high surface reaction [14]. This may favors to the formation of either amorphous, nanocrystalline or metastable phases that might have a huge impact in the processing of advanced functional materials having novel and unique structures and properties. During the process, aerosol droplets undergo evaporation, drying and solute precipitation in a single-step, enabling spherical, either hollow or dense, agglomerate-free, submicronic "secondary" particles to be obtained exhibiting the composite inner nanostructure and representing an assembly of primary nanoparticles. The size and size distribution of secondary particles are mainly influenced by the properties of precursor solutions and aerosol generation, while the size of primary particles depends on the timetemperature history of particle formation and materials properties [7]. There is a diversity of aerosol routes, depending mainly on the manner of aerosol formation and how the aerosol decomposition energy is transferred to the precursor system, reflecting on the most important particle formation parameters: residence time and temperature distribution [7]. Among them, flame synthesis represents a straightforward large-scale aerosol route for producing spherical nanoparticles in different oxide and non-oxide systems, enabling higher temperatures and shorter residence time to be obtained. It has been reported a successful processing of nanocrystalline up conversion phosphor particles in Yb (Tm, Er) doped-sodium vttrium fluoride and Sm-doped Gd₂O₃ by this route [13.15]. For the case of hot-wall flow reactor, a well-controlled temperature profile over long residence times can be achieved, however the direct processing of nanoscaled particles is limited and associated either with the precursor solution dilution or urea/salt assisted solution modification [7], which in turn influence on the powder production rates.

In our previous work, hot wall aerosol route has been recognized as successfull to obtain submicronic Eu^{3+} -doped nanocrystalline down-conversion Y_2O_3 , $(Y_{1-x}Gd_x)_2O_3$ and Gd_2O_3 phosphor particles with advanced structural, morphological and luminescent properties [8,9,16]. It has been demonstrated that the key particle formation parameters are the physico-chemical properties of precursor solution, the manner of aerosol generation and the process parameters like temperature, residence time, and atmosphere determining the mechanisms of aerosol formation, solute precipitation, nucleation, growth and primary nanoparticles aggregation into a spherical assemblage [7]. Recently we have presented the aerosol processing of temperature sensitive Y_2O_3 based nanocrystalline UCP particles, doped with Yb^{3+} and co-doped with either Tm^{3+} or Ho^{3+} [17]. Considering the diversity applications of nanocrystalline up-converting particles and especially their potential advantages over micro-scaled conventional materials, in this work we have prepared yttrium oxide co-doped with erbium and ytterbium by applying the same aerosol based conventional spray pyrolysis (CSP) method. Aiming to investigate the morphology aspect of UCP nanocrystalline particles, we have studied droplet-to-particle formation mechanisms in dispersed system and have discussed them in the framework of the obtained structural, morphological and spectroscopic properties.

2. Experimental

In order to synthesize Y_{1.94}Yb_{0.05}Er_{0.01}O₃ UCP particles, the precursor aqueous solutions ($c_i = 0.1 \text{ mol/dm}^3$) are prepared by dissolving the corresponding amounts of $Y(NO_3) \times 6H_2O_1$ $Yb(NO_3) \times 5H_2O$ and $Er(NO_3) \times 5H_2O$ having Yb/Er concentration ratio 5. All the chemicals are of the highest purity available (Aldrich, 99%); distilled deionized water is used with a resistivity of 18.2 M Ω cm⁻¹ (Milipore, UK). The obtained precursor solution is further ultrasonically atomized and such obtained aerosol is decomposed in the air stream in a high-temperature tubular flow reactor (tube geometry: D = 0.04 m; L = 1.9 m) equipped with the three temperature zones ($T_1 = 473$, $T_2 = 1173$, $T_3 = 1173$ K). The as-prepared powders are subjected to the additional thermal treatment in air at 1373 K for 12, 24 and 48 h (samples 5-2, 5-3 and 5-4), while 5-1 denotes as-prepared powder sample. The details regarding the processing route are given elsewhere [7] and schematic of the conventional spray pyrolysis experimental setup is presented at Fig. 1.

Physico-chemical properties of the precursor solutions are estimated at room temperature. Particle size distribution is analysed by laser particle sizer (Mastersizer 2000, Malvern Instruments). The morphological analysis and chemical purity are investigated by Field Emission Scanning Electron Microscopy, HITACHI SU-70 (FESEM) and Transmission Electron Microscopy, JEOL, JEM-2100F, 200 kV (TEM) coupled with energy dispersive X-ray Analysis and STEM mode. Structural evaluation is done by X-ray powder diffrac-

Fig. 1. Schematic representation of the laboratory setup of CSP with (1) carrier gas, (2) flow meter, (3) ultrasonic atomizer, 1.3 MHz, RBI (4) hot-wall reactor (5) diffusion dryer, TSI and (6) electrostatic precipitator.

tion (XRPD) analysis on Rigaku Ultima IV diffractometer operating with Cu Ka radiation at 40 mA and 40 kV. The measurements are performed in the 2θ range from 10° to 100° with a step scan of 0.02 and counting time of 10 s per each step. The Rietveld structural refinement is done in Topas Academic 4.1 [18] for the determination of microstructural parameters using the Fundamental Parameter Approach where FWHM based LVol (volume weighted mean column height) calculation is used for the determination of the intermediate crystallite size broadening modeled by a Voigt function. The photoluminescence spectra and decay time measurements are performed on spectroflurometer system having optical parametric oscillator excitation source, (Impulse laser -2 mJ per pulse, pulse duration 5.2 ns, repetition rate 10 Hz, EKSPLA NT 342, emission range 210-2300 nm), Cryostat (Advance Research Systems DE202-AE) equipped with Lakeshore model 331 controller, spectrograph FHR 1000 (Horiba Jobin-Yvon, 300 groove/mm grating) and ICCD detector (Horiba Jobin-Yvon 3771). The single exponential function is used for the decay time fitting.

3. Results and discussion

With the presumption that certain particle morphology is formed during the evaporation/drying stage of CSP [19,20], all calculations related to the aerosol transport regimes are estimated at 373.15 K. Moreover, considering a one-droplet- to one-particle conversion mechanism [21], the mean gas velocity and residence time were calculated from the gas flow rate and the geometry of hot-wall reactor aiming to analyze the conditions for particle generation in dispersed system. Based on that, the Reynolds number of the air flowing around single droplet/particle, defined as:

$$\operatorname{Re}_{t} = \frac{\rho_{a} \cdot d_{d} \cdot u_{a}}{\mu_{a}} \tag{1}$$

imply laminar gas motion; d_d is the droplet diameter, 3.217 µm, estimated in accordance to the Lang equitation and the solution

properties, [22–24], while the values and definition of other parameters are given in Table 1 and/or in Notations. It is assumed dropletto-droplet interaction are negligible because of the small droplet volume fraction in continuous phase [25].

The Reynold's number, which defines the regime of the aerosol transport within the system:

$$\operatorname{Re} = \frac{\rho_a \cdot D \cdot u_a}{\mu_a} \tag{2}$$

is calculated to be Re \sim 36.70 <2300, implying the aerosol transportation is done within the carrying gas into a laminar flux motion.

The temperature distribution along the radius of a droplet could be ignored for Biot number, Bi < 1, in accordance to the following equitation:

$$\operatorname{Bi} = \frac{h_t \cdot d_d}{6 \cdot k_w} \tag{3}$$

in which k_w (W m⁻¹ K⁻¹) is the droplet thermal conductivity, 0.683, taken for water at 373.15 K With assumption the droplet velocity is the same as that of the carrier gas, the heat transfer coefficient, h_t , is estimated based on Nusselt and Prandtl dimensionless numbers (Table 1) by combining the following equations:

$$Nu = 2 + 0.6 \cdot Re_r^{1/2} \cdot P_r^{1/3}$$
(4)

and

$$\mathbf{N}\mathbf{u} = \frac{h_t \cdot d_d}{k_w} \tag{5}$$

Because the resistance to heat flow within the droplet is small relative to the resistance presented by the convection processes at the surface, the temperature inside the droplet is uniform and assumed to be the same as the droplet surface, implying volume precipitation of solute inside the droplet. This implicates solid particle formation if the precolation criterion is fulfilled, enabling formation a continuous three-dimensional network of solute filling.

Table 1

The solution/gas properties and conditions for aerosol transport and particle generation.

The conditions for particle generation in a dispersed system Carrier Gas (air) flow rate, $F_a \times 10^5 \text{ (m}^3 \text{ s}^{-1})$ 2.667		Mean velocity of carrier g 0.02123	Residence time, τ (s) 89.5		
Physico-chemical and transport	properties of air at <i>T</i> = 373.15 K				
Density, $ ho_a$ (kg m ⁻³)	Shear viscosity, $\mu_a imes 10^6$ (Pas)	Pr	Re	Transport regime	
0.946	2.19	0.688	36.70	$<2.3 imes 10^3$ laminar	
Physico-chemical properties of t	he precursor solution at 298 K				
Concentration, c_i (mol dm ⁻³) Surface tension, $\gamma_i \times 10^3$ (N		N m ⁻¹) Viscosity, μ_i (m Pas)		Density, $ ho_i imes 10^{-3}$ (kg m $^{-3}$)	
0.1	65.8	1	.058	1.02217	
Values of dimensionless number	rs and heat transfer coefficient at <i>T</i> =	373.15 K			
$\text{Re}_t \times 10^3$ [1]	Nu [1] h _t	$ imes 10^{-5} (W m^{-1} K^{-1})$	Bi [1]	φ	
3.039	2.029 4.	183	0.338	0.00459 < 0.16	

Fig. 2. FESEM micrographs of as-prepared (a) and powders heat treated at 1373 K for 24 h (b and c); low magnification TEM image of the powder 1373 K for 24 h (d); the corresponding log-probability plot is given in inset.

Fig. 3. STEM image and EDS mapping of Y_{1.94}Yb_{0.05}Er_{0.01}O₃ UCP particles (SP 5-3).

However, for the conditions in this experimental work, the percolation criterion, φ is less than the critical volume fraction $\varphi^* = 0.16$ [20], implying the possibility for excessive porosity formation.

FE-SEM micrographs are presented at Fig. 2 for as-prepared and thermally treated powder samples. The presence of polydispersed spherical particles in submicronic range is evident. Either the sponge-like or desert-rose-like particle morphology prevailed for the as-prepared powders, while the prolonged heating leads to the better differentiation of primary particles as a result of their thermally induced growth, collision and aggregation. The as-prepared particle distribution is log-normal, as evident from Fig. 2a inset, with the D_{50} = 985 nm. The typical particle morphology after thermal treatment at 1373 K/24 h is presented at Fig. 2b and c, showing the blueberry-like structure of secondary particles representing an assembly of nanosized (<50 nm) primary particles. The primary particles are predominantly spherical in shape, colliding to the aggregates. Moreover, the increase of the annealing temperature and time additionally leads to the interparticle sintering that is more prominent at higher temperatures. Low magnification

Fig. 4. XRD pattern of $Y_{1.94}Yb_{0.05}Er_{0.01}O_3$ UCP particles annealed at 1373 K/24 h (SP 5-3).

Table	2

Rietveld refinement of Y_{1.94}Yb_{0.05}Er_{0.01}O₃ UCP particles (SP 5-3).

Lattice parameter (Å)	Crystallite size (nm)	^a Y ₁ :O bond length (Å)	^a Y ₂ :O bond length (Å)	Y ₁	0 ²⁻	Occ Y ₁ (Y3+)	$Occ Y_2(Y^{3+})$	R Bragg
10.59915 (6)	69 (1)	2.216 (4) 2.267 (4) 2.340 (4)	2.283 (4)	<i>x</i> - 0.0321(1)	x 0.3953 (4) y 0.1554 (3) z 0.3778 (3)	0.9693	0.9721	2.69

^a Y₁ corresponds to C₂ site; Y₂ corresponds to S₆ site in cubic crystal unit cell, S.G. *Ia*-3.

TEM implies the higher particle density at the surface implicating the particles predominantly aroused through the mechanism of surface precipitation [7]. Based on the elemental analysis (Fig. 3) it is evident a very homogeneous distribution of the constitutive elements: Y (L α , 1.9226 keV), O (K α 0.5249), Er (L α 6.9488 keV), Yb (M α 1.5215 keV). That represents one of the basic advantage of CSP showing no compositional segregation at the selected particle agglomerate presented in STEM image (upper left). Moreover, a uniform distribution of the Yb³⁺ and Er³⁺ ions into a host yttria matrix implicates high luminescence efficiency to be obtained.

XRPD analysis confirms the presence of a single cubic bixbyte crystal structure (S.G. Ia-3, PDF 87-2368) in all synthesized and thermally treated samples. The much narrower peak reflections are observed in thermally treated powders implying the increase of crystallinity with annealing temperature and time. Detailed microstructural analysis performed for SP-5-3 powder sample through Rietveld refinement (Fig. 4 and Table 2) revealed the crystal cell parameters did not change significantly after dopants incorporation in comparison to the Y_2O_3 phase (PDF 89-5591, a = 10.6 Å) due to the small differences in their ionic radii (Y³⁺ 0.104 Å, Yb³⁺ 0.100 Å, Er^{3+} 0.103 Å). After incorporation into the Y₂O₃ matrix, the Yb³⁺ and Er³⁺ ions could be randomly distributed into the two nonequivalent crystallographic sites: non-centrosymmetric C_2 at the 24d site and centrosymmetric S_6 (C_{3i}) at the 8a site [9]. With regards to that the Y³⁺ cation site occupancy refinements of both positions were performed, since the preferential occupation might influence on luminescence efficiency. The obtained results imply that substitution of Y^{3+} is more pronounced in the C_2 position than in S₆ position, as indicated by the lower values for C₂ site occupation with Y³⁺, Table 2. It is estimated the crystallite size of about 70 nm for the SP 5-3 sample thermally treated at 1373 K/ 24 h, confirming the powder nanocrystalline structure.

Fig. 5. Up-conversion emission spectra of nanocrystalline $Y_{1,94}Yb_{0.05}Er_{0.01}O_3$ powders excited at 978 nm as a function of annealing time at 1373 K, with the corresponding decay times, τ_{C} (ms). The annealing time dependence of green to red emission integrated area ratio is presented in inset. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

The up-conversion luminescence spectra upon excitation at 978 nm are presented at Fig. 5 as a function of annealing time at 1373 K. The green luminescence emission, assigned to the Er^{3+} (${}^{2}H_{11/2}$, ${}^{4}S_{3/2}$) $\rightarrow {}^{4}I_{15/2}$ electronic transitions is evident, peaking at 563 nm. The red emission at 660 nm is less intensive, and corresponds to the $Er^{3+} {}^{4}F_{9/2} \rightarrow {}^{4}I_{15/2}$ electronic transitions, while weak blue emission, assigned to the $Er^{3+} {}^{2}H_{9/2} \rightarrow {}^{4}I_{15/2}$ electronic transitions is almost negligible. The annealing time dependence of green to red emission integrated area ratio, presented at Fig. 5 in inset, increases linearly. It is assumed that due to the smallest energy levels band gap, the (${}^{2}H_{11/2}$, ${}^{4}S_{3/2}$) $\rightarrow {}^{4}I_{15/2}$ electronic transition is more affected by the phonons adsorbed at the surface comparing to the ${}^{4}F_{9/2} \rightarrow {}^{4}I_{15/2}$ ones [4]. By that, the thermally and kinetically provoked crystallite/particle growth and the surface defects diminishing manifest in increase of green to red emission ratio with annealing time.

The corresponding decay times at 300 K for the most prominent green emission, τ_{C} (ms), are presented at the Fig. 5, as well. For the rare earth ions is typical longer excited-state lifetimes, 10^{-6} – 10^{-3} s compared to 10^{-9} – 10^{-6} s for conventional ions [26]. The obtained decay time values associated with long emission implied very good up-conversion efficiency of powders and are improved in comparison to the reported values for nanocrystalline materials [11,27]. The higher value of 0.48 ms is obtained after 1373 K/24 h annealing. With no doubt, the observed relationship of the emission spectra and the decay times with annealing conditions are closely associated with the particle structure and morphology i.e. increasing the crystallite size associated with lowering of the defects and better accommodation of dopants into the lattice sites. In the same time, the counter current process of particle aggregation occurs, as evident by the neck formation and thickened with annealing, which causes the decrease of decay time after 48 h annealing. These altogether implies the optimum luminescence efficiency is a compromise of the time/temperature evolution of particle structure and morphology. The particles structural and morphological features (submicronic in size, spherical, nanostructured, having uniform distribution of the luminescent center) imply their application in different up converting phosphor technologies like security labeling, forensic, light emitting devices, temperature sensors, etc. [17]. Moreover, the particles composite inner structure, representing an assembly of nanosized primary particles, opens the possibility for particle surface modification and functionalization emphasizing the possibility in bioimaging and energy transfer applications [26].

4. Conclusions

Aerosol route as a bottom-up chemical approach for UCP phosphor particles processing is presented together with the corresponding process parameters that influence on the particle structure, morphology and composition. With the presumption that certain particle morphology is formed during the evaporation/drying stage of CSP, droplet to particle conversion and transport properties in dispersed system were followed using Re, Nu, Pr and Bi dimensionless numbers. The structural, morphological and functional properties, analyzed in accordance to XRPD, FESEM, STEM, TEM and spectroscopic measurements proved the feasibility of CSP for nanocrystalline phosphor particle processing.

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