Aerosol-assisted processing of hierarchically organized TiO_2 nanoparticles

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Abstract

Hierarchically assembled TiO_2 nanoparticles into larger spherical ones were obtained using aerosol-assisted processing method. Unagglomerated particles with the mean size of 440 nm were obtained from colloidal solution of TiO_2 nanoparticles (~4.5 nm) using ultrasonic spray pyrolysis at 550 ^{o}C. Their morphological complexity and structural polymorphism were investigated by using X-ray powder diffraction (XRPD), scanning electron microscopy (SEM), energy dispersive X-ray spectroscopy (EDS) and transmission electron microscopy (TEM) coupled with selected area electron diffraction (SAED) analysis. Pronounced evolution of nanocrystalline TiO_2(B) phase assembled together with the anatase building units (sized ~ 15 nm) in uniform submicrometric particles implicate their feasibility to be used in dye-sensitized solar cells and lithium ion batteries.

Keywords: TiO_2; titanium dioxide; aerosol processing; nanoparticles; hierarchically organized spherical particles; light scattering centers; lithium ion batteries.

1 Introduction

Titanium dioxide (TiO_2) based materials have significant large-scale applications as pigment, sensor, photocatalyst, etc (Nakata et al; 2012). The most important issue for the future development of the new relevance is the control of size, shape, structural and morphological properties of TiO_2 particles. It is well known that TiO_2 has four important crystallographic polymorphs: anatase (tetragonal), rutile (tetragonal), brookite (orthorhombic) and TiO_2(B) (monoclinic). Among them, rutile has the best thermodynamical stability (for particles > 35 nm), while anatase is the most photocatalytically efficient one. Brookite, as metastable phase that needs high processing temperature, has been rarely studied contrary to TiO_2(B) which is in the focus of many recent reports due to its potential application in energy storage systems. Titanium dioxide polymorphs are composed of many TiO_6 octahedra in which each titanium atom is coordinated in an octahedral configuration to six neighboring oxygen atoms. TiO_6 octahedra are also mutually co-coordinated (either corner or edge), forming different crystal symmetries (Landmann et al.; 2012). For the case of a TiO_2(B) phase, it is composed of corrugated sheets of edge-and corner sharing TiO_6 octahedra, thus forming a three-dimensional network. This open structure is characterized by large and continuous channels, which makes it well situated as a host for intercalation of lithium (Zhu et al., 2012). It is shown recently that hierarchically organized mesoporous TiO_2(B) microspheres, obtained *via* template assisted ultrasonic spray pyrolysis of titanium bis(ammonium lactato) dihydroxide with silica, have superior lithium storage performance which could meet the needs of electric vehicle batteries and other high power applications (Liu et al., 2011).

In generally, hierarchically organized TiO_2 nanoparticles, regardless of the crystal structure or shape have shown highly promising application in the energy and environmental-related fields such as: dye-sensitized solar cells (Zhang et al., 2012), lithium-ion batteries (Chen et al., 2010), gas sensing application (Wang et al., 2010), photocatalytic oxidation and water splitting (Lakshminarasimhan et al., 2007; Nakata and Fujishima, 2012). The common advantage of these nanostructures is their spherical morphology and submicrometer dimension, that offer high packing density and good particle mobility to form a compact electrode layer (Xu et al., 2013). The diverse levels of morphological and structural complexities of these hierarchically organized TiO_2 particles were usually established through sol-gel (Jiang et al., 2003), hydrothermal (Liu et al., 2012) and spray pyrolysis processing (Iskandar et al., 2007; Nedeljkovic et al., 1997). However, most of the syntheses were performed in the presence of hard templates (silica) or the soft ones (structure directing agents) providing generation of dense, mesoporous or hollow assemblies of primary nano sub-units with shape of sheets, tubes, particles, etc.

We have also shown that synthesis from the aerosol is found to be of the great value for manufacturing un-agglomerated nanostructured particles with pre-defined morphology and targeted chemical composition (Milosevic et al., 2009). This versatile technique is recently used for the synthesis of submicronic soft TiO_2 assemblages in the wide temperature range (Dugandzic et al., 2012). Their clustered substructure, controllable phase composition and high specific surface area enable surface modification of their primary anatase nano units (~ 4.5 nm) with different bidentate ligands making them to be effective for visible light absorption.

Here, we present detailed structural and morphological investigation of hierarchically organized TiO_2 spherical particles obtained through spray pyrolysis of TiO_2 colloidal solution. Their polycrystalline nature and presence of anatase and TiO_2(B) nano building blocks integrate advanced features of both TiO_2 polymorphs, extending their potential application in energy storage related fields.

2 Experimental techniques

2.1 Synthesis of TiO_2 hierarchically organized particles

A schematic view of the laboratory setup for ultrasonic spray pyrolysis used to prepare hierarchically organized TiO_2 particles was presented and described in our previous report (Dugandžić et al., 2013). Briefly, the fine and uniformly distributed droplets were continuously generated from precursor solution using the ultrasonic atomizer (RBI, France) operated at 1.7 MHz. As a precursor, TiO_2 colloidal solution with concentration of 0.05 M synthesized from titanium tetrachloride ($TiCl_4$) was used (Rajh, et al., 1996). The initial droplet size after atomization was calculated to be ~3 μm according to Lang equation (Lang, 1962; Peskin and Raco, 1963). Nitrogen (N_2) it used to introduce aerosol into tubular flow reactor and to provide short droplets residence time in the reaction zone (11 s). The temperature profile of reactor was maintained to be 150, 550 and 150^{o}C in three independently controlled zones. Additional particles drying at the reactor exit were performed in Diffusion Dryer unit 3062 (TSI Inc., USA) prior their collecting in electrostatic precipitator.

2.2 Particle characterization

The particle morphology was checked by scanning electron microscopy technique using Philips XL30 SEM (SEM Tech Solutions). The obtained images are analyzed using ImageJ software for the determination of the mean particle size. The elemental composition of the sample was analyzed with energy-dispersive X-ray spectroscopy (EDS) attached to the SEM. Transmission electron microscopy (TEM) images and selected area electron diffraction (SAED) pattern were taken using a JEM-2100 LaB_6 (JEOL Ltd.) operating at 200 kV. The powders phase composition were determined using a PW 1050 (Philips) diffractometer with CuKα radiation (α=1.5406) in the 2θ range from 15-95^o with a step scan of 0.05^o and scanning rate of 10 s per step. Structural refinement was done based on Rietveld analysis in Topas Academic 4.1 program (Cheary and Coelho, 1992). The background was refined by using the ninth-order Chebichev function, while peak profile shapes were convoluted using Lorentzian function for determination of the crystal size.

3. Results and discussion

The morphology of the obtained TiO_2 particles is shown in Figure 1(a). It is apparent that particles are highly spherical with quite uniform size distribution. As one could see from the particle size distribution, inset in Fig 1(b), non-aggregated submicron sized particles have the mean size diameter of ~ 440 nm. Characteristic surface morphology, notable at Figure 1(a), is a consequence of the close packing of primary building units and depends on their crystallinity. Typical EDS analysis, Figure 1(b), shows that the synthesized white color powders are composed of titanium (Ti) and oxygen (O) elements.

Rietveld refinement of the X-ray diffraction pattern of TiO_2 powder obtained through aerosol-assisted processing of TiO_2 nanoparticles at 550 ^{o}C is shown in Figure 2. In the Rietveld analysis the least squares refinements method is carried out until the best fit is obtained between the calculated patterns (red line, Figure 2), based on the refined structure models proposed (blue lines, Figure 2), and the observed diffraction pattern (black line, Figure 2). As one can see, it shows that synthesized powder is composed from anatase and TiO_2(B) phase in 28.5:71.5 wt. % ratio. Microstructural parameters of both phases are presented in Table 1. Small crystallites size of ~15 nm confirms nanocrystalline nature of spherically hierarchically organized TiO_2 structures. TiO_2(B) phase, characterized by the Freudenbergite type structure (Ishiguro, et al., 1978) is a monoclinic TiO_2 modification with a lower density and a structure characterized by combination of the edge- and corner-sharing TiO_6 octahedra forming the channels. It represented an intermediate step towards generation of the more stable TiO_2 rutile phase (Dugandžić et al., 2012), and, as it was mentioned above, it is one of the targeting phase for the synthesis since offers new possibilities for different ions accommodation in its structure (Dylla et al., 2013).

The inner structure of hierarchically organized TiO_2 particles was further investigated by transmission electron microcopy (TEM). Typical TEM images presented in Figure 3(a, b) confirm that spherical assemblies are comprised of much smaller building units whose dimension corresponds reasonably well with crystallite size determined by XRPD analysis. Additionally, the gradual change of contrast notable from the center to the edge in the individual spherical particle (Figure 3c) indicates their uniform self-organization within the bigger ones. The corresponding SAED patterns, Figure 3(d), reveals the presence of both TiO_2 phases: anatase (d=3.52 Å) and monoclinic TiO_2(B) (d=5.8 Å) crystal structures (d values correspond either to (101) or (200) crystal planes, respectively).

Based on the above presented results, a suggested formation mechanism of hierarchically organized TiO_2 particles generated through spray pyrolysis of the colloidal precursor solution is presented at Figure 4.

Starting from the assumption that during the spray pyrolysis process, one droplet yield one particle (Messing et al., 1993), each droplet generated from the colloidal TiO_2 precursor solution contains certain number of the colloidal TiO_2 nanoparticles. Due to the heating inside of the tubular hot-wall reactor, solute evaporates from the droplet surface while nanoparticles cluster and reorganize at droplet interior. With the further decrease of the droplet diameter nanoparticles come closer to each other forming the three-dimensional network. Sufficient heat input initiate further growth of anatase crystallites and partial transformation to the TiO_2(B) phase. Short particle residence time in reaction zone inhibits significant growth of nanobuilding units and intraparticle sintering, maintaining spherical shape and certain degree of nanoporosity in hierarchically organized sub-micron spherical particles.

Conclusions

We have shown the opportunities of the aerosol processing in the tailoring of morphology and phase content during synthesis of spherical, three-dimensional (3D) hierarchically organized TiO_2 particles from colloidal precursor solution. Their polycrystalline nature and presence of anatase and TiO_2(B) nano building blocks integrate advanced features of both TiO_2 polymorphs, extending their potential application in energy storage related fields.

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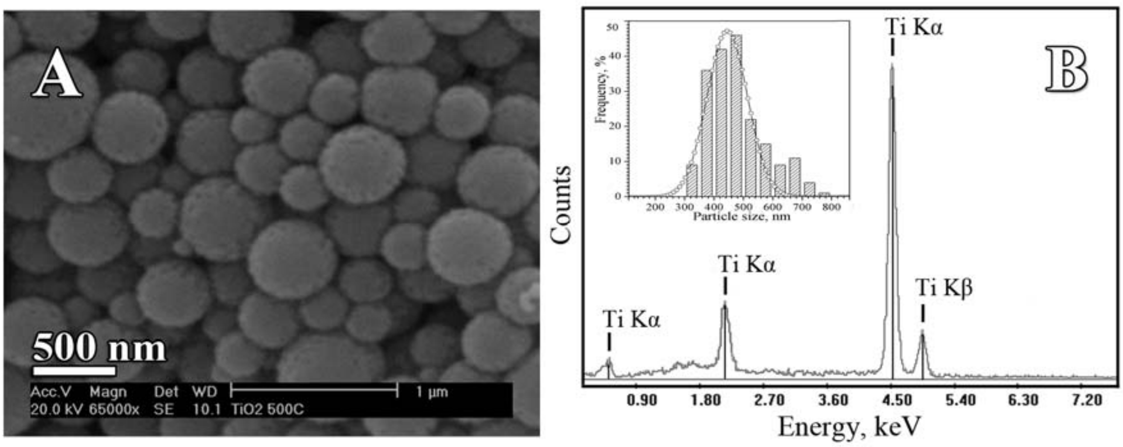

Figure 1 (a) SEM and the corresponding (b) EDS analysis of the hierarchically organized TiO_2 particles with the particle size distribution (inset)

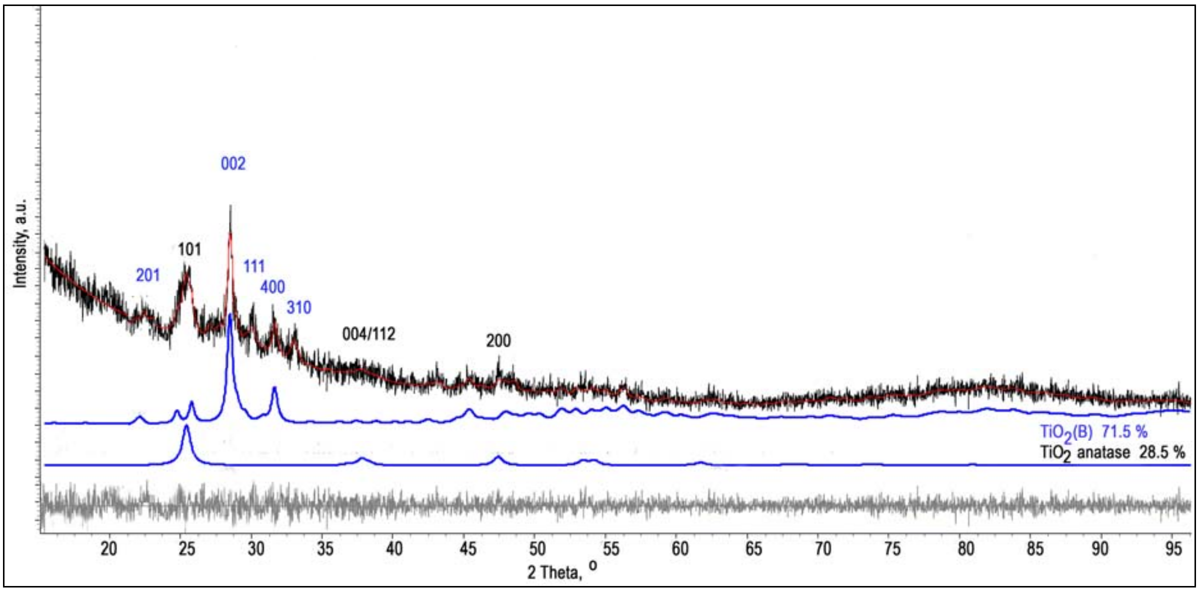

Figure 2 Rietveld refined X-ray powder diffraction (XRPD) pattern of the hierarchically organized TiO_2 nanostructured particles

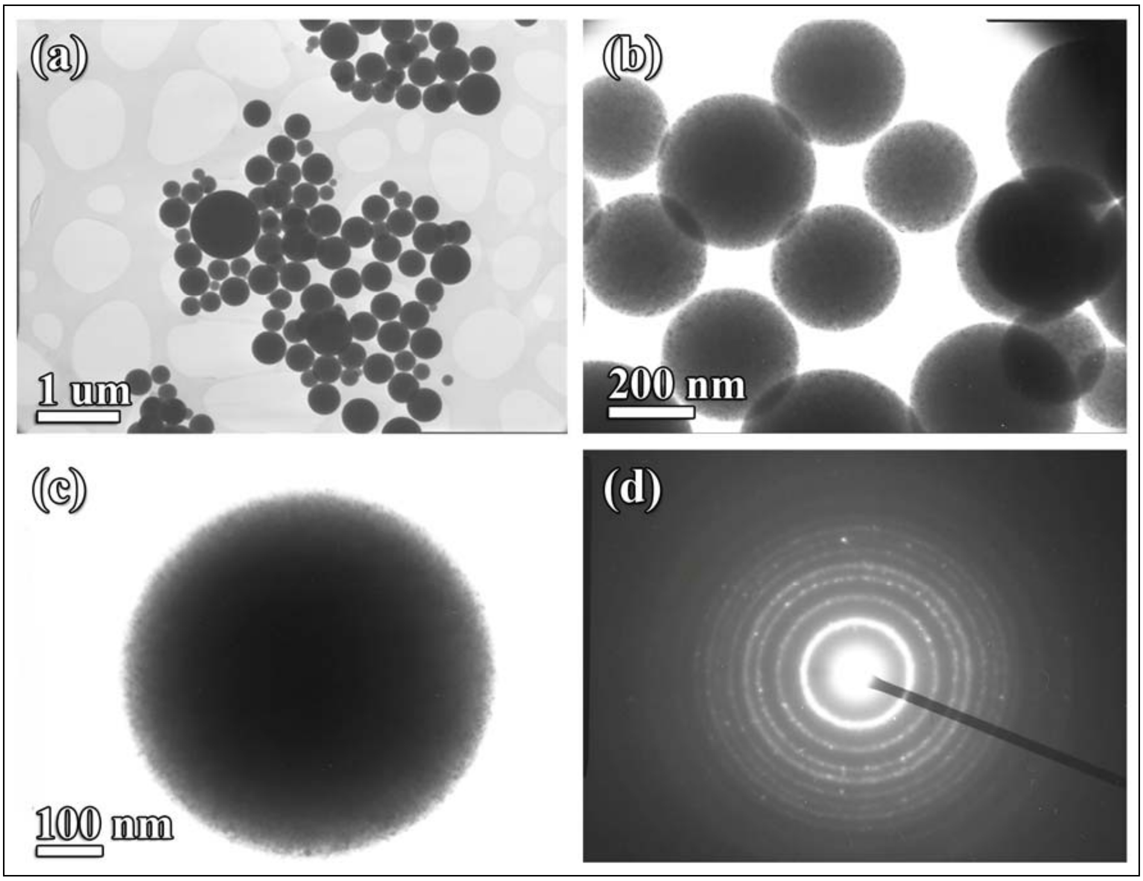

Figure 3 (a) (b) TEM images of hierarchically organized TiO_2 particles, (c) TEM image at higher magnification of single hierarchically organized particle and (d) corresponding selected-area electron diffraction (SAED) pattern

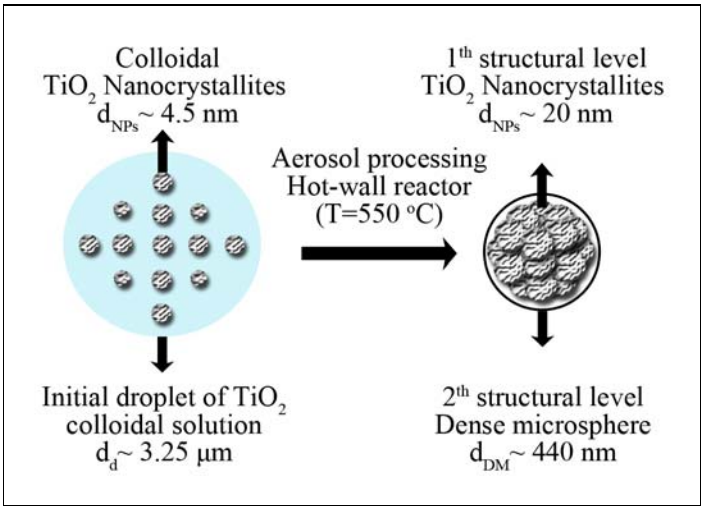

Figure 4 Schematic illustration of "one droplet to one particle" conversion mechanism of hierarchically organized sub-micron sphere formation

Table 1 Structural refinement and phase composition of TiO_2 powder

Polymorph	Cristal structure	Lattice parameters (Å)	CS (nm)	r_{bragg}	wt (%)
Anatase [a]	Tetragonal *I41/amdS*	*a*=3.901 [5] *c*=9.730 [2]	14 [1]	1.8	28.5
TiO_2 (B) [b]	Monoclinic *C2/m*	*a*=12.17 [2] *b*=3.746 [5] *c*=6.510 [1] *β*=107.5 [2]	15 [1]	1.6	71.5

r_exp = 10.157   r_wp = 10.622   gof = 1.046

[a] PDF 89-4921 *a = 3.777; c = 9.501;*

[b] PDF 74-1940 *a = 12.17; b = 3.741; c = 6.524;β= 107.05*