



Letter

Facile synthesis of hierarchical anatase microspheres

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ABSTRACT

A versatile synthesis method is proposed to fabricate hierarchical anatase microspheres under soft conditions and rendering batch volumes significantly large for practical scale-up preparation. The strategy is based on the use of non-aqueous conditions to prevent the accelerated hydrolysis of the Titanium precursor. Water traces from the air atmosphere are only incorporated during the vaporization stage, allowing a controlled precipitation process. Diluted precursor solutions and ethanolic medium promote the self-organization of the precipitated nanoparticles into stable units of spherical shape. The calcination of the obtained powder finally leads to a homogenous, monodisperse and easy to handle population of nanostructured anatase microspheres with high crystallinity and large surface area.

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1. Introduction

The fabrication of nanosized anatase with hierarchical structures of controlled size and morphology has attracted much attention in recent years due to its potential application as photocatalyst to environmental purification, hydrogen generation or solar energy conversion [1–3]. In general the formation and growth of TiO₂ nanoparticles starts with hydrolysis and condensation processes from different Ti-precursors. Then, depending on the assembling method the hierarchical structures may attain low density, high crystallinity, and large specific surface area, structural parameters which are all required to improve photocatalytic performance [4–7]. A suitable state of agglomeration of the TiO₂ nanoparticles with strong interparticle connectivity is also beneficial for the efficient hole-electron separation and the light harvesting properties [8]. But even gathering all these requirements, the extended use of TiO₂ suspensions in photocatalytic applications is restrained, mainly because the recovery of the nanoparticles from the treated water is still challenging [3]. One frequently adopted alternative consists in immobilizing the TiO₂ catalysts on a supporting material, but this limits its photocatalytic efficiency due to a significant loss in the contact area with the light source [3]. In this frame nanostructures assembled on a spherical morphology have shown

a high stability and a monodisperse nature which satisfies the above mentioned characteristics. The obtaining of such TiO₂ hierarchical spheres can be achieved through synthesis strategies involving the use of templates and/or hydrothermal or solvothermal conditions [9–12]. However, all these methods show substantial drawbacks for a scale-up production process. Reproducibility is still puzzle, but more than anything the amount of powder that can be produced is bare minimum and the size of the obtained spheres too low for easy handling. Therefore in this contribution we propose a facile synthesis method to produce significant batch volumes of solid hierarchical microspheres of anatase TiO₂, thus making viable a versatile large-scale fabrication and a handy product manipulation. In a first step soft non-aqueous ethanolic conditions are used to activate the Ti-alkoxy precursor. Then to promote the complete hydrolysis of the metal precursor the solution is left to freely vaporize at room temperature. In doing so only a minimized amount of water coming from the air atmosphere can enter the ethanolic system and the result is a controlled precipitation process taking place during the vaporizing step, but not before. In these conditions a monodisperse population of micron-sized TiO₂ spheres is obtained, which is further calcined under mild conditions to provide crystalline order to the anatase particles.

2. Materials and methods

The chemicals titanium (IV) tetrabutoxide (Ti(OBu)₄, Fluka, 98%) and anhydrous ethanol (EtOH, Merck, analytically pure) were used without further

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purification. $\text{Ti}(\text{OBut})_4$ was chosen as the Ti precursor since the butoxide chains slow down the hydrolysis reactions as compared with other alkoxide groups. In a typical procedure a solution of $\text{Ti}(\text{OBut})_4$ in 1 L of absolute ethanol is stirred under reflux at 78 °C; different amounts of tetrabutoxide were tested leading to different precursor concentrations: 1 M, 0.4 M and 0.1 M. Incorporation of water in this first step is prevented by using a closed reactor vessel (Labmax). After 8 h refluxing, the solution is transferred to a flat tray and evaporated to dryness at atmospheric conditions: 25 °C and less than 40% of humidity. In order to verify the robustness of the method the evaporation step was also conducted on a climate chamber at the same temperature but at a controlled humidity of 30% and 50%. In all cases a white precipitate evolves on vaporizing which is subsequently washed with water thoroughly. The obtained powder is further subjected to a firing step at 400 °C for 1 h.

Powder samples were initially characterized using a Hitachi TM1000 Tabletop scanning electron microscope working on backscattered mode. Field emission scanning electron microscopy was carried out on a Hitachi S-4700 Cold-FESEM working at 20 kV. High-resolution transmission electron microscopy images were obtained on a JEOL 2100F HRTEM operating at 200 kV. The analyses of the crystalline structure and the phase identification were performed by X-ray diffraction on a XRD Bruker D8 Advance diffractometer with a monochromatized source of $\text{Cu K}\alpha 1$ radiation ($\lambda = 1.5406 \text{ nm}$). Specific surface area was determined by the BET method in a

Monosorb Analyzer MS-13 QuantaChrome (USA). Nitrogen adsorption/desorption isotherms were carried out on an ASAP 2020-Micromeritics at 77 K. Samples were degassed at 150 °C during 48 h before analysis.

3. Results and discussion

As mentioned the synthesis starts with the activation of the Ti-alkoxy precursor under non-aqueous ethanolic conditions. The absence of water is initially advantageous since electropositive Ti cations are highly susceptible to nucleophilic attack by H_2O molecules, and this may uncontrollably accelerate the hydrolysis and lead to unrestrained precipitation and growth processes. Hence nucleation and growth essentially take place during the room temperature vaporization of the solvent, when as mentioned only water coming from the atmosphere incorporates to the system. Since the ethanol evaporation kinetics may be affected by the particular conditions of ambient air, experiments were also conducted on a climate chamber that controls the temperature and humidity conditions; the obtained results evidence a high reproducibility producing the desired anatase microspheres in all tested conditions (see experimental). Fig. 1 shows SEM backscattered micrographs (TM1000) of powders obtained when different concentrations of $\text{Ti}(\text{OBut})_4$ precursor are employed. Although in all cases a yield above 97% was attained, the influence of the precursor concentration on both the size and the morphology of the particles is manifest. When starting from a 1 M concentration of precursor, big ($\sim 8 \mu\text{m}$) and frequently fractured spheres can be observed embedded in a heterogeneous tangle of particles with undefined morphology. Dilution to 0.4 M of $\text{Ti}(\text{OBut})_4$ increases the proportion of these spheres but still the situation is not entirely homogenous. It is just when using a precursor concentration of 0.1 M when a homogenous population of spheres is finally obtained. The size of the spheres has substantially decreased ($\sim 2 \mu\text{m}$), and almost no fractured units are now observed. It should be noted that

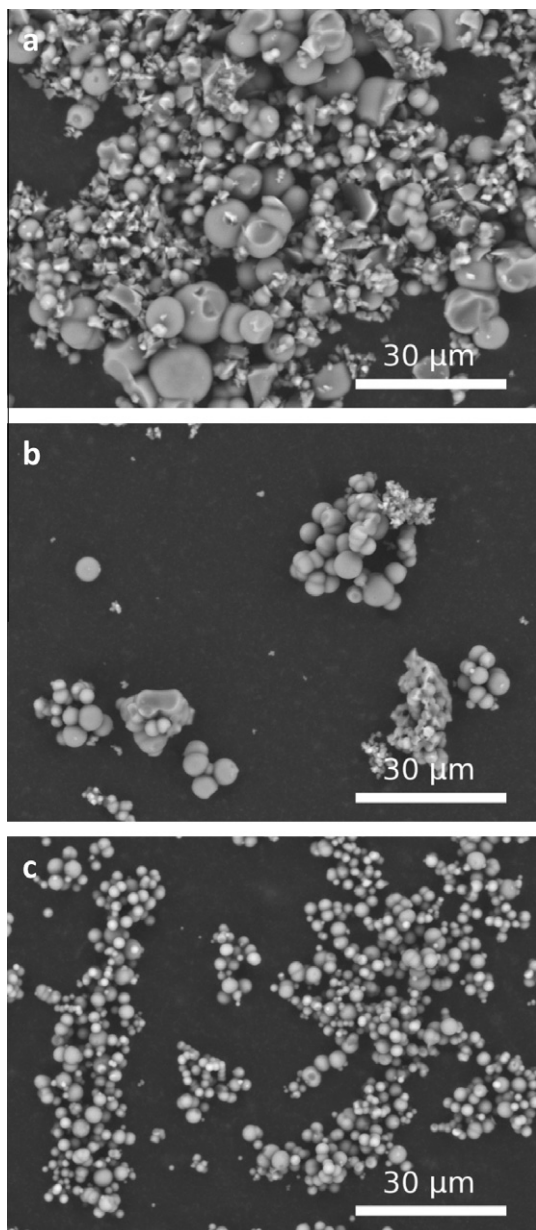


Fig. 1. SEM backscattered micrographs (TM1000) of powders obtained with different concentrations of $\text{Ti}(\text{OBut})_4$: (a) 1 M (b) 0.4 M and (c) 0.1 M.

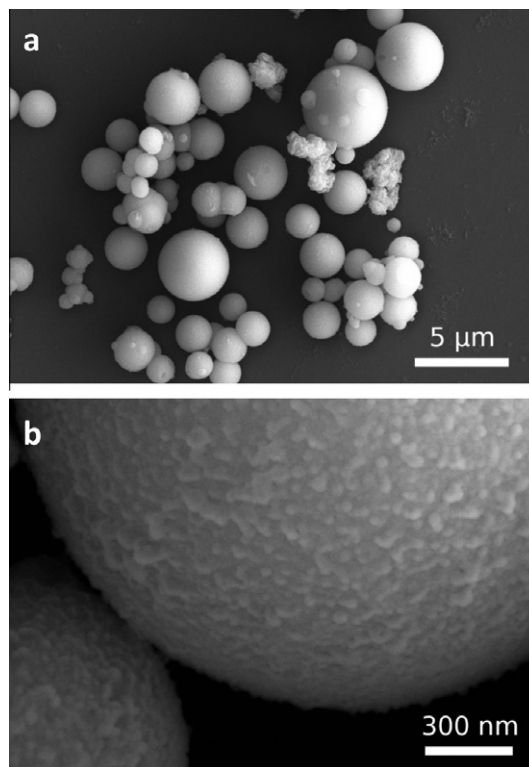


Fig. 2. FESEM micrographs of powder obtained with 0.1 M concentration of $\text{Ti}(\text{OBut})_4$.

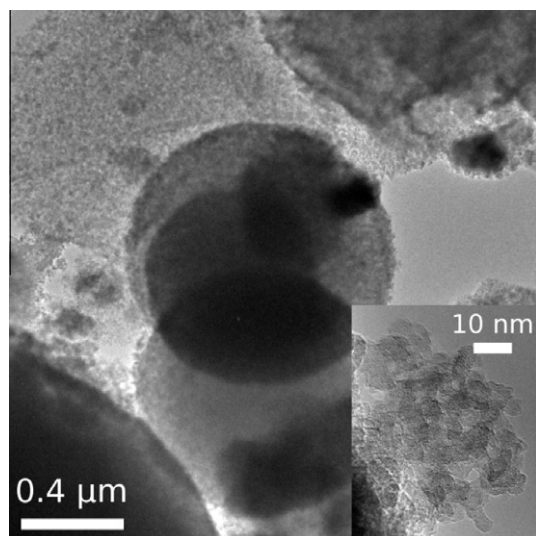


Fig. 3. HRTEM micrographs of the 0.1 M sonicated powder.

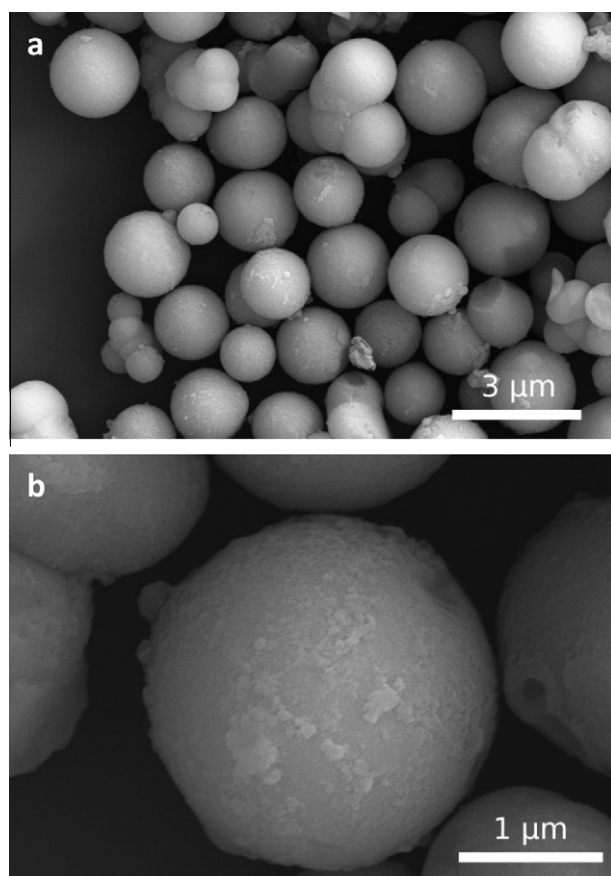


Fig. 4. Representative FESEM images of the 0.1 M calcined precipitate.

in all cases no trace of crystalline order was observed by XRD analyses of the obtained powders.

These results should be interpreted as follows. According to the designed experimentation the incorporation of water to the system is restricted to the vaporization stage. Thus, it is expected that the reaction between water and titanium may occur at the interface region between the atmosphere and the solution, where Ti-oxoalkoxy molecular clusters generate and migrate due to the Brownian

interaction and gravity [13]. Since no supplementary energy (e.g. mixing, stirring) is applied to the system during this room temperature vaporization process, the self-organization of the sol particles will be determined by the collisions among the formed nuclei. In this sense when high concentrations of titanium precursor are employed the amount of nuclei in the solution raises up, the collision frequency between these nuclei also increases and flocculation occurs. The consequence is a rapid growth process leading to the formation of an agglomerated mass without a prevailing morphology. But in addition to dilution, particle growth after nucleation is also affected by the solvent itself. The particle interaction potential varies with the dielectric constant of the solvent, thus affecting the colloidal stability and the development of precipitate morphology. In particular for nonoversaturated systems, it has been reported that water-rich conditions promote fine and highly agglomerated precipitates of irregular shape, whereas ethanol solutions with a lower dielectric constant encourage the aggregation of the fine precipitates on well dispersed spheres [13,14]. In our experiments, both dilution and the ethanolic medium promote the observed formation of fine nanoparticles assembled into stable spherical micron-sized units.

The powder with a 0.1 M starting concentration of $\text{Ti}(\text{OBut})_4$, hereafter the 0.1 M precipitate, was further analyzed by field emission scanning microscopy. Fig. 2 confirms that the formed spheres are actually composed by the agglomeration of a myriad of smaller nanoparticles. The specific surface area of the spheres is certainly elevated, up to $417 \text{ m}^2 \text{ g}^{-1}$, implying the existence of interparticle porosity. To better examine the inner nanostructure of the microspheres, the 0.1 M precipitate was subjected to a 5 min sonication

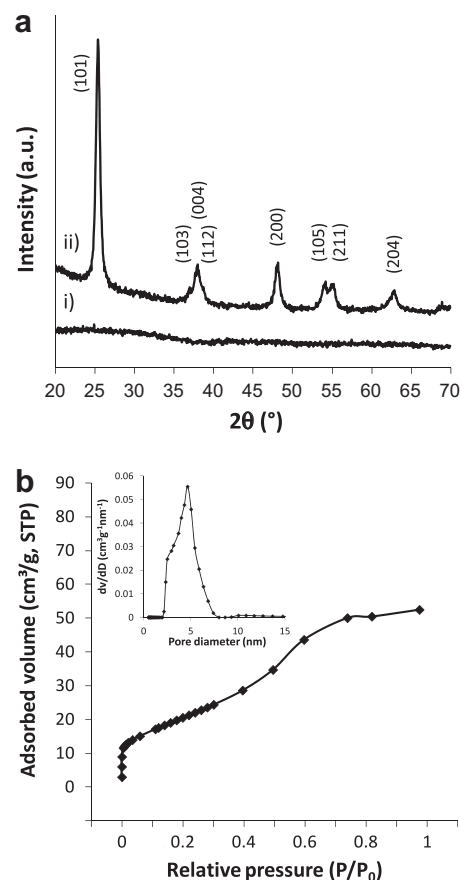


Fig. 5. (a) XRD diffraction patterns of the 0.1 M obtained precipitate (i) before and (ii) after calcination at 400°C . (b) N_2 adsorption-desorption BET isotherms. The inset shows the pore size distribution of meso- TiO_2 .

process that might cause the rupture of the microspheres. HRTEM of this sonicated powder is shown in Fig. 3. As observed some spheres have resisted the sonication and evidence a quite homogeneous distribution of particles, among which the interconnected nanoporosity can be reasonably envisaged. The high magnification image let us see some of these individual particles evidencing a primary crystallite size of about 5 nm.

But as mentioned before, none of the as-precipitated powders showed a degree of crystallinity that at least could be feasibly detected by XRD measurements. It happens that the initial formation of Ti-oxo (or Ti-oxoalkoxy) molecular clusters can only progress to form large Ti-oxo clusters or even TiO₂ nanoparticles when high amounts of water are used [13]. In our system the hydrolysis is however not completed (we have a minimized amount of water), so the initial precipitate may be still constituted by such Ti-oxo-alkoxides. Hence further energy needs to be provided to finally form the anatase nanoparticles. Subsequently the precipitated powders were subjected to a heat treatment at 400 °C during 1 h. FESEM micrographs in Fig. 4 correspond to the 0.1 M calcined precipitate and as observed the size and structure of the microspheres remains unaltered after the firing step.

Finally XRD analyses depicted also in Fig. 5a confirm the crystallization of a pure anatase phase (JCPDS File No. 21-1272). The specific surface area of the calcined microspheres also stays in high values, around 82 m² g⁻¹, therefore empowering the possibilities of these powders for photocatalytic applications. In addition, in order to investigate the pore structure of this sample, nitrogen adsorption/desorption isotherms were measured and the pore size distribution was calculated by the Density Functional Theory method (Fig. 5b). The pore size distribution is centered on 4.3 nm and shows a narrow shape pointing out that the mesoporous microspheres consist on densely packed primary nanoparticles with uniform agglomeration.

4. Conclusions

Crystalline and nanostructured TiO₂ anatase microspheres are produced by a facile and easy to scale synthesis method. The activation of the Ti-alkoxy precursor is initially conducted at 78 °C under ethanolic non-aqueous conditions that prevent a rapid and hence uncontrollable hydrolysis of the Titanium cations. Nucleation and growth of solid particles take place during the vaporiza-

tion stage, when only traces of atmospheric water can enter the system. The reaction between water and titanium occurs at the interface region between the atmosphere and the solution, where collisions among the formed nuclei lead to a self-organization of the particles. The use of diluted solutions of the Ti-alkoxy precursor and the ethanolic medium itself were found essential to obtain a monodisperse population of nanostructured micron-sized TiO₂ spheres. The system is finally calcined under mild conditions to provide crystalline order to the anatase particles. Hence, as a result of a simple cost-effective approach, an easy to handle powder consisting of hierarchical anatase microspheres is obtained in batch volumes significantly large for practical scale-up preparation.

Acknowledgments

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