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Synthesis of TiO_2 nanoparticles through the Gel Combustion process

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Abstract Nanosized titania particles have been synthesized through the Gel Combustion process. The synthesis was carried out by starting from a common and low-cost titanium precursor and hydrogen peroxide as combustible substance. The process led to a significant gas development and the as-synthesized nanoparticles showed a low degree of crystallinity and mean dimension of 20 nm. Different thermal treatments were performed so as to investigate their effect on the structural properties and on the particle size of the synthesized products. The optimal temperature was set at 300 °C, giving pure anatase TiO_2 nanopowders with a good level of crystallinity, an average particle size of 50 nm and a high value of specific surface area.

Introduction

Titanium dioxide TiO_2 has received in the last years growing attention thanks to its interesting properties that allow its employment in a wide range of applications, such as pigments [1], medical devices [2] and gas sensing [3]. In particular, the attention has been recently focussed on the semiconducting and photosensitive behaviour, exploited in several applications concerning the environmental field, such as purification of air and water from pollutants [4] and solar cells for low-cost photovoltaic devices [5]. The morphology of the TiO_2 particles significantly affects their catalytic and electrical behaviour, so that a great effort has been made in the development of innovative processes for obtaining nanosized particles. Several new processes and technologies have been developed in recent years for the production of titanium dioxide nanopowders, such as gas condensation [6], sol–gel [7] and hydrothermal synthesis [8]. The Gel Combustion process, belonging to the solution combustion syntheses, seems to be an interesting and powerful method for the synthesis of metal oxide nanoparticles. The process, developed at the beginning of the nineties, is performed in the middle between sol–gel and combustion, combining chemical gelation techniques and combustion processes. It is based on the Pechini synthesis [9] and it uses a redox mixture, containing an oxidizer and a fuel compound. The process involves an exothermic decomposition reaction of an aqueous gel and a thermally induced anionic redox reaction. The reaction produces nanostructured powders at rather low temperatures. The powders are slightly bonded into soft and very porous agglomerates. The Gel Combustion process has been extensively employed in the last years for the synthesis of nanoparticles of a number of metal oxides, such as SnO_2 [10, 11], NiO [12], yttria stabilized zirconia [13] and ferrites [14]. On the other hand, a limited number of studies have been dedicated to the investigation of the Gel Combustion synthesis for the preparation of both pure and doped titanium oxide nanopowders. Among the literature works related to similar methods, Sivalingam and co-workers synthesized nano-sized, high surface area TiO_2 by a solution combustion method for the photodegradation of poly(bisphenol-A-carbonate) in solution [15] and for the degradation of various dyes [16]. Yan et al. produced highly dispersed TiO_2 nanometric powders with controlled structure by a complex sol–gel auto-igniting chemical

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process [17]. The same researchers obtained anatase titania doped with cerium up to 5 mol% as nanometer-sized particles from a $TiO(NO_3)_2$–$Ce(NO_3)_2$–NH_4NO_3–citric acid compound system by a sol–gel auto-igniting synthesis process [18, 19]. Xiao et al. employed a similar sol–gel auto-combustion technique for preparing a nanocrystalline Sm^{3+}-doped TiO_2 showing high photocatalytic activity under visible light [20, 21]. Anuradha and Ranganathan achieved nanocrystalline TiO_2 by the combustion reaction involving titanyl nitrate and fuels like glycine and citric acid, comparing this route with the sol–gel method and the mechanochemical synthesis [22]. Wang et al. investigated the preparation of nanocrystalline TiO_2 powder by solution combustion method, optimizing the process conditions by employing the Taguchi robust design method [23].

All the afore mentioned works employed a well-established route, by using the titanyl nitrate as metal precursor and an organic fuel as reducer. Compared to the synthesis of other oxides, this approach involves an additional reaction between a common titanium precursor (isopropoxide, chloride) and nitric acid so as to form the titanyl nitrate necessary for the combustion.

In this work, the synthesis of TiO_2 nanopowders performed through an alternative method is discussed, by using titanium tetraisopropoxide $Ti(O\text{-}iPr)_4$ as titanium precursor and hydrogen peroxide H_2O_2 as fuel. Both reactants are common and low-cost, especially $Ti(O\text{-}iPr)_4$ which is widely used in the production of titanium dioxide by means of the sol–gel process. In this synthesis the titanium precursor acts as reducer and the hydrogen peroxide as oxidizer. The main advantage of the described method is the reduction of the number of processing steps and the cost-effectiveness of the starting reactants.

Experimental

Titanium tetraisopropoxide $Ti(O\text{-}iPr)_4$, hydrogen peroxide H_2O_2 and isopropyl alcohol C_3H_8O were used as starting materials. The Gel Combustion synthesis was carried out as follows. Titanium tetraisopropoxide and isopropyl alcohol were mixed and kept at room temperature in continuous stirring. Hydrogen peroxide was added drop by drop into the solution. The reaction occurring in this phase did not show any correspondence in the literature. So the reaction mechanism was supposed to be divided into two contemporary steps: the hydrolysis of Ti isopropoxide, causing the formation of titanium hydroxide (orthotitanic acid) $Ti(OH)_4$ precipitates (Eq. 1), and the oxidation of $Ti(OH)_4$ precipitates developing titanium peroxo-complex, assumed to be in the form $Ti(OOH)_4$ (Eq. 2). The reactions are the following:

$$\begin{aligned} &\mathrm{Ti}\left[\mathrm{OCH}(\mathrm{CH_3})_2\right]_4 + \mathrm{H_2O_2} + 4\mathrm{H_2O} \\ &\quad \rightarrow \mathrm{Ti}(\mathrm{OH})_4 + 4(\mathrm{CH_3})_2\mathrm{CHOH}\uparrow + \mathrm{H_2O_2} \end{aligned} \tag{1}$$

$$\mathrm{Ti}(\mathrm{OH})_4 + 4\mathrm{H_2O_2} \Rightarrow \mathrm{Ti}(\mathrm{OOH})_4 + 4\mathrm{H_2O} \tag{2}$$

The oxidation of $Ti(OH)_4$ is an exothermic reaction, thus increasing the temperature up to 150 °C, and promoted the evaporation of isopropanol and water with a significant development of gases after the isopropanol evaporation. The Ti peroxo-complex disposed in an inorganic gel. Among the various gel models reported in the literature, that of Ragai and Symons, shown in Fig. 1, was assumed [24, 25]. It appears like a strongly hydrated hydrogenated polymeric matrix, with an unusual structure due to the presence of some other electronegative species, i.e.O_2^-, coordinated to the Ti(IV) ion, besides the O^- and OH^- groups [26].

The gel was then dried and decomposed, giving softly agglomerated TiO_2 nanopowders. They were easily ground in an agate mortar and then thermally treated in air for 1 h at different temperatures in order to crystallize nanopowders and investigate the effect of the heat treatment on the particle size. The synthesis process is schematically summarized in Fig. 2.

The synthesized nanoparticles were characterized by X-ray diffraction (X'Pert Philips, range 2θ: 10–70°, radiation CuKα, $\lambda = 1.54056$ Å), thermogravimetric analysis (Mettler Toledo, 50–1000 °C, 10 °C/min, air) and differential thermal analysis (Perkin Elmer, 50–1000 °C, 10 °C/min, air), BET specific surface analysis by means of nitrogen adsorption-desorption at 77 K (Micromeritics ASAP 2010), field emission scanning electron microscopy (Hitachi S-4700) and transmission electron microscopy (Hitachi H-7100). The samples for electron microscopy observations were prepared by suspending some products in isopropanol through ultrasonic mixing for half an hour, and subsequently by placing a drop of the dispersion onto a copper grid coated with a layer of amorphous carbon. XRD peak broadening method based on the Scherrer Formula was used to determine the crystallite size.

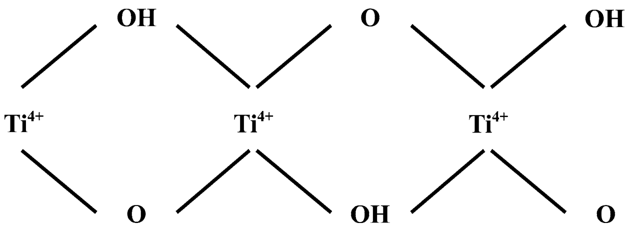

Fig. 1 Scheme of the $Ti(OOH)_4$ gel [17, 18] formed during the Gel Combustion process

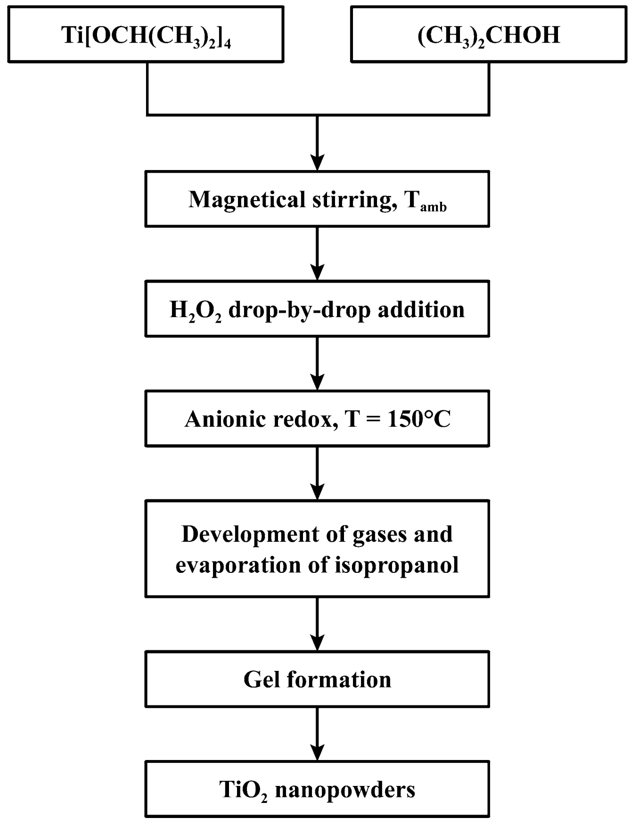

Fig. 2 Procedure scheme for the Gel Combustion synthesis of TiO_2 nanopowders

Results and discussion

XRD analysis on the as-synthesized TiO_2 nanopowders showed the formation of anatase phase, as illustrated in Fig. 3 [27]. The characteristic peaks at 25.4 and 38.54 two-theta degrees were recognized, corresponding to the hkl Miller index (101) and (112), respectively.

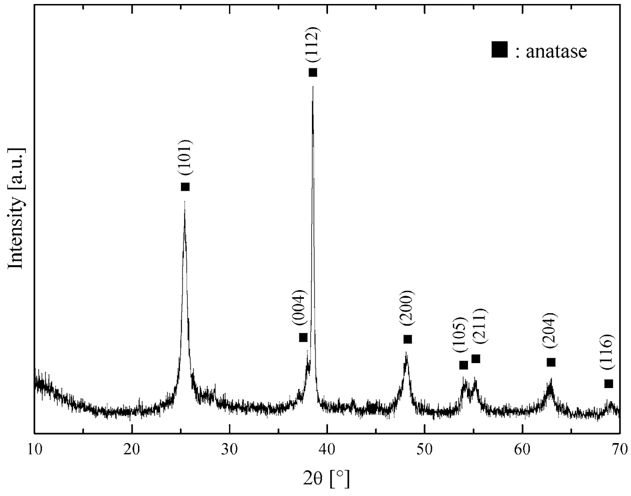

Fig. 3 XRD pattern of the as-synthesized TiO_2 nanopowders

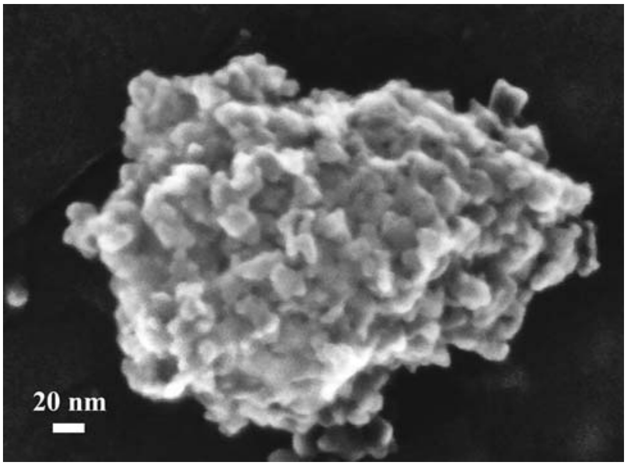

Fig. 4 FESEM micrograph of the as-synthesized TiO_2 nanopowders obtained by Gel Combustion (secondary electrons)

As can be noticed, the nanopowders showed a low degree of crystallization, and a thermal treatment was necessary in order to increase it and to stabilize the nanoparticles.

The FESEM analysis performed on the as-synthesized TiO_2 nanopowders, reported in Fig. 4, showed a low degree of agglomeration and an average particle size of about 20 nm, in good agreement with the crystalline domain dimension obtained from the XRD pattern through the Scherrer equation (see Table 1).

The effect of the heat treatment on phase composition and crystalline domain size was investigated in order to identify the best compromise between improvement of crystallinity and crystallite size growth. Figure 5 shows XRD pattern of the as-prepared and heat-treated TiO_2 nanopowders.

It can be observed that the heat treatment of the nanopowders largely affected the domain size, calculated through the Scherrer's formula, that was increased from 6 nm for the as-prepared nanopowders up to 137 nm for the TiO_2 treated at 900 °C, as reported in Table 1. At 700 °C the rutile phase peaks appeared in the XRD pattern. Treating the TiO_2 nanopowders at 900 °C it was possible to detect the presence of both anatase and rutile phases [28].

Table 1 Effect of heat treatment on crystallite size calculated by the Scherrer formula for the TiO_2 nanopowders

Thermal treatment	Crystalline domains size (nm)
As-prepared	6
250 °C	15
500 °C	27
700 °C	68
900 °C	137

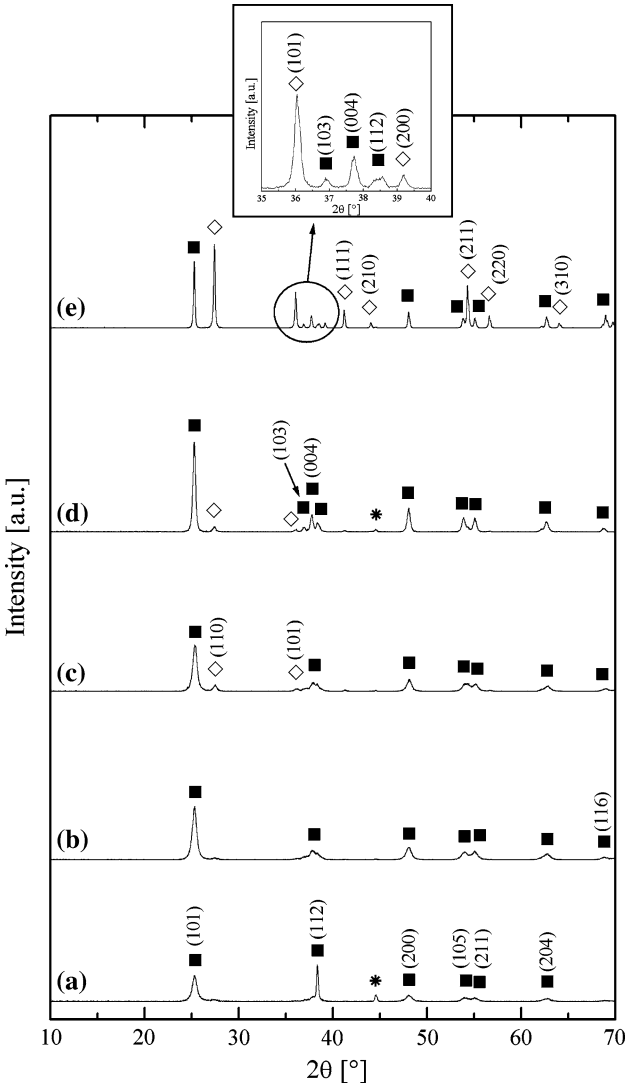

Fig. 5 XRD patterns of TiO_2 nanopowders as-prepared (**a**) and after heat treatment at 250 °C (**b**), 500 °C (**c**), 700 °C (**d**) and 900 °C (**e**). Phases identification: TiO_2 anatase (■), TiO_2 rutile (◇), Al sample holder (✳)

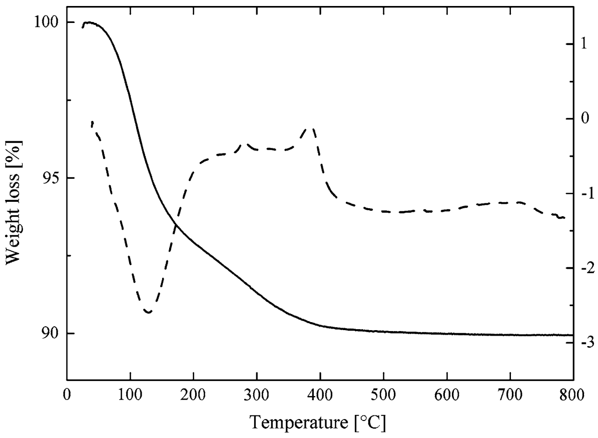

Fig. 6 TGA (solid) and DTA (dash) curves of as-prepared TiO_2 nanopowders

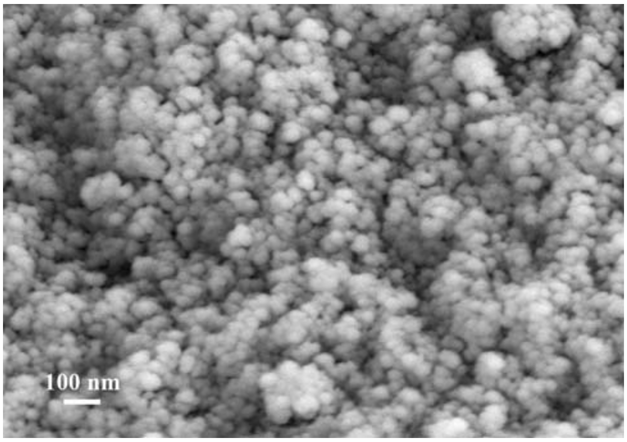

Fig. 7 FESEM micrograph of TiO_2 nanopowders obtained by Gel Combustion treated at 300 °C (secondary electrons)

The thermal analyses of the as-synthesized TiO_2 nanopowders through TGA and DTA are reported in Fig. 6. Thermogravimetric analysis showed a limited weight loss ($\sim$10%), due to evaporation of physically adsorbed water. DTA curve showed three peaks: the endothermic one, at about 110 °C, corresponded to the evaporation of adsorbed water, the exothermic one at about 400 °C corresponded to the crystallization of anatase and the third one, in the range between 600 and 800 °C, corresponded to the anatase-rutile transformation.

The evaluation of the XRD pattern and thermal analysis data allowed to select the heat treatment at 300 °C as an acceptable compromise between crystallinity of the final nanopowders and particle size growth.

The FESEM analysis after heat treatment at 300 °C showed TiO_2 nanopowders characterized by a particle size lower than 50 nm and softly agglomerated, as illustrated in Fig. 7. The weak agglomeration observed in the micrograph is in good agreement with that found out in previous

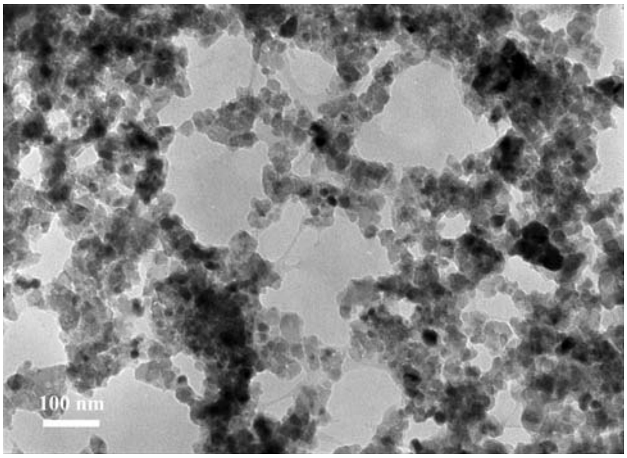

Fig. 8 TEM micrograph of TiO_2 nanopowders treated at 300 °C

works concerning the synthesis of nanosized oxides by Gel Combustion [10, 11, 29].

The TEM analysis confirmed the results obtained by FESEM, with a mean particle size of 50 nm, as shown in Fig. 8.

The high quantity of gases released during the Gel Combustion process yielded high values of specific surface area, as confirmed by BET analysis giving a value of 115 m^2/g.

Conclusions

- A Gel Combustion process has been set up for the synthesis of TiO_2 nanopowders starting from titanium tetraisopropoxide and hydrogen peroxide.
- The process yielded the formation of softly agglomerated powders characterized by particle size in the range between 6 and 130 nm and low degree of crystallinity.
- The thermal treatment of the powders was found to be optimal at 300 °C for 1 h, giving the best compromise between crystallinity of the nanopowders and limited growth of the crystallite size.
- The TiO_2 powders resulting from the heat treatment at 300 °C were characterized by a mean particle size of 50 nm and a specific surface area of 115 m^2/g.

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References

1. Feldman C (2001) Adv Mater 13:1301
2. Ferrari M (2005) Nat Rev Cancer 5:161
3. Fergus JW (2003) J Mater Sci 38:4259. doi:10.1023/A:1026318712367
4. Mills A, Le Hunte S (1997) J Photochem Photobiol A-Chem 108:1
5. O'Regan B, Grätzel M (1991) Nature 352:373
6. Siegel RW, Ramasamy S, Hahn H, Li Z, Lu T, Gronsky R (1988) J Mater Res 3:1367
7. Morales BA, Novaro O, Lopez T, Sanchez E, Gomez R (1995) J Mater Res 10:2788
8. Terwillinger CD, Chiang YM (1993) Nanostruct Mater 2:37
9. Pechini MP (1967) US Patent 3330697 1967
10. Fraigi L, Lamas DG, Walsöe de Reca NE (1999) Nanostruct Mater 11:311
11. Fraigi L, Lamas DG, Walsöe de Reca NE (2001) Mater Lett 47:262
12. Lian JS, Zhang XY, Zhang HP, Jiang ZH, Zhang J (2004) Mater Lett 58:1183
13. Yang J, Lian J, Dong Q, Guan Q, Chen J, Guo Z (2003) Mater Lett 57:2792
14. Yue Z, Li L, Zhou J, Zhang H, Gui Z (1999) Mater Sci Eng B-Solid 64:68
15. Sivalingam G, Madras G (2004) Appl Catal A-Gen 269:81
16. Sivalingam G, Nagaveni K, Hegde MS, Madras G (2003) Appl Catal B-Environ 45:23
17. Yan QZ, Su XT, Zhou YP, Ge CC (2005) Acta Phys-Chim Sin 21:57
18. Yan QZ, Su XT, Zhou YP, Ge CC (2005) Rare Metals 24:125
19. Yan QZ, Su XT, Huang ZY, Ge CC (2006) J Eur Ceram Soc 26:915
20. Xiao Q, Si ZC, Yu ZM, Qiu GZ (2007) Mater Sci Eng B-Solid 137:189
21. Xiao Q, Si Z, Zhang J, Xiao C, Zhiming Y, Qiu G (2007) J Mater Sci 42:9194. doi:10.1007/s10853-007-1919-9
22. Anuradha TV, Ranganathan S (2007) Bull Mater Sci 30:263
23. Wang CM, Wu H, Chung SL (2006) J Porous Mater 13:307
24. Ragai J, Selim SI (1986) J Colloid Interface Sci 115:139
25. Symons MCR (1987) Nature 325:659
26. Tengvall P, Lundström I, Sjöqvist L, Elwing H, Bjursten LM (1989) Biomaterials 10:166
27. JCPDS 21-1272
28. JCPDS 89-4202
29. Mimani T, Patil KC (2001) Mater Phys Mech 4:134