J Electroceram (2006) 17:37–40
DOI 10.1007/s10832-006-9932-y

Synthesis of TiO_2 nanospheres through microemulsion reactive precipitation

B. DeBenedetti · D. Vallauri · F. A. Deorsola · M. Martinez Garcia

Abstract In the present work the preparation of titania nanosized spherical powders through a microemulsion precipitation method was investigated. The process is based on the precipitation of particles from a solution containing low-cost precursor, previously emulsified in an immiscible liquid. The precipitates were obtained dropping an acqueous solution of $TiCl_4$ into a stable microemulsion containing a light mineral oil and a surfactant. Different mixing techniques were evaluated. The synthesized titania nanopowders were characterized by XRD, BET, TGA and DTA, SEM and TEM. The as-synthesized powders were mainly amorphous and were subjected to thermal treatment. Nanosized homogeneous spherical powders with average particle size of 6 nm after synthesis and 30 nm after heat treatment were obtained.

Keywords Titania · Precipitation synthesis · Microemulsion

Introduction

Nanostructured titanium oxide TiO_2 has played a key role in recent years because of its wide range of functional properties, that makes it the ideal candidate for a large variety of applications, such as white pigments [1, 2], catalysis [3, 4], photovoltaic cells [5, 6], medical devices [7] and gas sensing [8, 9].

Since the nanometric scale enhances TiO_2 properties, several methods with increased efficency were developed to obtain nanopowders, such as gas condensation [10] and sol-gel [11]. Nanosized spherical particles can be successfully prepared by wet chemical methods, although they require the use of high-cost raw materials. The emulsion technique is a simple and effective method for the synthesis of particles with spherical shape and narrow size distribution, starting from low-cost precursors [12, 13].

An emulsion is generally defined as a thermodynamically stable system composed of two immiscible liquids (water and oil) and a surfactant. Dispersed into the oil, the acqueous solution forms nanosized droplets, due to minimization of surface energy. Each droplet acts as a single nano-reactor, in which the precipitation of spherical and nanosized titania powders occurs by means of the thermal instability of the Ti precursor at high temperature [14]. In agreement with the literature, it is possible to obtain the formation of precipitates due to the interactive contact among nano-droplets, which aggregate and grow in a spherical shape. Moreover, during the precipitation each particle is coated by an emulsifier film preventing agglomeration [15].

In this paper the synthesis of nanosized spherical titania powders through the emulsion method is investigated. The process is carried out in presence of a $TiCl_4$ solution and a stable emulsion containing a light mineral oil and a surfactant. The thermal destabilization of the $TiCl_4$ precursor is exploited, without any further addition of precipitating components. Two different mixing techniques, magnetic and ultrasonic stirring, and their effect on structural, morphological and chemical properties of the particles are evaluated.

Experimental procedures

An acqueous solution of titanium chloride $TiCl_4$ was prepared by dropwise addition of $TiCl_4$ in stirred water cooled

B. DeBenedetti (✉) · D. Vallauri · F. A. Deorsola · M. Martinez Garcia
Dipartimento Scienza dei Materiali e Ingegneria Chimica, Politecnico di Torino, Corso Duca degli Abruzzi 24, I-10129 Torino, Italy
e-mail: bruno.debenedetti@polito.it

at 4°C. The concentration was adjusted to 2 M with respect to Ti^{4+}. The solution contained nanosized particles of hydrated titanium oxide $TiO_2 \cdot nH_2O$ and it was stable at room temperature. It was possible to prime the agglomeration process lowering the Ti concentration (in this case 0,25 M) or increasing the temperature.

A stable emulsion was prepared dissolving into light mineral oil a non-ionic emulsifier based on polyethylene glycol hexadecyl ether, which has a HLB (Hydrophile-Lipophile Balance) value of 5,3. The 0,25 M $TiCl_4$ solution was added drop by drop into the microemulsion at 50°C and was maintained for 15 h in continuous stirring. Two mixing techniques were compared: a traditional heated magnetic stirrer (1000 rpm) and an ultrasonic generator (Sonics, UCX750) used with a specific amplitude. Different water/oil/emulsifier weight ratios were tested. After precipitation, the emulsions were rotation-evaporated for water removal, centrifugated and washed with isopropanol three times at least. The so-obtained powders were dried at 80°C for 1 h.

The characterization of the synthesized nanoparticles was carried out by X-ray diffraction (X'Pert Philips, range 2θ: $10 \div 70^\circ$, radiation CuKα, $\lambda = 1{,}54056$ Å), thermogravimetric analysis (Mettler Toledo, $50 \div 1000$°C, 10°C/min, air) and differential thermal analysis (Perkin Elmer, $50 \div 1000$°C, 10°C/min, air), BET specific surface analysis by means of nitrogen adsorption-desorption at 77 K (Micromeritics ASAP 2010), scanning electron microscopy (LEO Supra 35) and transmission electron microscopy (JEOL JEM 2010).

Results and discussion

The emulsion properties and therefore the size and morphology of the particles are affected by several factors: the type of surfactant and oil phase, the oil/water/emulsifier (o/w/e) ratio, the concentration of the precursor solution and the stirring rate. Experimental tests were carried out with fixed kind of oil and of surfactant in order to investigate the effect of some parameters on the results.

At first, several o/w/e weight ratios were tested in order to establish the most suitable composition of the mixture. Concerning the emulsifier, a lower content leads to a larger size distribution. On the other hand, a high amount inhibits the droplets interaction and then the precipitation. Concerning the water amount, a stable emulsion can't be achieved when using an excessive quantity of aqueous solution.

Firstly the emulsifier amount was varied testing the 5, 10 and 15 wt%, fixing the water content to 20 wt% and balancing the remaining with oil. It was observed that the optimal condition to obtain nanosized spheres was 10 wt% of emulsifier, and further tests were carried out with this fixed content. Subsequently the water amount was considered. Different

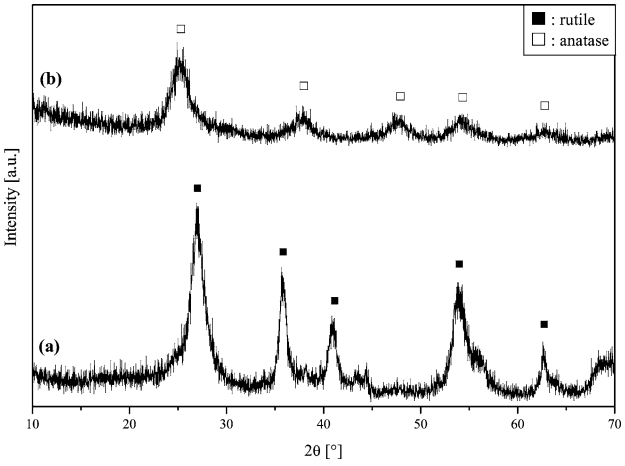

Fig. 1 XRD patterns of as-synthesized powders obtained through magnetic (a) and ultrasonic (b) stirring

contents (10, 20, 30 and 45 wt%) were evaluated, balancing the remaining with oil. All the water contents tested yielded to stable emulsions. It was observed that 70/20 and 60/30 ratios allowed to obtain spheres, but differently sized. Lower water content yielded smaller spheres. Increasing water amount more than 30 wt% gave bigger aggregates not spherically shaped. So the weight composition 70/20/10 gave the best results in terms of size and morphology of the powders obtained and it was adopted for further tests. Concerning the mixing technique, traditional hot plate stirrer and ultrasonic mixing were compared. Using a traditional hot plate stirrer the precipitation was carried out at 50°C and after 15 h a clear separation between precipitates and liquid phase was observed. XRD pattern in Fig. 1(a) showed the formation of the rutile phase. Morphological analysis by means of scanning electron microscopy showed the formation of spheres of average diameter of 400 nm (Fig. 2). Specific surface analysis resulted 100 m^2/g.

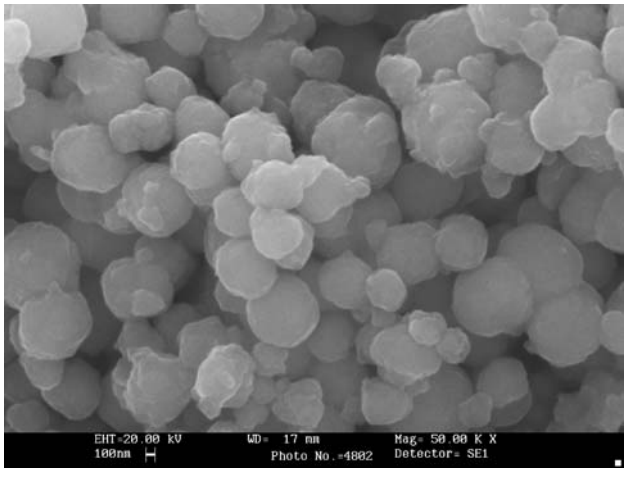

Fig. 2 SEM micrograph of TiO_2 nanospheres obtained using magnetic stirrer

An appreciable enhancement in the formation of droplets into the emulsion was achieved using an ultrasonic generator. Ultrasonic waves allowed to obtain nano-droplets and to prevent the aggregation of precipitates during the addition of the precursor solution into the emulsion. Moreover, the interaction between ultrasonic waves and liquid phase increased the temperature up to 80°C, making unnecessary the subsequent steps of heating and water removal through rotation and evaporation. The product was a cloudy suspension, in which particles couldn't precipitate because of the very small size. The precipitation was achieved by centrifugation in isopropanol before the washing step. The XRD pattern, reported in Fig. 1(b), showed the formation of anatase phase instead of the rutile. The change of crystalline phase was due to the different particle size yielded by the use of the two mixing techniques. In fact the high energy supplied in ultrasonic process favours high nucleation rate and is exploited to separate the nano-droplets, thus inhibiting particle agglomeration. Therefore highly dispersed and finer particles are yielded by the ultrasonic process with respect to the magnetic stirring. The different size of the nanospheres is the reason for the mechanism of TiO_2 phase formation during the two processes, as the anatase phase is more stable at nanosize, whilst rutile is the most thermodynamically stable phase in the case of big particles. This explanation is in accordance with several publications reporting that anatase is the thermodynamically stable phase if the particle size is less than 14 nm due to the significant increase of surface energy [16, 17].

TGA and DTA curves for crude powders are reported in Fig. 3. DTA plot indicates the endothermic peak due to physically absorbed water. The exothermic peak at 270°C corresponds to the decomposition of residual emulsifier, the condensation of ─OH groups and of non-bonded oxygen and the subsequent one at 390°C corresponds to the crystallization of anatase. Between 600 and 800°C the exothermic peak of the transformation anatase-rutile is evident. This was confirmed by XRD pattern of powders heat treated at 600°C for 1 h in air, reported in Fig. 4. As can be noticed, anatase and rutile phases were present.

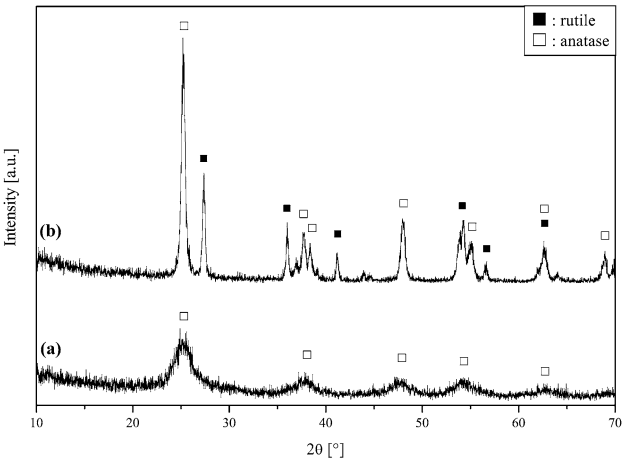

Fig. 4 XRD patterns of as-synthesized (a) and treated at 600°C (b) TiO_2 nanospheres obtained using ultrasonic generator

The DTA plot is in good agreement with the behaviour observed by Li et al. [18] on TiO_2 powders obtained through a slightly different process.

The TEM micrographs of as-synthesized and treated TiO_2 nanopowders are shown in Figs. 5 and 6 respectively. As can be noticed, particles with spherical shape and average size of 6 nm were formed. Specific surface area was very high, with a value of 280 m^2/g. Heat treatment allowed the re-crystallization of the powders without excessive particles growth, as shown in Fig. 6. After treatment the particles are characterized by average size of 30 nm, and the spherical shape is partially lost due to the particles growth. A high specific surface is maintained, with a value of 150 m^2/g.

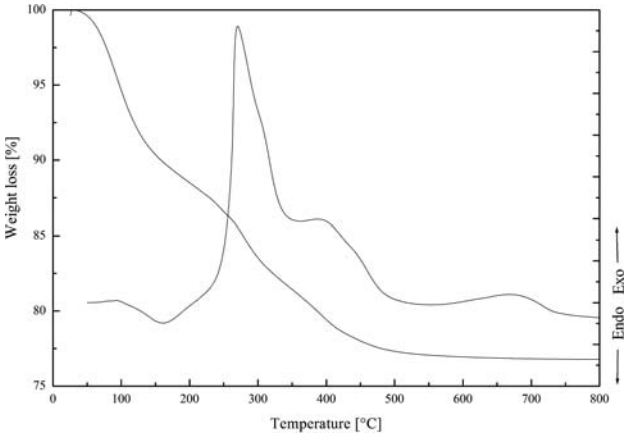

Fig. 3 DTA/TGA curves for as-synthesized TiO_2 nanospheres obtained using ultrasonic generator

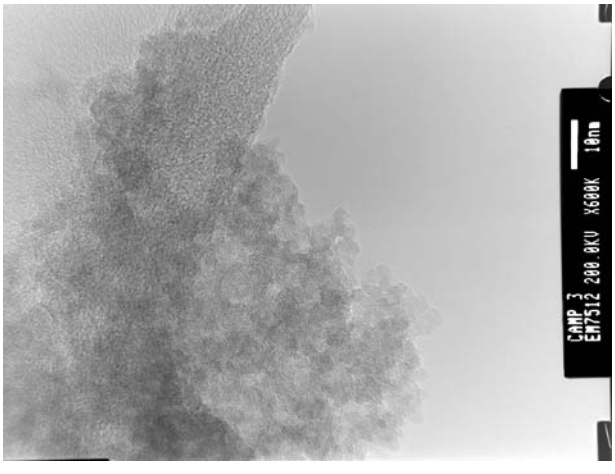

Fig. 5 TEM micrograph of as-synthesized TiO_2 nanospheres obtained using ultrasonic generator

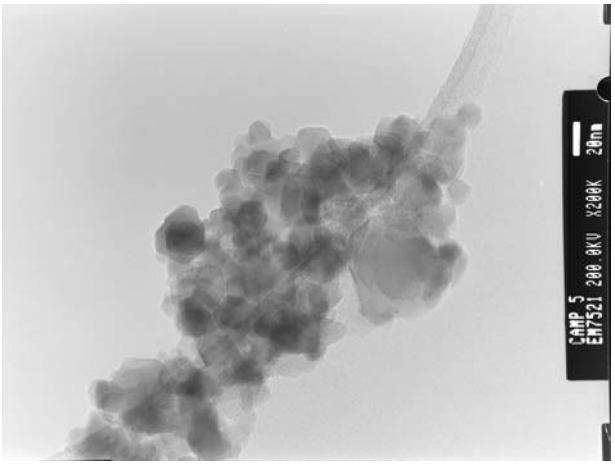

Fig. 6 TEM micrograph of TiO_2 nanospheres obtained using ultrasonic generator and heat treated at 600°C

Conclusions

Titanium oxide nanosized powders with spherical morphology were successfully synthesized through a microemulsion precipitation method. The oil/water/emulsifier ratio and the precursor solution concentration were optimized. Magnetic stirring yielded rutile nanosized spherical particles with average diameter of hundreds nm. The use of ultrasonic mixing gave remarkable improvement, decreasing the particle size to tens nm. The calcination treatment slightly affected particles size. The innovation of the present work consists of adopting the microemulsion precipitation method to obtain nanosized powders of TiO_2. Future developments will regard further study of some process parameters, particularly the effect of ultrasonic stirring on the phase formation of TiO_2.

Acknowledgment The authors are grateful to Dr. Paola Salvemini for the support in the experimental work.

References

1. C. Feldman, *Adv. Mater.*, **13**, 1301 (2001).
2. C. Feldman and H.O. Jungk, *Angew. Chem. Ind. Ed.*, **40**, 359 (2001).
3. W.J. Stark, K. Wegner, S.E. Pratsinis, and A. Baiker, *J. Catal.*, **197**, 182 (2001).
4. P. Panagiotopoulou and D.I. Kondarides, *J. Catal.*, **225**, 327 (2004).
5. M.J. Gratzel, *Sol-Gel Sci. Technol.*, **22**, 7 (2001).
6. A. Hagfeldt and M. Gratzel, *Acc. Chem. Res.*, **33**, 269 (2000).
7. M. Ferrari, *Nature Review, Cancer*, **5**, 1 (2005).
8. D. Morris and R.G.J. Edgell, *J. Mater. Chem.*, **11**, 3207 (2001).
9. J.W. Fergus, *J. Mater. Sci.*, **38**, 4259 (2003).
10. R.W. Siegel, S. Ramasamy, H. Hahn, Z. Li, T. Lu, and R. Gronsky, *J. Mater. Res.*, **3**, 1367 (1988).
11. B.A. Morales, O. Novaro, T. Lopez, E. Sanchez, and R. Gomez, *J. Mater. Res.*, **10**, 2788 (1995).
12. G.H. Maher, C.E. Hutchins, and S.D. Ross, *J. Mat. Proc. Tech.*, **56**, 200 (1996).
13. W. Bauer and G. Tomandl, *Ceram. Int.*, **20**, 189 (1994).
14. H. Herring and R. Hempelmann, *Mater. Lett.*, **27**, 287 (1996).
15. R. Zhang and L. Gao, *Mater. Res. Bull.*, **37**, 1659 (2002).
16. P.M. Oliver, G.W. Watson, E.T. Kelsey, and S.C. Parker, *J. Mater. Chem.*, **7**, 563 (1997).
17. B. Gilbert, H. Zhang, F. Huang, M.P. Finnegan, G.A. Waychunas, and J.F. Banfield, *Geochem. Trans.*, **4**, 20 (2003).
18. G.L. Li and G.H. Wang, *Nanostruct. Mater.*, **11**, 663 (1999).