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Soft solution fluorine-free synthesis of anatase nanoparticles with tailored morphology

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Abstract

TiO_2 nanoparticles with tailored morphology have been synthesized under exceptionally soft conditions. The strategy is based on the use of a non-aqueous alcoholic reaction medium in which water traces, coming either from the air (atmospheric water) or from an ethanol–water azeotropic mixture (ethanol 96%), are incorporated in order to accelerate hydrolysis of the Ti–precursor. Moreover, organic surfactants have been used as capping agents so as to tailor crystal growth in certain preferential directions. Combinations of oleic acid and oleylamine, which lead to the formation of another surfactant, dioleamide, are employed instead of fluorine-based compounds, thus increasing the sustainability of the process. As a result, TiO_2 nanostructured hierarchical microspheres and individual nanoparticles with exposed high-energy facets can be obtained at atmospheric pressure and temperatures as low as 78 °C.

Keywords: A. Powders: chemical preparation; A. Grain growth; B. Electron microscopy; D. TiO_2 anatase

1. Introduction

In recent years the number of published works dealing with obtaining TiO_2 nanoparticles with ultra-reactive surfaces has increased exponentially, mainly due to the great interest in their high reactivity that arises both from a scientific and technological point of view. The unique physicochemical properties of TiO_2 nanoparticles confer them with potential applications in a wide range of fields, acting as photocatalysts, dye-sensitive solar cells (DSCs), Li batteries, transparent conductors, gas sensors, and so on [1–13]. These properties depend not only on the crystal phase, particle size and distribution of the particles, but also on their specific morphology, since the latter can lead to a reduction in the formation of electron traps and thus facilitate the electron transfer in the semiconductor structure [1,2,14–19]. In particular, for photocatalytic applications materials based on high-energy faceted anatase nanocrystals or, as recently reported, on crystalline hierarchical TiO_2 hollow spheres [20–22] are required, in order to achieve a high efficiency. Accordingly, the synthesis of well-crystallized and nanostructured TiO_2 particles with tailored morphology represents a major challenge.

The formation and growth of TiO_2 nanoparticles is generally achieved through hydrolysis and condensation processes from different precursors. The major problem tailoring the morphology and size of these particles arises from the titanium ions themselves: Ti^{4+} cations are large and highly electropositive, and therefore prone to suffer a nucleophilic attack by water, which leads to a too fast hydrolysis and thus to uncontrolled growths and precipitations. One of the most effective ways to control the rate of hydrolysis is through the choice of the metal alkoxide, e.g. altering the OR groups. The alkoxy groups which are most frequently used in the synthesis of TiO_2 comprise from 2 (ethoxide) to 4 (butoxide) carbon atoms, and their

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reactivity during the hydrolysis decreases with increasing chain length. However, in the presence of excess of water, hydrolysis is still exothermic and quick and completed in seconds. A feasible way of further reducing this speed is by adjusting the $H_2O/M(OR)n$ ratio and stabilizing the formed colloids. What is more, the replacement of the alkoxy groups by less hydrolyzable ones may also contribute to decrease the rates of hydrolysis and condensation, affecting the crystallization behavior and increasing the control over the final particle size. Even with these procedures, the overall hydrolysis reaction of Ti^{4+} ions still remains too fast, and thus a very fine control of the reaction conditions is a necessary requirement, since any slight alteration of the reaction kinetics will cause dramatic changes in the size and morphology of the final material.

In order to overcome this drawback, non-hydrolytic processes have been described for obtaining TiO_2 nanoparticles with high crystallinity. The use of oxygen donor groups other than water may allow a better control of the reaction rate, leading to slow particle growth. The problem is that under these conditions the reaction rate is drastically reduced, the process becomes excessively slow and the possibility of tailoring the morphology of the synthesized particles is hindered by kinetic considerations [23–27]. In this sense a promising alternative which has been recently considered combines both hydrolytic and non-hydrolytic reactions: by adding a certain amount of water into a non-aqueous media, the size and morphology of the TiO_2 precipitated particles can be finely tuned [28].

However, for the particular case of high-energy faceted TiO_2 nanocrystals an extra problem needs to be faced: due to minimization of the surface energy, the number of highly reactive faces rapidly decreases during the crystallization process. This means that under normal conditions the synthesized TiO_2 crystals consist mainly of poorly reactive {101} faces, which are thermodynamically more stable than the desired {001} and {010} faces (Fig. 1). In order to reverse this situation, i.e. to stabilize the more reactive faces, a characteristic resource is the use of morphological agents that cap the growth in one or more faces, making the crystal develop only in certain directions and hence altering/controlling its morphology [29]. Hydrofluoric acid is one of these agents, and different experimental and theoretical studies have proved its efficiency producing faceted TiO_2 crystals with high percentages of {001} and {010} faces [30–33]. Most recent works on the synthesis of faceted TiO_2 follow this methodology, in which fluorine anions selectively adsorb on the surface of {010} and {001} faces, stabilizing them. However, the use of fluorinated compounds as morphological control agents also carries some disadvantages: first an input of pressure and temperatures around 180 °C are typically required so as to obtain the properly crystallized faceted particles. Moreover, during the reaction process a release of highly corrosive hydrofluoric vapors is always observed, which undoubtedly represents a major drawback for the large-scale synthesis of faceted TiO_2. In view of these facts, the substitution of fluorine-based compounds by organic capping surfactants which usually contain amine, amide or carboxylic groups, must be considered. Used either individually or combined [25–28,34–36], these molecules represent a more environmentally-friendly option to tune the morphology of the anatase particles. To be more precise, Dinh et al. [28] have recently proved different combinations of oleic acid and oleylamine to successfully synthesize TiO_2 crystals with different shapes. The problem with fluorine vapors is consequently eradicated when using this method, but temperatures around 180 °C and the use of a sealed autoclave reactor to autogenously increase the pressure are still required.

In this sense, herein we report a new synthetic approach based on a non-aqueous and fluorine-free technique to obtain TiO_2 nanocrystals with tailored morphology at atmospheric pressure and temperature clearly below 100 °C. Nanostructured hierarchical TiO_2 spheres as well as individual faceted anatase nanocrystals are successfully prepared at remarkably soft conditions. Oleic acid and oleylamine are combined and used as morphological control agents, and their capping role is analyzed and reinterpreted in terms of the formation of the dioleamide as a surfactant molecule.

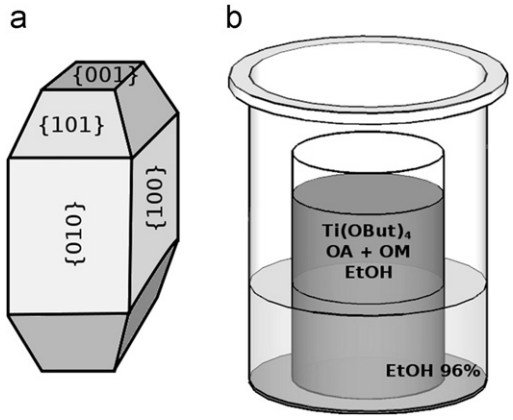

Fig. 1. (a) Anatase TiO_2 with {101}, {001} and {010}/{100} facets and (b) scheme of the reaction assembly for the nanoparticles synthesis.

2. Materials and methods

2.1. Chemicals

The chemicals titanium (IV) tetrabutoxide ($Ti(OBut)_4$, Fluka, 98%), ethanol (EtOH, Merck, analytically pure), oleic acid ((Z)-octadec-9-enoic acid, designated as OA, Fluka, analytically pure), and oleylamine ((Z)-octadec-9-en-1-amine, designated as OM, Aldrich, 70%) were used without further purification.

2.2. Synthesis of TiO_2 spheres (TiS)

A solution of $Ti(OBut)_4$ (10 mmol) in 200 mL of dry ethanol was stirred under reflux for 8 h. Then the solution

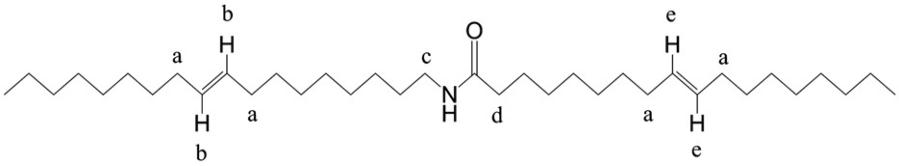

Fig. 2. Dioleamide (DO).

was evaporated to dryness, and the obtained white solid was washed with deionized water and dried at room temperature. The as-synthesized TiO_2 spheres were calcined at 300 and 400 °C for 4 h so as to remove organic products and promote crystallinity.

2.3. Synthesis of dioleamide (DO)

OA (3.55 g, 12.5 mmol) and OM (70%, 4.80 g, 12.5 mmol) were mixed in a flask under stirring, heat release was appreciated. The obtained yellow liquid was dried with $MgSO_4$. Yield: 99%. ^{1}H NMR (300 MHz, DMSO-d_6, δ): 7.35 (s, 2H, H_b), 5.28 (m, 3H, H_e+NH), 2.66 (s, 2H, H_c), 1.98 (s, 8H, H_a), 1.51 (s, 2H, H_d), 1.26 (s, 46H, CH_2), 0.85 (q, 6H, CH_3) (see Fig. 2).

2.4. Synthesis of TiO_2 nanoparticles (TiNP)

In a typical procedure, $Ti(OBut)_4$ (10 mmol) was added to a mixture of X mmol OA, Y mmol OM, in 5:5 or 6:4 ratios, and 200 mmol of dry ethanol. The Pyrex beaker containing the obtained mixture was placed into an automated laboratory reactor system (Mettler-Toledo LabMax) containing 80 mL of ethanol 96% (see Fig. 1). Then the reaction was heated under stirring at 78 °C for 8 h or 72 h. The obtained precipitate was washed with dry ethanol and deionized water several times and then dried at room temperature.

2.5. Surface surfactants removal from as-prepared anatase TiNP

Solid samples of the as-prepared anatase TiO_2 nanoparticles were heated at 200 °C for 30 min. The obtained orange solids were then washed with hot dry ethanol under stirring several times. Finally the obtained white precipitates were washed with deionized water and one last time with ethanol. The clean samples were dried at 80 °C in air.

2.6. Characterization

The analyses of the crystalline structure and phase identification were performed by X-ray diffraction (XRD Bruker D8 ADVANCE) with a monochromatized source of $CuK_{\alpha 1}$ radiation (λ=1.5406 nm) at 1.6 kW (40 kV, 40 mA). Samples were prepared by placing a drop of a concentrated ethanolic dispersion of particles onto a silicon single crystal. FESEM images were obtained with a Hitachi S-4700 field-emission scanning electron microscope (FESEM) working at 20 kV. Transmission electron microscopy (TEM) images were collected in a HITACHI H7100 microscope working at 125 kV and high-resolution transmission electron microscopy (HRTEM) images were obtained on a JEOL 2100F transmission electron microscope (TEM/STEM) operating at 200 kV and equipped with a field emission electron gun, providing a point resolution of 0.19 nm; samples were prepared by placing a drop of a dilute toluene or ethanol dispersion of nanoparticles onto a 300 mesh carbon-coated copper grid and evaporated immediately at 60 °C. ^{1}H NMR spectra were recorded on a spectrometer Bruker AMX-300 using DMSO-d_6 as solvent and TMS as internal reference.

3. Results and discussion

TiO_2 particles with distinct morphologies have been synthesized under soft, non-aqueous, ethanolic conditions. All reactions were carried out at 78 °C using $Ti(ButO)_4$ as the starting reagent. $Ti(ButO)_4$ was chosen as Ti precursor for its slow rate of hydrolysis, due to the butoxide group, which slows down the process of diffusion and polymerization compared to other alkyl groups. To obtain TiO_2 nanoparticles a new synthesis method was developed from the basis of that reported by Dinh et al. [28], with EtOH (96%) providing the water necessary to accelerate the hydrolysis reaction, and oleic acid (OA) and oleylamine (OM) as capping agents. Experiments were run in the absence of surfactants as well as with different ratios of oleic acid and oleylamine. In those experiments involving surfactants, the $Ti(OBut)_4$: surfactant molar ratio was kept constant at 1:10.

3.1. Growth in the absence of surfactants

When no surfactant is used, TiO_2 spheres with homogeneous sizes (2–4 μm) are obtained (Fig. 3). A more detailed analysis of the surface shows that the particles are in fact aggregates of TiO_2 nanocrystals with a spherical macrostructure (Fig. 3 (b), (d) and (f)), similar to those described in previous works [21,22,37]. This growth should be ascribed to the synthesis route: at low temperature and due to the limited amount of water from air, the formed TiO_2 crystals are small, and assemble in Ti microspheres with nanosized pores [20]. The crystallinity of the synthesized samples was examined by powder X-Ray diffraction. As shown in Fig. 4, the precipitate presents a low degree of crystallinity, which might be due to the small size of the

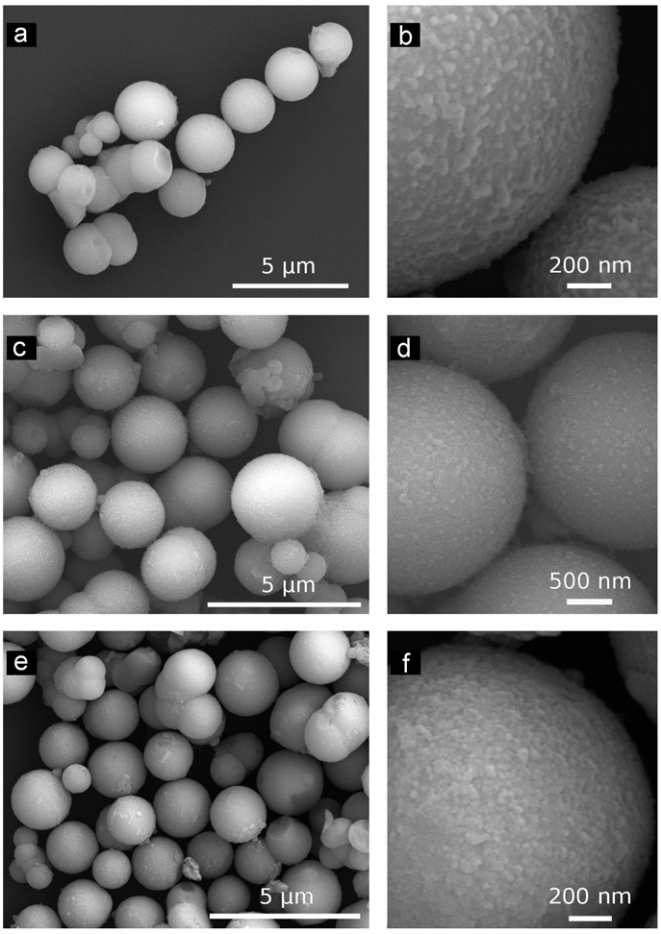

Fig. 3. (a) FESEM micrograph of the sample TiS, (b) detail of the surface of TiS, (c) FESEM micrograph of the sample TiS300, (d) detail of the surface of TiS300, (e) FESEM micrograph of the sample TiS400 and (f) detail of the surface of TiS400.

nanocrystals constituting the spheres (~5 nm). This fact is confirmed in the TEM micrographs (see Fig. 5), whereby the TiO_2 spheres, formed by small nanocrystals, show a cloud-like appearance. In order to improve the crystallinity of the obtained particles these samples were fired at temperatures of 300 °C (TiS300 samples) and 400 °C (TiS400 samples) for 4 h. As it can be seen in Fig. 4, the degree of crystallinity increases after calcination, due to a growth and consolidation of the nanoparticles (Fig. 3). In both cases crystallization of pure anatase phase (JCPDS File no. 21-1272) is observed, and FESEM micrographs confirm that the size and macrostructure of the spheres are maintained after calcination (Fig. 3). Therefore, this method of synthesis allows us to obtain crystalline TiO_2 spheres with homogeneity of sizes and shapes, similar to those described by other authors, but employing mild reaction conditions.

3.2. Effect of surfactants and surfactants ratio

The situation significantly changes when the reactions are carried out in the presence of oleylamine and oleic acid,

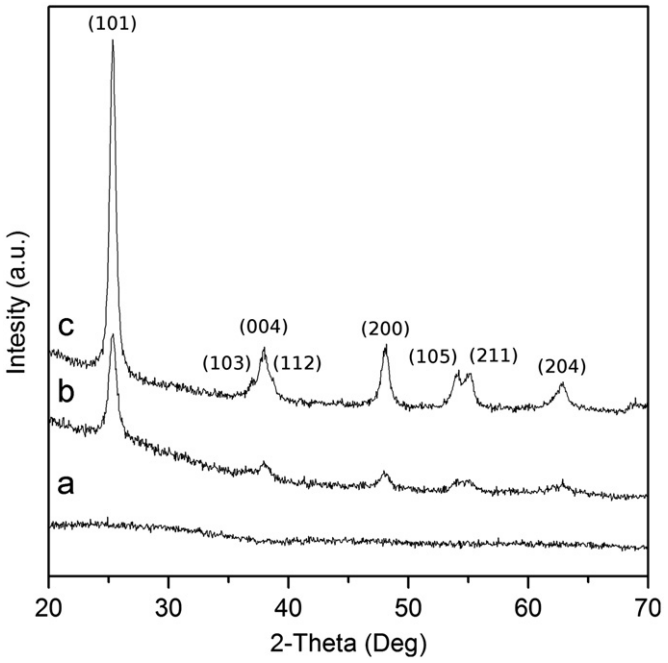

Fig. 4. XRD diffraction patterns of the TiS samples: (a) TiS, (b) TiS300 and (c) TiS400.

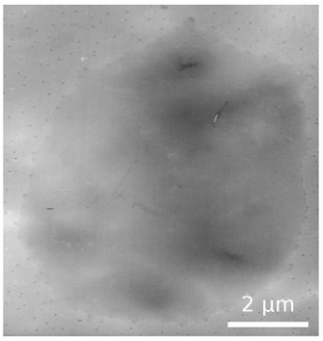

Fig. 5. Low-magnification TEM micrograph of an individual sphere of the sample TiS.

since now faceted nanoparticles of TiO_2 are obtained. More specifically, when the OA/OM ratio is 5:5 (TiNP5 samples), truncated rhombic-shaped TiO_2 nanoparticles are obtained, with a size of about 25 nm (Fig. 6(a)). A modification of the surfactants ratio to 6:4 (TiNP6 samples) leads to the formation of TiO_2 nanoparticles with similar size and morphology, together with the formation of TiO_2 nanorods (Fig. 6(b)). The crystallinity of the synthesized samples was verified by selected area electron diffraction (SAED) (Fig. 6(c)). This change in the growth habit with regard to the surfactant-free compositions must be interpreted as follows: as mentioned in the introduction, the shape of the final products is affected by the rate of the two main processes which control the formation of TiO_2, i.e. hydrolysis of the titanium precursor and the subsequent condensation reactions to form a Ti–O–Ti network [38]. By using surfactants with different functional groups and distinct binding strengths, the morphology of resulting

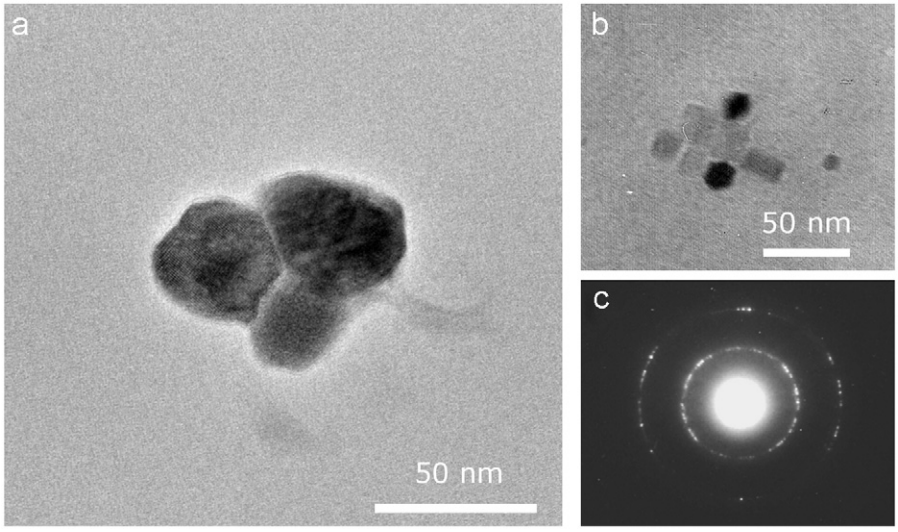

Fig. 6. Representative TEM images of: (a) TiNP5 obtained at 78 °C for 8 h, (b) TiNP6 obtained at 78 °C for 8 h and (c) SAED of truncated rhombic TiO_2 nanoparticles.

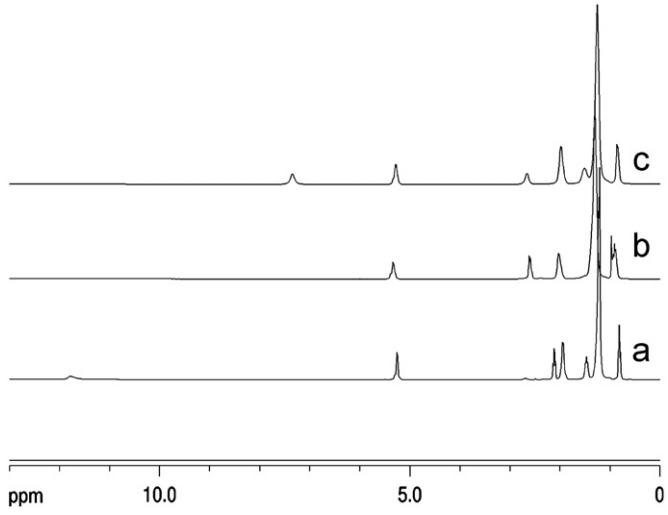

Fig. 7. ^{1}H NMR spectra in DMSO-d_6 of: (a) oleic acid (OA), (b) oleylamine (OM) and (c) dioleamide (DO).

particles could be controlled [39–41]. In our case it has been suggested that OA strongly binds to the TiO_2 {001} faces [25,28], whereas OM tends to adhere on the {101} ones [18]. Thus, varying the proportions of these compounds it is possible to modulate the rate of hydrolysis and promote the formation of TiO_2 nanoparticles with controlled shape and size [28]. Nevertheless, there is still a fact that must be considered: oleylamine and oleic acid condense exothermically in situ to form a long-chain amide, dioleamide (DO) [42], in a visible spontaneous process, which is confirmed by ^{1}H NMR spectroscopy. As shown in Fig. 7, after condensation the spectrum of the obtained product (DO) shows a new signal at 7.35 ppm, which corresponds to the H_e and NH group. Furthermore, the lack of any signal above 10 ppm confirms the loss of the hydrogen belonging to the carboxylic group. Finally, some signals are shifted compared to the free precursors. These

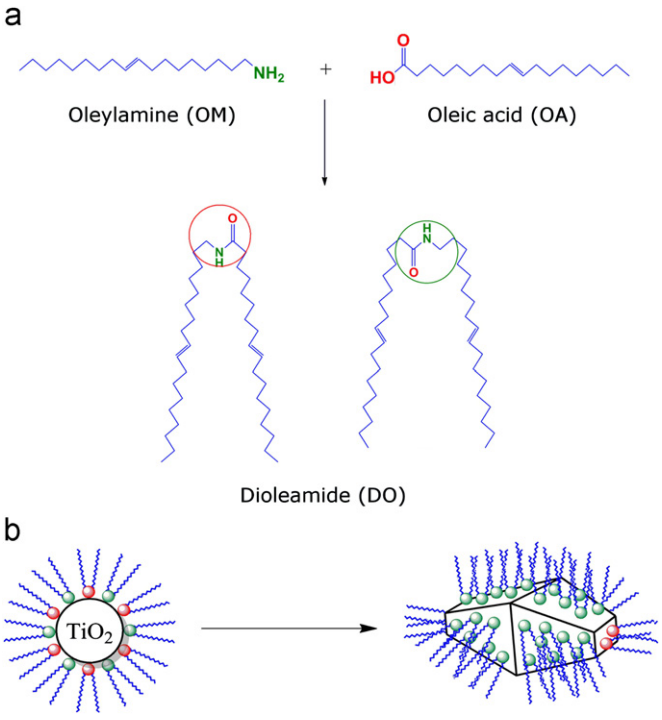

Fig. 8. (a) Oleic acid (OA) and oleylamine (OM) condensation and (b) shape control of dioleamide (DO) depending of the bond selectivity and strength.

facts confirm that the formation of DO was near completion after the addition of both compounds. This new formed molecule also plays a role as a surfactant [43], and according to our results it may also bind onto the TiO_2 faces with different strengths: more selectively to the {001} and {010} faces through the –C═O group and in a weaker way to the {101} faces through the –NH group (Fig. 8). These selective bindings of the DO molecule to different facets of the TiO_2 crystals restrict growth in the corresponding directions, as we have observed. On the

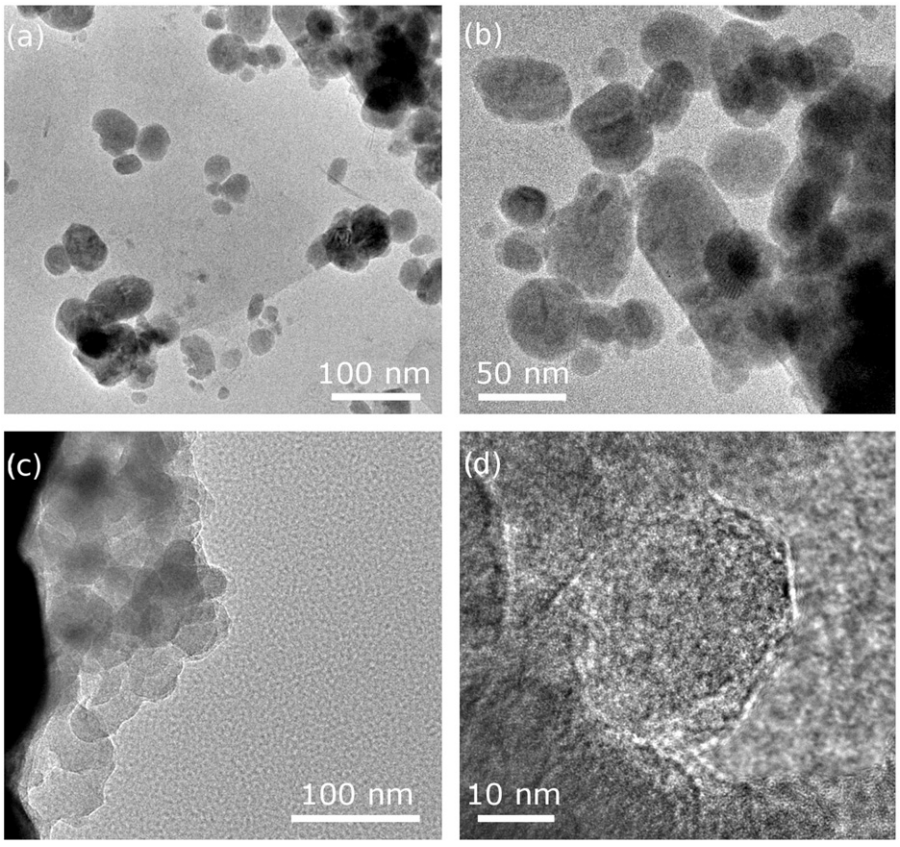

Fig. 9. TEM images of: (a) and (b) TiNP5 obtained at 78 °C for 72 h, (c) TiNP6 and (d) an individual particle of TiNP6 obtained at 78 °C for 72 h.

other hand, when the OA/OM mole ratio is changed to 6:4 (TiNP6 samples), there is an excess of unreacted OA and therefore an equilibrium is set between the binding of DO and OA to {001} faces. Due to the higher electronegativity of the carboxylic group belonging to OA, this probably binds more strongly and selectively to {001} faces, and as a result both TiO_2 truncated nanooctahedrons and TiO_2 nanorods are promoted.

3.3. Effect of reaction time

In order to evaluate how reaction time affects morphology of the particles, the reactions with 5:5 and 6:4 surfactants ratios were carried out, increasing the time up to 72 h (T=78 °C). As it can be observed in Fig. 9, the truncated rhombic nanoparticles retain their morphology, but no nanorods are observed this time. Once more crystallinity of the particles was verified by SAED (not depicted here). In the particular case of samples with 5:5 OA/OM molar ratio, merely an increase in the average particle size ($>$ 50 nm) is produced. However, in samples with 6:4 OA/OM molar ratio significant changes have been generated: the truncated octahedrons have been elongated in the [001] direction and this is due to the developing of new {010} facets (Fig. 9(c) and (d)). This situation can be ascribed to a kinetic regime [44], i.e. to the fact that the crystals grow faster on the faces with higher surface energy: {001} and {010}. Actually, our experiments with 6:4 OA/OM molar ratio (TiNP6 samples) suggest that the growth of the {001} faces is initially faster than that of the {010} ones, but beyond a certain point which we achieve by increasing the reaction time, the preferential growth switches to the {010} faces. Furthermore, Barnard et al. [45] also found that the formation of these new {010} facets is encouraged by conditions in which oxygenated surfaces are favored, something that we have in the TiNP6 samples with a higher amount of OA (6:4 M ratio) in the reaction medium.

4. Conclusions

A sustainable and versatile synthesis method has been developed which allows to obtain morphologically-tailored TiO_2 nanoparticles at extraordinarily soft solution conditions. Anatase nanostructured hierarchical spheres as well as individual nanoparticles with exposed high-energy facets ({001} and {010}) can be obtained at atmospheric pressure and temperatures as low as 78 °C. The strategy is based on the use of a non-aqueous alcoholic reaction medium with water traces to accelerate the hydrolysis of the Ti precursor. These water traces are incorporated either from the air (atmospheric water) or from the ethanol–water azeotropic mixture (ethanol 96%). Besides, organic surfactants based on a combination of oleic acid, oleylamine and the in situ formed dioleamide, have been employed to cap the growth in one or more crystal faces. Consequently the

particles develop only in certain directions, and hence tailoring their morphology. The absence of fluorine-based compounds, which are typically used as capping agents to control the morphology of the growing TiO_2 particles, makes the method here proposed a promising environmental-friendly alternative to current synthesis routes.

Acknowledgments

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References

[1] S. Liu, J. Yu, M. Jaroniec, Anatase TiO_2 with dominant high-energy {001} facets: synthesis, properties, and applications, Chemistry of Materials 23 (2011) 4085–4093.
[2] A. Hegazy, E. Prouzet, Room temperature synthesis and thermal evolution of porous nanocrystalline TiO_2 anatase, Chemistry of Materials 24 (2012) 245–254.
[3] J.J. Wu, X.J. Lü, L.L. Zhang, F.Q. Huang, F.F. Xu, Dielectric constant controlled solvothermal synthesis of a TiO_2 photocatalyst with tunable crystallinity: a strategy for solvent selection, European Journal of Inorganic Chemistry 19 (2009) 2789–2795.
[4] M. Li, Z.L. Hong, Y.N. Fang, F.Q. Huang, Synergistic effect of two surface complexes in enhancing visible-light photocatalytic activity of titanium dioxide, Materials Research Bulletin 43 (2008) 2179–2186.
[5] X.J. Lü, X. Mou, J.J. Wu, D.W. Zhang, L.L. Zhang, F.Q. Huang, F.F. Xu, S.M. Huang, Improved-performance dye-sensitized solar cells using Nb-doped TiO_2 electrodes: efficient electron injection and transfer, Advanced Functional Materials 20 (2010) 509–515.
[6] M. Grätzel, Photochemical cells, Nature 414 (2001) 338–344.
[7] X. Chen, S.S. Mao, Titanium dioxide nanomaterials: synthesis, properties, modifications, and applications, Chemical Reviews 107 (2007) 2891–2959.
[8] E.A. Rozhkova, I. Ulasov, B. Lai, N.M. Dimitrijevic, M.S. Lesniak, T. Rajh, A high-performance nanobio photocatalyst for targeted brain cancer therapy, Nano Letters 9 (2009) 3337–3342.
[9] D. Wang, D. Choi, J. Li, Z. Yang, Z. Nie, R. Kou, D. Hu, C. Wang, L.V. Saraf, J. Zhang, I.A. Aksay, J. Liu, Self-assembled TiO_2–graphene hybrid nanostructures for enhanced Li-ion insertion, ACS Nano 3 (2009) 907–914.
[10] X.J. Lü, F.Q. Huang, X.L. Mou, Y.M. Wang, F.F. Xu, A general preparation strategy for hybrid TiO_2 hierarchical spheres and their enhanced solar energy utilization efficiency, Advanced Materials 22 (2010) 3719–3722.
[11] D. Kim, A. Ghicov, S.P. Albu, P.J. Schmuki, Bamboo-type TiO_2 nanotubes: improved conversion efficiency in dye-sensitized solar cells, Journal of the American Chemical Society 130 (2008) 16454–16455.
[12] S.W. Kim, T.H. Han, J. Kim, H. Gwon, H.S. Moon, S.W. Kang, S.O. Kim, K. Kang, Fabrication and electrochemical characterization of TiO_2 three-dimensional nanonetwork based on peptide assembly, ACS Nano 3 (2009) 1085–1090.
[13] S. Joo, I. Muto, N. Hara, Hydrogen gas sensor using Pt- and Pd-added anodic TiO_2 nanotube films, Journal of the Electrochemical Society 157 (2010) J221–J226.
[14] H.G. Yang, C.H. Sun, S.Z. Qiao, J. Zou, G. Liu, S.C. Smith, H.M. Cheng, G.Q. Lu, Anatase TiO_2 single crystals with a large percentage of reactive facets, Nature 453 (2008) 638–641.
[15] H. Yang, G. Liu, S. Qiao, C. Sun, Y. Jin, S.C. Smith, J. Zou, H.M. Cheng, G.Q. Lu, Solvothermal synthesis and photoreactivity of anatase TiO_2 nanosheets with dominant {001} facets, Journal of the American Chemical Society 131 (2009) 4078–4083.
[16] X. Han, Q. Kuang, M. Jin, Z. Xie, L. Zheng, Synthesis of titania nanosheets with a high percentage of exposed (001) facets and related photocatalytic properties, Journal of the American Chemical Society 131 (2009) 3152–3153.
[17] Y. Dai, C.M. Cobley, J. Zeng, Y. Sun, Y. Xia, Synthesis of anatase TiO_2 nanocrystals with exposed {001} facets, Nano Letters 9 (2009) 2455–2459.
[18] J. Joo, S.G. Kwon, T. Yu, M. Cho, J. Lee, J. Yoon, T. Hyeon, Large-scale synthesis of TiO_2 nanorods via nonhydrolytic sol–gel ester elimination reaction and their application to photocatalytic inactivation of *E. coli*, Journal of Physical Chemistry B 109 (2005) 15297–15302.
[19] J. Li, L.W. Wang, Shape effects on electronic states of nanocrystals, Nano Letters 3 (2003) 1357–1363.
[20] X. Lü, S. Ding, Y. Xie, F. Huang, Non-aqueous preparation of high-crystallinity hierarchical TiO_2 hollow spheres with excellent photocatalytic efficiency, European Journal of Inorganic Chemistry (2011) 2879–2883.
[21] Z. Zheng, B. Huang, X. Qin, X. Zhang, Y. Dai, M. Jiang, P. Wang, M.H. Whangbo, Highly efficient photocatalyst: TiO_2 microspheres produced from TiO_2 nanosheets with a high percentage of reactive {001} facets, Chemistry—A European Journal 15 (2009) 12576–12579.
[22] Z. Zheng, B. Huang, J. Lu, X. Qin, X. Zhang, Y. Dai, Hierarchical TiO_2 microspheres: synergetic effect of {001} and {101} facets for enhanced photocatalytic activity, Chemistry—A European Journal 17 (2011) 15032–15038.
[23] J.N. Hay, H.M. Raval, Synthesis of organic–inorganic hybrids via the non-hydrolytic sol–gel process, Chemistry of Materials 13 (2001) 3396–3403.
[24] M. Niederberger, M.H. Bartl, G.D. Stucky, Benzyl alcohol and transition metal chlorides as a versatile reaction system for the nonaqueous and low-temperature synthesis of crystalline nano-objects with controlled dimensionality, Journal of the American Chemical Society 124 (2002) 13642–13643.
[25] Y.W. Jun, M.F. Casula, J.H. Sim, S.Y. Kim, J. Cheon, A.P. Alivisatos, Surfactant-assisted elimination of a high energy facet as a means of controlling the shapes of TiO_2 nanocrystals, Journal of the American Chemical Society 125 (2003) 15981–15985.
[26] Z. Zhang, X. Zhong, S. Liu, D. Li, M. Han, Aminolysis route to monodisperse titania nanorods with tunable aspect ratio, Angewandte Chemie International Edition 44 (2005) 3466–3470.
[27] R. Buonsanti, V. Grillo, E. Carlino, C. Giannini, T. Kipp, T.R. Cingolani, D. Cozzoli, Nonhydrolytic synthesis of high quality anisotropically shaped brookite TiO_2 nanocrystals, Journal of the American Chemical Society 130 (2008) 11223–11233.
[28] C.T. Dinh, T.D. Nguyen, F. Kleitz, T.O. Do, Shape-controlled synthesis of highly crystalline titania nanocrystals, ACS Nano 3 (2009) 3737–3743.
[29] M. Peiteado, T. Jardiel, F. Rubio, A.C. Caballero, Multipod structures of ZnO hydrothermally grown in the presence of Zn_3P_2, Materials Research Bulletin 45 (2010) 1586–1592.
[30] H.G. Yang, C.H. Sun, S.Z. Qiao, J. Zou, G. Liu, S.C. Smith, H.M. Cheng, G.Q. Lu, Anatase TiO_2 single crystals with a large percentage of reactive facets, Nature 453 (2008) 638–641.
[31] J. Pan, G. Liu, G.Q.M. Lu, H.M. Cheng, On the true photoreactivity order of {001}, {010}, and {101} facets of anatase TiO_2 crystals, Angewandte Chemie International Edition 50 (2011) 2133–2137.
[32] X.H. Yang, Z. Li, C. Sun, H.G. Yang, C. Li, Hydrothermal stability of {001} faceted anatase TiO_2, Chemistry of Materials 23 (2011) 3486–3494.

[33] C.Z. Wen, H.B. Jiang, S.Z. Qiao, H.G. Yang, G.Q. Lu, Synthesis of high-reactive facets dominated anatase TiO_2, Journal of Materials Chemistry 21 (2011) 7052–7061.
[34] Y. Yin, A.P. Alivisatos, Colloidal nanocrystals synthesis and the organic–inorganic interface, Nature 437 (2005) 664–670.
[35] S.G. Kwon, T. Hyeon, Colloidal chemical synthesis and formation kinetics of uniformly sized nanocrystals of metals, oxides, and chalcogenides, Accounts of Chemical Research 41 (2008) 1696–1709.
[36] X. Wang, Q. Peng, Y. Li, Interface-mediated growth of monodispersed nanostructures, Accounts of Chemical Research 40 (2007) 635–643.
[37] J.S. Chen, Y.L. Tan, C.M. Li, Y.L. Cheah, D. Luan, S. Madhavi, F.Y.C. Boey, L.A. Archer, X.W. Lou, Constructing hierarchical spheres from large ultrathin anatase TiO_2 nanosheets with nearly 100% exposed (001) facets for fast reversible lithium storage, Journal of the American Chemical Society 132 (2010) 6124–6130.
[38] J. Livage, M. Henry, C. Sanchez, Sol–gel chemistry of transition metal oxides, Progress in Solid State Chemistry 18 (1988) 259–341.
[39] E. Ramirez, S. Jansat, K. Philippot, P. Lecante, M. Gomez, A.M. Masdeu-Bulto, B. Chaudret, Influence of organic ligands on the stabilization of palladium nanoparticles, Journal of Organometallic Chemistry 689 (2004) 4601–4610.
[40] H.X. Mai, Y.W. Zhang, R. Si, Z.G. Yan, L.D. Sun, L.P. You, C.H. Yan, High-quality sodium rare-earth fluoride nanocrystals: controlled synthesis and opticals properties, Journal of the American Chemical Society 128 (2006) 6426–6436.
[41] J. Watt, N. Young, S. Haigh, A. Kirkland, R.D. Tilley, Synthesis and structural characterization of branched palladium nanostructures, Advanced Materials 21 (2009) 2288–2293.
[42] B.D. Fahlman, Nanoscale building blocks and applications, in: Materials Chemistry, 2nd ed., Springer-Verlag New York LLC, New York, 2008, pp. 517–518.
[43] H. Wu, Y. Yang, Y.C. Cao, Synthesis of colloidal uranium-dioxide nanocrystals, Journal of the American Chemical Society 128 (2006) 16522–16523.
[44] Y.W. Jun, Y.Y. Jun, J.J. Cheon, Architectural control of magnetic semiconductor nanocrystals, Journal of the American Chemical Society 124 (2001) 615–619.
[45] A.S. Barnard, L.A. Curtiss, Prediction of TiO_2 nanoparticle phase and shape transitions controlled by surface chemistry, Nano Letters 5 (2005) 1261–1266.