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High-Yield Preparation of Titanium Dioxide Nanostructures by Hydrothermal Conditions

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The effect of the neutral surfactant dodecylamine and octadecylamine on the synthesis of TiO_2-based nanostructures by the treatment of anatase with NaOH under hydrothermal conditions in the temperature range 120–150 °C and different reaction times was investigated. The products analyzed by electron microscopy, X-ray diffraction, FT-IR and elemental analysis contains—depending of the amine, the temperature and the duration of the hydrothermal treatment—spherical and tubular species containing the acid $H_2Ti_3O_7$. The formation of morphologically almost pure phases constituted by nanospheres and nanotubes were obtained at 130 °C after about 30 and 50 h respectively. Using dodecylamine, structurally fragile tubular amine containing nanocomposites are obtained, while in the case of the octadecylamine, notoriously stable purely inorganic nanotubes are formed. The role of the amine in these reactions is discussed.

Keywords: TiO_2-Based Nanostructures, Hydrothermal Treatment, Neutral Surfactant.

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1. INTRODUCTION

Nanostructured titanium oxide based materials like particles, wires and tubes have been the focus of great interest during the last years.[1–5] The development of simple chemical methods for producing large surface/volume ratio and high porosity titanium dioxide-based products has enhanced the potentiality of this broad band semiconductor in traditional applications like catalysis, pigments, cosmetics and optical materials as well as in the development of new advanced functional materials.[6,7] Much work on the preparation of nanotubes and nanowires by strong alkaline treatment of precursors like anatase or rutile under hydrothermal conditions has been reported.[8–10] However, reports on the role of surfactants as structure director, successfully used in oxides like V_2O_5,[11] are in the case of the titanium dioxide still scarce.

In this work we describe titanium oxide based nanostructures prepared via the reaction of anatase with NaOH in the presence of the long-chain neutral surfactants, dodecylamine (DDA) and octadecylamine (ODA), under different conditions. Inorganic nanotubes of pure $H_2Ti_3O_7$ as well as a nanocomposite with the amine are obtained with near quantitative yields.

2. EXPERIMENTAL DETAILS

0.4 g Anatase (Aldrich) and an equimolar amount of amine (DDA and ODA Aldrich 98%) were treated with 5 mL of 10 M NaOH (Merck) aqueous solution. The resulting suspensions were heated at temperatures in the range 120–150 °C in a Teflon lined autoclave. Solid products, obtained after about 12, 30, 50 and 72 h, were separated from the suspension by centrifugation, treated with a solution HCl 0.1 M for 24 h, and washed with deionised water repeatedly until pH 6 were analyzed by X-ray diffraction analysis (Siemens D-5000, Cu-Kα radiation), FT-IR (Bruker Vector 22 Fourier transform infrared spectrometer in the range 4000–250 cm^{-1} using KBr), SEM (Phillips XL-30), TEM (JEOL 100-SX) and Elemental analysis (SISONS ES-1108). The elemental analysis for selected samples: DDA 130 °C, 48 h: % Found (calculated for $(H_2Ti_3O_7)(DDA)_{0.4}$): C: 16.74 (16.75); H: 4.63 (4.63); N: 1.88 (1.63). ODA, 150 °C, 72 h: % Found (calculated for $(H_2Ti_3O_7)$): C: 0.31 (0.00); H: 1.22 (1.20), N: 0.16 (0.00).

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3. RESULTS AND DISCUSSION

The treatment of anatase with NaOH in the presence of the long-chain alkylamines, dodecylamine and octdecylamine, under hydrothermal conditions followed by the neutralization of resulting suspension leads to the formation of nanostructured products. The composition and shape of the products depend however on the nature of the amine as well as on the temperature and the reaction time of the hydrothermal treatment.

Best results, i.e., almost pure phases constituted by well defined nanostructures, were in general obtained at 130 °C. At this temperature depending on both, the reaction time and the amine carbon chain length, spheres or tubes with different aspect ratios and compositions may be obtained. In the reaction with dodecylamine (DDA) pure phases were obtained only at reaction times longer than 40 h. As observed in the TEM micrography in Figure 1 at *ca*. 30 h a mixture of pseudospherical arrangements and tubes are detected. The presence of particulate material is also present. However after 48 h a phase constituted solely by tubular structures illustrated in the SEM image in Figure 2(a) is obtained. The product is however somewhat fragile changing the aspect ratio by ultrasound radiation. Thus the TEM image in Figure 2(b) corresponding to the same product but sonicated in ethanol for 10 min shows nanotubes with lengths in the range 50–80 nm, shorter than those initially detected by SEM. The nanostructures in Figure 2(b) show internal and external diameters of 10 ± 0.5 and 7.2 ± 0.5 nm respectively. The aspect ratio of these nanostructures as well as the purity of the product is affected by the reaction time. Thus, preparations performed with hydrothermal reaction times of about 70 h lead to mixtures of relatively longer nanotubes and fibers. The elemental analysis of the nanotubes indicates the presence of DDA which is confirmed by the FT-IR spectrum, Figure 3(a), where the absorption bands ν(N-H), ν(C-H) and δ(N-H) corresponding to the amine are clearly detected. The product, which does not contain sodium, presents an X-ray diffraction pattern, Figure 4 in which, though the relatively low crystallinity of the sample, reflections corresponding to the acid $H_2Ti_3O_7$ may be detected. Thus, obtained nanotubes result to correspond to the organic–inorganic nanocomposite $H_2Ti_3O_7(DDA)_{0.4}$.

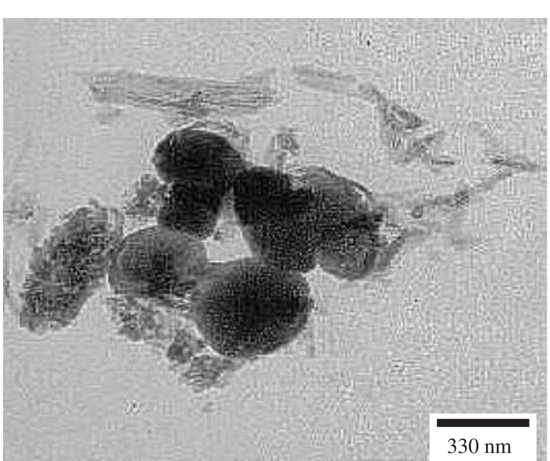


Fig. 1. TEM images of products obtained in the presence of DDA at 130 °C using a hydrothermal reaction time of 30 h.

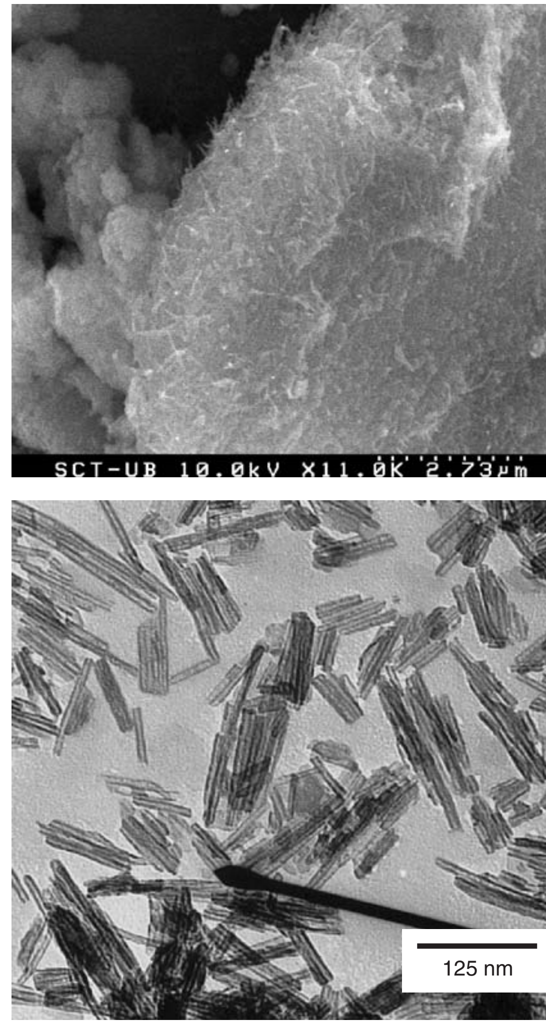
(a)
(b)


Fig. 2. Electron microscopy micrographies of nanotubes obtained using DDA at 130 °C after a hydrothermal reaction time of 48 h. (a) SEM micrograph of as prepared sample, (b) TEM image for the same product after sonication.

Results obtained from the reaction performed using octadecylamine (ODA) however differ from those discussed above. At the same reaction temperature, 130 °C, and a hydrothermal reaction time of about 30 h, a pure phase constituted by well defined spheres like those illustrated in Figure 5 with diameters in the range 150–350 nm is formed. Using a reaction time of about 50 h the formation of nanotubes with an almost quantitative yield is also observed. Contrasting with the DDA, the tubes prepared using ODA are much more stable and maintain their shape at higher hydrothermal reaction times. Thus at 72 h, pseudo-spherical aggregates like those illustrated in Figure 6(a) are observed. However these species

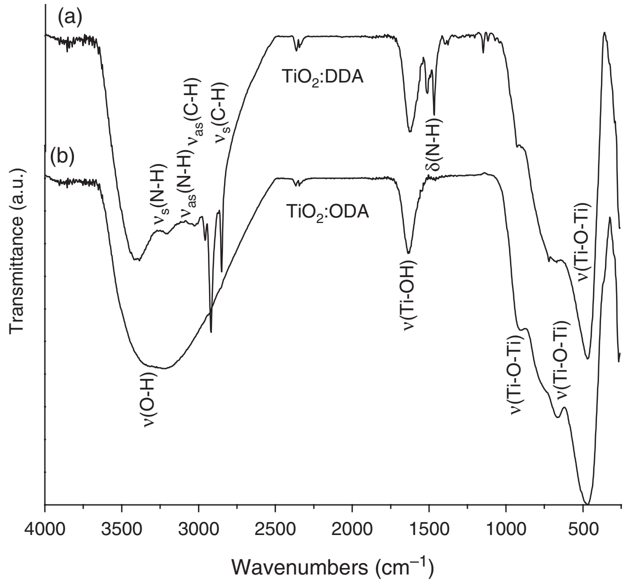


Fig. 3. FT-IR spectra of the products obtained in the presence of (a) DDA at 130 °C and 48 h and (b) ODA at 150 °C and 72 h.

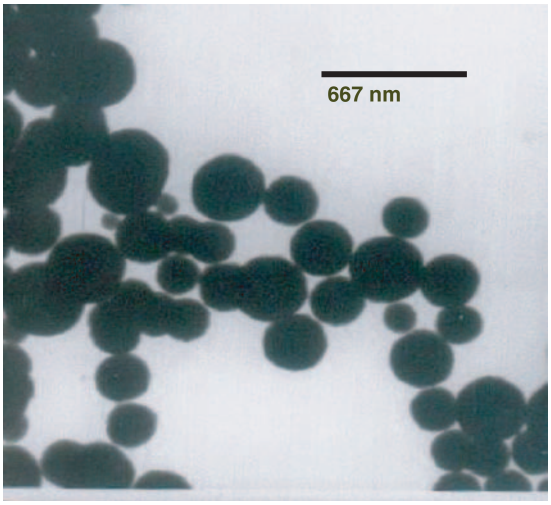


Fig. 5. TEM images of nanotubes obtained using ODA at 130 °C and 30 h.

are entirely formed by the aggregation of well formed tubular structures, Figure 6(b), with internal and external diameters of 9.5 ± 1 nm and 7 ± 1 nm respectively and lengths $\geq$100 nm. Moreover, preparations performed at 150 °C using reaction times of about 70 °C, i.e., conditions under which the preparation with DDA leads only to fibers and wires also result in the formation of nanotubes. The X-ray diffraction pattern of the product obtained at 130 °C is similar to that of the DDA derivative (Fig. 4). However the product obtained at 150 °C has a rather higher crystallinity bearing the more defined pattern shown in Figure 7 displaying reflections that, with slight shifts and intensity variations—frequently considered to be caused by the nanostructural nature of the products—essentially also

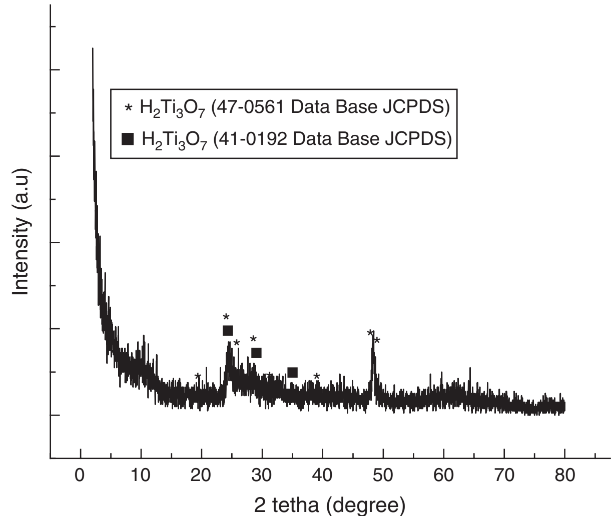


Fig. 4. X-ray diffraction analysis of the product obtained with DDA at 130 °C and 48 h.

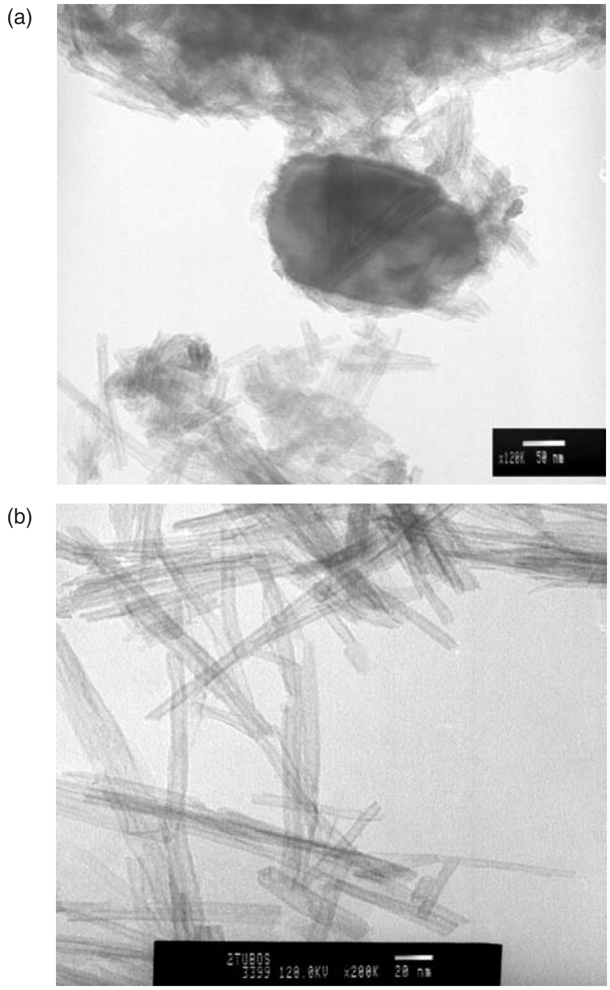


Fig. 6. (a) TEM image of spheres obtained using ODA at 130 °C and 72 h. (b) Image of the same sample at higher magnification.

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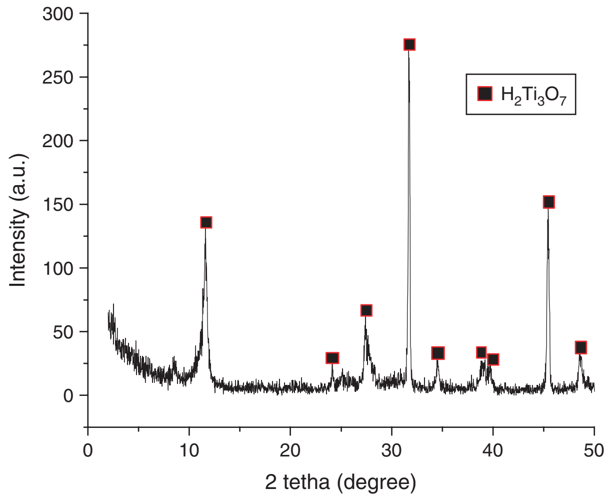

Fig. 7. X-ray diffraction pattern of nanotubes obtained using ODA at 150 °C and 72 h.

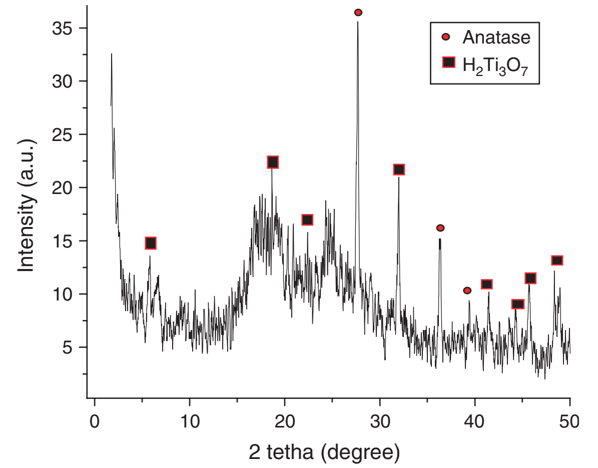

Fig. 9. X-ray diffraction pattern of the spheres produced using ODA at 130 °C and 30 h.

correspond to $H_2Ti_3O_7$. The FT-IR spectrum (Fig. 3(b)) and elemental analysis indicate the absence of ODA in the products. To test the role of the ODA in the formation of nanotubes, an experiment under the same conditions but without amine was performed. The result of this experiment is illustrated in Figure 8; only the formation of fibers was observed.

The nanospheres produced in the synthesis using ODA, contrarily to the tubular phases described above appear to be, as observed in the diffractogram in Figure 9, a mixture of $H_2Ti_3O_7$ and its precursor anatase. Thus they appear to be an intermediary in the formation of the tubes occurring at longer reaction times.

Results described above show that the first step in the formation of tubular nanostructures under strong alkaline conditions is always the formation of alkali titanates as being abundantly established in the literature,[12–14] independently of the presence of the amine described here. The role of the amine appears to be more related to the stabilization of new phases like the spheres and the tubes containing amine as well as of the conventional nanotubes which, under the same conditions but without amine, leads principally to fibers. However, the effect of the presence of amine strongly depends on the lengths of its carbon chain. The dodecylamine is able to produce a nanocomposite remaining inserted in the $H_2Ti_3O_7$ tubes, probably due to its molecular size permitting it to self-assemble in the available space. That however causes that under more drastic conditions the amine, disrupting its supramolecular structure, induces the inorganic tubular structure to collapse. In the case of longer amines like the ODA, a confinement into the tube would be unfavorable being thus forced to self-assemble around the inorganic tube forming a kind of vessel permitting an improved crystallization of the titanate which, finally, leads to more stable tubular inorganic species. The formation of almost perfect spheres observed at shorter reaction times would be also due to this micelle-like effect of this surfactant. The pseudo-spherical aggregates of the tubes observed under more drastic conditions may also find a similar explanation.

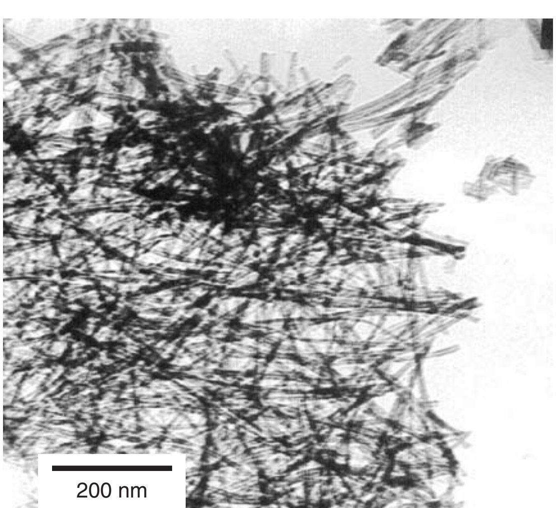

Fig. 8. TEM image of the product obtained at 150 °C and 72 h without amine.

4. CONCLUSIONS

The hydrothermal treatment of anatase with NaOH in the presence of a neutral surfactant like long-chain akylamines as the dodecylamine and the octadecylamine under relatively mild conditions, followed by a treatment with acid, leads to $H_2T_3iO_7$-based nanotubes. Although the formation of the titanate nanotubes appears to be independent of the presence of the amine, the latter plays a role in the properties of the products which however depend on the molecular length of the amine. Thus the dodecylamine may be inserted in the nanotube leading to relatively fragile tubular organic inorganic nanocomposites which under more drastic conditions collapse forming fibers. In the case

RESEARCH ARTICLE

of amines with a longer carbon-chain like the octadecylamine, the formation of an insertion product appears to be impossible. However it plays a role similar to a micelle which permit to stabilize spherical aggregates under both, the mildest and the most drastic of the used hydrothermal conditions. In between, intermediate reaction times lead to optimal stabilization of nanotubular structures. Furthermore, the use of ODA allows for the stabilization of nanotubes in conditions under which shorter chain amine lead to fibers. Further studies for determining the actual host-guest interactions involved in the effects described here are still in progress.

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References and Notes

1. Y. Lan, X. Gao, H. Zhu, Z. Zheng, T. Yan, F. Wu, S. P. Ringer, and D. Song, *Adv. Funct. Mater.* 15, 1310 (**2005**).
2. S. U. M. Khan, M. A. Shahry, and W. B. Ingler, Jr., *Science* 297, 2243 (**2002**).
3. M. Wagemaker, A. P. M. Kenetgens, and F. M. Mulder, *Nature* 418, 397 (**2002**).
4. A. R. Armstrong, G. Armstrong, J. Canales, R. Garcia, and P. G. Bruce, *Adv. Mater.* 17, 862 (**2005**).
5. S. Zhang, Q. Chen, and L. M. Peng, *Phys. Rev. B* 71, 014104 (**2005**).
6. K. Teraoka, T. Nonami, Y. Yokogawa, and T. Kameyana, *J. Mater. Res.* 15, 1243 (**2000**).
7. H. Masuda, K. Kamezawa, M. Nakao, A. Yokoo, T. Tamamura, T. Sugiera, H. Minoura, and K. Nishio, *Adv. Mater.* 15, 159 (**2003**).
8. Z. Y. Yuan, J. F. Colomer, and B. L. Su, *Chem. Phys. Lett.* 363, 362 (**2002**).
9. Y. X. Zhang, G. H. Li, Y. X. Jin, Y. Zhang, J. Zhang, and L. D. Zhang, *Chem. Phys. Lett.* 365, 300 (**2002**).
10. R. Yoshida, Y. Suzuki, and S. Yoshikawa, *J. of Solid Staen Chem.* 178, 2179 (**2005**).
11. C. O. Dwyer, D. Navas, V. Lavayen, E. Benavente, M. A. Santa Ana, G. González, S. B. Newcomb, and C. M. Sotomayor Torres, *Chem. Mater.* 18, 3016 (**2006**).
12. G. H. Du, Q. Chen, R. C. Che, Z. Y. Yan, and L. M. Peng, *Appl. Phys. Lett.* 79, 3702 (**2001**).
13. T. Kasuga, M. Hiramatsu, A. Hoson, T. Sekino, and K. Niihara, *Langmuir* 14, 3160 (**1998**).
14. T. K. Chen, W. T. Chen, M. Ch. Yang, and M. S. Wong, *J. Vac. Sci. Technol. B* 23, 2261 (**2005**).

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