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doi:10.1017/S1431927613009914

Microsc. Microanal. 19 (Suppl 2), 2013

Electron Microscopy Study of TiO_2 Hierarchical Structures Prepared by Hydrothermal Synthesis

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TiO_2 in the anatase crystal form is widely studied as a photocatalyst. Most effective in liquid (water) media is when it is in the form of nanoparticles dispersed in the polluted volume. Due to high surface area the probability for the contact between the photocatalyst and the pollutant is high. On the other hand nanoparticles are very hard to remove from the cleaned media and itself present unwanted pollution. One of possible solutions is to assemble nano building blocks into bigger structures without substantial lowering the surface-volume ratio which could be easily filtered from the suspension.

There are reports in the literature about preparation of TiO_2 hierarchical structures where shapes of corals [1], sea urchins [2,3], cactuses [4] or flowers [5,6], and microporous material [7,8] were obtained. Tian et. al. [5] prepared 3D flower-like structures with solvothermal synthesis at 180 °C for 0.5 h to 24 h, in ethanol/glycerol (in ratio 3:1) with tetrabutyl titanate as titania precursor, followed by calcination at 450 °C for 3 h. Material showed enhanced photocatalytic activity compared with commercial powder Degussa P25. Li et.al. [6] synthesized rutile chrysanthemums from titanium glycolate rods, heated at 400 °C for 4 h. Titanium glycolate rods were prepared solvothermally from titanium alkoxides in ethylene glycol at 170 °C for 2 h. In most cases the anatase or rutile crystals were relatively large and as a consequence the surface/volume ratio relatively small, specific surface was in the range of 50-100 m^2/g.

In the present work micro flower-like structures of TiO_2 were prepared solvothermally in glycerol. Structures were formed by self-assembly of twisted very thin amorphous sheets inside larger spherical, geode-like Ti-glycerolate particles. Transmission electron microscopy (Jeol 2010 F and Jeol 2100), electron diffraction and field emission scanning electron microscopy (Jeol 7600 F) revealed unique morphologies (Fig.1). Using different calcination temperatures the structures could be kept amorphous or crystalized in the form of anatase or rutile. Anatase started to form with calcination at 350 ºC and is single present phase in the sample till 550 °C, when rutile appeared. At 600 °C rutile was the only crystal modification left. After calcination the resulting anatase-based flower-like particles exhibited poor photocatalytic effect and the specific surface area was below 100 m^2/g. Using second hydrothermal step where amorphous flower-like structures and Ti-isopropoxide were starting materials 10-20 nm sized anatase nanoparticles were formed on the initial morphologies (Fig. 1 d-f). The specific surface area was 180 m^2/g. Photocatalytic effect was measured using caffeine and UV/Vis/NIR spectrophotometer. Amorphous micro TiO_2 structures were not photocatalytically active but when coated with anatase nanoparticles the effect was comparable to commercial TiO_2 powder (P25 from Evonik). Self-assembly, the nucleation and growth of flower-like structures inside micro-geode were followed using scanning and transmission electron microscopy. After second hydrothermal step beside shaping the material in the form of micron-sized flowers also organization of anatase nanoparticles on the each flower-leave was observed. Such nano-corn-cob morphology could be observed on Fig.1e. Possible explanations of such self-assembly and growth mechanisms will be presented and discussed.

References
[1] S. S. Mali, et al, Applied Surface Science **257** (2011), p. 9737.
[2] K. Hayashi, , et al, Material Letters **65** (2011), p. 3037.
[3] W. Wang, W. Wang and H. Hong, Chinese Physics Letters **28** (2011), p. 0781031.
[4] F. Guo, et al, Colloids and Surfaces A: Physicochemical and Engineering Aspects **395** (2012), p. 70.
[5] G. Tian, et al, CrystEngComm **13** (2011), p. 2994.
[6] Q. Li, et al, Journal of Alloys and Compounds **471** (2009), p. 477.
[7] J. Wu, et al, Journal of Crystal Growth **319** (2011), p. 57.
[8] X. Wang, et al, Langmuir **21** (2005), p. 2552.
[9] X. Wang and R. A. Caruso, Journal of Materials Chemistry **21** (2011), p. 20.
[10] This work is part of the PhD thesis of Ms. Barbara Horvat and was financially supported by the Slovenian Research Agency under Grant No. 1000-08-310086 and project J2-4309. Financed in part through the Slovenian Centre of Excellence Low Carbon Technologies (CO NOT)

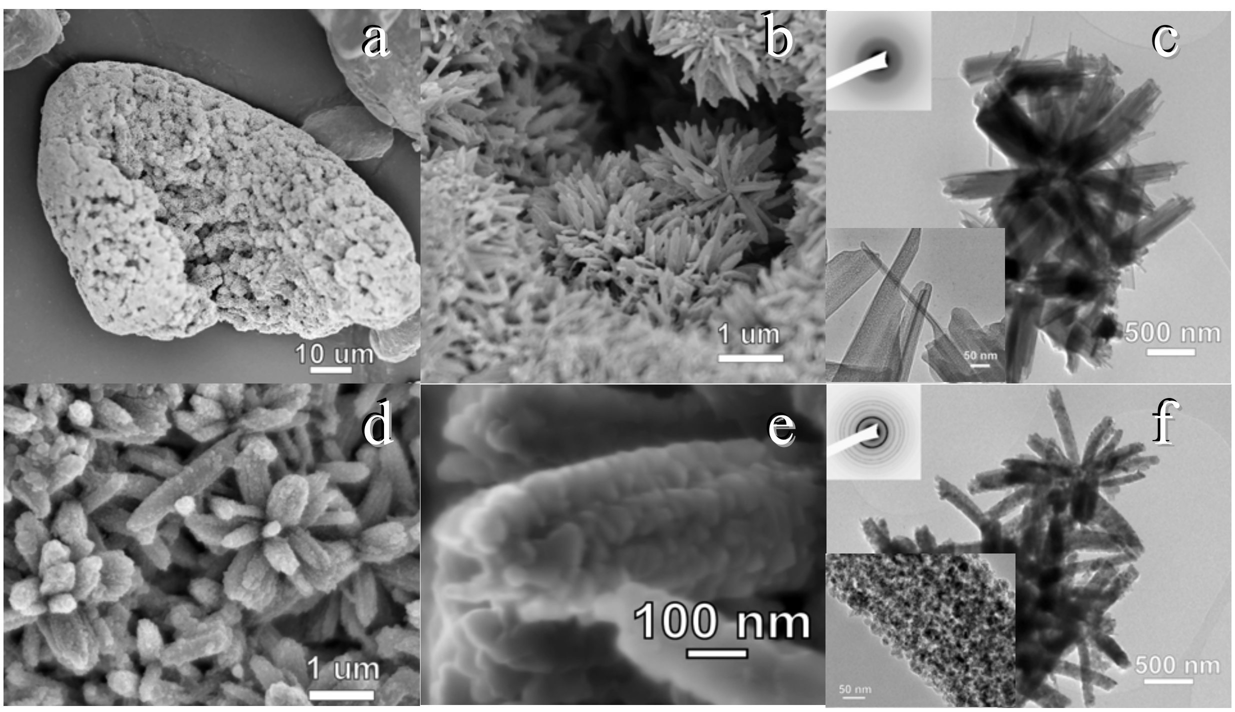

Fig. 1. SEM micrographs of geode-like structure (a) and flower-like hierarchical structures inside the geode (b). The flowers were made from twisted nanosheets of amorphous Ti-glycerolate as seen on TEM micrograph (c). Top inset represents selected area electron diffraction pattern, confirming that the sheets (bottom inset) are amorphous. After second hydrothermal step flower-like particles (d) were uniformly covered with 10 – 20 nm sized anatase nanoparticles forming nanocorn-cob shape (e). (f) - TEM image of this sample where diffraction pattern (top inset) corresponds to anatase crystal modification. Bottom inset shows TiO_2 nanoparticles arrangement.

https://doi.org/10.1017/S1431927613009914 Published online by Cambridge University Press