The synthesis and characterization of rutile titanium oxide nanoparticles

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Nanosized titanium oxide (TiO_2) exhibits unique physical and chemical properties which makes titanium oxide suitable for various applications, i.e. for photocatalysis, solar cells, luminescent materials, water photolysis, bactericidal use, dielectric materials, etc. Each application of nanosized titanium oxide requires a specific crystal structure (rutile or anatase), defined crystallites size and crystallites size distribution. This is why it is very important to develop and use synthesis methods which allow production of nanosized titanium oxide with controlled and predefined size, morphology and crystal structure. Among the used synthesis methods, the gel-sol and the sol-gel methods have proven to be promising and feasible processes to achieve control of the above-stated nanoparticle characteristics [1,2].

In our work we report on the synthesis of TiO_2 nanoparticles with the rutile crystal structure using both, the gel-sol and the sol-gel methods. With the gel-sol method, a highly viscous titanium-rich gel was used that was reacted at ~90ºC with a concentrated base forming a nanostructured titanate product. So prepared titanate was then treated with a suitable mineral acid which enabled the transformation of titanate to nanostructured rutile. The sol-gel method is different compared to the gel-sol method since nanoparticles form via heterogenous nucleation from a suitable solution rather than from a highly viscous gel as in the gel-sol method. Nevertheless, both reactions give high production efficiency and can be performed easily and quickly over a span of a few hours resulting in a formation of a viscous titanium oxide nanoparticle suspension. In both processing procedures the synthesized nanoparticles were isolated using centrifugation and repetitive decantation and re-suspension in water. After performing repetitive washing cycles, the nanoparticles were dried at 80ºC.

The obtained titanium oxide nanoparticles were characterized using X-ray powder diffraction (XRD), specific surface measurements (S_{BET}) and scanning and transmission electron microscopy (SEM, TEM). The XRD results showed that titanium oxide prepared either by the gel-sol or the sol-gel method crystallizes in the rutile crystal structure. Somewhat different width of the (110) diffraction in the XRD spectra peak indicated that both methods produced titanium oxide nanoparticles with different crystallite sizes. The specific surface measurements additionally showed that both methods produce titanium oxide nanoparticles having a high surface area ranging from 100-150 m^2/g, depending on the synthesis conditions. SEM and TEM images of titanium oxide nanoparticles prepared by the gel-sol method (Fig. 1) show that titanium oxide nanoparticles have a narrow size distribution and that they possess anisotropic shape. TEM observations (Fig. 1b) of anisotropically shaped particle further revealed that it is actually composed of well crystalline rutile nanoparticles ranging from 5 to 50 nm in size. The sol-gel method produces larger rutile nanoparticles having similar morphology as the gel-sol prepared nanoparticles (Fig. 2). Again, TEM observations (Fig 2b) showed that also these particles are composed from nanosized rutile crystallites with different size range, namely from 5 to 10 nm. No amorphous phase was

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observed in any of the observed specimens, regardless of the synthesis method. It was concluded that both, the gel-sol and the sol-gel methods are suitable for the preparation of titanium oxide nanoparticles with a large surface area and narrow size distribution. The obtained titanium oxide nanoparticles are well crystallized with the rutile structure and depending of the processing method show different degree of agglomeration.

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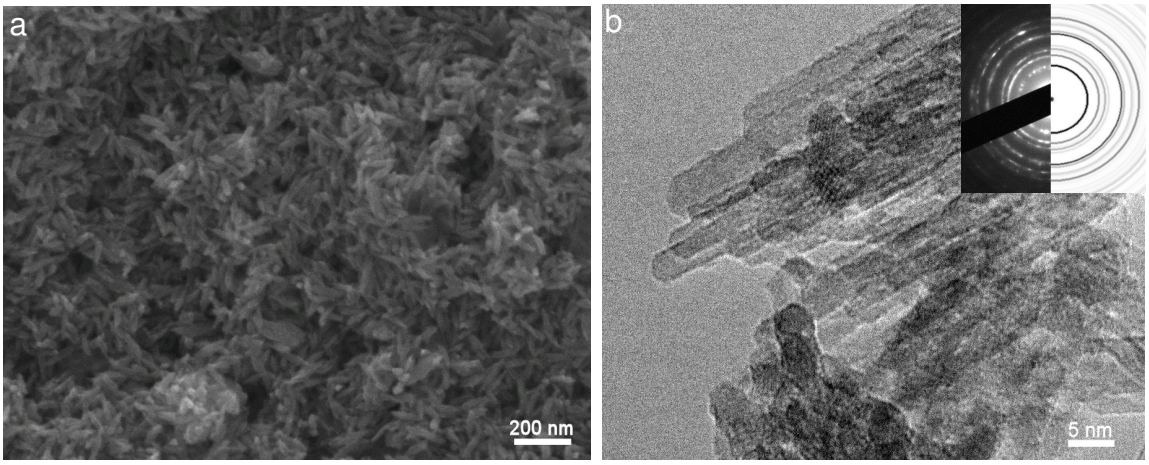

Figure 1. (a) SE image of titanium oxide nanoparticles prepared by the gel-sol method having very small sizes. (b) HRTEM image showing needle like shaped well crystalline nano-sized rutile particles with sizes ranging from 5 nm in width to 50 nm in length with the corresponding electron-diffraction pattern.

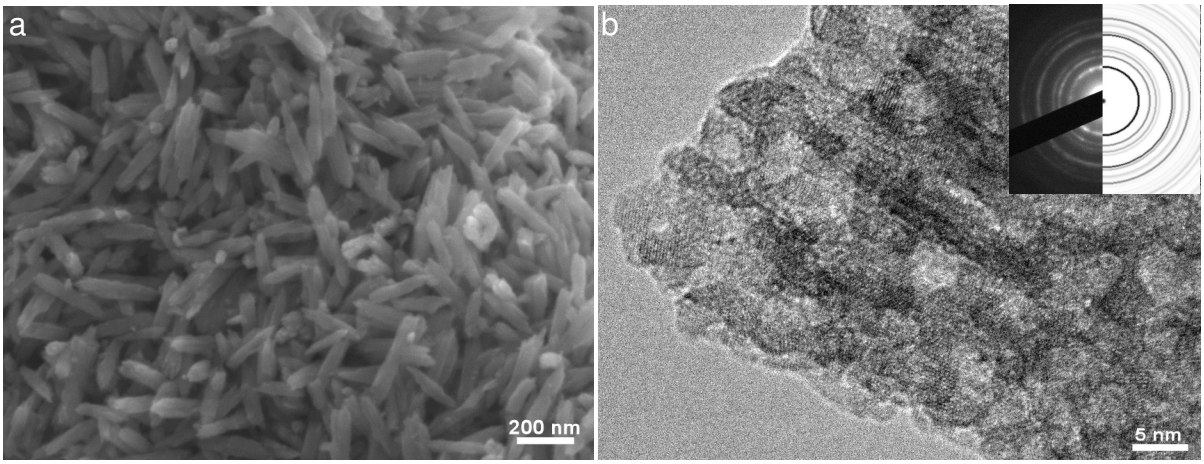

Figure 2. (a) SE image of titanium oxide nanoparticles prepared by the sol-gel method having larger sizes but similar morphology as the gel-sol prepared nanoparticles. (b) HRTEM image showing agglomerated well crystalline nano-sized rutile particles ranging from 5 to 10 nm in size with the corresponding electron-diffraction pattern.