Sc doped TiO_2 nanocrystals with core-shell morphology

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One of the most striking phenomena in nanoscience is the formation of self-assembled structures. Metal doped TiO_2 nanocrystals (NCs) display varying physiochemical properties based on their composition and structure. For instance, TiO_2 NCs made of a doped core have different photocatalytic properties than that doped core encased with a shell layer. This work discusses the choice of aliovalent Scandium (Sc) dopant in anatase host-lattice and the development of NCs with new *core/shell* morphology as a function of Sc diffusion and segregation during heat treatment of precipitated precursor from 200 to 1000 °C.

Rietveld refinement of powder X-ray diffraction patterns [1] confirmed that Sc (with a low dopant ratio of 4 at. %) is incorporated into a TiO_2 lattice at temperatures up to 800 °C. It was found that doping with Sc caused lattice stresses and structural defects (vacancies) due to misfit strain energy resulting from different ionic radii between Sc^{3+} (0.745 Å) and Ti^{4+} (0.605 Å). Annealing at 800 °C under air generated segregation of Sc into specific regions of NCs. This phenomenon can be explained by simultaneously diffusion and segregation processes of Sc dopant into a thin shell surrounding the TiO_2 core while maintaining to reduce the energy of the Sc-Ti-O system. To investigate the impact of Sc on the NCs morphology, complementary scanning transmission electron microscopy (STEM) and electron energy loss spectroscopy (EELS) were employed.

Figure 1a-b shown the *core/shell* growth of well-crystallized adjacent NCs. The corresponding FFTs (Fig.1b_1) shown the anatase (101) plane, connected to anatase indexed as (1 0 1), (103) and (112) (Fig.1b_2). The EELS profiles across the grain boundaries (GBs) were acquired to estimate the distribution of Sc dopant. Enrichment of the Sc at the shell near the GBs was observed (Fig.1c-d). The segregation shell was estimated to be on the order of a few nanometres.

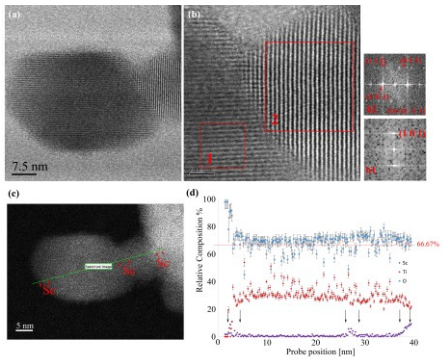

Figure 1. Morphology of Sc doped TiO2 at 800 °C. (a,b) STEM of Sc doped TiO2 NCs. (c,d) Relative composition by EELS showing the segregation of Sc as a thin shell (start and end of Sc rich area are marked by arrows)

Evaluation by STEM and EELS showed that the strain-energy driving process can be responsible for the energetically favored *core-shell* morphology transformation in Sc doped TiO_2 because of the relaxation of strain during NCs growth. The findings could be beneficial to understand the separated stages of NCs' nucleation and growth.

[1] Zenou, V., Bertolotti, F., Guagliardi, A., Toby, B.H., Von Dreele, R. B., Bakardjieva, S. (2020). *J. Appl .Cryst* **53**, 1452.

Keywords: TiO_2; nanocrystals; core-shell; segregation, doping

Acknowledgements: The research has received financial support from the GAČR Grant No. 181613S.

Acta Cryst. (2021), A**77**, C987