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## Non-thermal crystallization of TiO<sub>2</sub> thin films using supercritical carbon dioxide modified by ethanol-water mixture

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Thin films of titanium dioxide (TiO<sub>2</sub>) have attracted considerable attention in the past few years, since nanocrystalline TiO<sub>2</sub> shows outstanding properties (high photocatalytic activity, chemical stability, strong oxidation activity and non-toxicity) and has widespread application potential (self-cleaning surfaces, solar cells and energy conversion systems, gas and UV sensors, battery systems, etc.). All these applications rely on the semiconducting property of the TiO<sub>2</sub>, which is only found in crystalline TiO<sub>2</sub>. Crystalline TiO<sub>2</sub> has three natural crystalline modifications (named anatase, rutile and brookite), which differ in their semiconducting characteristics [1].

Method of preparation of crystalline TiO<sub>2</sub> thin films crucially affects their structural and microstructural properties influencing the TiO<sub>2</sub> (photo)catalytic performance. Since during commonly used method for the preparation of pure and crystalline TiO<sub>2</sub> thin films, calcination, an excessive sintering, crystallite growth or recrystallization occurs, this thermal processing is combined by supercritical carbon dioxide (scCO<sub>2</sub>) drying in last years. It was found that the pre-treatment of sol-gel derived metal oxide thin films as well as powders using supercritical carbon dioxide helps to enlarge surface area significantly and improve electronic properties showing enhanced photocatalytic performance [2].

To reduce the process temperature and to increase the thermal stability and the photocatalytic activity the TiO<sub>2</sub> thin films can be also directly crystallized by using scCO<sub>2</sub>, subcritical water, pressurized organic solvents or their combination in consecutive steps, as discussed recently [3, 4].

In this work, the scCO<sub>2</sub> modified by mixture of water and ethanol was used for a preparation of crystalline and pure nanostructured TiO<sub>2</sub> thin films in one step processing. All the experiments were performed over precursor titania thin films prepared by reverse micelles assisted sol-gel method, using hardly removable nonionic surfactant Triton X-114, however, forming uniform nano-domains. The effect of temperature (40-150 °C), pressure (10-30 MPa), modifier composition (20, 50 and 80 % w/w of water in ethanol) and concentration in scCO<sub>2</sub> (5-15 wt. %) and consumed amount of solvent (50-200 g) on microstructure and purity of TiO<sub>2</sub> thin films was thoroughly studied by means of Raman spectroscopy, X-ray diffraction, and contact angle measurements.

Anatase structure occurred in all tested TiO<sub>2</sub> thin films except those prepared at low temperature of 40 °C. When the processing was performed at lower temperatures than 100 °C, pressure below 20 MPa and solvent amount lower than 100 g the larger amount of surfactant residue in TiO<sub>2</sub> thin films was observed. The crystalline structure of anatase, which size changed from 1.2 to 7 nm in dependence on experimental conditions, was obtained without necessity of any additional thermal treatment of TiO<sub>2</sub> thin films. When scCO<sub>2</sub> modifier contained 80 % w/w of water the partial elution of TiO<sub>2</sub> film from glass substrate was observed.

[1] Forro L. et al. *J. Appl. Phys* 1994, 75, 633-635, [2] Wei M. D. et al. *J. Mater. Chem.*, 2007, 17, 3888-3893, [3] Sajfrtova M. et al. *J. Supercrit. Fluids* 2016, 117, 289-296, [4] Sajfrtova M. et al. *J. Supercrit. Fluids* 2018, 133, 211-217.