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Titanium dioxide has been extensively investigated for its promising applications in the form of thin films in solar cell [1] and also as a monoliths (blocks) for solar energy conversion [2]. The most important use of titania is associated with photocatalysis [3, 4] or as supporting material in the catalytic reactions [5]. Owing to the high photocatalytic activity, TiO_2 is an effective, easily available, relatively inexpensive and chemically stable photocatalyst. The photocatalytic activity of TiO_2 strongly depends on the structural properties such as crystal phase composition and crystallite size.

A commonly used method for the preparation of pure and crystalline TiO_2 is calcination (thermal treatment) [6, 7]. Nevertheless, this thermal treatment has some disadvantages such as excessive sintration, crystallite growth, recrystallization, or uncontrollable destruction of higly-porous structure of titania, commonly accompanied by the decrease of the surface area as well as of porosity.

The crystallization technique using modified supercritical carbon dioxide (SFC) opens up the possibility to prepare directly crystalline and highly pure nanostructured TiO_2 [8, 9] without any subsequent thermal treatment.

The motivation of this work is to utilize the SFC for the preparation of nanocrystalline titania thin films and aerogels of high purity. The crystallization with pure and modified $scCO_2$ by water (5–30 wt. %) and/or organic solvent (10 wt. %) was tested. The temperature (40–150 °C), pressure (10–30 MPa) and the volume of CO_2 (50–200 g) passed through the extractor were optimized with respect to the microstructure and purity of TiO_2 thin films and aerogels.

The purity and crystallinity of prepared TiO_2 thin films and aerogels were estimated by Raman spectroscopy. The crystallite size and the phase composition were determined by X-ray diffraction. Textural properties of aerogels such as the surface area and the pore-size distribution were characterized by nitrogen physisorption and helium pycnometry measurements.

Both, TiO_2 thin films and aerogels prepared with pure $scCO_2$ were amorphous. The crystallization of TiO_2 thin films was achieved at 150 °C with 100 g of $scCO_2$ modified by 30 wt. % of water. In case of aerogels, the temperature of 40 °C and lower concentration of water in $scCO_2$ (5 or 15 wt. %) were sufficient for the crystallization. The best results in terms of crystallization and the purity of titania were obtained during the process combine $scCO_2$, water and organic solvent.

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