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Preparation of Nanocrystalline Titania Thin Films by Using Pure and Modified Supercritical Carbon Dioxide

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Titania films are materials of great interest, as TiO_2 anatase crystal structure shows a high photocatalytic activity, chemical stability, strong oxidation activity, and non-toxicity. Anatase can be used in environmental applications, such as air- and water-purification [1] or for the decomposition of organic compounds.[2] The photocatalytic efficiency of thin films depends not only on their phase composition but also on hydrophilicity, specific surface area, crystallinity and crystallite-size. These properties can be significantly influenced by the preparation method used.

The commonly applied method for the preparation of pure and crystalline TiO_2 thin films is calcination.[3] Nevertheless, this thermal treatment presents some disadvantages, such as recrystallization, excessive sintration, crystallite growth, and a decrease in the specific surface area. Furthermore, the properties or photocatalytic performance cannot be easily controlled.

Therefore, calcination has been combined with supercritical fluid extraction (SFE) or pressurized liquid extraction (PLE). It was found that the pre-treatment using supercritical carbon dioxide ($scCO_2$) proposed for lowering the process temperature of sol-gel derived metal oxide film helps to increase the thermal stability and photocatalytic activity of films.[4]

The motivation of this work is to utilize the SFE for the direct preparation of highly pure TiO_2 thin films without any subsequent thermal processing. Extraction with pure and modified $scCO_2$ was tested and compared with PLE. Different types of liquid solvents (water, ethanol, acetone etc.) were used as $scCO_2$ modifiers at concentrations from 0 to 30 mass %. The effect of extraction temperature (40–150 °C), pressure (10–65 MPa) and the volume (50–200 g) and flow rate (0.3–1.8 g/min) of solvents passed through the extractor on microstructure and purity of TiO_2 thin films were examined.

The prepared thin films were characterized with respect to the (micro)structural properties by Raman spectroscopy. The most promising

thin films were analyzed by means of X-ray diffraction to determine the crystallite size, the phase composition, and the film thicknesses. The contact angles of films were measured to obtain the information about surface wettability.

When pure $scCO_2$ or pressurized hot water was used as the solvent no crystallization occurred. The addition of a small amount of water to $scCO_2$ at optimum extraction conditions (T=150 °C, p=30 MPa) led to the direct crystallization of films. The modification of $scCO_2$ by organic solvents resulted in the removal of organic precursors and thus in the increase of the TiO_2 thin film purity. When SFE was terminated by pure $scCO_2$ drying, the crystal size of 12 nm was achieved.

References

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