

Limited grain-growth during annealing of nanocrystalline anatase used in photovoltaic solar cells.

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Raising cost, limited reserves, and environment impact of fossil fuels push research toward the exploitation of new energy sources. In the last decades, renewable energy becomes one of the most important and studied fields, and photoelectric devices development, such as Dye Sensitized Solar Cells (DSSC), a promising and feasible reality. Nano-anatase thin films are employed as electrodes in DSSC, where they must ensure a suitable porosity and specific surface area to allow impregnation with organic dyes. Such films, applied in form of paste with specific rheological properties, are engineered through an accurate control on nanocrystal growth during sintering on conductive glass. In fact, the anatase crystal size affects both efficiency of DSSC devices and their transparency when employed as full-length windows. Therefore, the understanding of the grain growth evolution as function of the temperature and time variables is one of the main goals during the electrode development. Along with this technological application, the assessment of kinetic and energetic properties of nanocrystal growth is currently investigated to better understand the well known dependence of phase stability fields upon size besides the classic intensive thermodynamic variables, pressure and temperature. The present study deals with the characterization of two nano-anatase powders (labelled as LP1 and Q-05) obtained at reflux temperature of organic solvents. Anatase nanocrystals, having similar starting grain size (i.e. on average 7.0 and 5.3 nm for LP1 and Q-05, respectively), were synthesized by using the same TiO₂ precursor with different solvents and catalysers. Both samples were characterized by in-situ and ex-situ high-temperature X-ray powder diffraction experiments. Three isotherms for each sample were collected. Thermal treatments revealed substantial difference in the grain-growth evolution of the two powders. LP1 displays isothermal grain-growth curves as function of both time and temperature, showing trends that are reproducible by the Höfler and Averbach equation [1]. As a matter of fact, after 20 hours of treatment the crystal size is 2 to 2.5 times coarser than the starting one for the 400 and 500 °C isotherm, respectively. Differently, the Q-05 sample reveals a grain-growth behaviour that is a transition from a locked situation (i.e. up to 500 °C no growth occurs) to isotherms characterized by a very small size growth (i.e. at maximum 1.3 times the starting value, for the isotherm collected at 600 °C). As a matter of fact, the 500 °C isotherm cannot be correctly fitted through the Höfler and Averbach equation (as for the LP1 and the Q-05-550 and -600 °C isotherms) but it follows in a better way the trend described by the Michels equation [2] where a locking in the crystal size is assumed. A correct fitting of each isotherm allowed to calculate the grain-growth activation energy. For both LP1 and Q-05 samples, a value of about 30 kJ/mol was obtained. This latter value agrees with previous literature data [4,5]. These results indicate that Q-05 keeps the grain size during the sintering, that is a goal in the development of high performance titania film for DSSC applications. The locked crystal growth of Q-05 can be related to the pinning effect caused by organic residual species [5] or chlorine ions on the nanocrystal surface [6]. This highlights the remarkable effects of organic interactions to stabilize the nanosize.

References

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