New insights into the ultrafast charge carrier dynamics of nanostructured TiO_2 photoanodes under operando conditions

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Nanostructured TiO_2 films are widely used in various applications, such as photoelectrocatalysis, where charge-carrier lifetimes strongly influence their performance. However, although the impact of morphology on material properties is known, its exact influence on the ultrafast dynamics of photogenerated species in operando conditions is not yet fully understood. Therefore, in this work, the ultrafast dynamics of different photogenerated species in mesoporous and dense (non-mesoporous) TiO_2 films with different stacked layers were studied through transient absorption spectroscopy with sub-picosecond time resolution under oxygen evolution reaction conditions (OER) and different bias from open circuit potential (OCP) to 1.81 V_{RHE}. Steady state photo electrocatalysis tests reveal that dense films have a higher photocurrent than mesoporous films, independently of the number of stacked layers. The photocurrent for dense films at 1.23 V_{RHE} increases with the number of stacked layers. However, the photocurrent of mesoporous films beyond a 1-layer decreases notably. In operando measurements reveal that the ultrafast dynamics of photogenerated species in dense and mesoporous films are not significantly affected by the applied bias during the first two picoseconds after light excitation. Nonetheless, at longer delay times (>1 ns), the decay time of electrons probed at 890 nm and 660-690 nm in thin dense films notably decreases as the applied bias increases, contrary to what is observed for thick dense and mesoporous films. These results show that structural organization and applied bias govern ultrafast carrier processes, guiding the design of improved TiO_2 photoanodes.