Supporting Information.

Experimental Details

Film deposition: A stock solution of the titanium peroxo complex was prepared by adding 9 ml of freshly distilled TiCl₄ (82.07 mmol) dropwise to an ice-cooled solution of 14.45 ml 35 vol. % H₂O₂ (164.1 mmol) in 100 ml of water. Afterwards further water was added to fill up to a total volume of 500 ml.

A solution of vanadic acid was always freshly prepared by dissolving 0.731 g NH₄VO₃ (5 mmol) in 50 mL distilled water at 353 K. Subsequent acidification was performed through Amberlite IR-120 proton exchange resin. Further water was added to a total volume of 250 mL to receive a 0.025 M solution.

Reaction solutions for the deposition were prepared by mixing the appropriate amounts of the titanium peroxo complex and vanadic acid as well as 1 M hydrochloric acid (Riedel-de-Haën, Fixanal) and distilled water.

For the film deposition the substrates were immersed in 10 ml aliquots of the deposition solution, covered and placed in an oil bath at 353 K.

Although the adherence of the films was not quantified, it should be noted, that a simple tape-peel test with commercial adhesive tape or ultrasonication in water could not remove the films.

Zeta potential measurements: A Zetasizer Malvern 3000 HSₐ was used to measure the electrophoretic mobility. Suspensions of titania and vanadia, respectively were obtained by reaction of the above mentioned reaction solutions. Powders were collected by centrifugation, washed and redispersed in an aqueous solution of 150 mM HCl without prior drying. The pH was changed during data collection by addition of a 250 mM KOH solution. To improve the reliability, a series of three separate measurements (298 K) was collected for each system.
Film characterization:

XPS: X-ray Photoelectron spectra were recorded using a Thermo VG Thetaprobe system employing monochromatic incident Al Kα radiation (hv=1486.68 eV; spot size 400 μm). The energy scale of the concentric hemispherical analyzer was calibrated with high-purity reference samples of Au, Ag and Cu, by setting the corresponding binding energy (BE) positions of the Au 4f7/2, Ag 3d5/2 and Cu 2p3/2 main peaks at their recommended values of 83.98 eV, 368.26 eV and 932.67 eV, respectively. Detailed spectra of the Ti 2p, V 2p, O 1s, and C 1s photoelectron lines were measured with a pass-energy of 100 eV and a step size of 0.1 eV. Charge compensation of the insulating samples during the XPS analysis was achieved by irradiation of the sample surface with a diffuse beam of low energy electrons (kinetic energy of 5 eV; emission current ~35 μA) using a Floodgun. For data evaluation, the BE scale of each measured XPS spectrum was corrected for charging effects by setting the corresponding C 1s main peak for adventitious carbon to the recommended value of 284.6 eV.

SEM: Secondary Electron Images were recorded with a JEOL JSM 6500F JAMP-7830F scanning Auger electron microscope equipped with a field emission gun, while employing a primary electron beam of 10 keV and 11 nA.

Auger: Auger Electron Spectroscopy (AES) was applied. The oxide-film composition as a function of depth below the oxide surface was determined by Auger Electron Spectroscopy (AES) depth profiling. To this end, the V LMM, Ti LMM, Si KLL, O KLL and C KLL peaks were recorded with a JAMP-7830F scanning Auger electron microscope using a primary electron beam of 10 keV and 11 nA, an analysis area of 10×10 μm², and employing a sputter interval of initially 20s, and subsequently 60s (1 keV Ar+ beam with a beam current of 170 nA; 300×300 μm² raster). For quantification, the linear least squares fitting procedure in the Phi Multipack software package (version 5.0) was used, while employing
the peak-to-peak heights of the differentiated spectra in combination with the appropriate sensitivity factors for O, V, Ti and Si, as given by the manufacturer.