Electronic Supplementary Information

Ageing mechanisms of highly active and stable nickel-coated silicon photoanodes for water splitting

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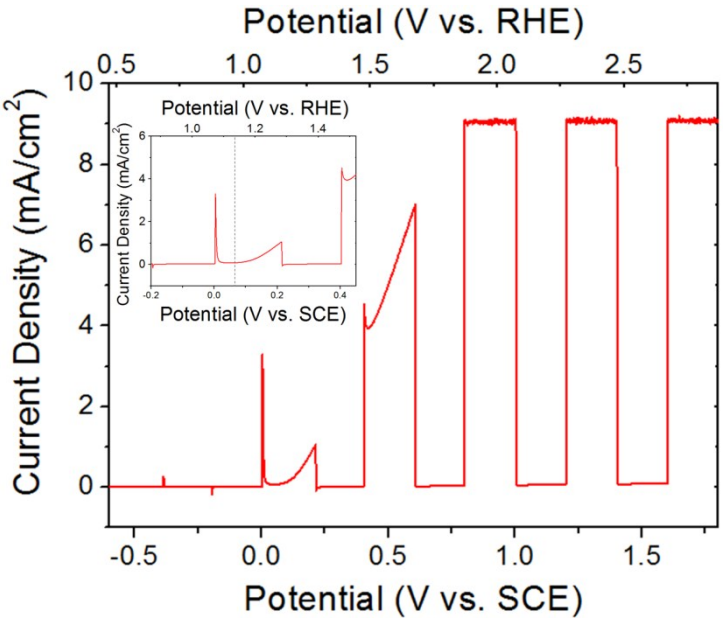

Fig. S1 Cyclic voltammogram and linear sweep voltammetry (LSV) recorded for a 2 nm Ni coated silicon photoanode under an illumination of 50 mW/cm^2. In the LSV, the light is being chopped.

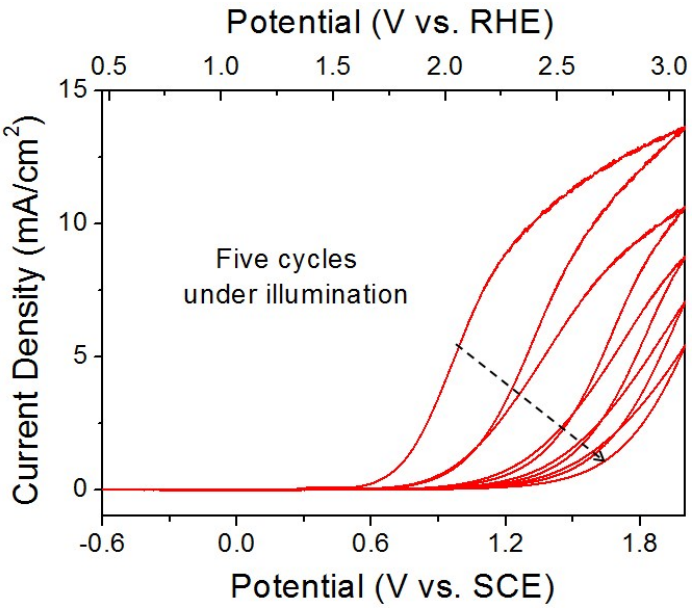

Fig. S2 Consecutive five cycles cyclic voltammograms recorded for a 2 nm Ni coated silicon photoanode (without native SiO_2) under an illumination of 50 mW/cm^2. The native SiO_2 was etched by HF solution before nickel deposition. The fast decay indicates that SiO_2 is beneficial to the stability of the photoanode.

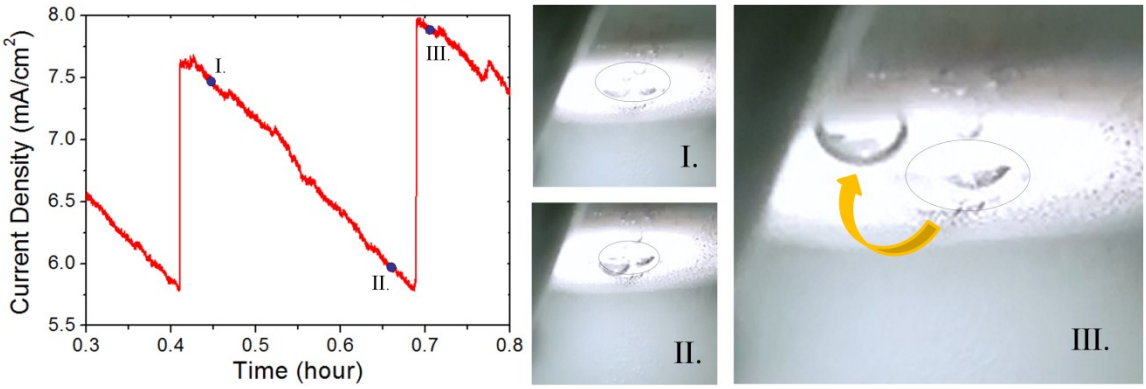

Fig. S3 Amperometric I-t curve measured at 1.8 V vs. SCE for the 2 nm Ni photoanodeunder an illumination of 50 mW/cm^2. The I-t curve clearly displays the typical saw tooth shape related to the formation process of a bubble. On the right, the digital camera pictures of the detachment of a bubble in the points I, II and III highlighted in the I-t curve.

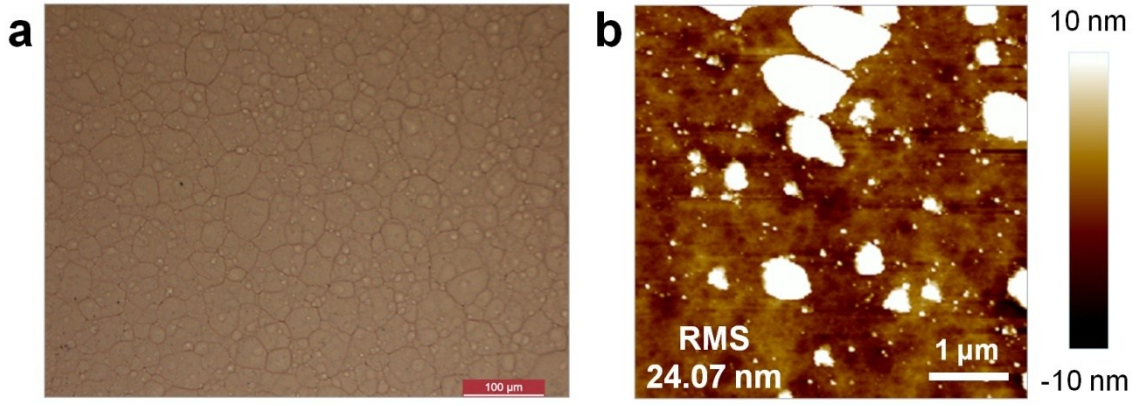

Fig. S4 (a) Optical microscope and (b) AFM images of a piece of silicon corroded in potassium hydroxide during 5 days, showing a high surface roughness.

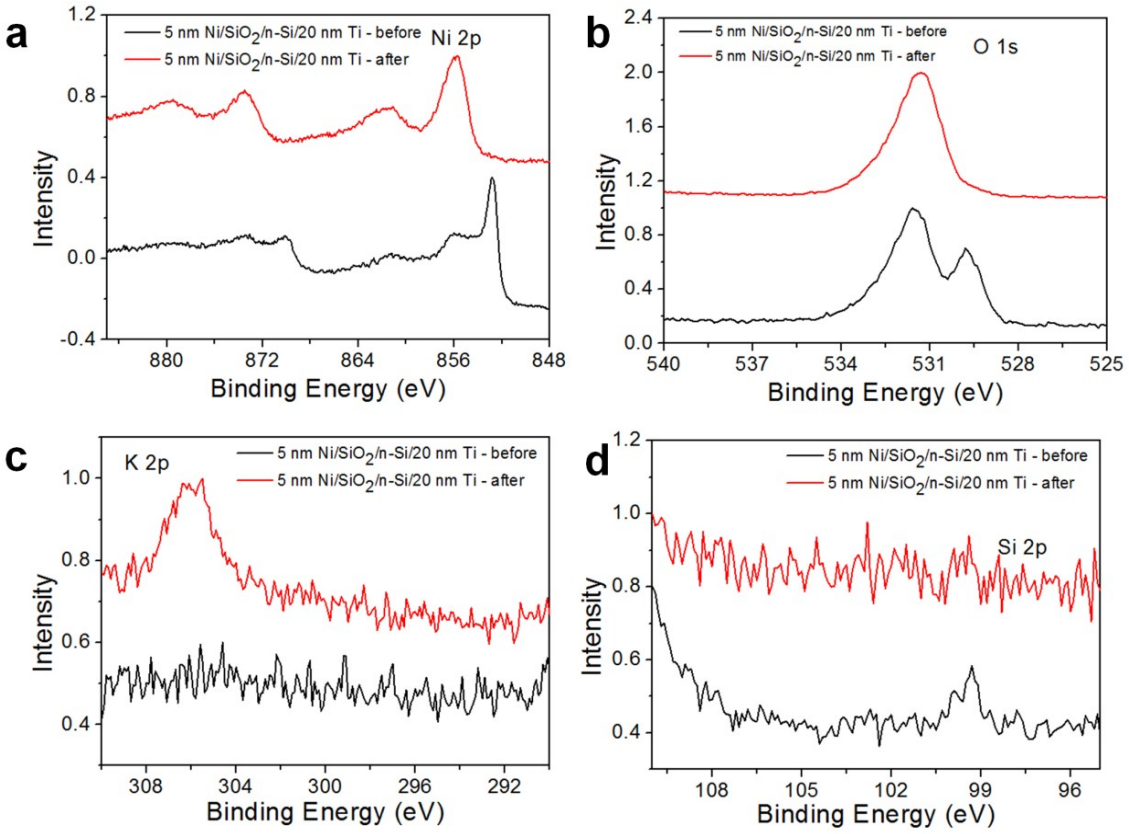

Fig. S5 XPS spectra for the 5 nm Ni photoanode after 24 h PEC tests (red line). The spectra of the fresh sample are also showed as reference (black).

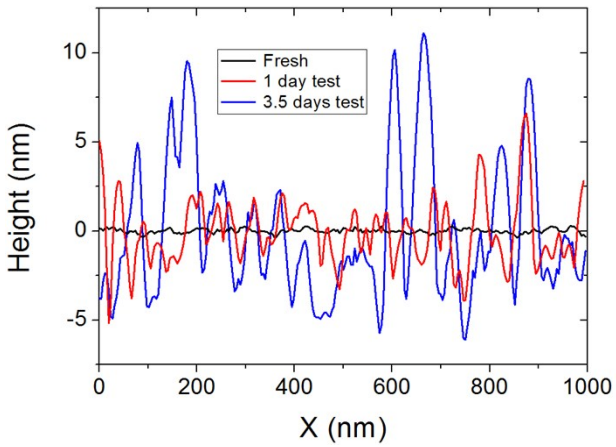

Fig. S6 Cross section of the topographic map collected for 5 nm Ni coated nSi photoanodes before and after test. The surface of the sample stressed during 1 day reveals typical thickness fluctuations between ± 2 nm, with some local hillocks that may correspond to degradation at pinholes. Therefore, this analysis indicates that the change on the thickness displayed in Figure 3b of the manuscript may be susceptible to some nanometric deviations.

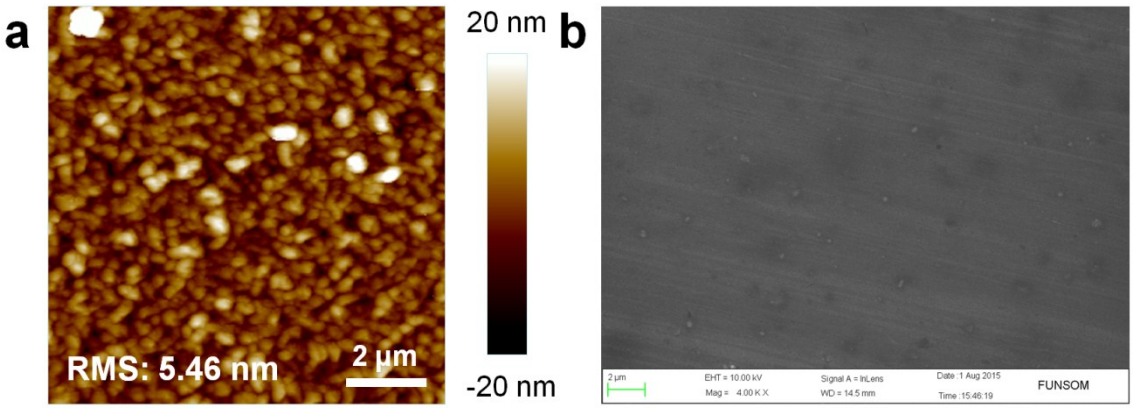

Fig. S7 (a) AFM and (b) SEM images for the 10 nm sample after 11 days OER test under 50 mW/cm^2 illumination. The AFM image corroborates the increase of the surface roughness.

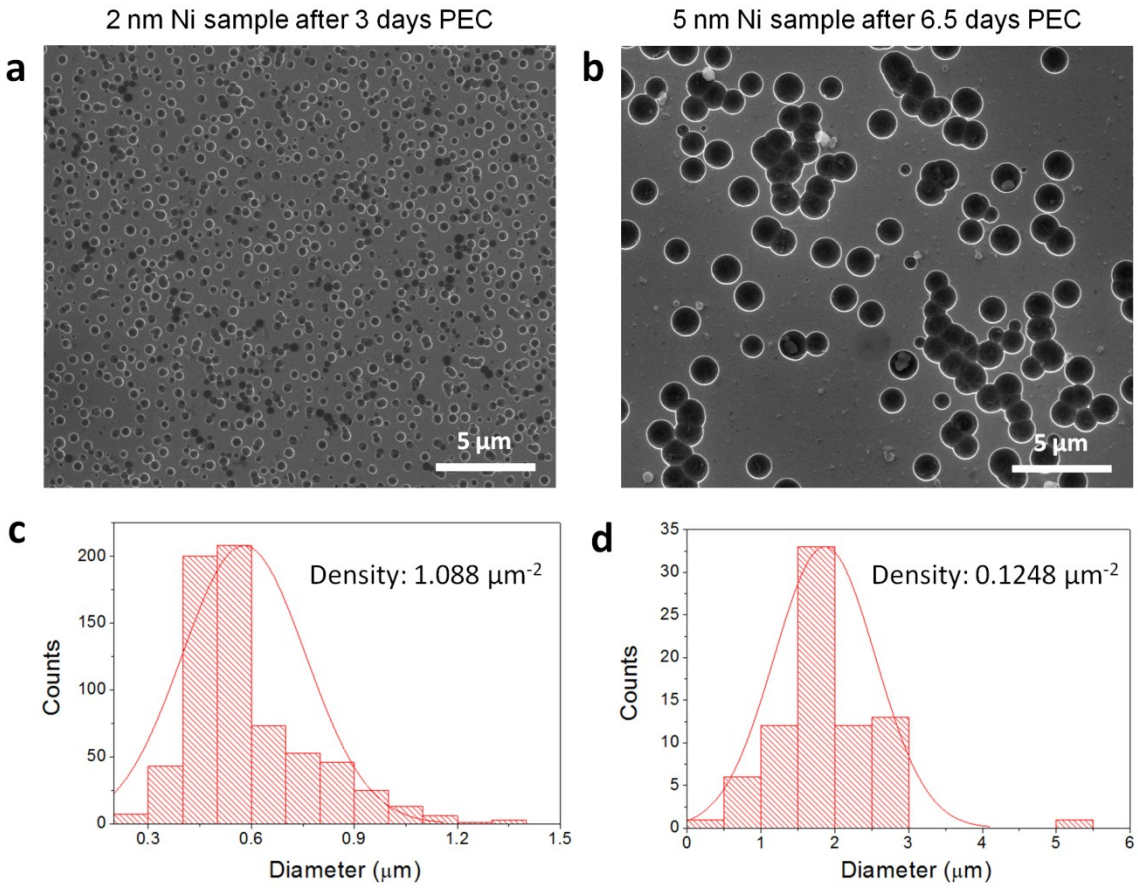

Fig. S8 SEM images of the twophotoanodes fabricated in this work after different testing times under 50mW/cm^2 light illumination. The corrosion-related holes start to appear at different times and they have different sizes. Also the amount of holes per µm^2 is different.

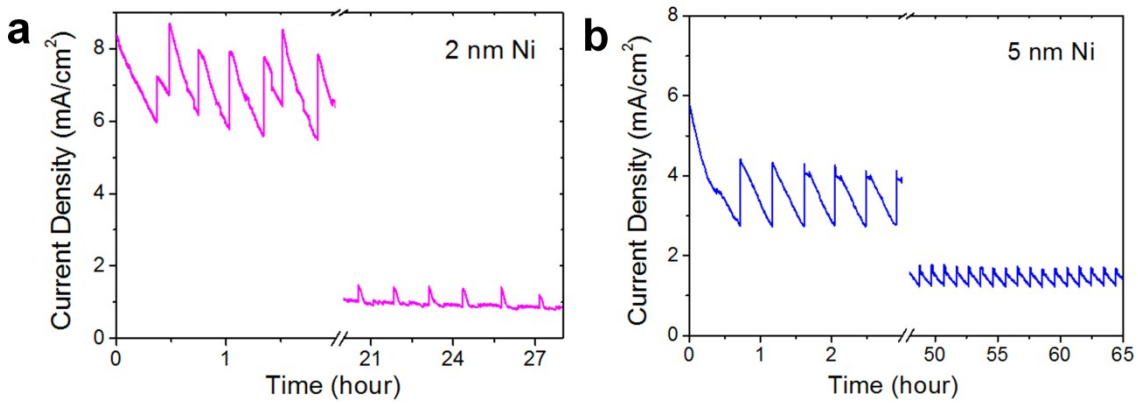

Fig. S9 I-t curves measured for the 2 nm and 5 nm nickel-coated silicon photoanodes under collected under 50 mW/cm^{2}light intensity in KOH by applying 1.8 V vs. SCE. The plots display the different shapes (conduction mechanisms) of the I-t curve for initial and final times.

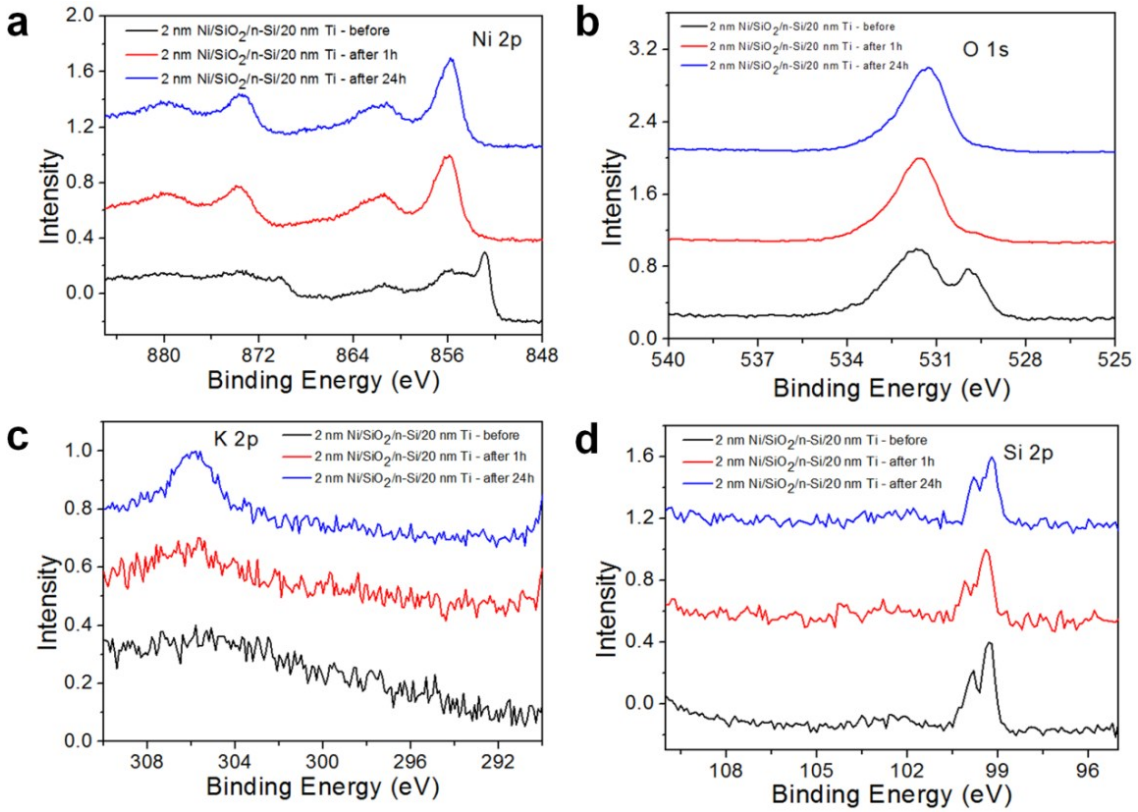

Fig. S10 XPS spectra for the 2 nm Ni photoanodes after 1 h (red) and 24 h (blue) PEC tests. The spectra of the fresh sample are also showed as reference (black).