## Substitution of native silicon oxide by titanium in Ni-coated silicon photoanodes for water splitting solar cells

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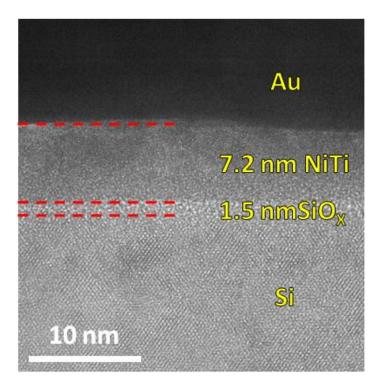


Fig. S1. Another typical cross-sectional TEM images of the activated 2 nm Ni/2 nm Ti/nSi photoanodes (without the native  $SiO_X$ ), which has been protected by depositing 50 nm Au right after the PEC tests. The Ni and Ti interface disappeared at these positions, and the thickness of the mixed layer is around 7.2 nm. There is also one layer formed below the mixed layer, that we attribute to  $SiO_X$ .

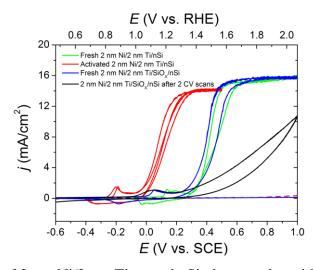


Fig. S2. CV scans of 2 nm Ni/2 nm Ti coated nSi photoanodes without (green and red lines) and with (blue lines) the native  $SiO_X$  layer. The 2 nm Ni/2 nm Ti coated nSi photoanodes without  $SiO_X$  shows an activation process (red lines), however the one without  $SiO_X$  doesn't show any activation, it decays after each CV scan (black lines). All the CVs are in 1M KOH electrolyte under 1 sun illumination. The CVs were obtained at a scan rate of 100 mV/s with iR compensation.

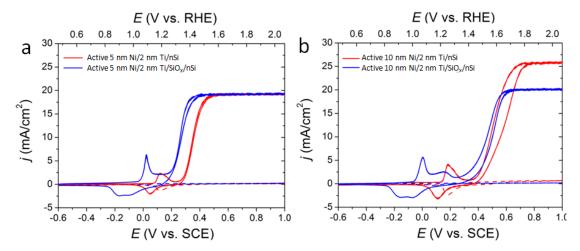


Fig. S3. Activity comparison of activated 5 nm (a) and 10 nm (b) Ni/2 nm Ti based nSi photoanodes without (red lines) and with (blue lines) the native  $SiO_X$  layer in 1 M KOH electrolyte. After activation, the 5 and 10 nm Ni/2 nm Ti coated sample with native  $SiO_X$  shows a slightly better activity than the counterpart without the native  $SiO_X$ . The CV scans were obtained at a scan rate of 100 mV/s with iR compensation.

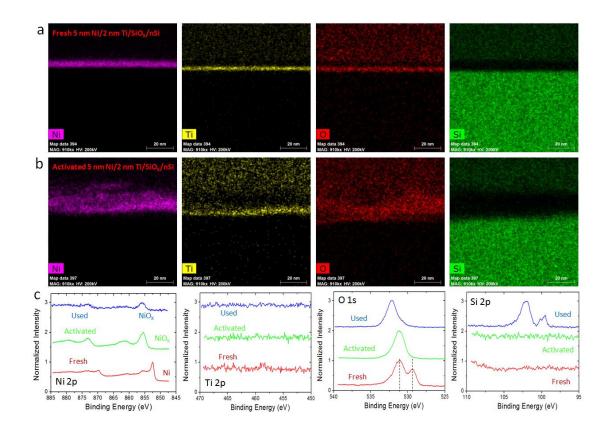


Fig. S4. Chemical composition analysis of the 5 nm Ni/2 nm Ti/SiO<sub>X</sub>/nSi photoanodes before and after the PEC activation process. Cross-sectional EDS maps of (a) fresh and (b) activated 5 nm Ni/2 nm Ti/SiO<sub>X</sub>/nSi photoanodes. The Ni, Ti, O and Si element composition maps are exhibited in both (a) and (b) to observe the difference between these two samples. (c) XPS spectra of fresh (red), activated (green) and used (blue) 5 nm Ni/2 nm Ti/SiO<sub>X</sub>/nSi photoanodes. The binding energy regions of Ni 2p, Ti 2p, O 1s and Si 2p are all shown to track the change of each sample after the each period of the PEC tests.