Electronic Supplementary Material (ESI) for Physical Chemistry Chemical Physics

Supporting Information:

Si Photoanode Protected by Metal Modified ITO with Ultrathin NiO_x for Solar Water Oxidation

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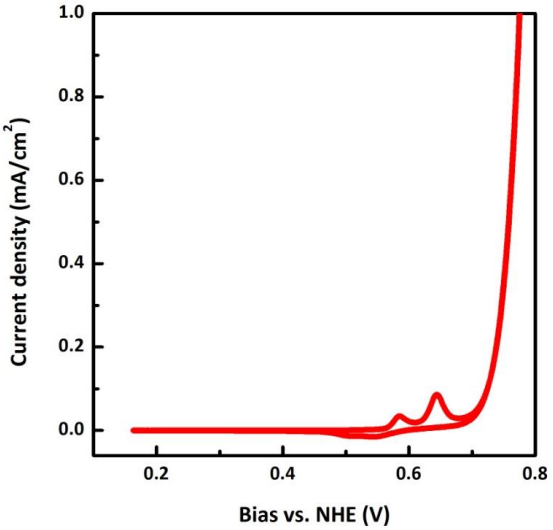


Figure s1 Development of two oxidation peaks on the NiO_x-TX catalyst after 500 cycles of CV scans (scan rate 10 mV/sec)

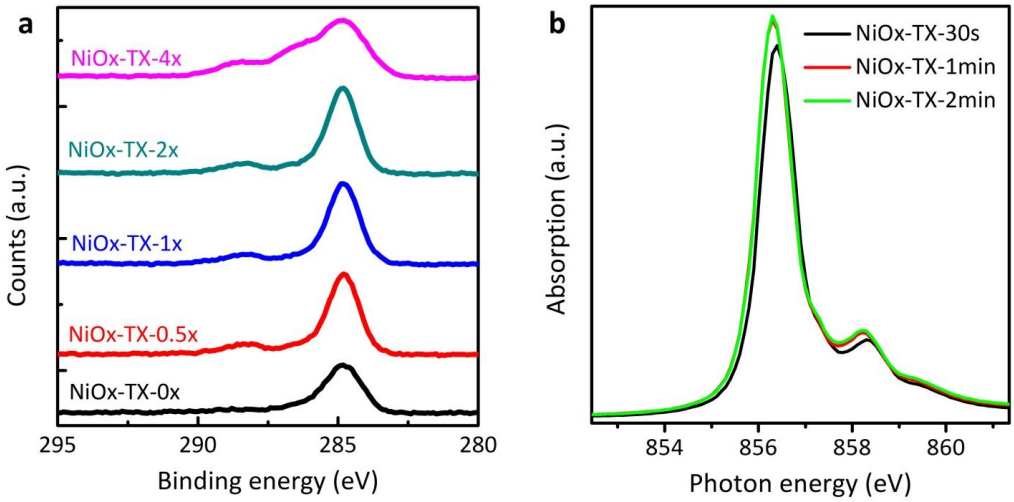


Figure s2 (a) XPS spectra of C 1s peaks show that the carboxylate component at the binding energy of 284.8 eV also present in samples prepared with a higher concentration of complexing agent, (b) the XANES Ni k-edge spectra on samples annealed for various times.

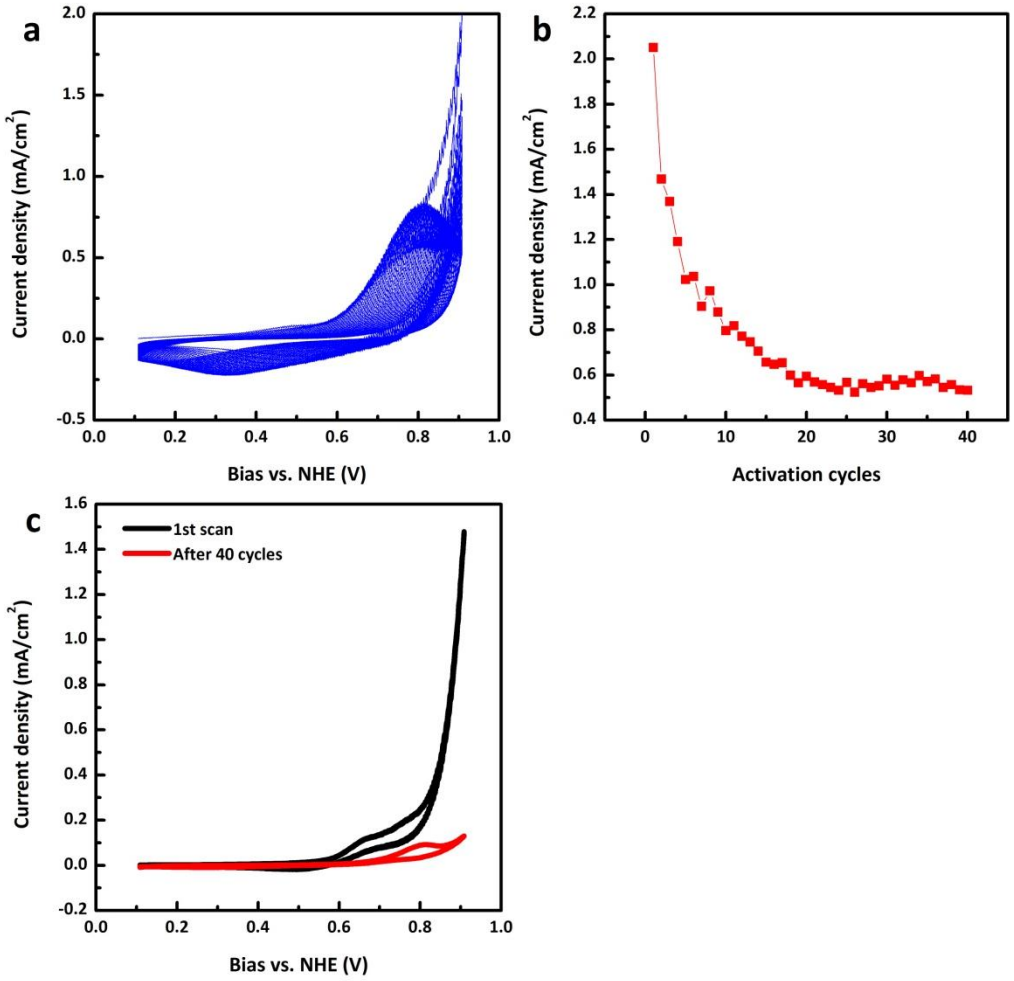


Figure s3 Stability study of the NiO_x-TX directly coated p^+-Si substrate in the dark. (a) 40 cycles of CV scans (scan rate 100 mV/sec), (b) current density at the overpotential of 493 mV, and (c) CV scans before and after the activation process (scan rate 10 mV/sec).

To prove this, degenerately doped p+ (100) Si directly coated with NiOx-TX catalysts was tested without removal of the native Si oxides. During the typical activation process, the redox peaks became more pronounced (Figure s4a) and only negligible photoactivity was noticed on this device. However, different from that of NiOx-TX coated FTO glass, its OER current dropped continuously (Figure s4b). Presumably, attacks on the native oxide and then underneath Si may cause the loss of catalysts. This was actually noticed during the in-situ XANES measurements, during which the Ni signal became undetectable after continuous running for less than 5 minutes (in-situ XANES measurement data not shown here). This resulted in a significant lower current density after the activation process (Figure s4c).

To utilize the outstanding OER catalytic activity of the ultrathin alkaline catalyst, a stabilized n-Si photoanode that is chemically inert to the alkaline environment is required.

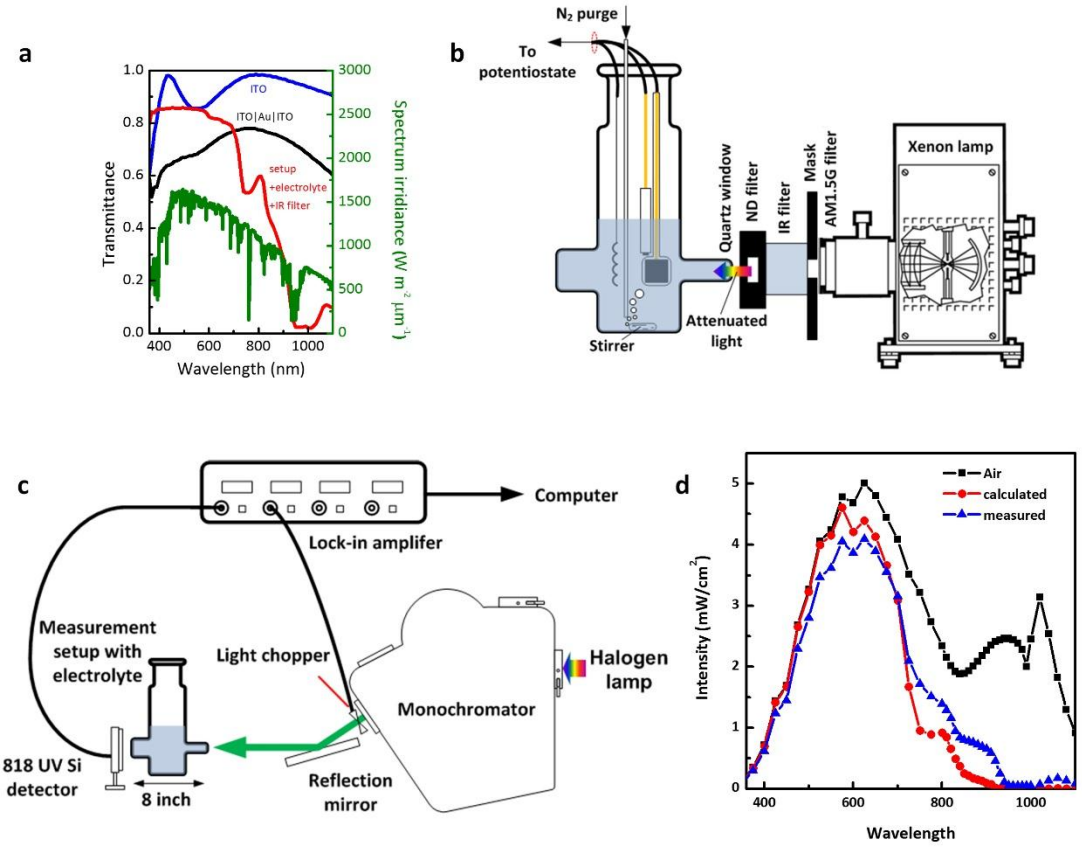


Figure s4 (a) Transmittance of the s-TCO, a bare ITO, the measurement setup, and the AM 1.5G solar irradiance spectrum (green curve, data from NREL). Schematics showing the setup for the PEC measurement (b) and for the characterization of the light loss by electrolyte (c). (d) Change of the light spectrum from the solar simulator after attenuated by the liquid water.

Besides optical modulation by water, glassware, scattering for particles, effects from the OD filter and the mask are not ignorable, which in total contributing a loss of light intensity at the sample position. Transmittance of the three components was measured. The calculated light intensity based on the water absorption coefficient reported by Hale and Querry[1] and the measured light intensity showed a great consistency. In addition, the light intensity modulation also includes the reflection at interfaces, scattering at particles, diffusion in random directions and absorption of other components. Calculations based on a

calibration Si photodiode showed about 48.8% light loss under masked illumination, resulting in a light intensity of 51.2 mW/cm2 at the sample position in the PEC measurement setup.

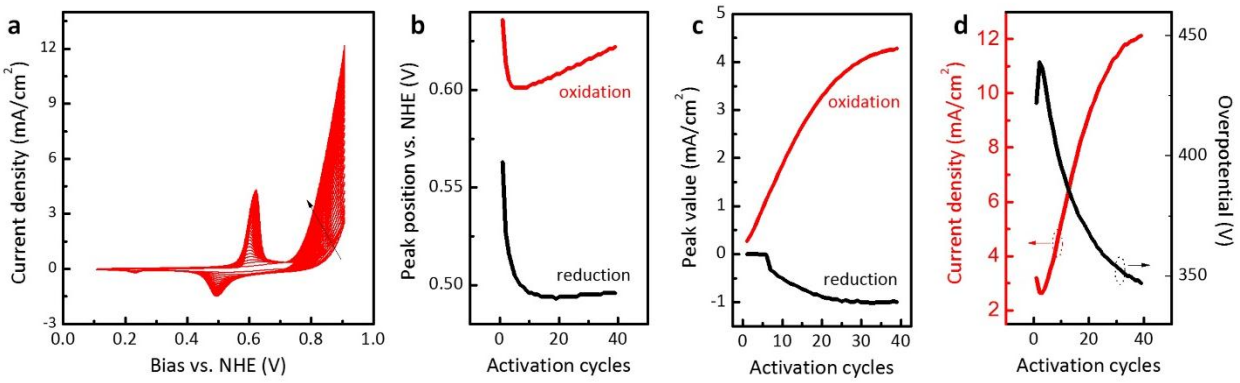
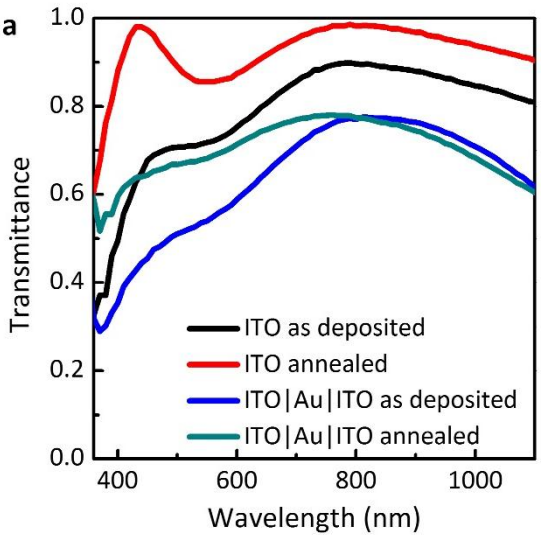


Figure s5 CV scan of a typical NiO_x-TX OER catalyst activation process (100 mV/sec) for 40 cycles through the activation contact (shown in a), where one can see a shift of the oxidation/reduction peak position (b), the magnitude of peaks (c), as well as the water oxidation current density at the overpotential of 493 mV (red curve), and overpotential to drive 1 mA/cm^2 current density (black curve) (d) *vs.* the activation cycles.

a



b

TCO structure	As prepared	Annealed
ITO	1.6 mΩ-cm	2.4 mΩ-cm
ITO|Au|ITO	0.52 mΩ-cm	0.43 mΩ-cm

Figure s6 Transmittance and resistivity of ITO and ITO|Au|ITO before and after annealing

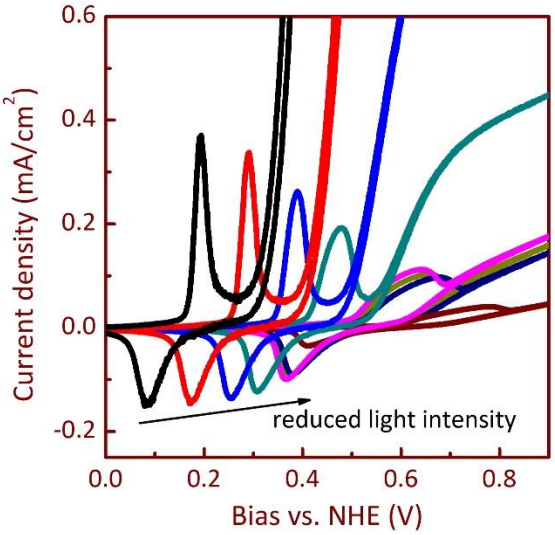


Figure s7 Magnification on the Ni redox region of Fig.5c showing changes on the redox peaks and onset current *vs.* the light intensity.

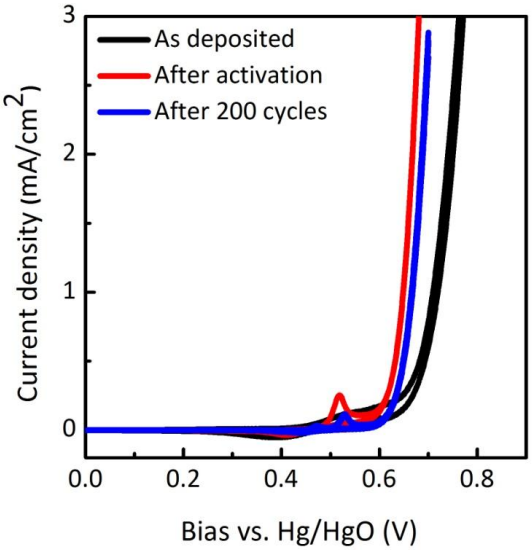


Figure s8 Stability test of NiO_x-TX catalyst through a consecutive CV scans showed a degradation after 200 cycles.

Reference:

1. G. M. Hale and M. R. Querry, *Appl. Opt.*, 1973, **12**, 555-563.