

Supporting document for “NiO functionalized silicon for efficient photo-oxidation of water”

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1. **Si substrate preparation:** Si substrates used in this report are single side polished phosphors doped n-type [100] 4 inch Si wafer with a thickness of 450 μm and a resistivity of 0.3-0.5 ohm-cm. Si wafers were diced into 1.27 \times 1.27 cm^2 for fabrication of photoelectrodes. Surface native oxide on Si was not etched before deposition, unless specifically mentioned, to smoothen the transition from Si to the coating material¹.

2. **NiO_x sol-gel preparation and film spin-coating:** The precursor solution of sol-gel nickel oxide was prepared by dissolving Ni acetate tetrahydrate (Sigma-Aldrich[®]) 0.4 M in a mixture of dimethylethanolamine (dmaeH, Sigma-Aldrich[®]) and mono-ethanol amine (MEA, Sigma-Aldrich[®]) in the ratio of 9:1. The dmaeH was chosen as a precursor and MEA was added as a stabilizer. The solution was refluxed at 70 °C for 2 hr. As prepared solution was dark green. The precursor solution was filtered to remove large undissolved species and then aged for 24 hr before being used. Prepared sol-gels were drop casted on cleaned sample surface and spun at 4000 rpm for 30 s. samples were first dried on hotplate in air at 300 °C for 10 min and were placed in annealing furnace with N₂ flow at 200 sccm and annealed at 400 °C for 1 hr. For certain samples, Ir metal deposition was also performed using sputtering (see section 3). Figure S1 shows a SEM

image with small magnification showing a large-scale uniform, smooth and crack-free surface of annealed NiO_x film on Si.

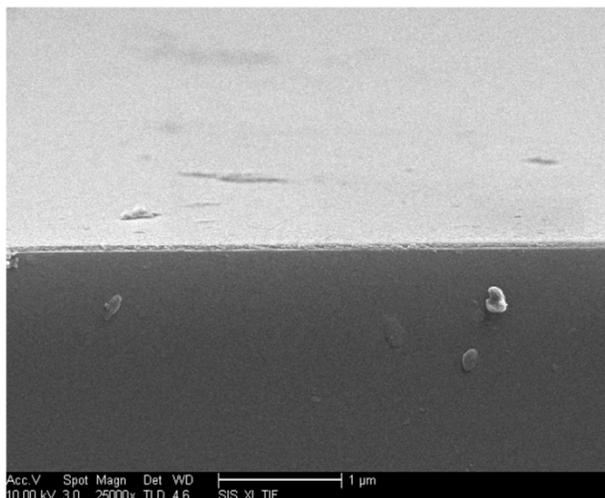


Figure S1. SEM image on the right shows the large scale view of the NiO_x film surface.

3. **Film deposition:** ITO film was sputtered using Denton® RF magnetron sputtering. Target (tin doped indium oxide 99.95%) was bombarded pre-cleaned using RF power (300 W) at high pressure (10 mTorr) prior to the deposition on Si samples to remove surface impurities. The films were deposited in an Ar environment. Sputtering was started till base pressure reached 4×10^{-4} mTorr. During actual deposition on Si samples, chamber working pressure was kept at 5.4 mTorr and deposition power was 300 W. Substrates were held at room temperature in all runs. Deposition rate at this condition was about 3 Å/s. Films were deposited simultaneously at different substrates for electrochemical, Hall, SEM/EDX, and optical transmittance measurement, including polished Si, glass, and Ti foil. All substrates were pre-cleaned using acidic solution and standard solvent, and rinsed in DI water, finally dried for deposition. Ti foils were etched in diluted HCl solution at room temperature for 5 min and then rinsed in DI water to remove surface oxides.

NiO_x film was also obtained using RF sputtering for comparison with a stoichiometric NiO target (99.95%) obtained from Able Target Ltd. (China). Ar gas was used to ignite the plasma under a base pressure of 4.5×10^{-6} Torr and during deposition pressure of the chamber was maintained at 5.5 mTorr. RF power was kept at 200 W and deposition rate under this condition was around 0.78 Å/s. To get a comparable thickness as the 1 layer spin-coated sol-gel film, 8 mins sputtering deposition was used to get 34.8-nm NiO_x film on Si substrates.

Ir metal was deposited using EMLtech® K575X DC sputtering equipped with turbo pump (BOC Edwards® model Ext70H24V). Chamber working pressure was kept at 7.5 mTorr during deposition. Deposition time was counted 3 sec after pressure was stabilized. Ultrapure Ar gas was used to purge the chamber. Samples were kept at a distance of 3 cm away from the target.

TiO₂ film was deposited using hot wall, flow through reaction chamber atomic layer deposition (Beneq® TFS200 ALD). Precursors were DI water and TiCl₄. N₂ was used as carrier gas. Pulse time for each precursor was 100 msec. Purge time between each precursor was 500 msec.

Reactor chamber pressure was kept at 1 Torr during the deposition. Deposition temperature was kept at 250 °C. Deposition rate at this condition was around 0.464 Å/cycle.

4. **XANES measurement:** The XANES were obtained on the spherical grating monochromator (SGM) beamline ($\Delta E/E: \sim 10^{-4}$) at the Canadian Light Source Inc. (CLS) in a surface sensitive, total electron yield (TEY) mode using specimen current. Data were normalized to the incident photon flux, which were collected with a refreshed gold mesh (evaporation of a fresh Au layer prior to the measurements).

5. **XPS measurement:** Ex situ XPS measurement of the O 1s and Ni 2p levels were performed on NiO_x thin film coated n-type Si photoelectrodes before and after high temperature annealing in N₂ environment. XPS measurement were conducted at Beijing electron spectrum center lab (Tsinghua University, Beijing China), equipped with Al K α source 25 W energy. The base pressure of analysis chamber was 4.5 $\times 10^{-10}$ mTorr. The binding energy scale was calibrated to carbon line of 284.8 eV. All XPS spectra were recorded with a resolution of 0.51 μ eV. Each data set was first corrected for the non-linear emission background. The data was then fitted with Gaussian function to find the peak positions.

6. **SEM and EDXS measurement:** The scanning electron microscopy (SEM) and energy-dispersed x-ray spectroscopy (EDXS) measurement were done using Phillips XL30 ESEM equipped with Oxford EDX unit. X-ray spectra were collected using Inca Software for elemental analysis.

7. **Hall measurement:** The Hall measurement was done on a home-built Hall setup using the van der Pauw method were performed at room temperature. In or In/Zn alloy were used for contact to the films depending on the type of conduction. Carrier concentration and mobility were calculated.

8. **Optical transmittance measurement:** Room temperature optical transmittance study was conducted using a monochromator (Horiba Jobin Yvon® iHR 550) equipped with a 150 W Xenon lamp as an illumination source with and a 1200 groove/mm grating with 300 nm blaze providing monochromatic light in 300-500 nm. For a longer wavelength range above 500 nm, a 100 W halogen lamp and a 600 groove/mm grating with 500 nm blaze were used for a higher efficiency of obtaining monochromated light. A lock-in amplifier (Stanford Research® SR530) was used to isolate the signal component arising specifically from the incident illumination. A pre-amp (Ithaco 1211 current preamplifier) with various gains depending on the current levels were also used. The transmitted light spectrum of the monochromatic illumination was calibrated using a Si p-i-n photodiode (Newport® 818-UV with OD3 attenuator). Illumination was incident at 90° to the sample surface with light spot size around 0.05 cm². As seen below in Figure S2, sol-gel film gives better transmittance in the range of 400-600 nm. At 600 nm, the

transmittance is above 90% indicating a highly transparent film. Optical band gaps were extracted from the transmittance data and sol-gel NiO_x after annealing gave about 3.2 eV energy band gap.

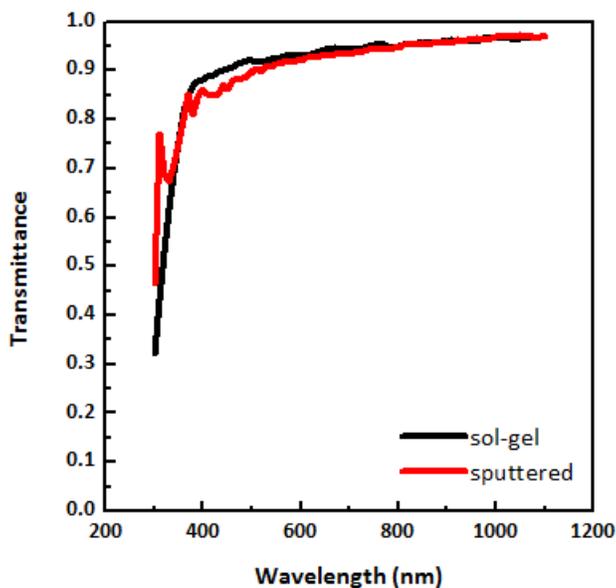


Figure S2. Transmittance of sol-gel (37.4 nm) and sputtered (34.8 nm) NiO_x films.

9. PEC measurement setup: Prior to measurement, indium paste was applied at the back of the sample providing an ohmic electrical contact and then fixed on a home-made measurement setup. An optical image of our homemade sample holder and a schematic of our measurement setup are shown in Figure S3. A copper wire was pushed against to the sample indium contact and sealed with front surface exposed to electrolyte. Exposed area was controlled by the PDMS window mold which was kept constant for every sample at 1 cm². For electrochemical measurement, the counter electrode (CE) was Pt coil wire and reference electrode (RE) was Ag/AgCl with 1 M KCl solution. Measurement was done in one-compartment cell setup. A xenon lamp from a solar simulator providing an output light intensity at 100 mW cm⁻² at a distance of 22.86 cm. Electrochemical behavior of samples was measured using a two-channel potentiostat (Digi-Ivy® DY2300) with a slow scan rate (10 mV/s). All data were recorded using software DY2300. In all experiments, electrolyte solution was 0.25 M Na₂SO₄ buffered with PBS (pH=7.2) at room temperature. pH of the solution at room temperature was measured using Oakton® pH5 pH meter.

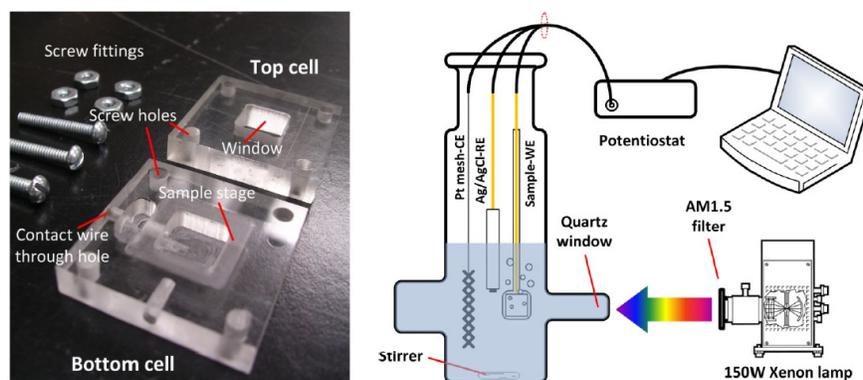


Figure S3. a) home-made sample holder, and b) schematic of measurement setup.

10. **TiO₂ performance degradation:** 5 consecutive scans were collected using linear sweep voltammetry with a scan rate of 50 mV/s and minimum stabilization time of 20 min between each scan after one cyclic voltammetry scan (Figure 2 curve 3). Current density at 2 V dropped from 0.3 (from 1st CV scan) to 0.07 mA/cm² (Figure S4).

Current monitoring over 1 hour period showed that TiO₂ sample was disabled after 5 min. However ITO coated Si can function for more than 1 hr without significant degradation of photocurrent. One can also find the unprotected n-Si with and without native oxides in Figure S4. One can see after removing oxides with HF, current level was initially higher than the one with native oxides. But both unprotected Si with and without native oxides were disabled in less than 1 min under a constant bias of 2 V.

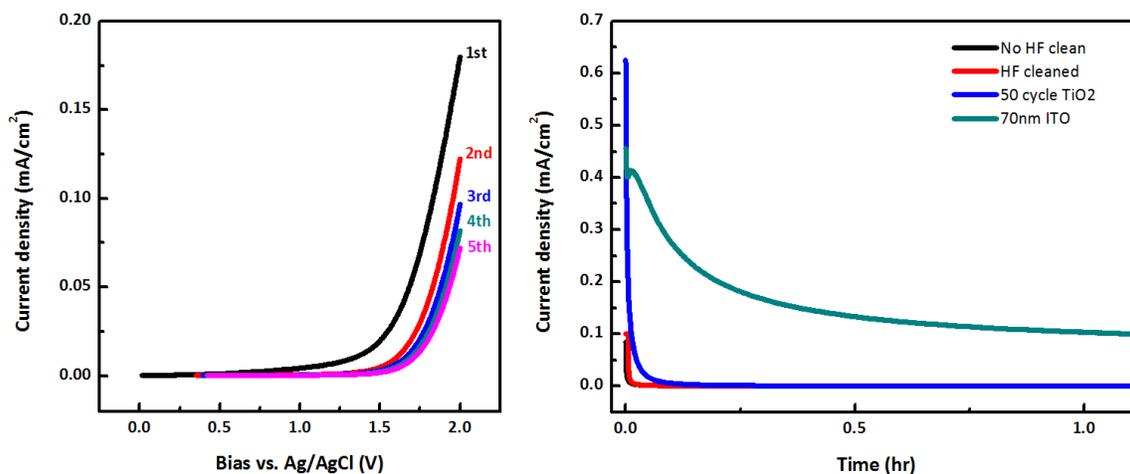


Figure S4. TiO₂ performance degradation demonstrated using 5 consecutive linear scans.

11. **Voltammetric behavior of n-Si with various structures:** Figure S5 shows the Voltammetric behavior of various n-Si photoelectrodes. n-Si|ITO (blue ▲) showed highest onset potential. n-Si|NiO_x, on the other hand, showed negative-shifted onset potential lower to the thermodynamic water oxidation level (red ●). Further coating with Ir, a well-know electrocatalyst, did not show significant improvement (black ■). Applying NiO_x catalyst on n-Si|ITO showed also negative-shifted onset potential indicating an electrocatalytic effect from

NiO_x (magenta ◀). Comparing to Ir coated *n*-Si|ITO (dark cyan ▼), *n*-Si|ITO|NiO_x showed higher onset potential.

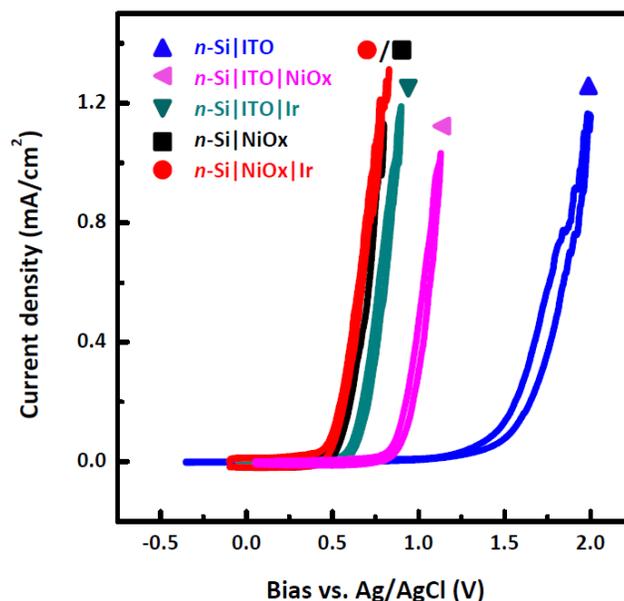


Figure S5. Voltammetric behavior of *n*-Si|ITO, *n*-Si|NiO_x, *n*-Si|ITO|Ir, *n*-Si|ITO|NiO_x, and *n*-Si|NiO_x|Ir under illumination at 100 mW/cm²

12. Solid-state device fabrication and measurement: ITO top contact on NiO_x was sputter-coated using the same condition as described above. IV measurements under dark and illumination were measured using Agilent® B1500 semiconductor device analyzer. Sample position was kept at a constant distance from the light source as the PEC measurement. Top ITO contact area is 0.47 cm². Device response in dark and under illumination is shown in Figure S6. Solar simulator (Newport®) equipped with a UV-enhanced Xenon lamp was used and AM1.5 solar spectrum with 1 sun intensity was obtained using an AM1.5 filter. It was found that the Voc = 300mV.

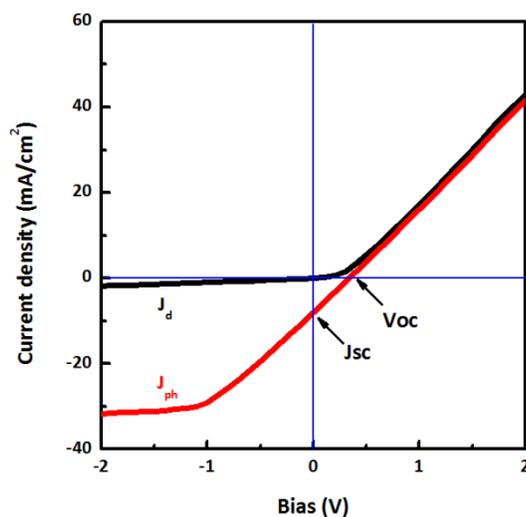


Figure S6. IV curve of the solid state device measurement showing ITO top contact for NiO_x and Si junction after annealing and its response to light.

13. Setup attenuation factor measurement: In order to estimate the power conversion efficiency of the device as pointed out by previous research², actual light strength arrived at the sample through the solution was first approximated using the calibrated Si photodetector. To do this, the single compartment cell filled with electrolyte was placed between the monochromatic light and Si photodiode. Spectral photocurrent of the Si photodetector measured before (I_{in}) light entering the quartz window and the one after (I_{out}) light exiting on the other side were collected (Figure S7). The attenuation coefficient of the cell filled with electrolyte can be then calculated using equation 1:

$$\alpha = -\frac{1}{z} \log_e \frac{I_{out}}{I_{in}} \quad (1)$$

where α is the attenuation coefficient of the cell with electrolyte and z is the distance between the positions where two spectrum were measured (35.56 cm). Attenuation coefficient of the water was demonstrated before by Hale and Querry in 1973³. The attenuation coefficient measured in this work and absorption of water reported in ref 3 are illustrated in Figure S6, in which we can see the two curves are showing matched peak positions. The difference between the curves is believed due to the setup. This confirmed that light spectrum was modulated by the absorption of electrolyte solution as well as the container, assuming no interference from particles and air bubbles and also change of light spot size was ignored (due to the higher refractive index of water than light incident media, which was air). Light spot size from monochromator was fixed to 0.25 cm² on samples as well as on Si photodiode. One can see from our measurement that water has major absorption at the IR range and ignorable effects in the wavelength below IR. Based on the calculated coefficient, light spectrum at the sample (distance to the quartz window was kept around 5.08 cm) was able to be evaluated using equation 2 below.

$$I_s = I_{in} \cdot e^{-\alpha \cdot z_s} \quad (2)$$

where I_s is the spectral photocurrent at the sample position and z_s is the distance between sample and quartz window. Using the light spectrum measured and calculated attenuation coefficient, spectral photocurrent at sample position in the electrolyte virtually measured using Si photodiode was able to be accurately estimated. This approach leads to a good approximation and improved evaluation accuracy of PEC device performances (e.g., conversion efficiency). It is worthwhile to point out that errors can be significant if setup attenuation was not carefully considered.

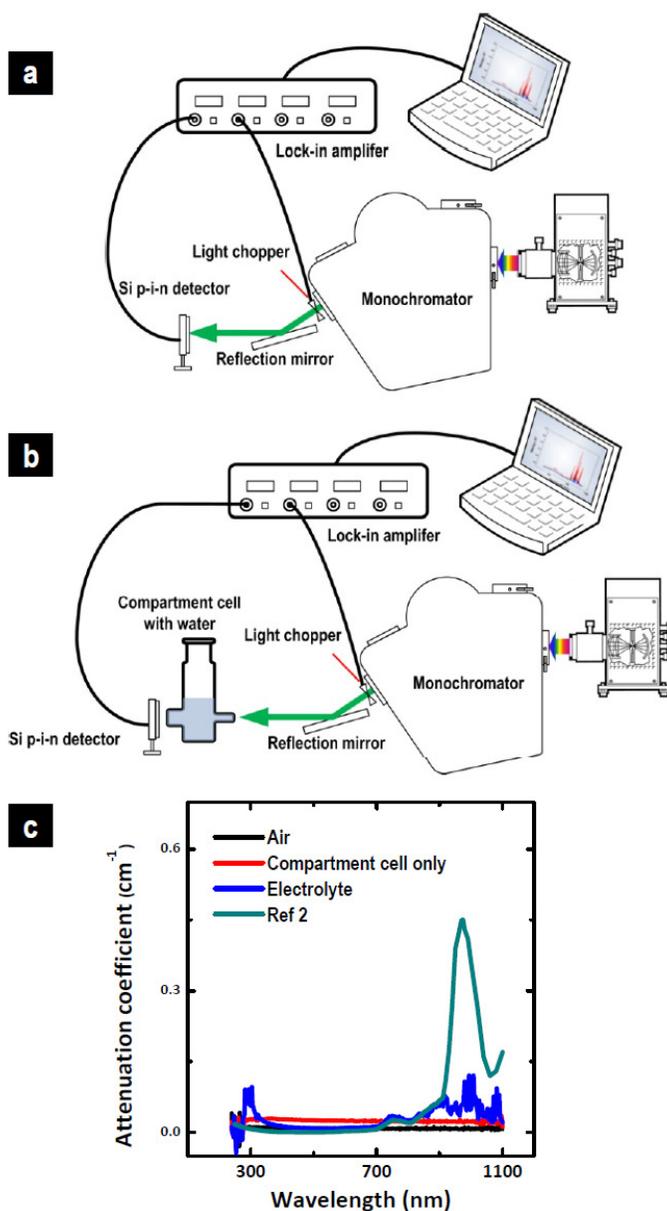


Figure S7. Setup attenuation coefficient measurement at room temperature and 70% humidity a) with and b) without compartment cell, c) setup attenuation spectra under different conditions.

14. Two-electrode measurement: Power conversion efficiency was calculated based on the two-electrode I-V measurement results in Figure S8. The bias scale vs. Ag/AgCl 1 M KCl is converted to reversible hydrogen electrode (RHE). Note that potential vs. reversible hydrogen electrode (RHE) (top x-axis in Figure 1), which is independent of pH can be converted from Ag/AgCl electrode using the equation of

$$E(\text{RHE})=E(\text{Ag/AgCl})+0.059 \times \text{pH}+E^0(\text{Ag/AgCl}) \quad (3)$$

where $E^0(\text{Ag/AgCl})$ is the potential difference to standard hydrogen potential, which is 0.236 V. One can see that metal coating effectively move the onset potential, where current density exceeds 0.1 mA/cm^2 , below zero RHE level.

Different from what we observed from three-electrode measurement, $n\text{-Si|ITO|NiO}_x$ showed nearly identical IV curves as the $n\text{-Si|ITO|Ir}$ electrode. Reasons are clear to us at this point.

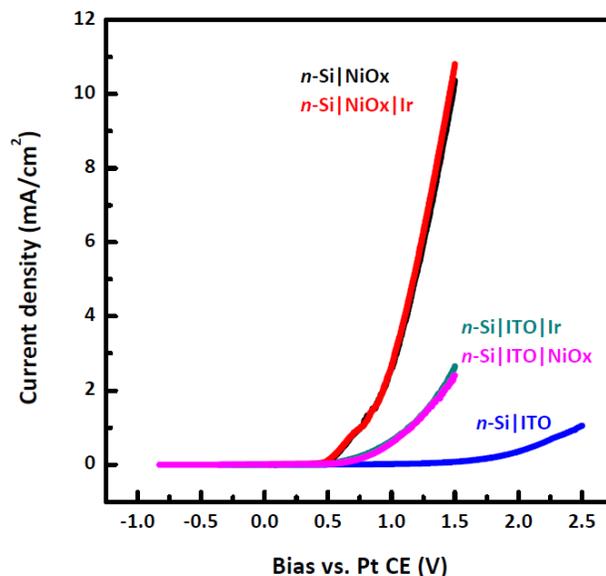


Figure S8. Voltammetric behavior of $n\text{-Si|ITO}$, $n\text{-Si|NiO}_x$, $n\text{-Si|ITO|Ir}$, $n\text{-Si|ITO|NiO}_x$, and $n\text{-Si|NiO}_x|\text{Ir}$ under illumination at 100 mW/cm^2 under two-electrode measurement setup.

15. Long term stability: Intermittent current monitoring over 3 days under a fixed bias on sol-gel NiO_x protected $n\text{-Si}$ is shown in Figure S9. Current degraded over the time of study was observed. Very fast decays in photocurrent at the beginning and eventually level up. The device remained to be functional after 4 hour operation, although only about 1/6 of photocurrent remained. The possible reasons behind this observation are under investigation.

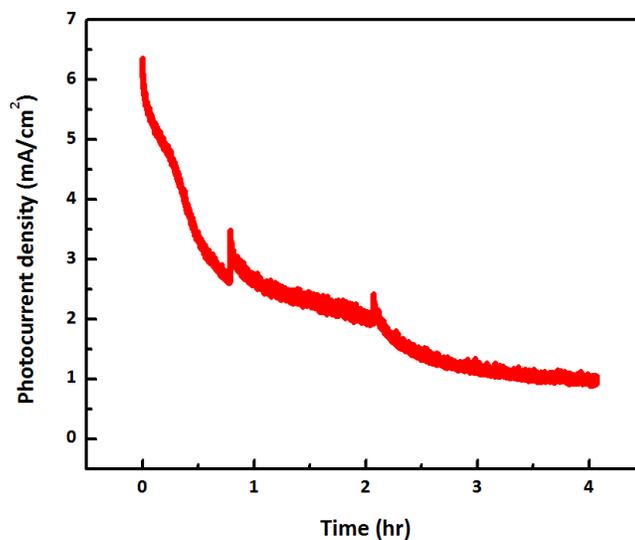


Figure S9. Stability measurement of sol-gel NiO_x enabled *n*-Si photoelectrode under a constant bias at 1.3 V for 4 hours operation over a 3-day period.

References:

1. G. Hodes, L. Thompson, J. DuBow and K. Rajeshwar, *J. Am. Chem. Soc.*, 1983, **105**, 324-330.
2. A. Wolcott, W. A. Smith, T. R. Kuykendall, Y. Zhao and J. Z. Zhang, *Adv. Funct. Mater.*, 2009, **19**, 1849-1856.
3. G. M. Hale and M. R. Querry, *Appl. Opt.*, 1973, **12**, 555-563.