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A nearly transparent Ni-based oxygen-evolving catalyst for photoelectrocatalysis

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Chemicals

High-purity transition metal salts ($NiCl_2·6H_2O$, $Ni(NO_3)_2·6H_2O$), and high-purity sodium hydroxide (NaOH) were purchased from Sigma-Aldrich. 2,2'-Bipyridine (bpy) and anhydrous ethanol were purchased from Alfa Aesar. In all experiments, ultrapure water was used (Milli-Q, 18.2 MΩ cm). All NaOH solutions were purified to remove the Fe impurities according to the literature method.[1] All other reagents were used as received without further purification.

Preparation of transition metal-bipyridine complexes

In a typical synthesis, 0.2 mM of Ni^{2+} and 0.7 mM of bpy were dissolved in 50 mL degassed deionized water. Upon magnetic stirring at room temperature, the aqueous solution was mixed with 50 mL pre-prepared iron-free 2.0 M NaOH to form an M-bpy alkaline electrolyte. Following this procedure, Ni-bpy alkaline electrolytes with different metal concentrations and stoichiometric Ni:bpy ratios were prepared. In all cases, Ni-bpy solutions were freshly prepared for experiments.

Fabrication of silicon photoanodes

Phosphorus-doped [100] n-type (0.3 – 0.5 Ω·cm, 525 μm thickness) and heavily arsenic-doped [100] n++-type (< 0.005 Ω·cm, 525 μm thickness) silicon wafers were purchased from Sil'tronix. The silicon wafers were cut into 1.5 × 2.5 cm^2 pieces. Subsequently, the wafers were transferred into a beaker and washed with ethanol and deionized water to remove trace organics, and finally dried by nitrogen blowing. After this process, around 2 nm nickel films were sputtered on silicon substrates by a sputter coater (Safematic CCU-010, Switzerland). The unpolished backside was scraped by a diamond pen dipped with gallium indium alloy (InGa, Alfa Aesar, 99.99%) for conductivity, and a copper tape was adhered to the back side for electrochemical measurements.

Anchoring of Ni-bpy pre-catalysts on electrodes

Ni-bpy complex was self-immobilized on fluorine-doped tin oxide (FTO, sheet resistance < 15 ohm sq^{-1}, Kalvo FTO-P003, China) substrates and silicon photoanodes upon the electrochemical oxidation process during catalytic water oxidation. Specifically, in a Ni-bpy alkaline electrolyte, a constant potential within the oxygen-evolving range, for instance, 1.72 V (versus RHE) or a constant current density was applied to the bare FTO (the detailed electrochemical configuration see below), allowing the anchoring of Ni-bpy pre-catalysts onto

FTO substrates. To determine whether anchored Ni species dissolved from the FTO surface, after applying a potential of 1.72 V for 10 min, a subsequent interval of 10 min at open circuit potential was applied, and we repeated the anchoring-and-desorption process three times. Prior to the loading of catalysts, all as-received FTO substrates were ultrasonically cleaned by ethanol and H_2O for 5 min and flushed with nitrogen gas. For silicon substrates, the anchoring of Ni-bpy pre-catalyst was carried out by applying a constant bias, ~1.1 V under illumination on n-type and ~1.6 V in the dark on n^{++}-type silicon electrodes, respectively, which corresponded to their OER onset potential in 1.0 M NaOH solution.

Preparation of other nickel catalysts on FTO

To compare the activity and long-term stability of Ni-bpy derived catalyst with widely reported Ni-based film catalysts, here the amorphous NiO_x, sputtered Ni, and electrodeposited NiOOH films were fabricated. The atomic loading of Ni on the Ni-based films was calculated to be ~300 nM cm^{-2}, close to the amount of Ni-bpy derived catalysts after 60 hours of operation.

Spin-coating of NiO_x films: 0.05 M $NiCl_2 \cdot 6H_2O$ solution was dissolved in ethanol as a precursor. The precursor solution was spin-coated on FTO substrates using a Laurell WS650MZ-23NPPB spin coater at 3000 rpm 1.0 min for the formation of a film. This film was irradiated with 254 nm light for 15 hours and then annealed at 150 °C in the air for 1 hour to obtain an amorphous NiO_x film.[2]

Sputtering of Ni films: ~2 nm of Ni films were sputtered on thoroughly cleaned FTO substrates at a deposition rate of ~0.1 Å s^{-1} using an electron beam evaporation system (SPECS EBE-4) at room temperature.

Electrodeposition of NiOOH: NiOOH was electrochemically deposited on the FTO substrate by following a previously reported method.[1] Briefly, the electrodeposition was performed in a nitrogen-purged plating solution containing 0.1 M $NiSO_4 \cdot 6H_2O$ solution with a pH 6.5-7.2 (adjusted by 0.1 M NaOH) at 1.2 V vs. Ag/AgCl (Sat. KCl) at 70 °C until the passing of ~8.2 mC total charge. After deposition, the NiOOH films were rinsed with H_2O before the electrochemical test.

Purification of NaOH Solution

To eliminate the interference of Fe impurities in the NaOH electrolyte, the electrolyte is strictly treated with iron removal, and the purification process includes the following steps.[2]

A centrifuge tube was thoroughly cleaned with dilute sulfuric acid and deionized water to remove any residual contaminants. A high-purity $Ni(OH)_2$ precipitate was prepared by dissolving 2 g of 99.999% $Ni(NO_3)_2 \cdot 6H_2O$ in 4 mL of deionized water, followed by the addition of 20 mL of 1.0 M NaOH. The mixture was oscillated and centrifuged to obtain the precipitate. The $Ni(OH)_2$ precipitate was washed three times by dispersing it in 20 mL of deionized water and 2 mL of 1.0 M NaOH, followed by oscillation and centrifugation. Finally, 50 mL of 1.0 M NaOH was added to the purified $Ni(OH)_2$ precipitate, and the mixture was oscillated, centrifuged at high speed for 10 minutes, and left to settle for at least 3 hours. The supernatant, now free of Fe impurities, was carefully decanted into a clean container for use in the electrochemical tests.

Electrochemical characterization

Electrochemistry was performed in a typical three-electrode configuration using an SP-300 potentiostat (Bio-logic). All experiments were carried out at room temperature (25 ± 2 °C) in 1.0 M NaOH or M-bpy containing 1.0 M NaOH in a custom-designed Cappuccino Teflon cell with a quartz window (Fig. 3b), where an Ag/AgCl (saturated KCl) as reference electrode and a platinum gauze as counter electrode. FTO and silicon used as working electrodes were exposed by a fixed circular 0.2826 cm^2 area. For n-type silicon, the simulated solar illumination was achieved by passing light from a 300 W Xenon lamp (LOT-Quantum Design GmbH) through an AM 1.5G filter set, and the incident sunlight density was calibrated to 100 mW cm^{-2} (equal to 1.0 sun) by using a Si certified reference photodiode. The applied potentials reported were converted to the reversible hydrogen electrode (RHE) using the following equation:

$$E\ (\text{vs. RHE}) = E\ (\text{vs. Ag/AgCl}) + 0.197\ \text{V} + 0.059 \times \text{pH}$$

Where the E (vs. Ag/AgCl) is the experimentally measured potential, and 0.197 V is the potential of the Ag/AgCl reference electrode against a normal hydrogen electrode (NHE) at 25 °C. The pH of the electrolyte was measured with an Ohaus Starter 2100 pH meter.

Cyclic voltammetry (CV) curves were recorded in the potential range of 0.75−1.75 V (for silicon, 0.75−2.0 V) at a sweep rate of 10 mV s^{-1}. The stability tests were determined by chronopotentiometry with an applied constant current density of 1.0 mA cm^{-2}. For FTO electrodes, magnetic stirring at 1500 rpm was used to dislodge O_2 bubbles during electrochemical testing, while the silicon photoanodes were performed without magnetic stirring.

The turnover frequency (TOF) value at an overpotential (η) of 300 mV was calculated using the equation:

$$\text{TOF} = (j \times A)/(4 \times F \times n)$$

where j is the current density at η = 300 mV, A is the geometric area of the electrode (0.2826 cm^2), F is the Faraday constant (96485.3 C mol^{-1}), and n is the mole number of Ni atoms on the surface of the electrode. The η was calculated by the formula: η = E (vs. RHE) – 1.23 V. For Ni-bpy derived catalyst, the n is calculated based on the integration of Ni redox couples.

In-situ UV-vis spectroelectrochemistry

The UV-vis measurements were collected using a QE Pro UV-visible spectrometer (Ocean Optics) equipped with an HL2000 light source that was connected via fibre-optic cables (200 μm fibre core diameter). A homemade quartz cuvette cell constituted a pre-cut FTO slide (coated to a fixed 0.35 cm^2 area by epoxy resin), an Ag/AgCl reference and a platinum mesh were utilized. The spectroelectrochemical cell was mounted along the vertical direction of the beam path, which allowed the pass of the UV-vis light through the front face of the FTO. The variation of absorbance intensity was synchronously monitored while performing the electrochemical experiments. The CV curves and the anchoring and desorption processes of catalysts were measured using the above-mentioned setups. All in-situ UV-vis absorption spectra were blanked versus the absorption of Ni-bpy alkaline electrolyte and bare FTO at an applied potential of 1.72 V.

Materials characterizations

Light transmittances of Ni-based catalysts on FTO after stability tests were evaluated on a QE Pro UV-visible spectrometer and the reported spectra were obtained by deducting the background from cleaned bare FTO. The crystal structures were measured by X-ray diffraction (XRD) patterns in a range of 5-90° using an X'Pert PRO MPD diffractometer equipped with a Cu-Kα radiation source. Surface morphology changes on FTO substrates during the anchoring and desorption of Ni-bpy catalyst were photographed using a field emission scanning electron microscopy (FESEM, JEOL JSM-7500F, Japan) that coupled with an energy dispersive X-ray (EDX) spectrometer. Compositional information (Ni/N ratio) of Ni-bpy derived catalysts was determined by an Escalab 250Xi X-ray photoelectron spectroscopy (XPS) microprobe (Thermo Fisher Scientific) with an Al Kα (hν = 1486.6 eV) monochromated source, and the binding energies were calibrated using the adventitious carbon by shifting the C 1s peak to 284.8 eV. To minimize the effect on the desorption of Ni-bpy derived catalyst, the FTO electrodes were immediately taken out after electrochemical testing, dried by nitrogen gas, and stored in a vacuum before analysis. The Ni-bpy catalyst distribution maps were determined by a Bruker M4 Plus Tornado micro-X-ray fluorescence (μ-XRF) spectrometer, operating at 50 kV and 600 μA with an Rh anode X-ray source. The amount of loaded Ni was confirmed by a PerkinElmer Optima 5300 DV inductively coupled plasma-atomic emission spectrometer (ICP-AES).

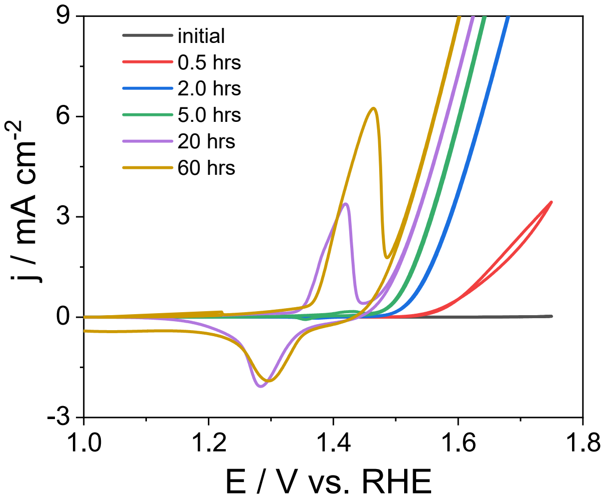


Figure S1. The catalyst loading process and TOF calculations. j-V curves of Ni-bpy derived catalysts after different operating times under OER turnover at a constant current density of 1.0 mA cm^{-2} in 1.0 M NaOH Ni:bpy 2:7 solutions at 10 mVs^{-1}.

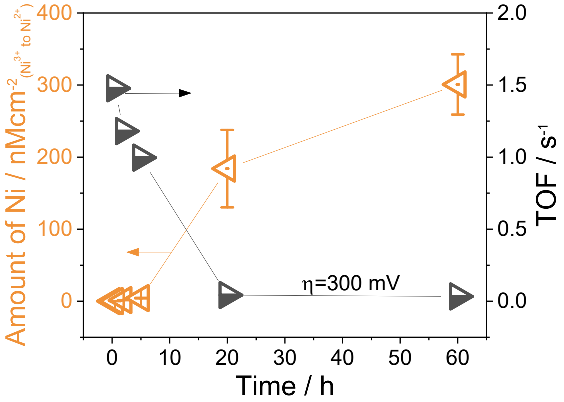


Figure S2. The loaded Ni sites were calculated based on the integration of the redox couple in Figure 1, and the TOF values were calculated according to the Ni sites on FTO electrodes with an overpotential of 300 mV.

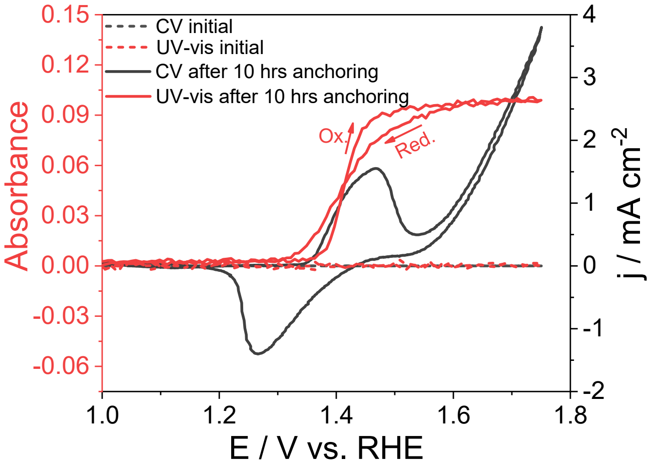


Figure S3. The CV-absorption curves present that the catalyst charging (Ni^{2+} to Ni^{3+}) leads to the spectral absorption and the OER starts after the absorption plateau above 1.5 V.

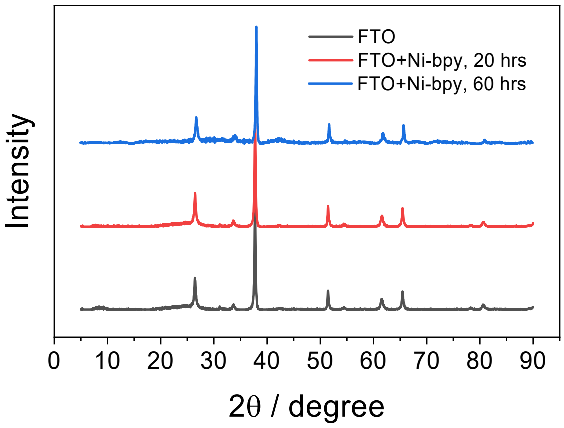


Figure S4. XRD pattern of Ni-bpy catalyst upon 20 and 60 hours loading shows only the typical peaks of bare FTO, demonstrating the amorphous structure of Ni-bpy-based catalysts.

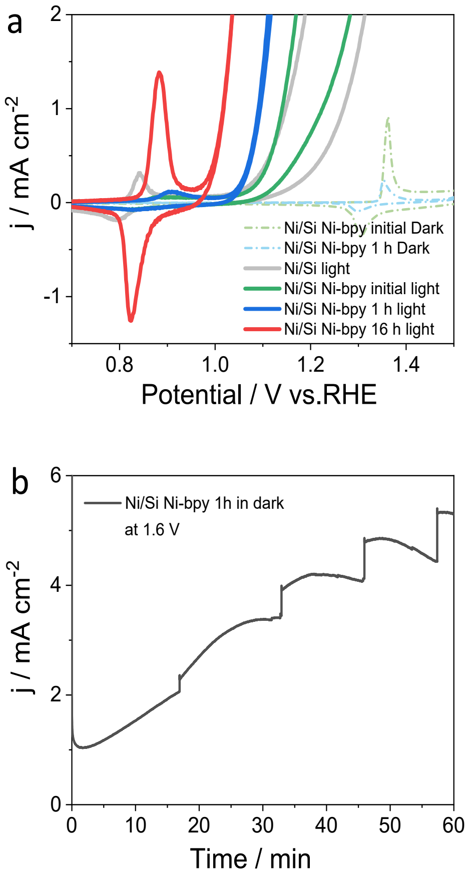
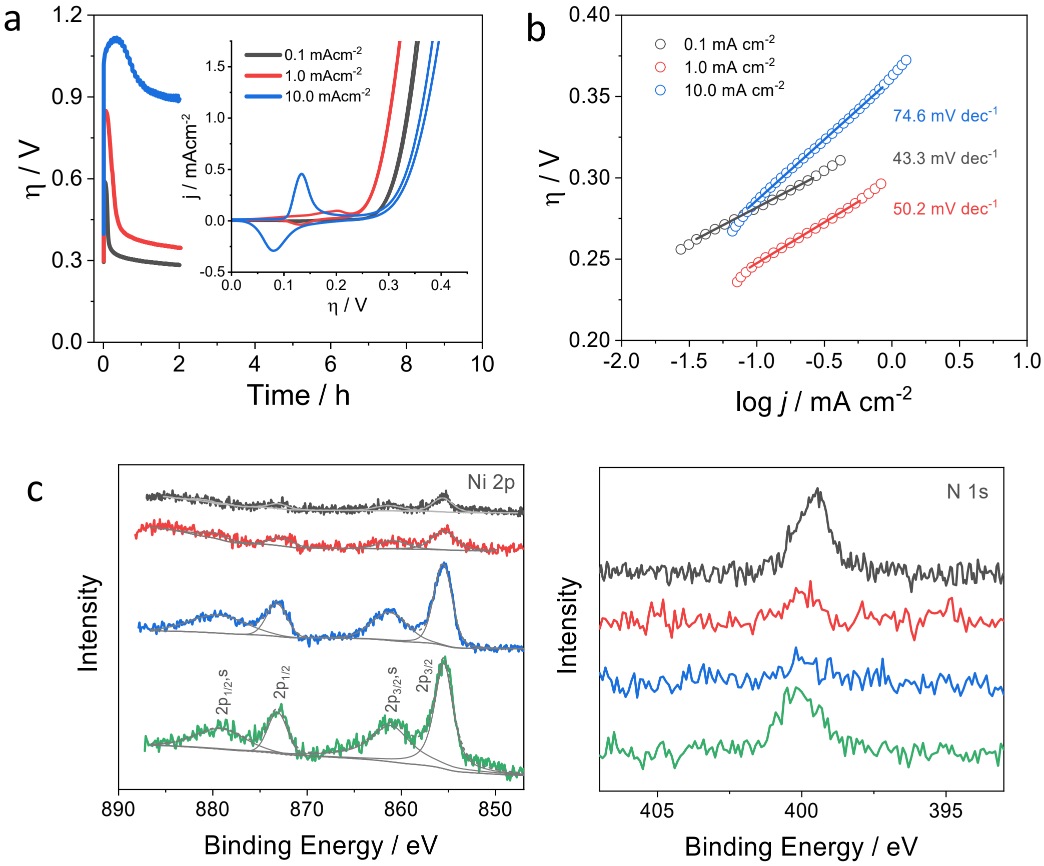


Figure S5. The increased activities of both photoelectrode and dark electrodes in the presence of Ni-bpy. (a), Redox couples through amplifying the CV curves of the Ni redox range. The redox couples were used to evaluate the Ni sites. The introduction of Ni-bpy highly increases the active sites presented by the increased redox peak (red line). Meanwhile, as exhibited in the main text, the Ni-bpy-derived Ni-containing catalyst has higher OER activity. The increased active sites and the higher specific OER activity improve the final performance. (b), The increase of current density in the dark at 1.6 V in the presence of Ni-bpy in 1.0 M NaOH.



Atomic % Samples	C 1s	O 1s	Ni 2p	N 1s	Ni/N Ratio
▬ 0.1 mA cm^{-2}, 2.0 hrs	44.59	51.90	1.08	2.43	0.44
▬ 1.0 mA cm^{-2}, 2.0 hrs	33.0	65.36	1.13	0.51	2.22
▬ 10.0 mA cm^{-2}, 2.0 hrs	29.58	67.37	2.64	0.42	6.29
▬ 1.0 mA cm^{-2}, 20 hrs	43.55	51.24	4.16	1.06	3.93

Figure S6. The effect of current density (applied initial bias) on the activity of Ni-bpy derived catalysts. (a), A high current density means a high initial bias on bare FTO at the same electrolyte (Ni:bpy 2:7+1.0 M NaOH). After 2 hours of reactions, with different current densities from 0.1, 1.0 to 10.0 mAcm^{-2} under catalytic turnover, the loading of Ni sites is reasonably different from recorded redox couples in the inset. Though we are not able to evaluate TOF between 0.1 and 1.0 mAcm^{-2} owing to the difficulty in identifying the redox couples, we could clearly say that the solution Ni-bpy under high current density or high initial bias is more inclined to form less active Ni sites (blue curve in the inset). (b), Tafel slopes of the samples after 2 h of operations via different current densities. (c), X-ray photoelectron spectra of the corresponding samples. Higher current density and longer operating time cause a stronger hydroxylation, which was evidenced by a higher Ni/N ratio.

References

1. T. W. Kim and K.-S. Choi, *Science*, 2014, **343**, 990-994.
2. L. Trotochaud, S. L. Young, J. K. Ranney and S. W. Boettcher, *J. Am. Chem. Soc.*, 2014, **136**, 6744-6753.