Supporting Information

Dye-Sensitized Photocathodes for Oxygen Reduction: Efficient H_2O_2 Production and Aprotic Redox Reactions

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Table of Contents

Transmittance of NiO and BH4/NiO films

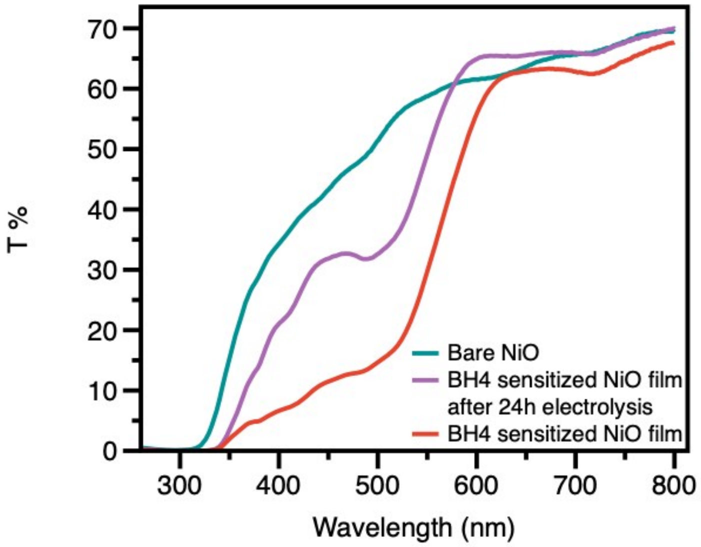

Figure S1. Transmittance of a bare NiO film (green line), a BH4 sensitized NiO film (red line), and a BH4 sensitized NiO film after 24h electrolysis (purple line)

Adsorption isotherm

The adsorption isotherm was done by measuring the absorbance of soaking solutions before and after NiO film sensitization. BH4 soaking solutions were prepared in 0.001 mM, 0.002 mM, 0.005 mM, 0.01 mM and 0.015 mM concentrations in DMF.

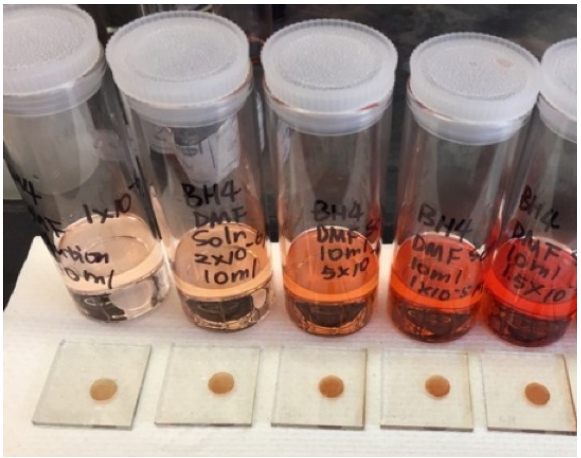

Figure S2. BH4 soaking solutions (0.001 mM, 0.002 mM, 0.005 mM, 0.01 mM and 0.015 mM in DMF) and sensitized NiO films.

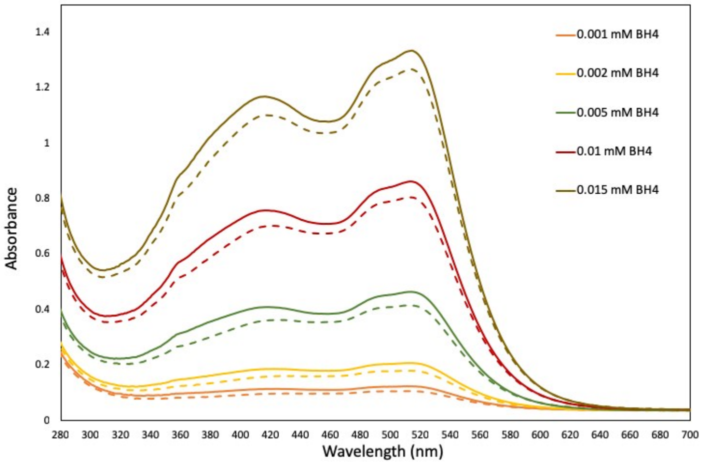

Figure S3. UV-Vis of BH4 soaking solutions before (solid line) and after soaking (dash line)

Langmuir model of adsorption[1]

$$q = q_{\mathrm{m}} \frac{K \cdot c}{1 + K \cdot c}$$

Parameter	Bare NiO
K (M^{-1})	378
q_m (nanomol/cm^2)	22.6
R^2	0.993

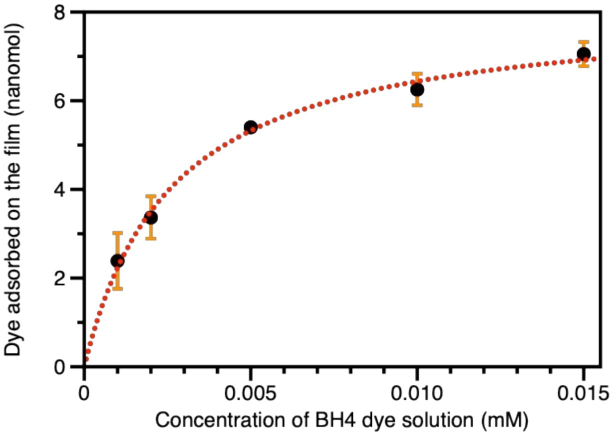

Figure S4. Adsorption isotherm of BH4 on NiO films and fitting result by using Langmuir model of adsorption. q is the quantity of adsorbate (BH4) on NiO film(adsorbent). q_m is the maximum quantity of adsorbate on NiO film, K is the binding affinity between adsorbate and adsorbent.

Transmittance of porphyrin/NiO films

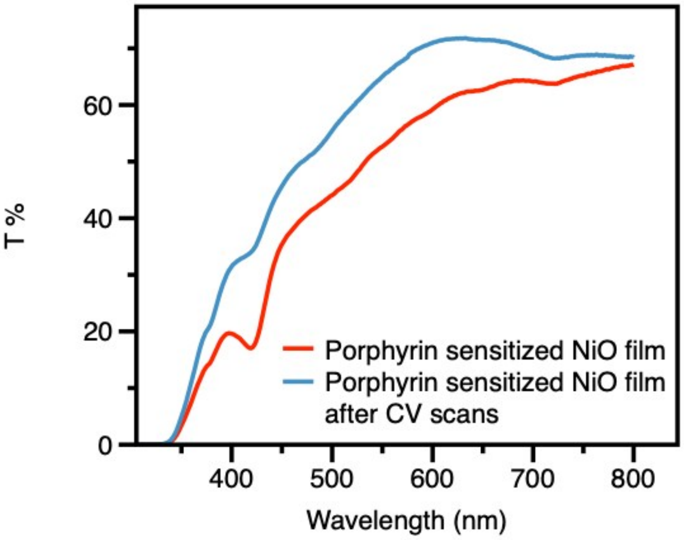

Figure S5. Transmittance of porphyrin sensitized NiO films before and after cyclic voltammetry measurements.

Long-term electrolysis of a BH4/NiO electrode

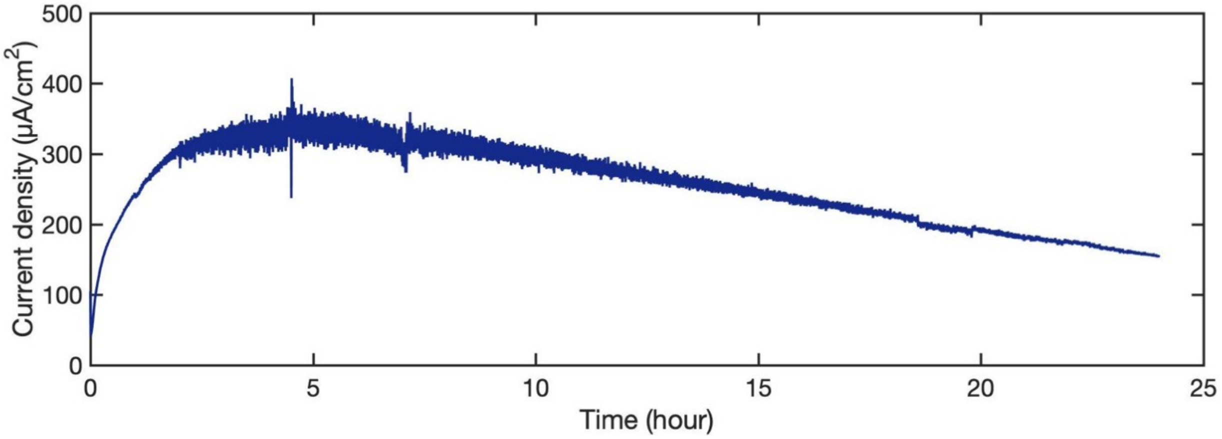

Figure S6. Controlled-potential coulometry of a BH4 sensitized NiO electrode at an applied bias at 0.42 V vs RHE under 1 sun condition in MOPS buffer, the electrolyte was constantly purging

O_2 to maintain an O_2-saturated solvent. 7.94 C of charge was accumulated during the course of 24 hours.

The calibration curve for H_2O_2 quantification

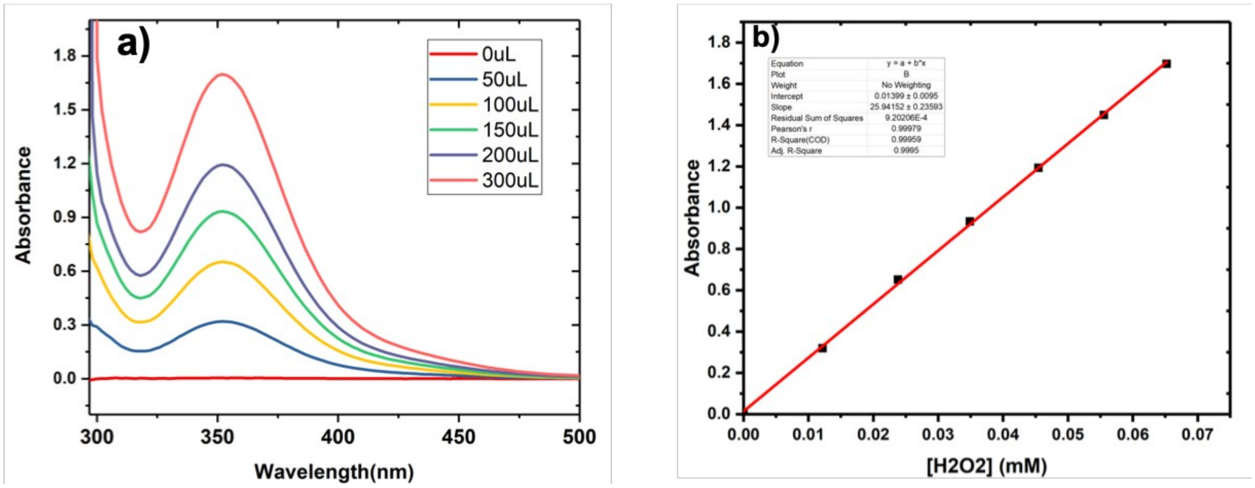

Figure S7. a) UV-Vis absorbance spectra of an aqueous KI solution with increasing amounts of added H_2O_2. b) Calibration curve: absorbance at 352nm vs concentration of H_2O_2.

TiO(SO_4) titration for H_2O_2 quantification

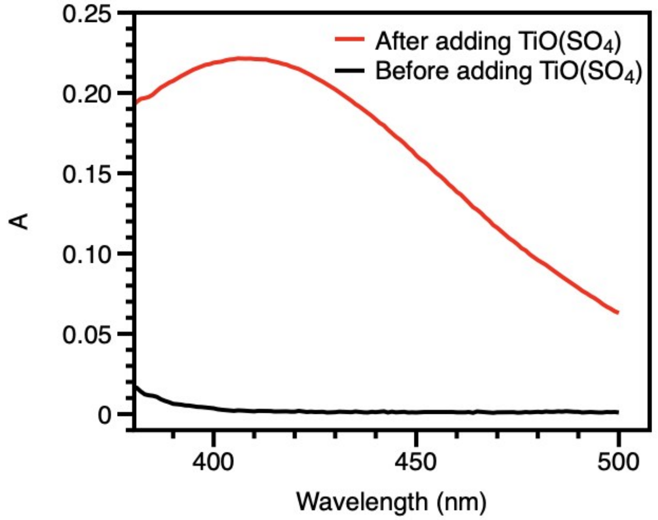

Figure S8. TiO(SO_4) titration for the calculation H_2O_2 concentration after 24h electrolysis. 2 ml titanium (IV) oxysulfate solution was added to a cuvette followed by a 1 ml aliquot of electrolyte after 24 h electrolysis. The absorbance at 405 nm is 0.22. Calibration curve is y=0.668x, y is the concentration (mM) of H_2O_2 in cuvette, x is the absorbance.[2] Calculated concentration of H_2O_2 in electrolyte is 0.963 mM.

Iodometric titration for H_2O_2 quantification

$$H_2O_2 + 2KI + 2H_2SO_4 \xrightarrow{\text{cat.}} 2H_2O + I_2 + 2KHSO_4$$
$$I_2 + I^- \longrightarrow I_3^-$$

Iodometric titration was applied in quantifying the amount of H_2O_2.[3,4] Hydrogen peroxide can oxidize potassium iodide (KI) with catalytic $(NH_4)_6Mo_7O_{24}$ to give triiodide, which absorbs light at 352 nm. Aliquots of electrolyte were collected at regular intervals, and KI and $(NH_4)_6Mo_7O_{24}$ were added. From the increased absorbance of triiodide at 352 nm, the concentration of H_2O_2 in bulk electrolyte and faradaic efficiency were calculated based on a calibration curve obtained from standard H_2O_2 solutions.

The electrolysis for H_2O_2 quantification in the main text was done in 20 mM MOPS pH=6 buffer solution and the voltage applied is at 0.42 V vs RHE. The following figure S9 and S10 show the quantification of H_2O_2 during electrolysis in different conditions as indicated below.

In 0.1 M citrate pH=5 buffer, applied 0.26 V vs RHE bias

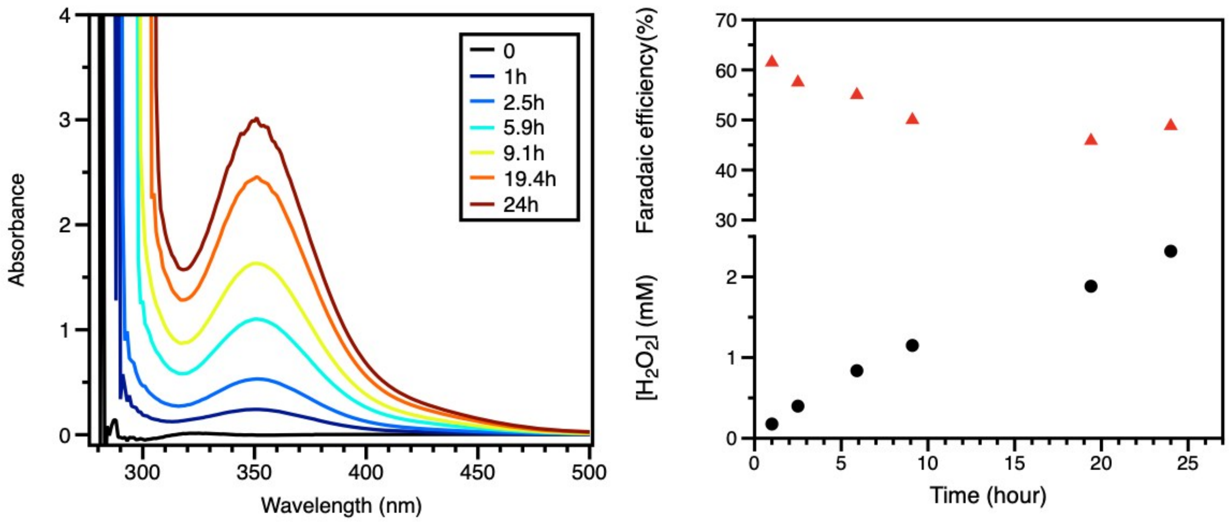

Figure S9. (a)Absorbance of triiodide (generated from reaction with H_2O_2) at different times (0h, 1h, 2.5h, 5.9h, 9.1h, 19.4h, 24h) (b) Concentration of H_2O_2 from titrations and corresponding faradaic efficiency during bulk electrolysis in 0.1 M citrate buffer (pH=5) with applied bias at 0.26V vs RHE under 1 sun light illumination.

In 20 mM MOPS pH=6 buffer, applied 0.32 V vs RHE bias

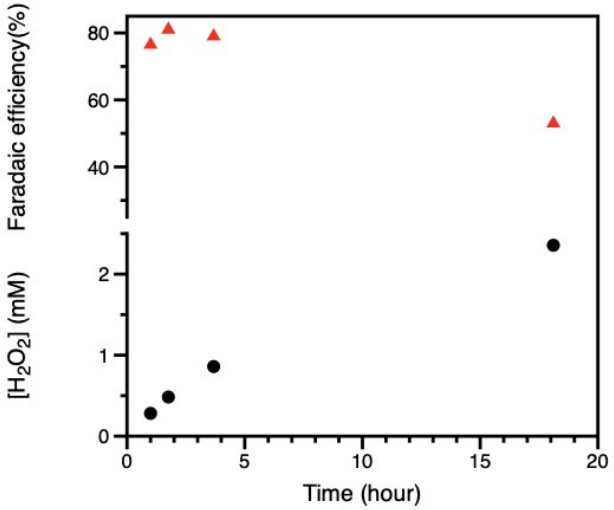

Figure S10. Concentration of H_2O_2 from titrations (bottom) and corresponding faradaic efficiency (top) during bulk electrolysis in 20 mM MOPS pH=6 buffer with applied bias at 0.32 V vs RHE under 1 sun light illumination

Photocathode degradation in aprotic solvents

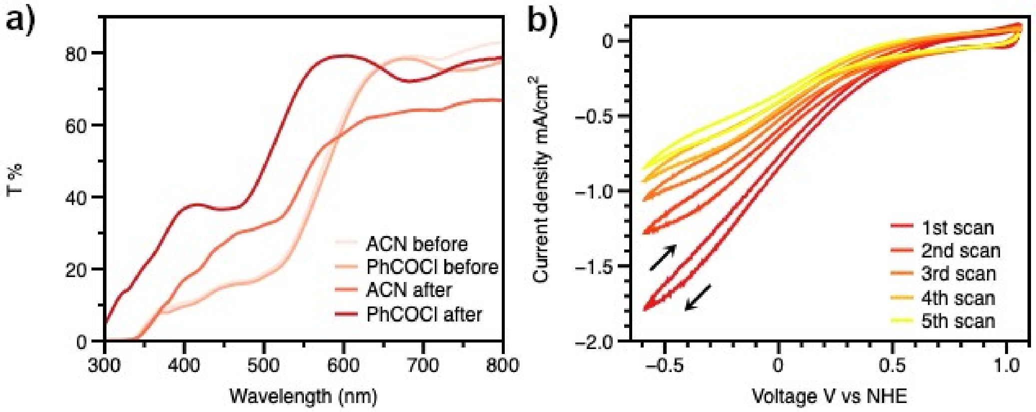

Figure S11. (a)Transmittance of BH4 sensitized NiO film before (two light orange lines) and after cyclic voltammetry scans (Orange line is in the pure acetonitrile solution, red line is in the 0.1 M benzoyl chloride (BzCl) acetonitrile solution) (b) cyclic voltammograms of BH4 sensitized NiO film in 0.1M benzoyl chloride, 0.1M $TBAPF_6$ acetonitrile solution, five continuous CV scans in O_2, light condition. Light: Xe lamp, 400 nm long path filter, 1 sun intensity

Reactions between KO_2 and BH4/NiO

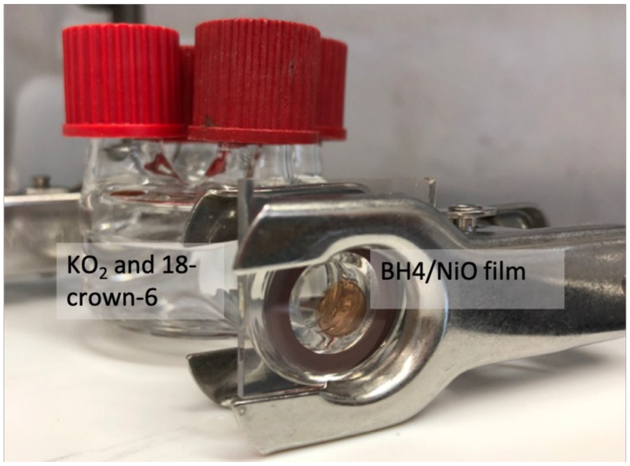

Figure S12. The setup to mimic the reaction between superoxide and BH4/NiO/FTO. Potassium dioxide (KO_2, 119 mg) and 18-crown-6 (399 mg) were added to the cell containing 15 ml dry acetonitrile under N_2. The BH4 sensitized NiO film on FTO glass was attached to the side of cell and soaked in the solution. After 3h stirring, the color of the film changed from red to colorless, which indicates the desorption of BH4 from the electrode.

NMR for product detection

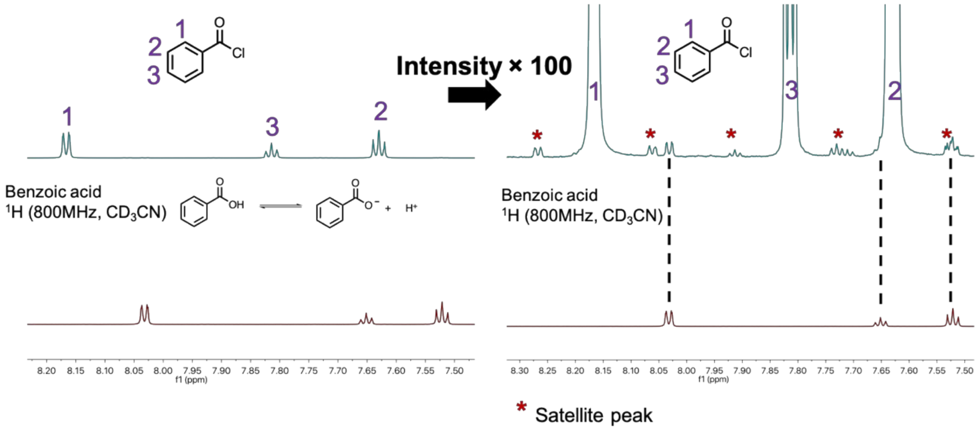

Figure S13. 800MHz NMR (90%CH3CN+10%CD3CN). The green curve shows the NMR of electrolyte containing excess amount of benzoyl chloride after 30 min electrolysis. The red curve is a standard NMR spectrum of benzoate. Compared with the two samples, benzoate was observed as the final product in the electrolyte.

Bare NiO films for comparison

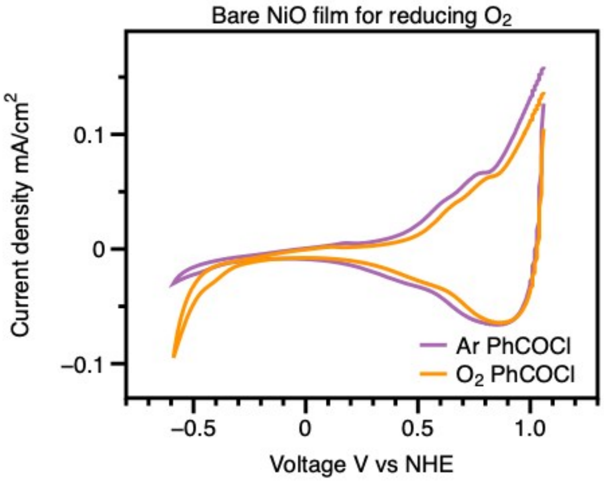

Figure S14. The CV of bare NiO film under 1 atm Ar (purple), and under 1 atm O_2 (orange) in 0.1M BzCl, 0.1M $TBAPF_6$ in dry acetonitrile.

Al_2O_3 overlayers for protecting the electrode surface

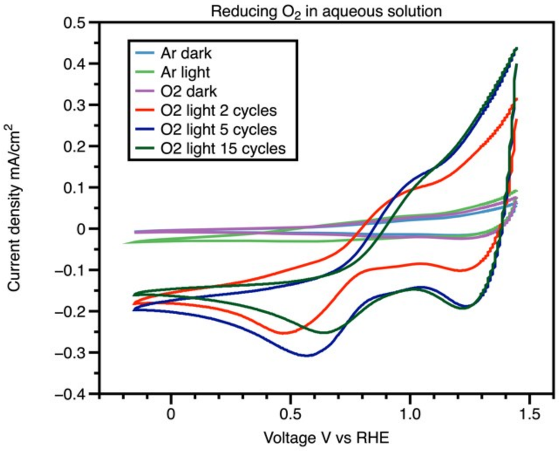

Figure S15. The CV of Al_2O_3/BH4/NiO films. Al_2O_3 was coated on top of BH4/NiO by 2(red), 5(blue) and 15(green) cycles of atomic layer deposition at 200°C. Electrolyte: 0.1 M citrate buffer at pH=5. Light: Xe lamp, 400 nm long path filter, 1 sun intensity. The electrodes were stable during CV scans, but the currents were lower compared with without Al_2O_3 coatings.

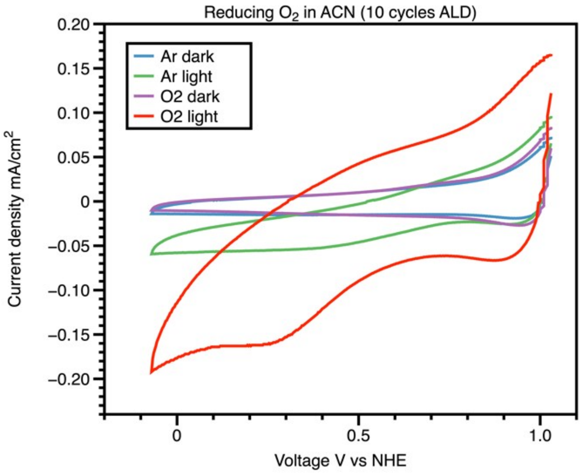

Figure S16. The CVs of Al_2O_3/BH4/NiO films. Al_2O_3 was coated on top of BH4/NiO by 10 cycles of atomic layer deposition at 200°C. Electrolyte: 0.1 M TBAPF6 in acetonitrile with 0.1M benzoyl chloride. Light: Xe lamp, 400 nm long path filter, 1 sun intensity. The electrode was colorless after CV scans which indicates its instability.

Nanosecond TA for BH4-sensitized NiO film

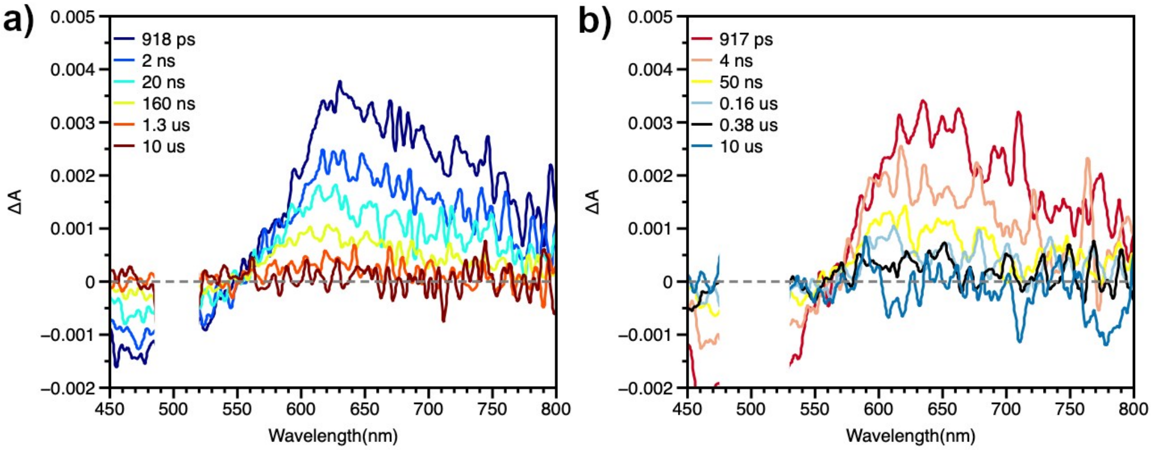

Figure S17. Nanosecond TA spectra of the BH4-sensitized NiO film in (a) Ar (b) O_2. Excitation: 500 nm

Single wavelength analysis of TA for BH4-sensitized NiO film

The fitting of the kinetic trace at 615 nm is by Kohlrausch-Williams-Watts (KWW) function as shown followed.[5–7]

$$A(t) = A_0 e^{-(t/\tau_{KWW})^{\beta_{KWW}}} \qquad (1)$$

$$\tau_{obs} = \frac{\tau_{KWW}}{\beta_{KWW}} \Gamma\left(\frac{1}{\beta_{KWW}}\right) \qquad (2)$$

$$\Gamma(x) = \int_0^{\infty} u^{x-1} e^{-u} du \qquad (3)$$

A_0 is the initial absorption, τ_{KWW} is the characteristic lifetime, β_{KWW} is the stretching parameter. τ_{obs} is the averaged lifetime obtained from equation 2.

	τ_{KWW} (μs)	β_{KWW}	R^2	RMSE	τ_{obs} (μs)
Ar	0.15	0.3	0.93	0.041	1.3
O_2	0.10	0.38	0.79	0.063	0.38

Table S1. Fitting parameters of the $BH4^{\bullet-}$/NiO film by a KWW function at 615 nm.

Calculation of kinetic rate constant

$$BH4^{\bullet-} + h^+ \xrightarrow{k_r} BH4 \qquad (4)$$

$$BH4^{\bullet-} + O_2 \xrightarrow{k_e} BH4 + O_2^{\bullet-} \qquad (5)$$

In Ar, charge recombination is the only pathway of dye decay (4), the reaction is the first order of $BH4^{\bullet-}$ concentration (6). k_r is the charge recombination rate constant and k_e is the electron transfer rate constant

$$\text{Rate} = k_r [BH4^{\bullet-}] \qquad (6)$$

In O_2, a one-electron transfer also happens from $BH4^{\bullet-}$ to O_2. To simplify the equation, we assume the reaction is the first order of the concentration of $BH4^{\bullet-}$ since O_2 is in excess. Therefore, the reaction rate is obtained from a combination of electron transfer and charge recombination.

$$\text{Rate} = (k_e + k_r) [BH4^{\bullet-}] = k_{obs} [BH4^{\bullet-}] \qquad (7)$$

k_{obs} is the observed rate constant in O_2 and it is equal to $k_e + k_r$. From table S1, we can obtain the lifetime of $BH4^{\bullet-}$ in both Ar and O_2, thus, we can calculate the rate constant which is equal to $\frac{1}{\tau}$.

$$k_r = \frac{1}{\tau_{obs,Ar}} = 7.7 \times 10^5\ \mathrm{s}^{-1},$$

$$k_{obs} = \frac{1}{\tau_{obs,O_2}} = 2.6 \times 10^6\ \mathrm{s}^{-1},$$

$$k_e = k_{obs} - k_r = 1.8 \times 10^6\ \mathrm{s}^{-1}.$$

The recombination rate constant (k_r) is determined to be $7.7 \times 10^5\ \mathrm{s}^{-1}$. We can also determine the k_e which is equal to $1.8 \times 10^6\ \mathrm{s}^{-1}$ from τ_{obs} in O_2.

References

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