Supporting information

Optimized H_2 -evolving dye-sensitized LaFeO₃ photocathodes prepared via the layer-by-layer assembly of dye and catalyst

Ximeng Xu,ª Yingzheng Li,ª Chang Liu,ª Peili Zhang,ª Ke Fan,ª Xiujuan Wu,ª Yu

Shan^a and Fusheng Li^{*a}

a) State Key Laboratory of Fine Chemicals, Institute of Artificial Photosynthesis, Institute for Energy Science and Technology, Dalian University of Technology, 116024 Dalian, China. *fusheng@dlut.edu.cn*

Experimental section

Materials

Lanthanum nitrate hexahydrate (La(NO₃)₃·6H₂O, 99.9%), iron nitrate nonahydrate (Fe(NO₃)₃ 9H₂O, 99%), Ethyl cellulose were purchased from Aladdin[®]. High-purity water (18.2 MΩ·cm⁻¹) supplied by a Milli-Q system (Millipore, Direct-Q 3 UV) was used in all experiments. Fluorine-doped tin oxide (FTO, NSG 10Ω 10 mm × 25 mm × 2.2 mm) substrates were purchased from a local foreign trade company, and were ultrasonically cleaned in deionized water, acetone and ethanol for 15 min, respectively. The Dubois-type [Ni(P₂N₂)₂]²⁺ (NiP) catalyst was synthesized according to literatures.^{1, 2} The quinacridone and other chemicals were purchased from Aladdin[®] and used as received. Organic solvents used during the experiment were analytical reagent grade and were of the highest available purity.

Physical Characterization Instruments

The morphology and transmission electron microscopy (TEM) images of all

films was characterized by field emission scanning electron microscopy (HITACHI UHR FE-SEM SU5000, operated at 5 and 15 kV) and HT7700 EXALENS transmission electron microscope (Hitachi Ltd., Japan), respectively. A Smart Lab 9KW diffractometer using Cu Kα radiation (Rigaku Corp., Japan) was used to detect X-ray diffraction (XRD) patterns. The absorption spectra of photocathodes were obtained by a solid UV-visible (UV-vis) spectrometer (Thermo Scientific Evolution 200). ¹H-NMR and ¹³C-NMR spectra were taken by a Bruker DRX-500 instrument at 298 K. Fourier transform infrared spectra (FT-IR) were measured by Nicolet 6700 Flex (Thermo Fisher™). The binding energy of relevant elements was analyzed by X-ray photoelectron spectroscopy (XPS, Thermo Fisher ESCALAB[™] Xi+). The catalyst loading amount of catalyst was obtained by inductively coupled plasma-atomic emission spectroscopy (ICP-AES, AVIO 500 PerkinElmer[™]). The pH of the electrolyte was measured by the 914 pH/conductometer (Metrohm[™]).

Fabrication of LaFeO₃ (LFO)photocathode

Mesoporous LFO films were prepared by template spray pyrolysis method, using a homemade electronic-controlled spraying device. The parameter settings are consistent with previous reports.³ After 12-15 spraying cycles, the films were then further annealed at 600 °C for 3 h in the air to remove the ethyl cellulose template.

Synthesis of PQA Dye



Figure S1. Synthetic route of PQA

Synthesis of compound 1

The synthesis of PQA is conducted in four steps with moderate yields as shown in *Figure S1*. Firstly, quinacridone (9.36 g, 30 mmol), C₄H₉Br (13.7 g, 100 mmol), cetyltrimethylammonium bromide (2 g, 9 mmol) (CTAB), toluene (120 mL) and KOH (22.4 g, 400 mmol) were added into a 250 mL round-bottom flask. Then, the mixture was heated to 90°C for 10 h. After the reaction was cooled to room temperature, the mixture was poured into a large amount of water and stirred vigorously. A red solid was obtained after washing with HCl (1 M), water and methanol as the product, yielding 10.94 g (86%). ¹H NMR (500 MHz, CD₂Cl₂): 8.79(s, 2H), 8.56 (dd, *j* = 8 Hz, 2 Hz, 2H), 7.83 (td, *j* = 15 Hz, 5 Hz, 2H), 7.60 (d, *j* = 10 Hz, 2H), 7.33 (t, *j* = 10 Hz, 2H), 4.59 (t, *j* = 10 Hz, 4H), 2.07-2.01 (m, 4H), 1.71-1.67 (m, 4H), 1.16 (t, *j* = 5 Hz, 6H). ¹³C NMR(500 MHz, CD₂Cl₂): 178.05, 142.69, 136.14, 134.78, 128.10, 126.68, 121.01, 115.18, 113.70, 46.41, 29.46, 20.64, 14.09. HRMS (ESI) calculated *m/z* of [M+H]⁺: 425.2229; found 425.2223.



Figure S2.1H-NMR spectrum of compound 1

Synthesis of compound 2

Compound 1 (5 g, 13.5 mmol), KI (2.6g, 15.7 mmol) and KIO₃ (1.5g, 7 mmol) were transferred into a single-necked flask and dissolved in acetic acid (120 mL). The mixture was heated at 100°C for 12 h, and then was poured into the water. A red solid was obtained after washing with water, yielding 8.12 g (89%). ¹H NMR (500 MHz, CD₂Cl₂): 8.75 (s, 2H), 8.62 (s, 2H), 7.97 (d, *j* = 10 Hz, 2H), 7.30 (d, *j* = 10 Hz, 2H), 4.45 (t, *j* = 5 Hz, 4H), 2.0-1.94 (m, 4H), 1.65-1.60 (m, 4H), 0.93 (t, *j* = 5 Hz, 6H). ¹³C NMR (600 MHz, CD₂Cl₂, CF₃COOH): 178.78, 145.72, 143.04, 137.76, 136.76, 126.89, 122.72, 118.82, 115.84, 86.67, 48.08, 30.47, 21.27, 14.76. HRMS (ESI) calculated *m/z* of [M+H]⁺: 677.0162; found 677.0156.



Figure S3.1H-NMR spectrum of compound 2

Synthesis of compound 3

Compound 2 (1g, 1.6 mmol), diethyl phosphite (7 mL), Pd(PPh₃)₄ (360 mg, 0.3 mmol), triethylamine (1 mL) and toluene (12 mL) were added into a 15 mL microwave reaction bottle. The mixture was heated to 130°C for 3 h under Ar in a microwave reactor (Biotage Initiator⁺). After removing the solvent by a rotary evaporator, the residues were purified by chromatography using a silica-gel column with CH₂Cl₂:MeOH (10:1) as an eluent, yielding 791 mg (71%). ¹H NMR (500 MHz, CD₂Cl₂): 8.91 (d, *j* = 15 Hz, 2H), 8.80 (s, 2H), 8.10 (t, *j* = 10 Hz, 2H), 7.65 (d, *j* = 10 Hz, 2H), 4.56 (t, *j* = 10 Hz, 4H), 4.17-4.12 (m, 8H), 2.04-1.98 (m, 4H), 1.71-1.64(m, 4H), 1.34 (t, *j* = 5 Hz, 12H), 1.12 (t, *j* = 10 Hz, 6H). ¹³C NMR(500 MHz, CD₂Cl₂): 177.60, 144.67, 138.82, 136.48, 133.18, 127.22, 121.72, 120.16, 115.60, 114.48, 62.63, 46.63, 29.38, 20.54, 16.62, 14.01. HRMS (ESI) calculated *m/z* of [M+H]⁺: 697.2808; found 697.2802.



Synthesis of PQA

Compound 3 (0.4g, 0.7 mmol), bromotrimethylsilane (1 mL) and chloroform (10 mL) were added into a 30 mL single-necked flask. The mixture was heated to 45°C and maintained for 10 h. Then 2 mL of methanol was added to quench the reaction. A bright red solid was collected and washed with dichloromethane as the product, 372.7 mg (91%). ¹H NMR (500 MHz, D₂O, NaOD): 8.65 (d, *j* = 10 Hz, 2H), 8.23 (s, 2H), 7.96 (t, *j* = 10 Hz, 2H), 7.26 (d, *j* = 10 Hz, 2H), 4.80 (s, 4H), 3.94 (t, *j* = 5 Hz, 4H), 1.58-1.52 (m, 4H), 1.37-1.29 (m, 4H), 0.87 (t, *j* = 5 Hz, 6H). ¹³C NMR(500 MHz, D₂O, NaOD): 179.35, 141.90, 137.94, 134.65, 133.59, 128.32, 124.98, 118.97, 115.43, 113.24, 45.30, 28.40, 19.28, 13.15. FT-IR (u cm⁻¹): 1621 ($u_{C=O}$), 1281 (u_{C-N}), 1113 ($u_{P=O}$), 1007 (u_{P-O}). HRMS (ESI) calculated *m/z* of [M-H]: 5831399; found 583.1416.





Figure S6. Fourier transform infrared (FT-IR) spectra of PQA

Preparation of (NiP-m+PQA-n)@LFO photocathodes

PQA-n@LFO were fabricated via layer-by-layer (LBL) assembly on LFO films. LFO films were immersed in a PQA solution (1.5 mM in methanol) for 45 min; after being washed with methanol, PQA-1@LFO was obtained. Then, by immersing the PQA-1@LFO electrode into a $ZrOCl_2$ solution (2 mM in methanol) for 30 min and washing with methanol, (PQA-1+ Zr^{4+})@LFO was obtained. (PQA-1+ Zr^{4+})@LFO was subsequently immersed in the solution of PQA for 45 min, PQA-2@LFO was obtained. Multilayers of dye were constructed by repeating the above steps. Multilayers of catalyst could also be fabricated through the same procedure; a NiP solution (2 mM in methanol) and a ZrOCl₂ solution (2 mM in methanol) were used. (NiP-m+PQA-n)@LFO photocathodes with different numbers of dye layers (m) and catalyst layers (n) could be constructed on the surface of LFO.

Performance Measurements

PEC measurements were evaluated in a typical three-electrode cell with a Ag/AgCl as the reference electrode and a graphite rod as the counter electrode. The simulated solar light was obtained by an Oriel LCS-100 solar simulator (Newport) with an AM 1.5G filter (100 mW cm⁻²). A 0.1 M pH=7.0 phosphate buffer solution was used as the electrolyte. All the potential values were calculated to a reversible hydrogen electrode (RHE) according to $E_{RHE} = E_{Ag/AgCl} + 0.059 \text{ pH} + E_{(Ag/AgCl vs RHE)}$, where $E_{(Ag/AgCl vs RHE)}$ is 0.196 V.

The Applied Bias Photon-to-current Efficiency (ABPE) of the photocathodes used in the test was calculated according to the following equation by converting the LSV curves.

$$ABPE(\%) = \frac{\left(0 - V_{RHE}\right) * (j_{light} - j_{dark})}{P_{light}} \times 100\%$$
equation

S1

Where V_{RHE} is the applied potential versus RHE (V), j_{light} and j_{dark} are the measured photocurrent and dark current, respectively. P_{light} is the power density (100 mW cm⁻²).

In order to quantitatively determine charge recombination behavior, a normalized parameter (D) was calculated using the following equation:

-

...

$$D = (I_t - I_{st})/(I_{in} - I_{st})$$
 equation S2

where I_t , I_{st} and I_{in} are the time-dependent, steady-state and initial photocurrent, respectively. In D = -1 was defined as a transient time constant(*T*), which embodies the behavior and lifetime of charge carriers.⁴

The Faradaic efficiency (FE) of hydrogen evolution could be expressed by the following equation.

$$FE(\%) = \frac{2eN_A n_{H_2}}{Q} \times 100\%$$
 equation S3

Where *e* is the elementary charge, N_A is the Avogadro constant, n_{H2} is the amount of hydrogen determined by gas chromatography, and *Q* is the integrated charge passed through the photoelectrodes in 60 minutes.

The turnover frequencies (TOF) of the photoelectrons were calculated from the following equation.

$$TOF = \frac{TON}{t} = \frac{n_{H_2}}{t * n_{NiP}}$$
 equation S4

Where n_{H_2} is the amount of hydrogen determined by gas chromatography, n_{NiP} is the amount of NiP by ICP-AES and t is the duration of the electrolysis process.



Figure S7. (a) XRD patterns of LFO. (b) The top view SEM image of LFO, the insert shows the side view image. (c) UV–vis absorption spectrum of LFO, and the inset shows the corresponding Tauc plot. (d) Mott-Schottky plots of LFO, measured in a 0.1 M pH=7.0 phosphate buffer solution.



Figure S8. (a) UV-vis absorption spectrum of PQA, and differential pulse voltammetry spectra (DPV, the insert). (b) UV-vis absorption spectroscopy of LFO with 0, 1, 2, 4, 6, and 8 layers dye.



Figure S9. I–V plot of LaFeO₃ with 0, 2, 4, 6, 8 layers dye (a) in a 0.1 M phosphate buffer solution containing [Co(NH₃)₅CI]Cl₂ (20 mM) (pH=7.0), and (b) for H₂ generation in 0.1 M phosphate buffer solution (pH=7.0) purged with Ar.



Figure. S10. The HAADF-STEM image and corresponding EDS elemental mapping of (a) PQA-6@LFO and(b) (NiP-4+PQA-6)@LFO.



Fig. S11. (a)XPS spectra of survey spectrum, (b) N 1s, (c) P 2p, (d) Ni 2p high-resolution XPS spectra of (NiP-4+PQA-6)@LFO photocathodes.



Figure S12. The LSV curves under continuous illumination with a scan rate of 15 mV s⁻¹ of LFO, PQA-6@LFO, NiP-4@LFO, (NiP-4+PQA-6)@LFO photocathode in an Ar-saturated 0.1 M pH=7.0 phosphate buffer solution.



Figure S13. The LSV curves of (NiP-4+PQA-6)@LFO and (NiP-1+PQA-6)@LFO with a scan rate of 15 mV s⁻¹.



Figure S14. The controlled potential photo-electrolysis trace of (NiP-4+PQA-6)@LFO and (NiP-1+PQA-6)@LFO (a), PQA-6@LFO(b), NiP-4@LFO, LFO photocathodes held at 0.5 V vs. RHE in an Ar-saturated 0.1 M pH=7.0 phosphate buffer solution under simulated solar light.

| Table S1 The performances of different photocathodes | | | | | | |
|--|--------------------------------|---|------|-----|--|--|
| NiP loading/ nmol.cm ⁻² | Charge/ mC.cm ⁻² | H ₂ production nmol.cm ⁻² | FE/% | TON | | |
| | | | | | | |

| (NiP-1+PQA-6) @LFO | 5.79 | 46.1 | 96 | 40 | 16.5 |
|--------------------|------|------|-----|----|------|
| (NiP-4+PQA-6) @LFO | 13 | 62.2 | 170 | 53 | 13.1 |
| NiP-4@LFO | 9.49 | 51.2 | 119 | 45 | 12.6 |
| PQA-6@LFO | - | 42.4 | 81 | 36 | - |
| LFŌ | - | 27.6 | 36 | 25 | - |

REFERENCES

- U. J. Kilgore, J. A. S. Roberts, D. H. Pool, A. M. Appel, M. P. Stewart, M. R. DuBois, W. G. Dougherty, W. S. Kassel, R. M. Bullock and D. L. DuBois, *J. Am. Chem. Soc.*, 2011, **133**, 5861-5872.
- 2. T. E. Rosser, M. A. Gross, Y.-H. Lai and E. Reisner, *Chem. Sci.*, 2016, **7**, 4024-4035.
- F. Li, R. Xu, C. Nie, X. Wu, P. Zhang, L. Duan and L. Sun, *Chem. Commun.*, 2019, 55, 12940-12943.
- 4. C. Liu, F. Li, L. Wang, Z. Li, Y. Zhao, Y. Li, W. Li, Z. Zhao, K. Fan, F. Li and L. Sun, *Fundamental Research*, 2022, DOI: https://doi.org/10.1016/j.fmre.2022.03.013.