Supporting Information

Epitaxial Encapsulation of Homodispersed CeO₂ in a Cobalt-Porphyrin Network Derived Thin Film for Highly Efficient Oxygen Evolution Reaction

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Experimental Section

Materials and instrumentation

All the reagents and solvents employed were commercially available and were used as received without further purification.

The samples grown on functionalized Au substrate were characterized with infrared reflection absorption spectroscopy (IRRAS). IRRAS data were recorded using a Bruker Vertex 70 FTIR spectrometer with 2 cm⁻¹ resolution at an angle of incidence of 80° relative to the surface normal. Powder X-ray diffraction (PXRD) analysis was performed on a MiniFlex2 X-ray diffractometer using Cu-K α radiation ($\lambda = 0.1542$ nm) with a scanning rate of 0.5° min⁻¹. Transmission electron microscope (TEM) images and EDS recorded for the samples were used JEM-2010F. Scanning electron microscope (SEM) images for the morphology of thin films were measured by JSM6700. Electrochemical measurement was carried out by Zahner-Zennium IM6 and the CHI760e electrochemical workstation (Shanghai Chenhua Instrument China). The NEXAFS measurements were carried out at the BL12b bending magnet beamline at the National Synchrotron Radiation Laboratory (NSRL) in a total electron yield (TEY) mode by collecting the sample drain current. The base pressure of the UHV chamber was better than 5 × 10⁻⁸ Pa. The synchrotron beam was monochromatized via a varied line-spacing plane grating and refocused by a toroidal mirror. An energy range from 100 to 1000 eV was supplied with an energy resolution of approximate 0.2 eV at the C K-edge.

Preparation of functionalized FTO substrates

The functionalized FTO substrates were treated with a mixture of concentrated KOH(2mmol) aqueous solution and hydrogen peroxide (30%) with a volume ratio 3:1 at 80 °C for 30 minutes and then cleaned with deionized water and dried under nitrogen flux for the next preparation.

Fabrication of PIZA-1 and Ce(pdc)₃@PIZA-1 thin films

The thin film was fabricated using the following diluted ethanolic solutions: cobalt (II) acetate (1 mM) and TCPP (0.1 mM) and. The spray times were 15s, 25s for $Co(OAc)_2$ and TCPP solution, respectively. There was waiting time for 30s between steps and each step was followed by a 3s spray step with pure ethanol to remove residual reactants.

The functionalized FTO substrate was sprayed by cobalt acetate (1 mM) and TCPP (0.1 mM) and Ce(pdc)₃ (0.1 mM) ethanol solutions sequentially. The spray times were 15s, 25s and 10s for Co(OAc)₂, and Ce(pdc)₃ solutions, respectively. There was waiting time for 30s between steps and each step was followed by a 3s spray step with pure ethanol to remove residual

reactants. A total of 20 growth cycles were used for in situ LPE layer-by-layer Ce(pdc)₃ encapsulation in PIZA-1 (Ce(pdc)₃@PIZA-1) thin film in this work.

Synthesis of powder PIZA-1

Powder MOF PIZA-1 was synthesized by mixing 0.37 g (1.5 mmol) cobalt acetate and 0.8 g (1 mmol) TCPP (5,10,15,20-Tetra(4-carboxyphenyl)porphyrin) in 10 ml pure ethanol (drops of pyridine) in a sealed glass bottle. The reagents were mixed and dissolved in an ultrasonic bath for 30 min, followed by heating at 65 °C for 2 days and cooling to room temperature. The resulting powder was washed with pure ethanol and dried in nitrogen. The XRD data of PIZA-1 powder was consistent to the simulated XRD of PIZA-1 (Figure S5).

Synthesis of Ce(pdc)₃

A mixture of $Ce(NO_3)_3 \cdot 6H_2O$ (0.25 mmol), pyridine-2,6-dicarboxylic acid (H₂pdc 0.75 mmol) and dimethylamine (0.75 mmol) were placed in a 20 mL of sealed glass bottle with 5 mL pure water. The mixture was ultrasonicated for 30 min and then was heated at 60°C for overnight, resulting in the formation of a clear solution. After evaporation of this solution, the colorless powder crystal of compound Ce(pdc)₃ was obtained and charaterized by PXRD. Here the guest molecules in the complexes were omitted in this study.

Fabrication of PIZA-1-400 and CeO2@PIZA-1-400 thin film on FTO

The sample of PIZA-1 and $Ce(pdc)_3$ @PIZA-1 thin films was put in tubular furnace and calcinated at 400 °C with flowing N₂ for 5 h. after cooling down the sample to room temperature, the PIZA-1-400 and CeO₂@PIZA-1-400 thin film on FTO were obtained.

Electrochemical Tests

Electrochemical measurements were carried out in a three-electrode system on an electrochemical workstation in 1.0 M KOH aqueous solution at room temperature where Pt wire served as the counter electrode, Ag/AgCl as the reference electrode and the sample@FTO were directly selected as the working electrode without any ancillary materials. The electrochemical behaviors of the prepared electrodes were characterized by cyclic voltammetry (CV), Linear-sweep voltammetry (LSV), chronoamperometry and electrochemical impedance spectroscopy (EIS). CV curves were measured in a potential range from 0 to 0.6 V(vs. Ag/AgCl) at different scan rates(10-100mV/s) and Linear-sweep voltammetry (LSV) were performed by sweeping the potential from 0 to 0.9 V(vs. Ag/AgCl) at a sweep rate of 5 mV s⁻¹. Gas bubbles appeared on the surface of the sample electrodes, showing a phenomenon of water spitting. The bubbles were confirmed to be oxygen by gas chromatography with a fluorescence-based oxygen sensor. All samples were performed under the same measurement, all potentials were converted to reversible hydrogen electrode (RHE) via calibration and all currents were corrected with by iR compensation. The chronoamperometry were conducted at 0.7 V(vs. Ag/AgCl) for PIZA-1-400 thin film on FTO and the chronoamperometric response of CeO₂@PIZA-1-400 thin film on FTO was obtained at 0.6 V (vs. Ag/AgCl) under the current density of about 10mA cm⁻¹. Electrochemical impedance spectroscopy (EIS) measurements were carried out in a frequency range from 0.01 Hz to 100 kHz by applying an AC voltage with an amplitude of 5 mV at 0.6 V(vs. Ag/AgCl). Besides, the potentials in this work were referenced to a reversible hydrogen electrode (RHE) according to the Nernst equation : E(RHE) = E(Ag/AgCl) + 0.0591 pH +0.197.

More experimental and characterization details, additional figures and images, XRD patterns, IR spectrometry and SEM images are provided in the Supplemental Information.



Figure S1. The structure of of PIZA-1 along [100] (a), [110] (b) and [010] (c) orientations.



Figure S2. Top: The process of PIZA-1 (top) and PIZA-1-300 (down) powder deposited on glassy carbon in the 1.0 M KOH electrolytes for OER measurement.



Figure S3. The sample of PIZA-1/FTO before and after immersing in the 1.0 M KOH electrolytes during the OER measurement.



Figure S4. The sample of PIZA-1-400/FTO before and after immersing in the 1.0 M KOH electrolytes during the OER measurement.



Figure S5. The XRD pattern of of PIZA-1 and PIZA-1-400.

To confirm the component, calcinated PIZA-1 were characterized by IR, Raman spectra and NEXAFS spectra. The absorbance at 3000 cm⁻¹ in the IR (Figure S6) and Raman spectra (Figure 1b) disappeared, indicating that the -OH was lost after calcination at 400 °C. However, there was an intense absorbance at 1200~1600 cm⁻¹ that can be observed, which could demonstrate that the metalloporphyrin groups still retain in the sample at 400~500 °C calcination.^[1, 2] The NEXAFS spectra were obtained in a total electron yield mode by collecting the sample drain current. Since there were Co-N and Co-O bonds in the samples, the N K-edge (Figure S8) rather than Co L-edge (Figure S7) spectra were recorded in order to verify whether the CoN₄ core structure still remained after the calcination. In Figure S8, the N K-edge spectra of PIZA-1 and PIZA-1-400 samples were rather similar, dominantly comprised of three resonances in the low-energy region near 399 eV, followed by a doublepeak between 400 and 402 eV and a broad hump around 406 eV. These experimental results were very close to that of meso-tetraphenylporphyrinato-cobalt (II) (CoTPP) sample that Schmidt et al reported [N. Schmidt et al, J. Chem. Phys., 2010, 133, 054703]. This rather comparable N K-edge structures for PIZA-1 sample before and after calcination under 400 °C indicated the presence of metalloporphyrin groups.



Figure S6. The IR spectra of PIZA-1 powder before and after calcination at 400 °C, 500 °C and 600 °C under nitrogen atmosphere.



Figure S7. Co L_{2,3}-edge spectra of PIZA-1 and PIZA-1-400 thin films.



Figure S8. N K-edge spectra of PIZA-1 and PIZA-1-400 thin films.



Figure S9. The SEM image of PIZA-1 thin film before (a) and after (b) calcination at 400 °C.



Figure S10. The thicknesses of PIZA-1 thin films with 10, 20, 30 and 35 cycles LPE cycles characterized by cross section of SEM (top) and the a linear function of the thickness vs LPE cycles (down).



Figure S11. Electrochemical impedance spectra (EIS) of PIZA-1-400/FTO with different cycles recorded in a frequency range from 0.01 to 100 kHz with an AC potential amplitude of 5 mV at 1.6 V potential vs. RHE



Figure S12. The Tafel plots from the LSV curves of PIZA-1-400/FTO with different cycles (1, 5, 10, 15, 20, 25, 30 and 35 cycles).



Figure S13. Chronopotentiometric curves of PIZA-1-400 (20L)/FTO.

Thickness/cycles	OER: E (V vs RHE) at I = 10 mA/cm ²	OER: overpotential (mV) at I = 10 mA/cm ²
0		
1	1.825	595
5	1.735	505
10	1.725	495
15	1.704	474
20	1.660	430
25	1.675	445
30	1.686	456
35	1.693	463

Table S1. The potential and overpotential (current density at 10 mA/cm²) of the PIZA-1-400 sample with different LPE cycles.

When the LPE cycles increased from 1, 5, 10 to 20 cycles, the potential decreased from 1.825 to 1.66 V (at the current density of 10 mAcm⁻²) continuously. This maybe because that the increased cycles of porous thin film would provide large electrochemical surface area and more channel and pore for enhancing the mass transfer. It was obvious that PIZA-1-400(20L) had the best electrocatalystic performance of OER with the overpotential of ~ 430 mV. With the increasing of LPE cycles from 20 to 35 cycles, then the potential increased to 1.693 V. We hypothesize that many gas bubbles have occupied the pores in the porous PIZA-1-400 thin film, which would block the mass transfer in the channels and lead to a low utilization of the electrochemical surface area. To verify that the PIZA-1 thin film calcinated under 400 °C has best OER performance, the 20 cycles of PIZA-1 thin film calcinated under 400, 500, 600 °C were prepared for electrochemical measurement. The result of LSV, ESI and Tafel plots showed that PIZA-1-400 (20L)/FTO has the best OER performance, which is consistent to the behavior in the case of powder PIZA-1. The stabilized current density indicates no obvious deactivation of PIZA-1-400 (20L)/FTO after 10000 s as shown in Figure S13, suggesting that present sample exhibits a good catalytic stability under strong base conditions.



Figure S14. High-temperature in situ XRD measurements of Ce(pdc)₃ from 30 to 400 °C.



Figure S15. (a) The scheme illumination from $Ce(pdc)_3$ to CeO_2/C material; (b) the XRD of calcianted $Ce(pdc)_3$ at 400 °C under N₂ atmosphere and simulated XRD of CeO_2 ; (c) The TEM images of CeO_2 prepared by calcianting the $Ce(pdc)_3$ at 400 °C under N₂ atmosphere; (d) The size distribution of CeO_2 NPs in $CeO_2@PIZA-1-400$ thin film catalyst.



Figure S16. The XPS of Ce³⁺ in Ce(pdc)₃@PIZA-1 thin film.



Figure S17. The XPS of Co²⁺/Co³⁺ in calcinated Ce(pdc)₃@PIZA-1 thin film under 400 °C.



Figure S18. The element mapping of Ce(pdc)₃@PIZA-1 thin film with 20 LPE cycles characterized by SEM.



Figure S19. The water contact angles of FTO substrate, PIZA-1, PIZA-1-400, Ce(pdc)₃@PIZA-1 and CeO₂@PIZA-1-400 thin film grown on FTO substrates.

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Figure S20. CV curves of the CeO₂@PIZA-1-400/FTO sample (20 cycles) measured at different scan rates from 10mV/s to 100 mV/s.



Figure S21. The plots of peak current density of $CeO_2@PIZA-1-400/FTO$ sample (20 cycles) with different scan rate, the double layer capacitance was then estimated from the slope of the fitted the linear region.

catalyst	electrodes	Overpotential	References
		at 10mA cm ⁻²	
		(mV vs.RHE)	
CeO ₂ @PIZA-1-400	FTO	370	This work
Co-AIM NU-1000	FTO	566	ACS Appl. Mater. Inter.
			2015 , 7, 28223
Co-ZIF-9	FTO	510	Nanoscale, 2014 , 6, 9930.
NiCo-UMOFNs	glassy-carbon	250	<i>Nat. Energy</i> 2016 , 1, 16184
UTSA-16	glassy-carbon	408	ACS Appl. Mater. Inter.
			2017 , 9, 7193
FeTPyP-Co	glassy-carbon	351	J. Am. Chem. Soc. 2016,
			138, 3623
Fe/NiBTC	Ni Foam	270	ACS. Appl. Mater. Inter.
			2016 , 8, 16736
$[Co(C_{12}H_6O_4)(H_2O)_4]$	Cu Foam	520	J. Am. Chem. Soc. 2014,
			136, 13925
MAF-X27-OH	glassy-carbon	461	J. Am. Chem. Soc. 2016,
			138, 8336.
Co-WOC-1	glassy-carbon	390	Angew. Chem. Int. Ed.
			2016 , 55, 2425.
Fe ₃ -Co ₂	glassy-carbon	283	J. Am. Chem. Soc. 2017, 139, 1778

 Table S2. Comparison of the overpotential of known MOF-based catalysts on the substrates.



Figure S22. The thicknesses of PIZA-1 thin films with 10, 20, 30 and 35 cycles LPE cycles characterized by cross section of SEM (top) and the a linear function of the thickness vs LPE cycles (down).

[1] Y. Chen, G. Royal, E. Flahaut, S. Cobo, V. Bouchiat, L. Marty, N. Bendiab, *Advanced materials (Deerfield Beach, Fla.)* **2017**.

^[2] K. Mittra, A. Singha, A. Dey, *Inorg. Chem.* **2017**, *56*, 3916.