

Electronic Supplementary Information

Full water splitting by nanoporous CeO₂ nanowire array under alkaline condition

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Experimental section

Materials: TM was provided by Hangxu Filters Flag Store, Hengshui, Hebei. Pt/C (20 wt% Pt on Vulcan XC-72R), was purchased from Alfa Aesar (China) Chemicals Co. Ltd. $\text{Ce}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$, $\text{CO}(\text{NH}_2)_2$, KMnO_4 , $\text{MnSO}_4 \cdot \text{H}_2\text{O}$, oxalic acid and KOH were purchased from Sigma-Aldrich Chemino) benzcal Reagent Co., Ltd. Hydrochloric acid (HCl) and ethanol were purchased from Aladdin Ltd. (Shanghai, China). Nafion 115 membrane (DuPont) was purchased from HESEN Co., Ltd. (Shanghai, China). Ultrapure water used throughout all experiments was purified through a Millipore system.

Preparation of MnO_2 - CeO_2 and np- CeO_2 : (1) A certain amount of MnO_2 and CeO_2 with a mass ratio of 7.6:1 were mechanical mixed and grinded in agate mortar. Such composite was named as MnO_2 - CeO_2 ; (2) 30 mL mixture of $\text{Ce}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$ and $\text{CO}(\text{NH}_2)_2$ and 30 mL suspension liquid of $\text{MnSO}_4 \cdot \text{H}_2\text{O}$ and KMnO_4 were mixed. The following processes were the same as those of CeO_2 . The prepared sample was denoted as MnO_2 - CeO_2 ; Then the solution and a piece of Ti mesh (1 cm \times 4 cm in size) were put into a Teflonlined autoclave and kept at 120 °C for 5 h. When the autoclave cooled down naturally, the resulting sample was dried 2 h at 60 °C in air and followed by calcination at 300 °C under Ar atmosphere for 120 min. To prepare np- CeO_2 /TM, the resulting MnO_2 - CeO_2 /TM was put in 0.6 M oxalic solution for 1.5 h and then dried for 4 h at 60 °C.

Preparation of Pt/C based work electrode: Pt/C ink was prepared by dispersing 20 mg of catalyst into 490 μL of water/ethanol (v/v = 1:1) and 10 μL of 5 wt% Nafion using sonication for 30 min. Then 11.5 μL of the Pt/C ink (containing 452 μg of Pt/C) was loaded onto a bare TM of 0.25 cm^2 in geometric area.

Preparation of RuO_2 loading on TM (RuO_2 /TM): RuO_2 was prepared in accordance with reported work. Briefly, 2.61 g of $\text{RuCl}_3 \cdot 3\text{H}_2\text{O}$ and 1.0 mL KOH (1.0 M) were added into 100 mL distilled water and stirred for 45 min at 100 °C. Then the above solution was centrifuged for 10 minutes and filtered. The precipitates were collected by centrifugation and washed with water for several times, followed by

drying at 70°C. Finally, the product was annealed at 300°C for 3 h under air atmosphere. RuO₂ ink was prepared by dispersing 20 mg of catalyst into 490 μL of water/ethanol (v/v = 1:1) and 10 μL of 5 wt% Nafion using sonication for 30 min. Then 11.3 μL of the RuO₂ ink (containing 452 μg of RuO₂) was loaded onto a bare TM of 0.25 cm² in geometric area.

Characterizations: XRD patterns were obtained from a Shimazu XRD-6100 diffractometer with Cu Kα radiation (40 kV, 30 mA) of wavelength 0.154 nm (Japan). SEM images were collected from the tungsten lamp-equipped SU3500 scanning electron microscope at an accelerating voltage of 20 kV (HITACHI, Japan). TEM images were obtained from a Zeiss Libra 200FE transmission electron microscope operated at 200 kV. XPS measurements were performed on an ESCALABMK II X-ray photoelectron spectrometer using Mg as the exciting source. The absorbance data of spectrophotometer were measured on SHIMADZU UV-1800 ultraviolet-visible (UV-Vis) spectrophotometer.

Electrochemical measurements: Electrochemical measurements are performed with a CHI 660D electrochemical analyzer (CH Instruments, Inc., Shanghai) in a standard three-electrode system, using np-CeO₂/TM as the working electrode, a graphite plate as the counter electrode and a SCE as the reference electrode. In all measurements, the SCE reference electrode was calibrated with respect to reversible hydrogen electrode (RHE). In 1.0 M KOH, E (RHE) = E (SCE) + 1.068 V.

Where j is current density (A cm⁻²) at defined overpotential of the electrochemical measurement in 1 M KOH; A is the geometric area of the testing electrode; 2 indicates the mole of electrons consumed for evolving one mole H₂ from water; F is the Faradic constant (96485 C mol⁻¹); m is the number of active sites (mol), which can be extracted from the linear relationship between the oxidation peak currents and scan rates by the equation (2):

$$\text{slope} = n^2 F^2 A \Gamma_0 / 4RT \quad (2)$$

where n is the numbers of electron transferred; $m = A\Gamma_0$; Γ_0 is the surface concentration of active sites (mol cm⁻²); R and T are the ideal gas constant and the

absolute temperature, respectively.

TOF_{avg} calculations:

The electrochemical active surface area (ECSA) is calculated using the following formula:

$$A_{ECSA}^{CeO_2} = \frac{C_{dl}}{40 \mu F cm^{-2} per cm_{ECSA}^2}$$
$$TOF_{avg} = \frac{(3.12 \times 10^{15} \times \frac{H_2}{cm^2} per \frac{mA}{cm^2}) \times j}{1.24 \times 10^{15} \times A_{ECSA}}$$

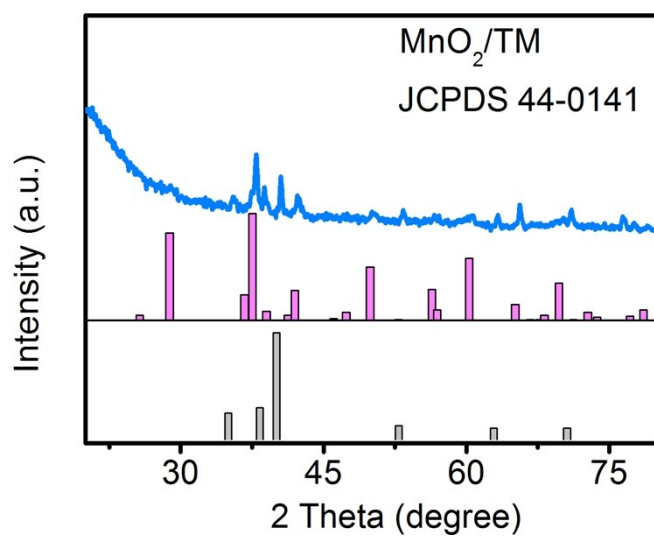


Fig. S1. XRD patterns for MnO₂

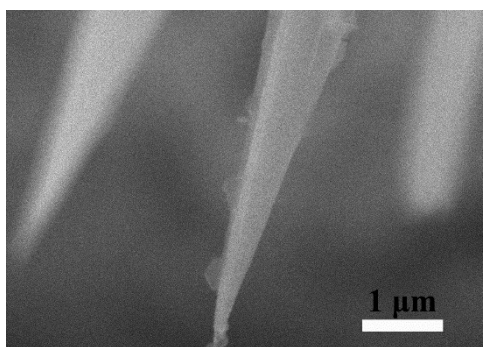


Fig. S2. The SEM image of MnO₂-CeO₂/TM

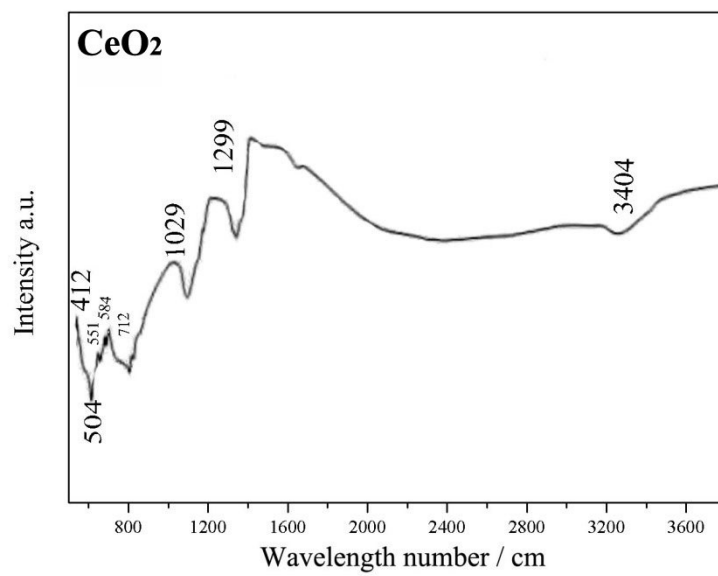


Fig. S3. FTIR spectrum of np-CeO₂

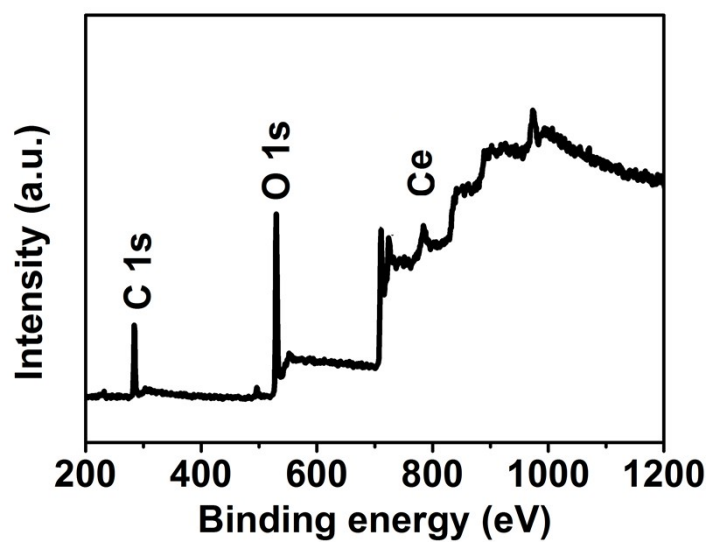


Fig. S4. XPS analysis spectrum for np-CeO₂.

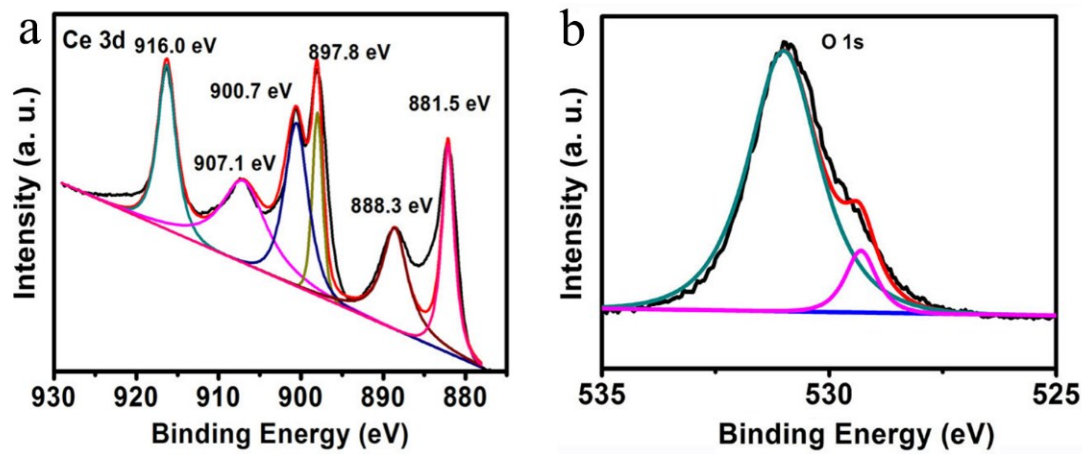


Fig. S5. XPS spectra for np-CeO₂ in the (a) Ce 3d and (b) O 1s regions.

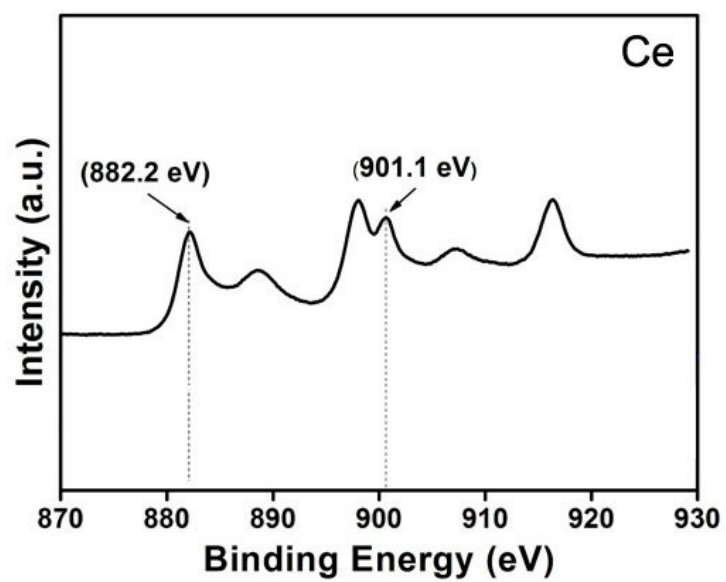


Fig. S6. XPS spectra for MnO₂-CeO₂ in the Ce 3d.

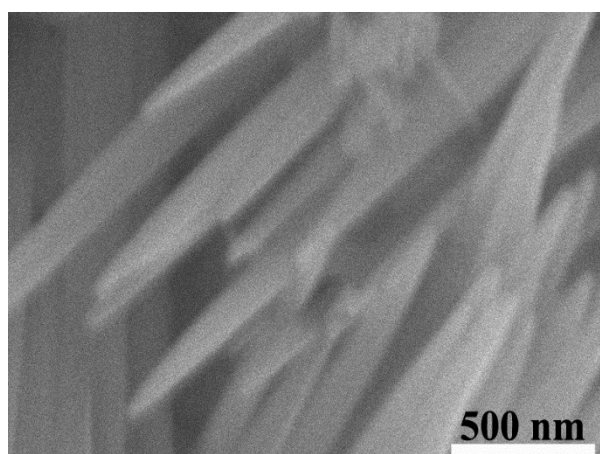


Fig. S7. The SEM image of np-CeO₂ after the long-term test.

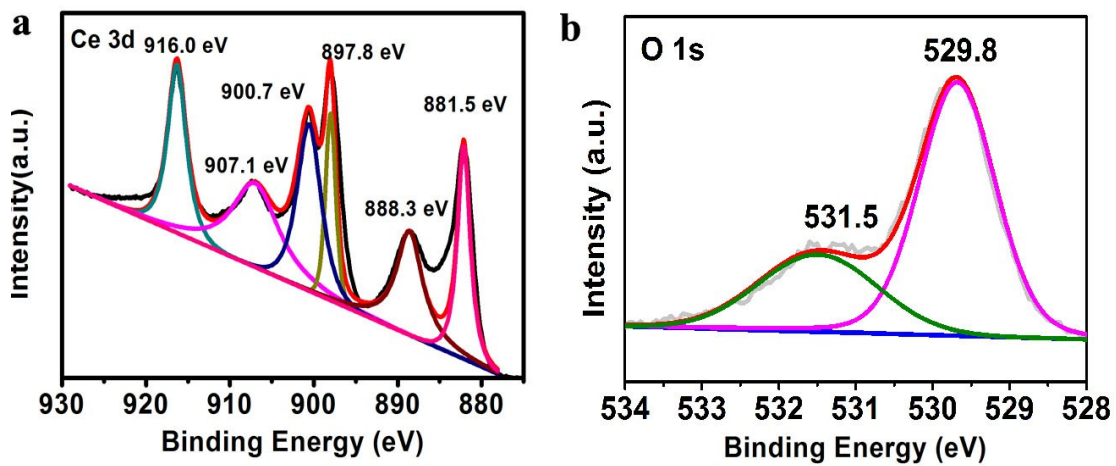


Fig. S8. The XPS spectra for np-CeO₂ after the long-term test.

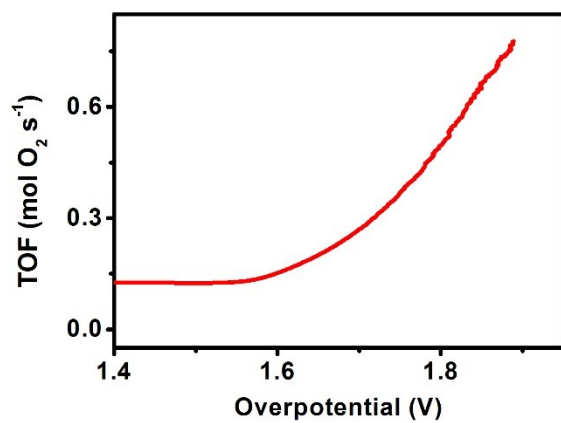


Fig. S9. TOF_{avg} calculation of np-CeO₂/TM.

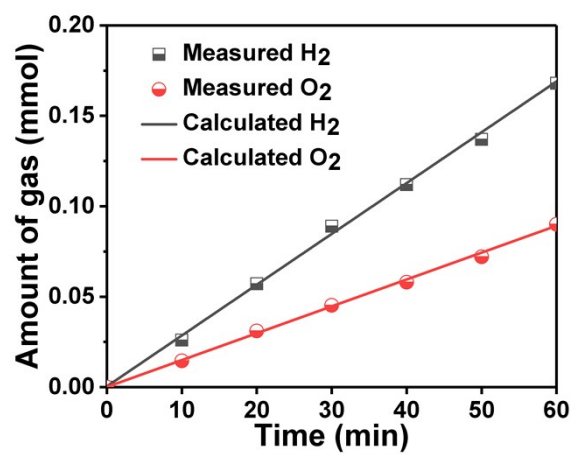


Fig. S10. The amount of gas theoretically calculated and experimentally measured versus time of overall water splitting for np-CeO₂||np-CeO₂.

Table S1. Comparison of HER performance for np-CeO₂/TM with other non-noble-metal electrocatalysts in alkaline electrolytes.

Catalyst	loading (mg cm ⁻²)	<i>j</i> (mA cm ⁻²)	<i>η</i> (mV)	Electrolyte	Reference
np-CeO ₂ /TM	1.9	10	91	1.0 M KOH	This work
	1.9	20	112		
NiCo ₂ S ₄ NA/CC	0.43	20	228	1.0 M KOH	2
Co-NRCNTs	0.28	20	~360	1.0 M KOH	3
Mo ₂ C	0.80	20	~360	1.0 M KOH	4
FeP NAs/CC	1.50	20	~370	1.0 M KOH	5
CoO _x @CN on GCE	0.42	20	~393	1.0 M KOH	6
PCPTF	0.10	20	~807	1.0 M KOH	7
Ni ₂ P	0.28	20	205	1.0 M KOH	8
WP ₂ SMPs	2	10	153	1.0 M KOH	9
MoS ₂ /Mo	1.2	10	184	1.0 M KOH	10
Ni ₃ S ₂ nanosheet/NF	1.6	10	223	1.0 M KOH	11

Table S2. Comparison of OER performance in alkaline electrolytes for np-CeO₂/TM with some reported non-noble-metal OER electrocatalysts.

Catalyst	loading (mg cm ⁻²)	<i>j</i> (mA cm ⁻²)	<i>η</i> (mV)	Electrolyte	Reference
np-CeO ₂ /TM	1.9	10	279	1.0 M KOH	This work
	1.9	20	323		
Co ₃ O ₄ NCs	0.35	20	~360	1.0 M KOH	12
Co-P	1	20	~370	1.0 M KOH	13
NiCo LDH	0.23	20	~393	1.0 M KOH	14
NiCo ₂ O ₄ NNs	0.53	20	~807	1.0 M KOH	15
Co-S/Ti mesh	--	10	340	1.0 M KOH	16
CoMn LDH	--	10	324	1.0 M KOH	17
CoCo LDH		10	393	1.0 M KOH	18

Table S3. Comparison of overall water splitting performance in 1.0 M KOH for np-CeO₂/TM with some reported non-noble-metal bifunctional electrocatalysts.

Catalyst	<i>j</i> (mA cm ⁻²)	<i>Voltage</i> <i>s</i> (V)	Reference
np-CeO ₂ /TM	10	1.57	This work
NiMo HNRs/TM	10	1.64	19
NiCo ₂ O ₄ microcuboid	10	1.65	20
EG/Co _{0.85} Se/NiFe-LDH	20	1.71	21
Ni-B/Ni foam	15	1.69	22
CoOx@CN	20	1.70	23
NiCoP NSAs	50	1.77	24
TiN@Ni ₃ N/Ti foil	10	1.67	25
NiFe/NiCo ₂ O ₄ /NF	10	1.67	26
CP/CTs/Co-S	10	1.743	27

References:

- 1 L. Niu, Z. Li, Y. Xu, J. Sun, W. Hong, X. Liu, J. Wang and S. Yang, Simple s of amorphous NiWO₄ nanostructure and Its application as a novel cathode material for asymmetric supercapacitors *ACS Appl. Mater. Interfaces*, 2013, **5**, 8044–8052.
- 2 D. Liu, Q. Lu, Y. Luo, X. Sun and A. M. Asiri, NiCo₂S₄ nanowires array as an efficient bifunctional electrocatalyst for full water splitting with superior activity *Nanoscale*. 2015, **7**, 15122–15126.
- 3 X. Zou, X. Huang, A. Goswami, R. Silva, B. R. Sathe, E. Mikmeková and A. Asefa, Nanoporous molybdenum carbide nanowire as an electrocatalyst for hydrogen evolution reaction. *Angew. Chem., Int. Ed.*, 2014, **53**, 4461–4465.
- 4 H. Vrubel and X. Hu, Molybdenum boride and carbide catalyze hydrogen evolution in both acidic and basic solutions. *Angew. Chem., Int. Ed.*, 2012, **51**, 12875–12878.
- 5 Y. Liang, Q. Liu, A. M. Asiri, X. Sun and Y. Luo, Self-supported FeP nanorod arrays: A cost-effective 3D hydrogen evolution cathode with high catalytic activity. *ACS Catal.*, 2014, **4**, 4065–4069.
- 6 H. Jin, J. Wang, D. Su, Z. Wei, Z. Pang and Y. Wang, In situ Cobalt–Cobalt Oxide/N–doped carbon hybrids as superior bifunctional electrocatalysts for hydrogen and oxygen evolution. *J. Am. Chem. Soc.*, 2015, **137**, 2688–2694.
- 7 Y. Yang, H. Fei, G. Ruan and J. M. Tour, Cobalt-based thin film as a bifunctional catalyst for hydrogen generation and oxygen generation. *Adv. Mater.*, 2015, **27**, 3175–3180.

- 8 E. J. Popczun, J. R. McKone, C. G. Read, A. J. Biacchi, A. M. Wiltrout, N. S. Lewis and R. E. Schaak, Nanostructured nickel phosphide as an electrocatalyst for the hydrogen evolution reaction *J. Am. Chem. Soc.*, 2013, **135**, 9267–9270.
- 9 Z. Xing, Q. Liu, A. M. Asiri and X. Sun, High-efficiency electrochemical hydrogen evolution catalyzed by tungsten phosphide submicroparticles. *ACS Catal.*, 2015, **5**, 145–149.
- 10 Z. Pu, Q. Liu, A. M. Asiri, Y. Luo, X. Sun and Y. He, 3D macroporous MoS₂ thin film: in Situ hydrothermal preparation and application as a highly active hydrogen evolution electrocatalyst at all pH values. *Electrochem. Acta.*, 2015, **168**, 133–138.
- 11 L. Feng, G. Yu, Y. Wu, G. Li, H. Li, Y. Sun, T. Asefa, W. Chen and X. Zou, High-index faceted Ni₃S₂ nanosheet arrays as highly active and ultrastable electrocatalysts for water splitting. *J. Am. Chem. Soc.*, 2015, **137**, 14023–14026.
- 12 S. Du, Z. Ren, J. Zhang, J. Wu, W. Xi, J. Zhu and H. Fu, Amorphous cobalt phyllosilicate with layered crystalline motifs as water oxidation catalyst. *Chem. Commun.*, 2015, **51**, 8066–8071.
- 13 N. Jiang, B. You, M. Sheng and Y. Sun, Metal–organic framework derived hybrid Co₃O₄–Carbon porous nanowire arrays as reversible oxygen evolution electrodes *Angew. Chem., Int. Ed.*, 2015, **54**, 6251–6255.
- 14 H. Liang, F. Meng, C. A. Miguel, L. Li, A. Forticaux, L. Xiu, Z. Wang and S. Jin, Hydrothermal continuous flow synthesis and exfoliation of NiCo layered double hydroxide nanosheets for enhanced oxygen evolution catalysis. *Nano. Lett.*, 2015,

- 15**, 1421–1427.
- 15 H. Shi and G. Zhao, Water oxidation on spinel NiCo₂O₄ nanoneedles anode: microstructures, specific surface character, and the enhanced electrocatalytic performance. *J. Phys. Chem. C*, 2014, **118**, 25939.
- 16 T. Liu, Y. Liang, Q. Liu, X. Sun, Y. He and A. M. Asiri, Electrodeposition of cobalt-sulfide nanosheets film as an efficient electrocatalyst for oxygen evolution reaction. *Electrochem. Commun.*, 2015, **60**, 92–96.
- 17 F. Song and X. Hu, Ni₂P as a janus catalyst for water splitting: The oxygen evolution activity of Ni₂P nanoparticles. *J. Am. Chem. Soc.*, 2014, **136**, 16481–16488.
- 18 F. Song and X. Hu, Exfoliation of layered double hydroxides for enhanced oxygen evolution catalysis. *Nat. Commun.*, 2014, **5**, 4477.
- 19 J. Tian, N. Cheng, Q. Liu, X. Sun, Y. He and A. M. Asiri, Self-Supported NiMo hollow nanorod array: An efficient 3D bifunctional catalytic electrode for overall water splitting *J. Mater. Chem. A*, 2015, **3**, 20056–20059.
- 20 X. Gao, H. Zhang, Q. Li, X. Yu, Z. Hong, X. Zhang, C. Liang and Z. Lin, hierarchical NiCo₂O₄ hollow microcuboids as bifunctional Electrocatalysts for overall water-splitting *Angew. Chem., Int. Ed.*, 2016, **55**, 6290–6294.
- 21 Y. Tan, H. Wang, P. Liu, Y. Shen, C. Cheng, A. Hirata, T. Fujita, Z. Tang and M. Chen, Nanoporous bimetallic phosphides towards electrochemical water splitting *Energy Environ. Sci.*, 2016, **9**, 2257–2261.
- 22 Y. Liang, X. Sun, A. M. Asiri and Y. He, Mn Doping of CoP Nanosheets Array:

- An Efficient Electrocatalyst for Hydrogen Evolution Reaction with Enhanced Activity at All pH Values. *Nanotechnol.*, 2016, **27**, 12LT01.
- 23 H. Jin, J. Wang, D. Su, Z. Wei, Z. Pang and Y. Wang, In situ Cobalt–Cobalt Oxide/N-Doped Carbon Hybrids as Superior Bifunctional Electrocatalysts for Hydrogen and Oxygen Evolution. *J. Am. Chem. Soc.*, 2015, **137**, 2688–2694.
- 24 Y. Li, H. Zhang, M. Jing, Y. Kuang, X. Sun and X. Duan, Ternary Nicop Nanosheet Arrays: An Excellent Bifunctional Catalyst for Alkaline Overall Water Splitting. *Nano Res.*, 2016, **9**, 251–2259.
- 25 Q. Zhang, Y. Wang, Y. Wang, A. M. Alenizi, A. A. Elzatahry and G. Zheng, Myriophyllum-Like Hierarchical Tin@Ni₃N Nanowire Arrays for Bifunctional Water Splitting Catalysts *J. Mater. Chem. A*, 2016, **4**, 5713–5718.
- 26 C. Xiao, Y. Li, X. Lu and C. Zhao, Foam Electrodes with Triple Hierarchy and Double Synergies for Efficient Whole Cell Water Splitting. *Adv. Funct. Mater.*, 2016, **26**, 3515–3523.
- 27 J. Wang, H. Zhong, Z. Wang, F. Meng and X. Zhang, Integrated Three-Dimensional Carbon Paper/Carbon Tubes/Cobalt–Sulfide Sheets as an Efficient Electrode for Overall Water Splitting *ACS Nano.*, 2016, **10**, 2342–2348.