Electronic Supplementary Information

Experimental section

Materials: Lithium chloride anhydrous, selenium dioxide, nickel acetate tetrahydrate and ruthenium chloride hydrate were purchased from Aladdin Ltd. (Shanghai, China). Pt/C (20 wt% Pt on Vulcan XC-72R) and Nafion (5 wt%) were purchased from Sigma-Aldrich Chemical Reagent Co., Ltd. KOH, ethanol, and HCl were purchased from Tianjin Chemical Corporation. All chemicals were used as received without further purification. Copper foam was purchased from Kunshan Desco Electronics Co., Ltd. The water use throughout all experiments was purified through a Millipore system (18.2 MΩ).

Preparation of Ni_3Se_2 on Cu foam (Ni_3Se_2/CF): Before Ni_3Se_2 electrodeposition, copper foam was pretreated by 3 wt% HCl for 2 h at ambient atmosphere. Then, the obtained HCl-treated copper foam was rinsed with deionized water purged with Ar and dried in vacuum oven. The obtained copper foam (CF) was kept under Ar atmosphere. The electrodeposition was performed in a typical three-electrode cell configuration, where the reference electrode is a saturated calomel electrode (SCE) and the counter electrode is graphite flake, using a CHI 660E electrochemical analyzer (CH Instruments, Inc. Shanghai). Ni_3Se_2/CF catalyst was prepared according to reported method with minor modifications.[1,2] The electrolyte bath comprised of 13 mmol nickel acetate tetrahydrate, 7 mmol selenium dioxide and 40 mmol lithium chloride anhydrous (200 mL). The experiment was performed at room temperature (25˚C) under N_2 blanket without stirring. The pH was maintained at 3.5 using HCl. HCl can also prevent the formation of hydroxyl species and insoluble compound. Electrodeposition was effected by CF (1 cm × 1 cm) potentiostatically biasing the CF at a potential of -0.5 V vs. SCE for 1 h at ambient atmosphere. After deposition, the sample was removed from the compression cell and rinsed with deionized water and ethanol several times and then dried at 60 °C for 10 h in vacuum oven.

Preparation of Pt/C and RuO_2 loaded electrodes: RuO_2 catalyst was prepared according to reported method.[3] In brief, 0.1 M $RuCl_3 \cdot 3H_2O$ was put into a flask and maintained at 100°C for 10 min under air atmosphere and then the addition of 1 mL KOH solution (1 M). The mixture was maintained at this temperature under stirring for another 45 min. After that, the solution was centrifuged and filtered to get precipitate. The obtained precipitate was then washed several times with deionized water to remove the remaining chlorides. The resulting Ru-hydroxide was dried for 5 h at 80°C and then calcined in air at 300°C for 3 h to obtain RuO_2. To prepare Pt/C and RuO_2 loaded electrodes, 20 mg Pt/C or RuO_2 and 10 μL 5 wt% Nafion solution were dispersed in 1 mL 1:1 v water/ethanol solvent by 30-min sonication to form an ink finally. Then 150 μL catalyst ink was loaded on a CF with a catalyst loading of 3.0 mg cm^{-2}.

Characterizations: XPS measurements were performed on an ESCALABMK II X-ray photoelectron spectrometer using Mg as the exciting source. XRD measurements were performed using a RigakuD/MAX 2550 diffractometer with Cu Kα radiation (λ=1.5418 Å). SEM images were taken on a XL30 ESEM. TEM measurements were made on a HITACHI H-8100 electron microscopy (Hitachi, Tokyo, Japan) with an accelerating voltage of 200 kV. Gas chromatography (GC) measurements were conducted on GC-2014C (Shimadzu Co.) with thermal conductivity detector and nitrogen carrier gas. The generated gas was confirmed by GC analysis.

Electrochemical characterization: Electrochemical measurements are performed with a CHI 660D electrochemical analyzer. A typical three-electrode cell was used. The Ni_3Se_2/CF used as the working electrode, a saturated calomel electrode (SCE) used as the reference electrode, and graphite plate used as the counter electrode. The measurements were conducted in 1.0 M KOH solution. All the potentials reported in our work were vs. the reversible hydrogen electrode (RHE) according to E (RHE) = E (SCE) + 0.059 pH + 0.242 V. The long-term durability test was performed using chronopotentiometric measurements. All currents presented are corrected against the ohmic potential drop.

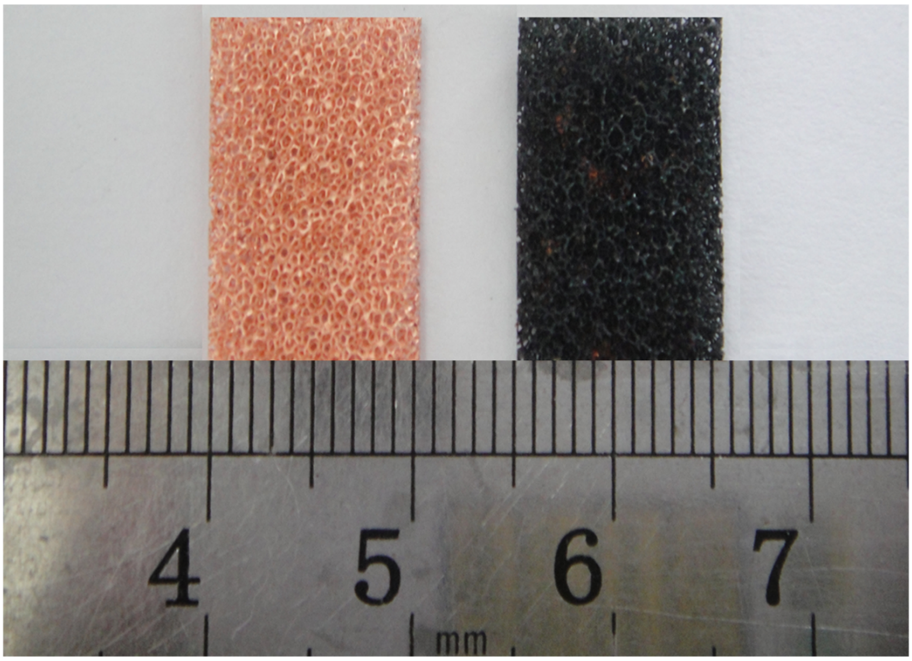
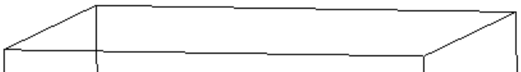


Fig. S1 Photograph of the bare CF (left) and Ni_3Se_2/CF (right).

Fig. S2 Arrangement of Ni and Se atoms in the rhombohedral unit cell for Ni_3Se_2.



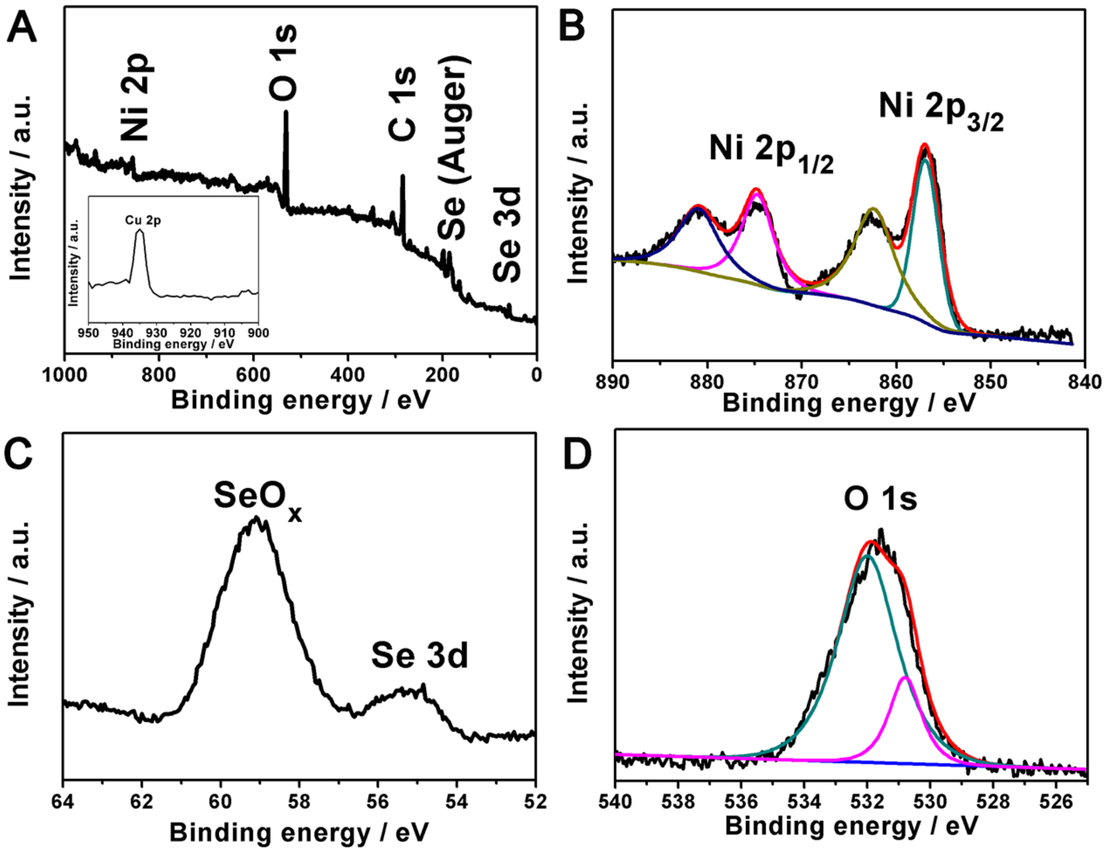


Fig. S3 (A) XPS survey spectrum for Ni_3Se_2/CF. Inset: zoom in window of the survey spectrum (900-950 eV). XPS spectra in the (B) Ni 2p, (C) Se 3d, and (D) O 1s regions.

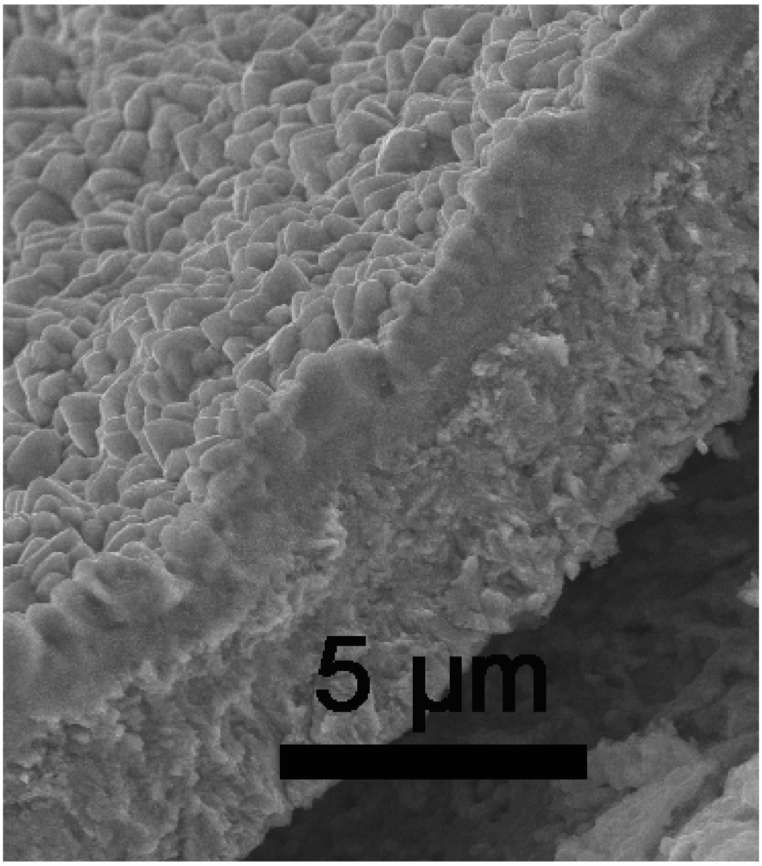


Fig. S4 Cross-section SEM image of Ni_3Se_2/CF.

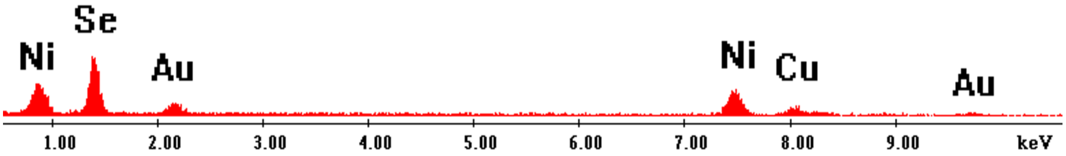


Fig. S5 EDX spectrum of the Ni_3Se_2/CF.

Catalyst	η@10 mA cm^{-2}（mV）	Ref
Ni_3Se_2/CF	100	This work
Ni_2P particles	~220	4
Ni_2P	~175	5
Ni_5P_4	~150	6
NiFe LDH/NF	~210	7
CoO_x@CN	232	8
Co-P	94	9
PCPTF	~380	10

Table S1 Comparison of HER performance in 1.0 M KOH for Ni_3Se_2/CF with other electrocatalysts.

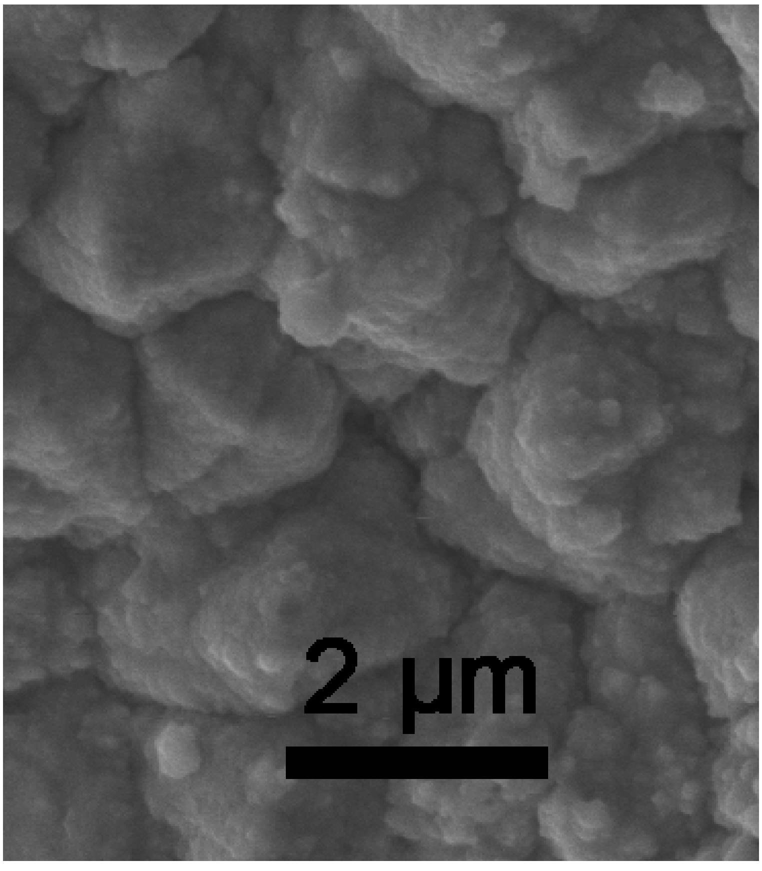

2 µm

Fig. S6 SEM image of the post-HER Ni_3Se_2/CF in 1.0 M KOH.

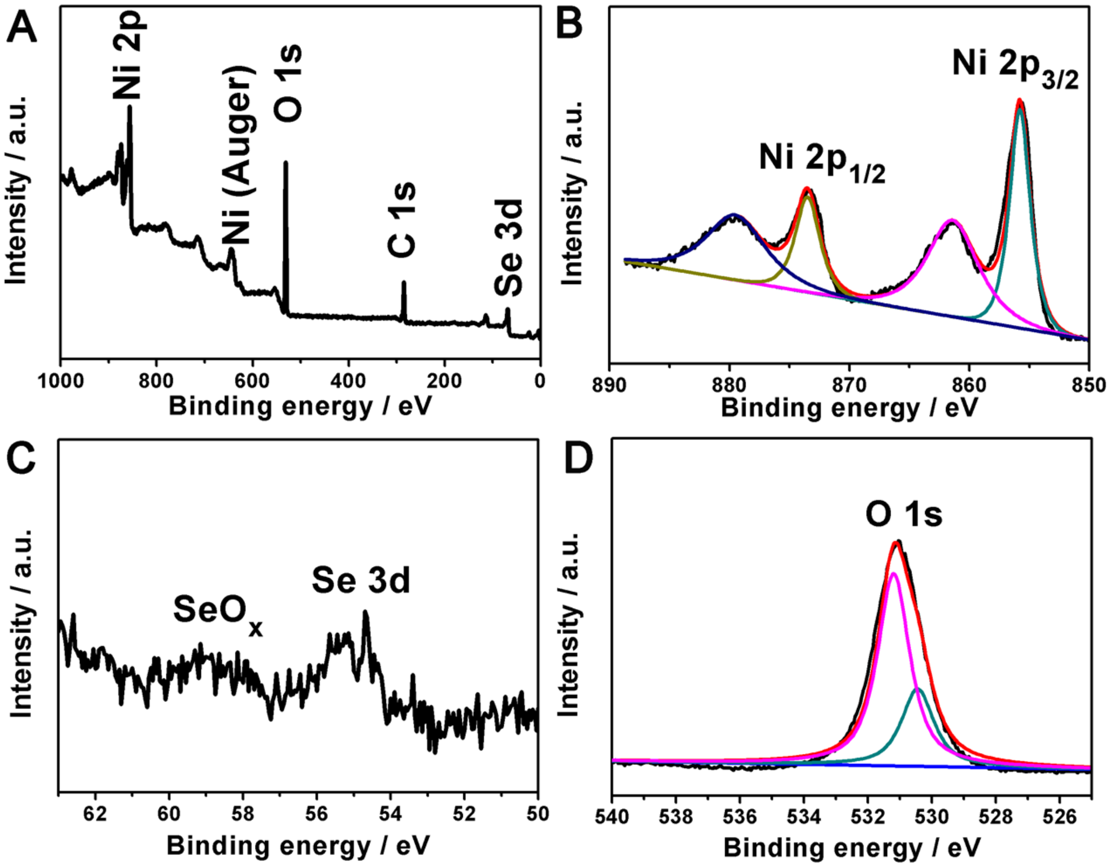


Fig. S7 (A) XPS survey spectrum of the post-HER Ni_3Se_2/CF. XPS spectra in the (B) Ni 2p, (C) Se 3d, and (D) O 1s regions.

Table S2 Comparison of OER performance in alkaline for Ni_3Se_2/CF with other electrocatalysts.

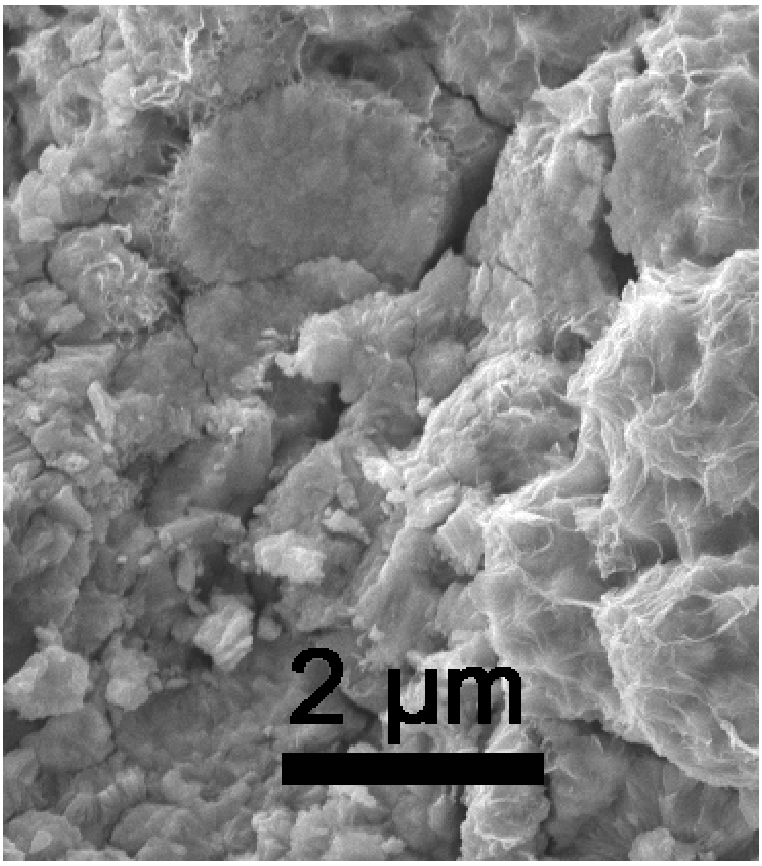


Fig. S8 SEM image of the post-OER Ni_3Se_2/CF in 1.0 M KOH.

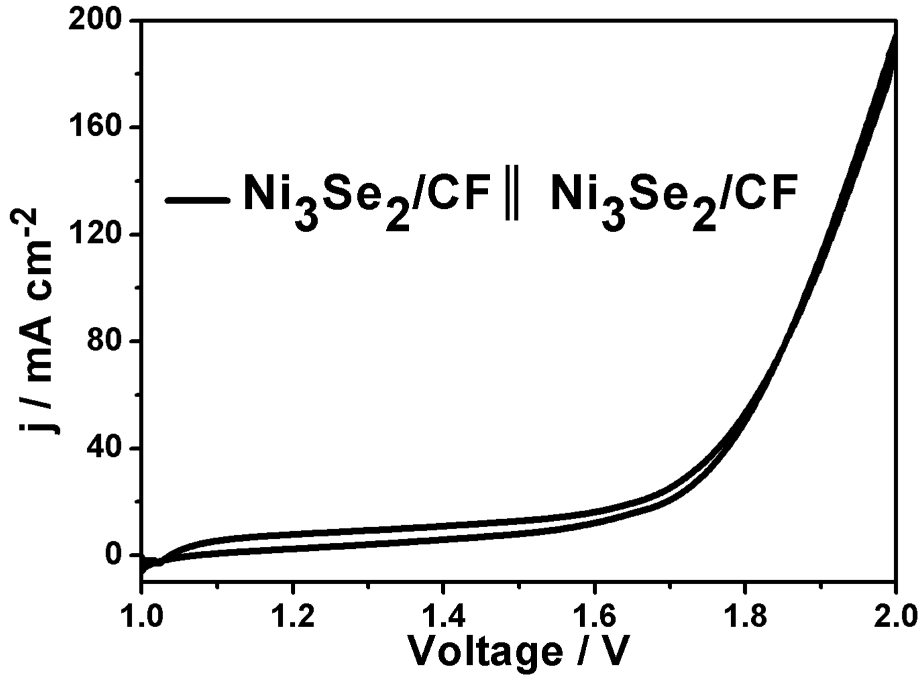


Fig. S9 CV curve for Ni_3Se_2/CF‖Ni_3Se_2/CF in a two-electrode configuration at a scan rate of 10 mV s^{-1} in 1.0 M KOH solution.

Table S3 Comparison of overall water splitting performance in alkaline for Ni_3Se_2/CF with other electrocatalysts.

Catalyst	Electrolyte	Voltage@10 mA cm^{-2} (V)	Ref
Ni_3Se_2/CF	1.0 M KOH	1.65	This work
Ni_2P	1.0 M KOH	1.63	5
Ni_5P_4	1.0 M KOH	1.7	6
NiFe LDH/NF	1.0 M KOH	1.70	7
Co-P	1.0 M KOH	1.65	9
Co_3O_4NCs/carbon fiber paper	1.0 M KOH	1.91	11
$Ni_{0.33}Co_{0.67}S_2$	1.0 M KOH	~1.72	13

Reference

1 K. Anuar, Z. Zainal, N. Saravanan and A.R. Kartini, *AJSTD,* 2004, **21**, 19.

2 A. I. Carim, F. H. Saadi, M. P. Soriaga and N. S. Lewis, *J. Mater. Chem. A,* 2014, **2**, 13835.

3 J. C. Cruz, V. Baglio, S. Siracusano, V. Antonucci, A. S. Aric, R. Ornelas, L. Ortiz-Frade, G. Osorio-Monreal, S. M. Durn-Torres and L. G. Arriaga, *Int. J. Electrochem. Sci.,* 2011, **6**, 6607.

4 L. Feng, H. Vrubel, M. Bensimon and X. Hu, *Phys. Chem. Chem. Phys*., 2014, **16**, 5917.

5 L-A. Stern, L. Feng, F. Song and X. Hu, *Energy Environ. Sci.,* 2015, **8**, 2347.

6 M. Ledendecker, S. Krick Calderón, C. Papp, H. P. Steinrück, M. Antonietti, and M. Shalom, *Angew. Chem. Int. Ed.,* 2015, **127**, 1.

7 J. Luo, J.-H. Im, M. T. Mayer, M. Schreier, M. K. Nazeeruddin, N. G. Park, S. D. Tilley, H. Fan and M. Grätzel, *Science*, 2014, **345**, 1593.

8 H. Jin, J. Wang, D. Su, Z. Wei, Z. Pang and Y. Wang, *J. Am. Chem. Soc.*, 2015, **137**, 2688.

9 N. Jiang, B. You, M. Sheng and Y. Sun, *Angew. Chem. Int. Ed.*, 2015, **54**, 6251.

10 Y. Yang, H. Fei, G. Ruan and J. M. Tour, *Adv. Mater.,* 2015, **27**, 3175.

11 S. Du, Z. Ren, J. Zhang, J. Wu, W. Xi, J. Zhu and H. Fu, *Chem. Commun.,* 2015, **51**, 8066.

12 M. Shalom, D. Ressnig, X. Yang, G. Clavel, T. P. Fellinger and M. Antonietti, *J. Mater. Chem. A,* 2015, **3**, 8171.

13 Z. Peng, D. Jia, A. M. Al-Enizi, A. A. Elzatahry and G. Zheng, *Adv. Energy Mater.,* 2015, **1402031,** 1.