Electronic Supplementary Information (ESI)

Template synthesis of CoSe₂/Co₃Se₄ nanotubes: tuning the crystal structures for photovoltaics and hydrogen evolution in alkaline medium

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Fig. S1 Thermogravimetric curve of Co_3Se_4 NTs samples. This TGA has four distinct stage of weight losses. The first weight loss stage (A stage) ended at ~85 °C, stemming from evaporation of trace water. The second weight loss (B stage) at the temperature ranging from 85 to 340 °C was attributed to the Co_3Se_4 reacting with Se to form o- $CoSe_2$. The third weight loss (C stage) at the temperature ranging from 340 to 410 °C may be associated with the evaporation of Se. Following this, the o- $CoSe_2$ converted to c- $CoSe_2$ companying with the evaporation of Se at the temperature ranging from 410 to 600 °C (D stage).



Fig. S2 XRD patterns of the $Co(CO_3)_{0.35}Cl_{0.20}(OH)_{1.10} \cdot 1.74H_2O$ sample.



Fig. S3 SEM images of the (a) o-CoSe₂ and (b) Co₃Se₄ NPs.



Fig. S4 TEM images of the (a) o-CoSe₂ and (b) c-CoSe₂.



Fig. S5 (a) The survey spectrum of o-CoSe₂, c-CoSe₂ and Co₃Se₄ NTs. (b) Co 2p XPS spectra of c-CoSe₂. (c) Se 3d XPS spectra of c-CoSe₂.



Fig. S6 N_2 adsorption-desorption isotherm of Co_3Se_4 NPs.



Fig. S7 (a) and (b) SEM images of Co_3Se_4 after the DSSC and HER tests, respectively. (c) and (d) SEM images of o-CoSe₂ after the DSSC and HER tests, respectively.



Fig. S8 XRD patterns of the Co_3Se_4 NTs and $o-CoSe_2$ after the HER stability test in 1.0 M KOH.



Fig. S9 Cyclic voltammograms of (a) o-CoSe₂, (b) c-CoSe₂, (c) Co₃Se₄ NTs and (d) Co₃Se₄ NPs at different scan rates (10, 20, 40, 60, 80, 100 and 120 mV s⁻¹) in 1.0 M KOH.



Fig. S10 Calculation of exchange current density of o-CoSe₂, c-CoSe₂, Co₃Se₄ NTs and Co₃Se₄ NPs.

The exchange current density (J_0) was calculated using extrapolation methods. When the overpotential value is 0, the log (J) values for o-CoSe₂, c-CoSe₂, Co₃Se₄ NTs and Co₃Se₄ NPs are -0.83, -0.89, -0.96 and -1.12, respectively. Based on Tafel equations, J_0 values for o-CoSe₂, c-CoSe₂, Co₃Se₄ NTs and Co₃Se₄ NPs were calculated to be 0.15, 0.13, 0.11 and 0.08 mA cm⁻², respectively.

| Catalysts | Onset potential | $\eta_{10}(\mathrm{mV})$ | Tafel slope | References |
|--------------------------------------|-----------------|--------------------------|--------------------|------------|
| | (mV) | | $(mV decade^{-1})$ | |
| Ni ₂ P | 100 | 225 | 100 | 1 |
| nanoparticles | | | | |
| Ni-Co-P-300 | | 150 | 60.6 | 2 |
| CoP nanowire | 80 | 209 | 129 | 3 |
| arrays | | | | |
| Co@N-C | | 210 | 108 | 4 |
| Ni ₅ P ₄ films | | 150 | 53 | 5 |
| CoO _x /CN | 85 | 232 | 114 | 6 |
| NiP ₂ nanosheet | 74 | 102 | 65 | 7 |
| arrays | | | | |
| WN nanorod | | 285 | 170 | 8 |
| arrays | | | | |
| MoB | 140 | 225 | 59 | 9 |
| Co-Ni-B | | 133 | 121 | 10 |
| CoS ₂ pyramids | | 244 | 133 | 11 |
| CoSe ₂ /CF | | 95 | 52 | 12 |
| o-CoSe ₂ | 54 | 124 | 65.9 | This work |

Table S1 Comparison of HER performance in alkaline medium for as-obtained samples with other non-noble metal-based catalysts.

References

- L. G. Feng, H. Vrubel, M. Bensimon and X. L. Hu, *Phys. Chem. Chem. Phys.*, 2014, 16, 5917–5921.
- 2 Y. Feng, X.-Y. Yu and U. Paik, Chem. Commun., 2016, 52, 1633-1636.
- 3 J. Q. Tian, Q. Liu, A. M. Asiri and X. P. Sun, J. Am. Chem. Soc., 2014, 136, 7587– 7590.
- 4 J. Wang, D. F. Gao, G. X. Wang, S. Miao, H. H. Wu, J. Y. Li and X. H. Bao, *J. Mater. Chem. A*, 2014, **2**, 20067–20074.
- 5 M. Ledendecker, S. Krick Calderon, C. Papp, H. P. Steinruck, M. Antonietti and M. Shalom, *Angew. Chem., Int. Ed.*, 2015, **54**, 12361–12365.
- 6 H. Y. Jin, J. Wang, D. F. Su, Z. Z. Wei, Z. F. Pang and Y. Wang, *J. Am. Chem. Soc.*, 2015, **137**, 2688–2694.
- 7 P. Jiang, Q. Liu and X. P. Sun, Nanoscale, 2014, 6, 13440–13445.
- 8 J. L. Shi, Z. H. Pu, Q. Liu, A. M. Asiri, J. M. Hu and X. P. Sun, *Electrochim. Acta*, 2015, **154**, 345–351.

- 9 H. Vrubel and X. L. Hu, Angew. Chem., Int. Ed., 2012, 51, 12703-12706.
- 10 S. Gupta, N. Patel, R. Fernandes, R. Kadrekar, A. Dashora, A. K. Yadav, D. Bhattacharyya, S. N. Jha, A. Miotello and D. C. Kothari, *Appl. Catal.*, *B*, 2016, **192**, 126–133.
- 11 H. C. Zhang, Y. J. Li, G. X. Zhang, P. B. Wan, T. H. Xu, X. C. Wu and X. P. Sun, *Electrochim. Acta*, 2014, **148**, 170–174.
- 12 C. S. Sun, Q. C. Dong, J. Yang, Z. Y. Dai, J. J. Lin, P. Chen, W. Huang and X. C. Dong, *Nano Res.*, 2016, **9**, 2234–2243.