Electronic Supplementary Material (ESI) for Inorganic Chemistry Frontiers.


**Electronic Supplementary Material**

# Rational design of Co-S-P nanosheet arrays as bifunctional electrocatalysts for both ethanol oxidation reaction and hydrogen evolution reaction

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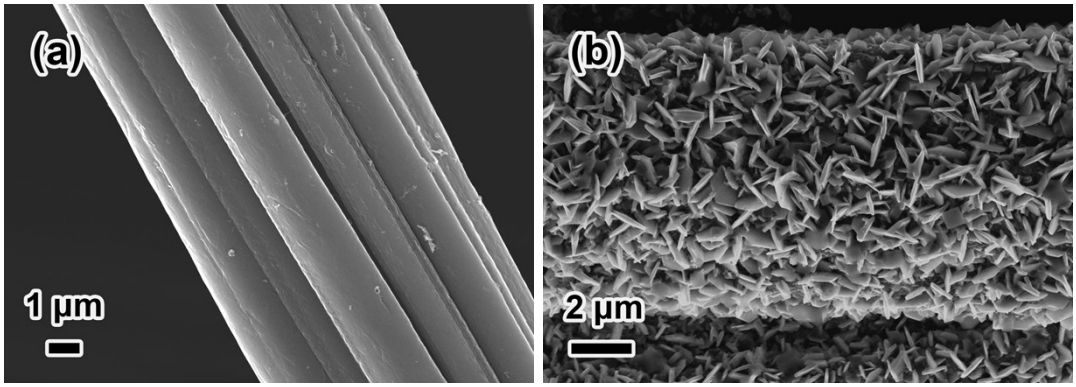


**Fig. S1.** SEM images of bare carbon cloth (a) and $CoS_2$/CC electrode (b).

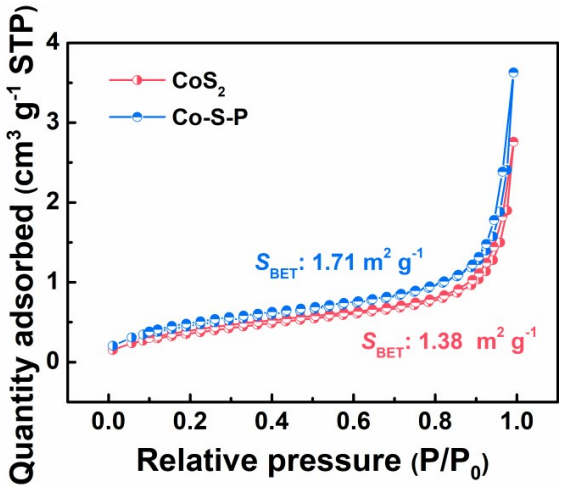


**Fig. S2.** Nitrogen adsorption-desorption isotherms of $CoS_2$ and Co-S-P.

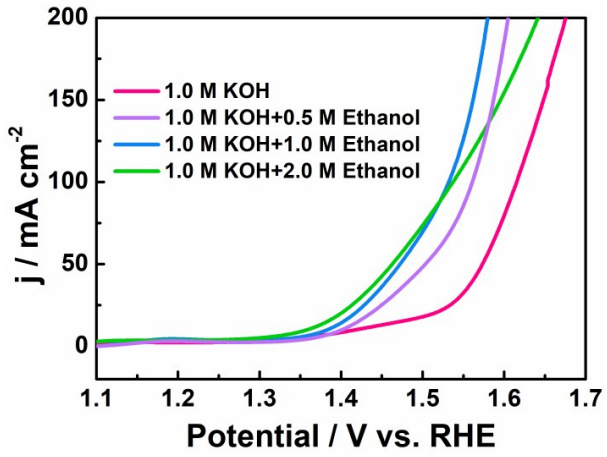


**Fig. S3.** LSV curves of Co-S-P/CC electrode for OER, EOR and collected using various contents of ethanol as an electrolyte.

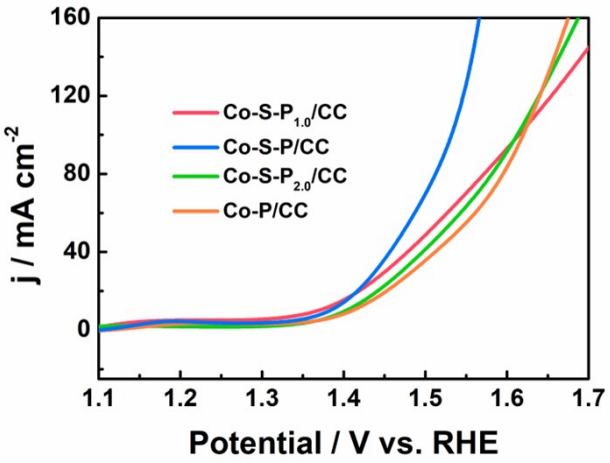


**Fig. S4.** LSV polarization curves of the Co-S-$P_{1.0}$/CC, Co-S-P/CC, Co-S-$P_{2.0}$ and CoP/CC toward EOR.

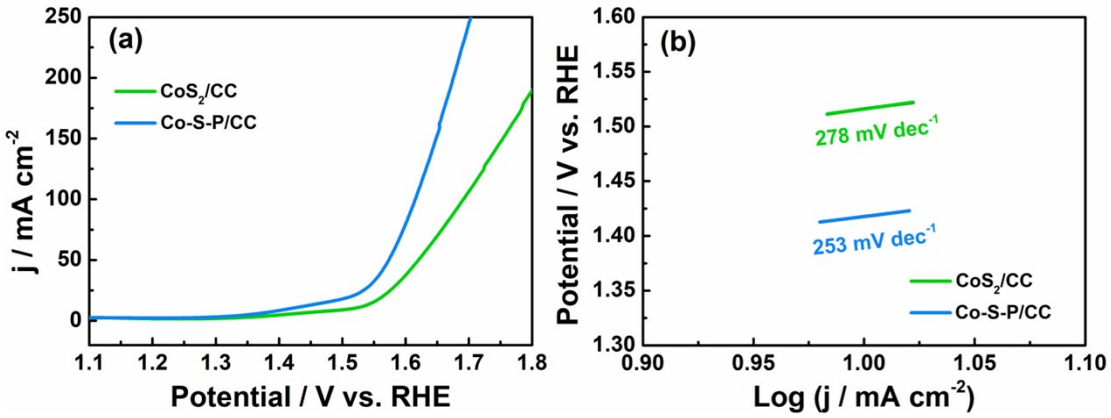


**Fig. S5.** (a) LSV polarization curves of the $CoS_2$/CC and Co-S-P/CC in 1.0 M KOH electrolyte. (b) The corresponding Tafel plots.

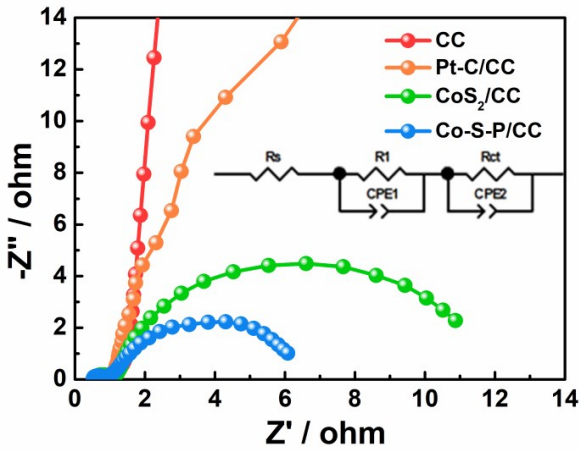


**Fig. S6.** Nyquist plots of the bare CC, $CoS_2$/CC, Co-S-P/CC catalysts for EOR process at 1.38 V vs. RHE.

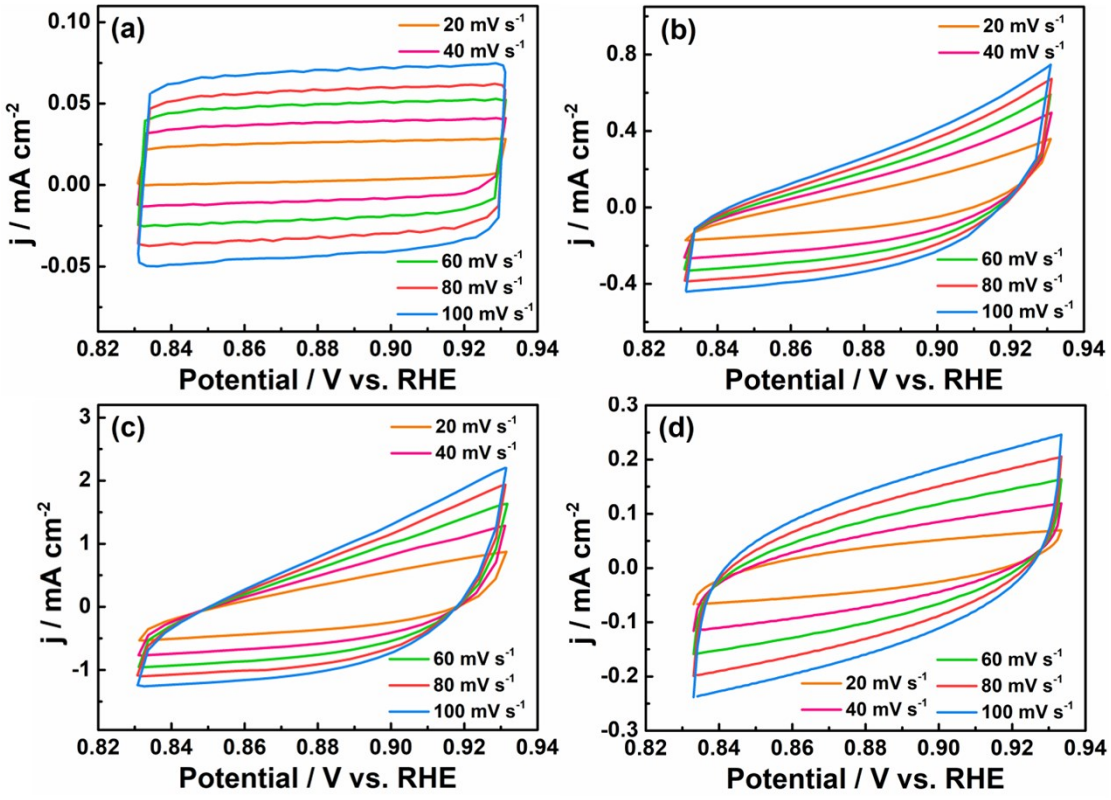


**Fig. S7.** CV curves for (a) bare CC, (b) $CoS_2$/CC, (c) Co-S-P/CC and (d) Pt-C/CC electrodes in a potential range of 0.83~0.93 V vs. RHE with scan rates from 20 to 100 mV $s^{-1}$ upon EOR catalysis.

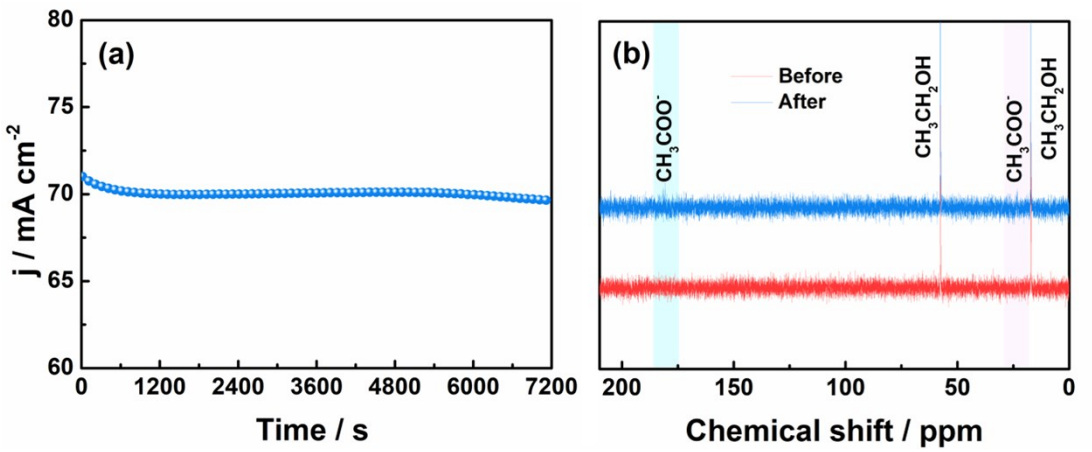


**Fig. S8.** (a) Chronoamperometric curves of Co-S-P/CC electrode at a potential of 1.5 V vs. RHE for 2 h. (b) $^{13}C$ NMR spectra of electrolyte before and after oxidation reaction.

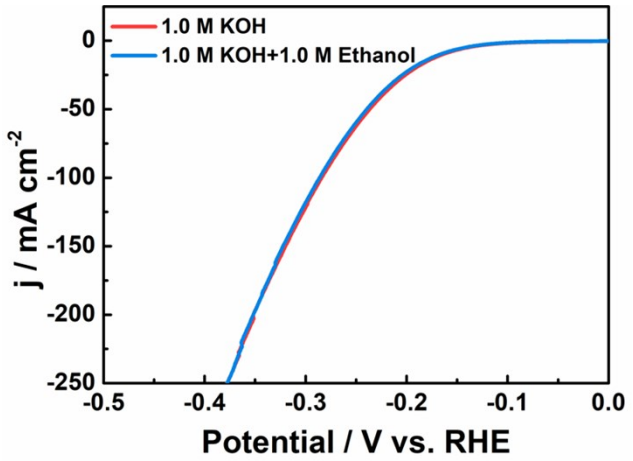


**Fig. S9.** LSV polarization curves of the Co-S-P/CC electrode at a scan rate of 5 mV $s^{-1}$ in 1.0 M KOH with and without 1.0 M ethanol for HER.

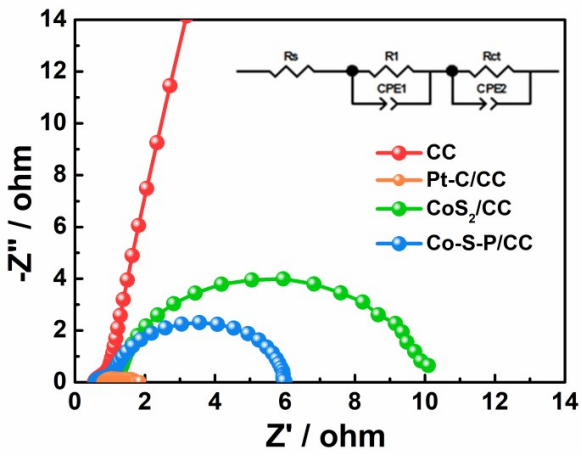


**Fig. S10.** Nyquist plots of the bare CC, $CoS_2$/CC, Co-S-P/CC catalysts at an overpotential of 200 mV toward HER.

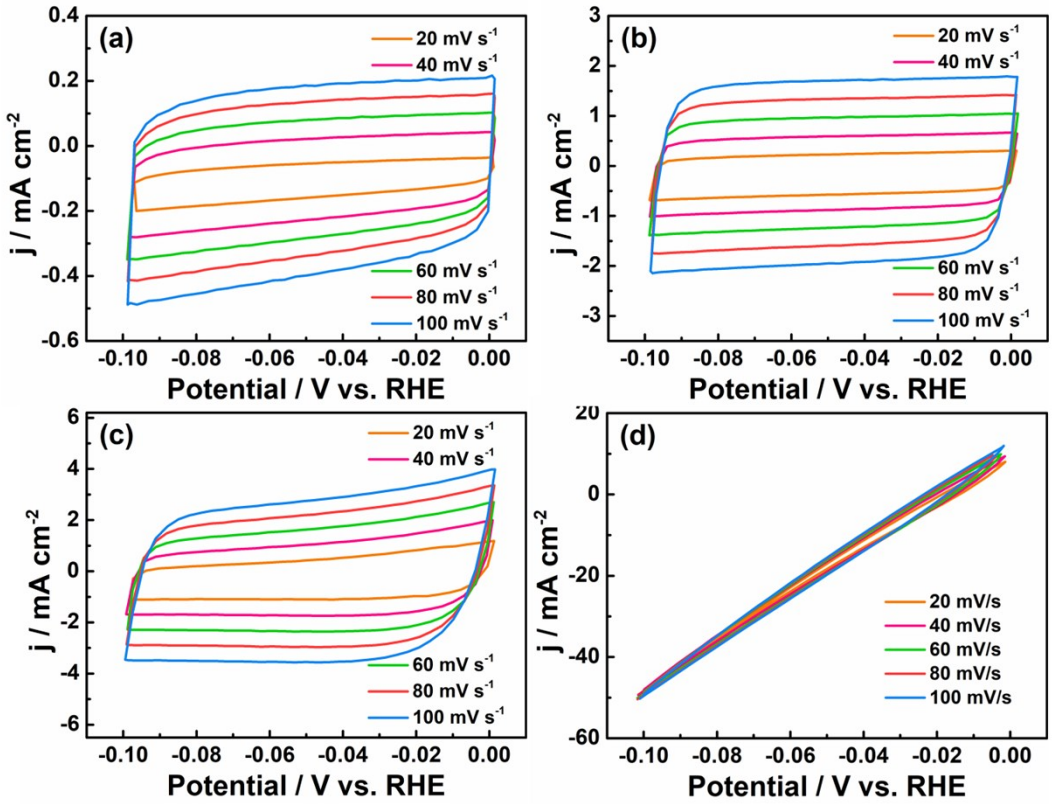


**Fig. S11.** CV curves for (a) bare CC, (b) $CoS_2$/CC, (c) Co-S-P/CC and (d) Pt-C/CC electrodes in a potential range of –0.1~0 V vs. RHE with various scan rates for HER catalysis.

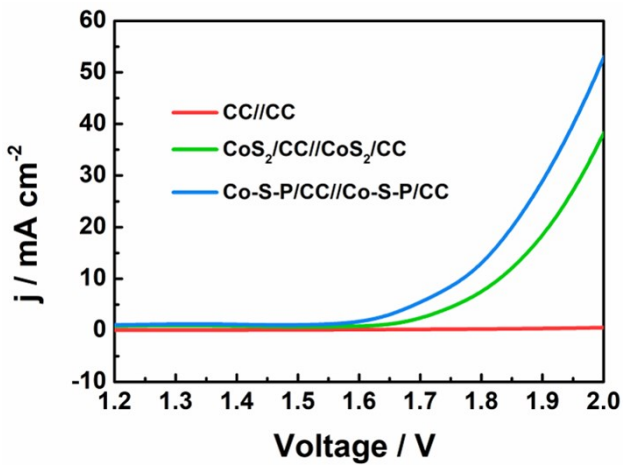


**Fig. S12.** Full water splitting performance of the CC, $CoS_2$/CC and Co-S-P/CC in a two-electrode system.

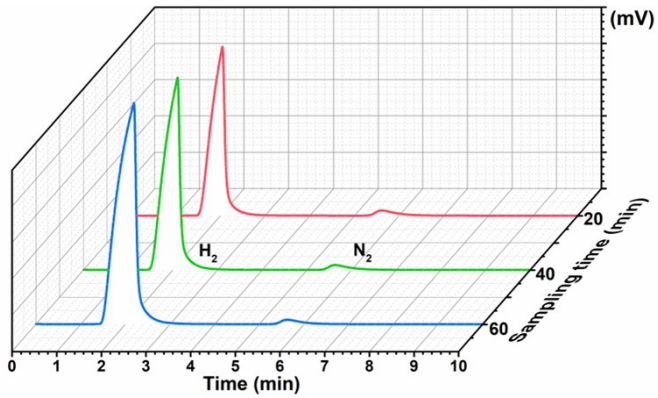


**Fig. S13.** Chromatograms of real-time electrolysis product of Co-S-P/CC//Co-S-P/CC electrolyser.

**Table S1.** Comparison with the performance of electrocatalytic ethanol oxidation catalysts reported in the previous literature

| Catalysts | Electrolyte | Current density at 1.5 V vs. RHE (mA $cm^{-2}$) | Potential at 10 mA $cm^{-2}$ (V) | Electrolyte product | Ref. |
|---|---|---|---|---|---|
| Perforated CoNi hydroxide nanosheets | 1.0 M KOH with 1.0 M ethanol | 57 | 1.39 | acetic acid | 1 |
| NGr–NiO/ITO | 0.5 M NaOH with 1.0 M ethanol | 3 | - | - | 2 |
| MgFe layered double hydroxide | 1.0 M NaOH with 1.0 M ethanol | 2.2 | - | - | 3 |
| NiAl layered double hydroxide | 1.0 M NaOH with 1.0 M ethanol | 40 | 1.72 | Acetaldehyde acetic acid | 4 |
| NiFe layered double hydroxide | 1.0 M KOH with 1.0 M ethanol | 1.2 | - | - | 5 |
| NiFe LDH@$MnO_2$ spheres | 1.0 M KOH with 1.0 M ethanol | 4 | >1.70 | - | 5 |
| **Co-S-P/CC** | 1.0 M KOH with 1.0 M ethanol | 70 | 1.38 | acetic acid | This work |

**Table S2.** Comparison with the performance of electrocatalytic HER catalysts reported in the previous literature

| Catalysts | Electrolyte | Overpotential at 10 mA $cm^{-2}$ | Tafel slope ($mV\ dec^{-1}$) | Ref. |
|---|---|---|---|---|
| PdCu Alloy Nanosheets | 1.0 M KOH | 106 mV | 124 | 6 |
| PdCu Alloy Nanoparticles | 1.0 M KOH | 182 mV | 170 | 6 |
| $Ni_3S_2$ | 1.0 M KOH | 335 mV | 97 | 7 |
| $CoNi_2S_4$@$CoS_2$/NF | 1.0 M KOH | 173 mV | 51 | 8 |
| $CoNi_2O_4$@$Co_3O_4$/NF | 1.0 M KOH | 206 mV | 92 | 8 |
| $NiS_2$/CFC | 1.0 M KOH | 210 mV | 114 | 9 |
| Carbon Paper/Carbon Tubes/C-S Sheets | 1.0 M KOH | 190 mV | 131 | 10 |
| **Co-S-P/CC** | 1.0 M KOH with 1.0 M ethanol | 167 mV | 86 | This work |

**Reference**


1. W. Wang, Y. B. Zhu, Q. Wen, Y. Wang, J. Xia, C. Li, M. W. Chen, Y. Liu, H. Li, H. A. Wu and T. Zhai, Modulation of molecular spatial distribution and chemisorption with perforated nanosheets for ethanol electro-oxidation, *Adv. Mater.*, 2019, **31**, 1900528.
2. A. A. Daryakenari, D. Hosseini, Y. L. Ho, T. Saito, A. Apostoluk, C. R. Müller and J. J. Delaunay, Single-step electrophoretic deposition of non-noble metal catalyst layer with low onset voltage for ethanol electro-oxidation, *ACS Appl. Mater. Interfaces*, 2016, **8**, 15975-15984.
3. M. Shao, F. Ning, J. Zhao, M. Wei, D. G. Evans and X. Duan, Hierarchical layered double hydroxide microspheres with largely enhanced performance for ethanol electrooxidation, *Adv. Funct. Mater.*, 2013, **23**, 3513-3518.
4. L. Xu, Z. Wang, X. Chen, Z. Qu, F. Li and W. Yang, Ultrathin layered double hydroxide nanosheets with Ni(III) active species obtained by exfoliation for highly efficient ethanol electrooxidation, *Electrochim. Acta*, 2018, **260**, 898-904.
5. Z. Jia, Y. Wang and T. Qi, Hierarchical Ni-Fe layered double hydroxide/$MnO_2$ sphere architecture as an efficient noble metal-free electrocatalyst for ethanol electro-oxidation in alkaline solution, *RSC Adv.*, 2015, **5**, 83314-83319.
6. X. Zhao, L. Dai, Q. Qin, F. Pei, C. Hu and N. Zheng, Self-supported 3D PdCu alloy nanosheets as a bifunctional catalyst for electrochemical reforming of ethanol, *Small*, 2017, **13**, 1602970
7. N. Jiang, Q. Tang, M. Sheng, B. You, D. Jiang and Y. Sun, Nickel sulfides for electrocatalytic hydrogen evolution under alkaline conditions: a case study of crystalline NiS, $NiS_2$, and $Ni_3S_2$ nanoparticles, *Catal. Sci. Technol.*, 2016, **6**, 1077-1084.
8. R. Huang, W. Chen, Y. Zhang, Z. Huang, H. Dai, Y. Zhou, Y. Wu and X. Lv, Well-designed cobalt-nickel sulfide microspheres with unique peapod-like structure for overall water splitting, *J. Colloid Interface Sci.*, 2019, **556**, 401-410.
9. T. Wu, X. Zhu, G. Wang, Y. Zhang, H. Zhang and H. Zhao, Vapor-phase hydrothermal growth of single crystalline $NiS_2$ nanostructure film on carbon fiber cloth for electrocatalytic oxidation of alcohols to ketones and simultaneous $H_2$ evolution, *Nano Res.*, 2017, **11**, 1004-1017.
10. J. Wang, H. X. Zhong, Z. L. Wang, F. L. Meng and X. B. Zhang, Integrated three-dimensional carbon paper/carbon tubes/cobalt-sulfide sheets as an efficient electrode for overall water wplitting, *ACS Nano*, 2016, **10**, 2342-2348.