

## Supporting Information

### Metal Organic Frameworks (MOFs) Derived Iron Phosphide as Highly Stable and Efficient Catalyst for Hydrogen Evolution

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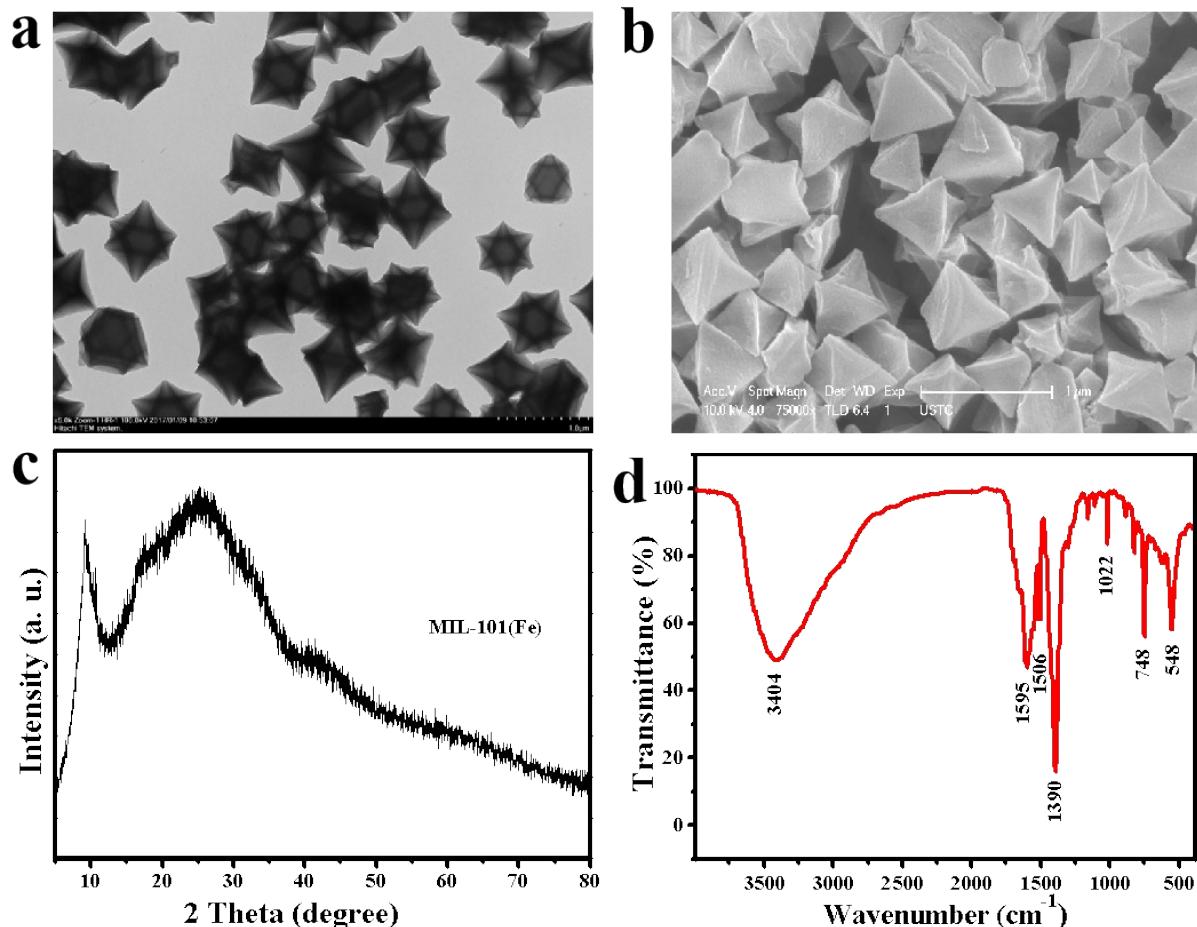
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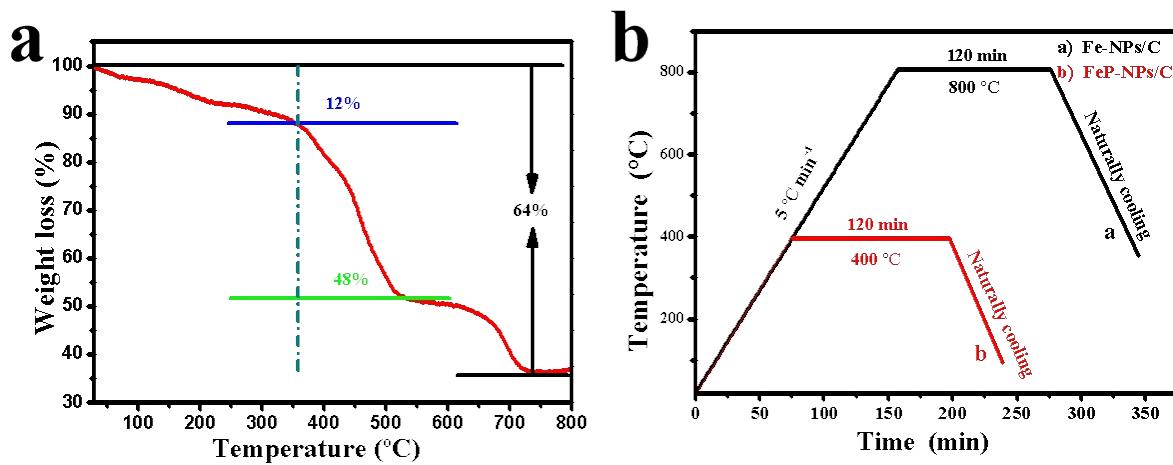
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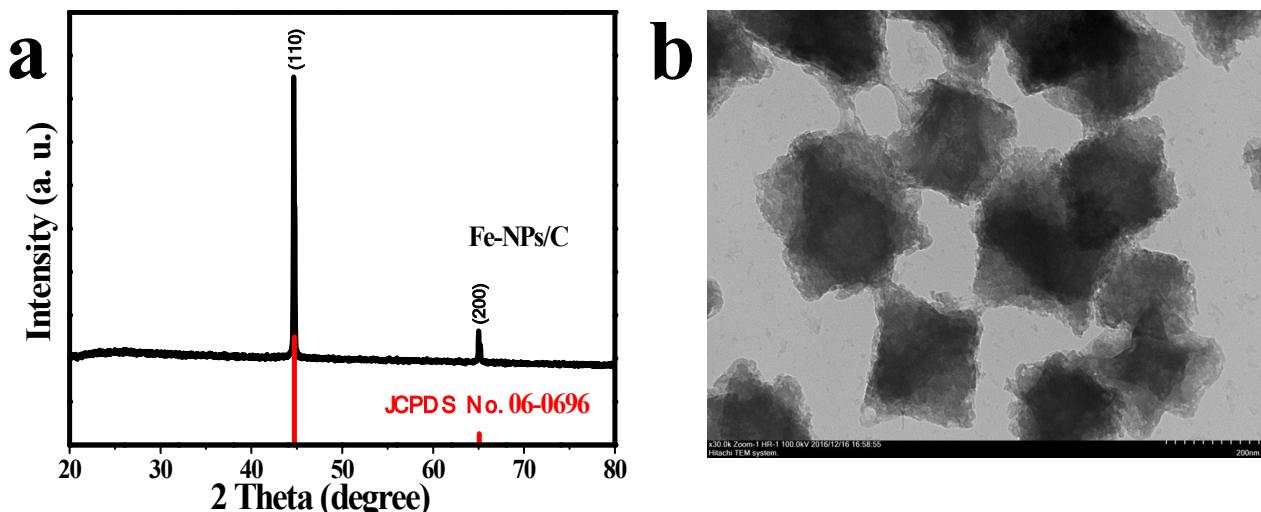
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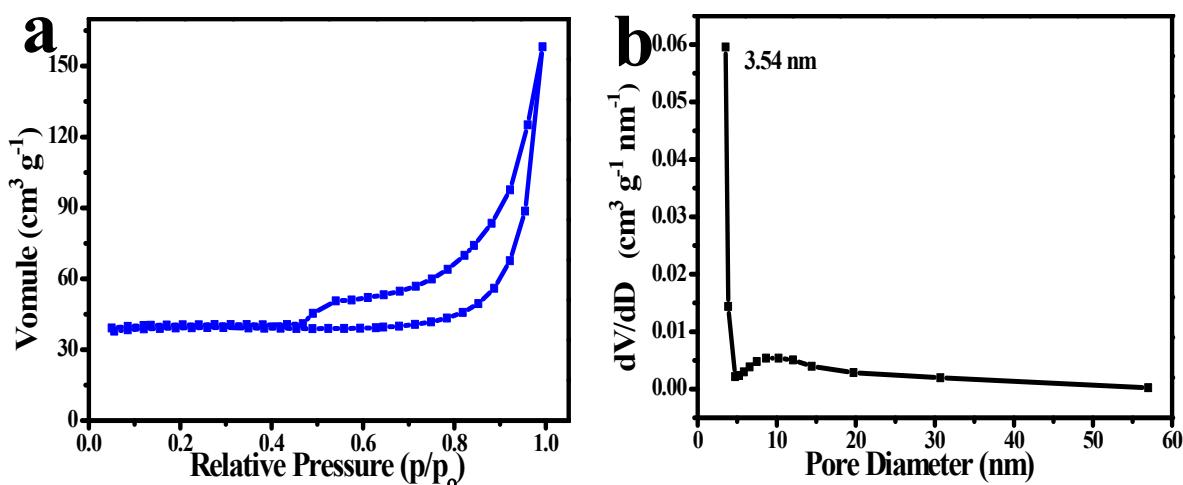
**Fig. S1.** (a) TEM and (b) SEM image, (c) XRD pattern and (d) FT-IR spectrum of MIL-101(Fe).



**Fig. S2.** (a) TG curve of MIL-101(Fe), (b) program temperature procedure applied for the synthesis of Fe-NPs/C and FeP-NPs/C.



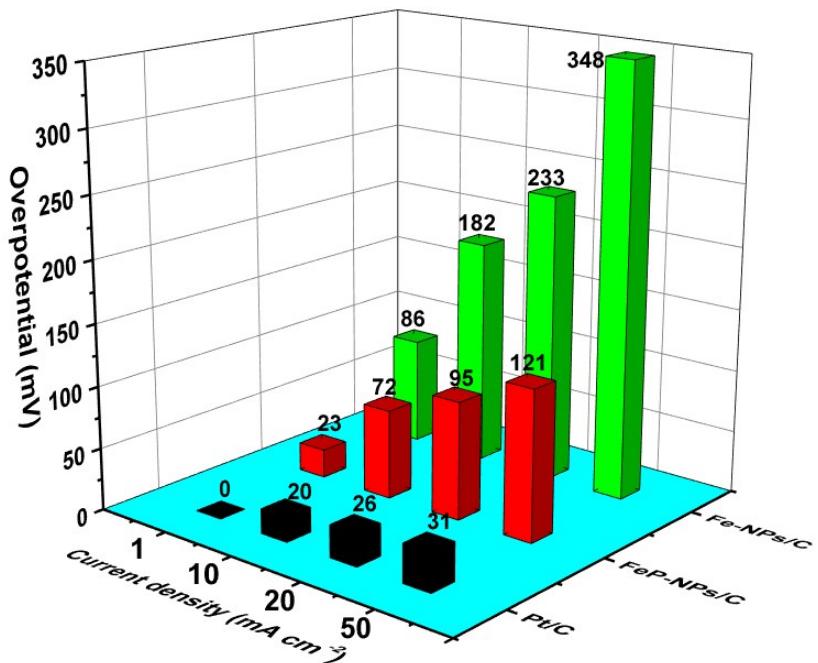
**Fig. S3.** (a) XRD pattern and (b) TEM image of Fe-NPs/C.



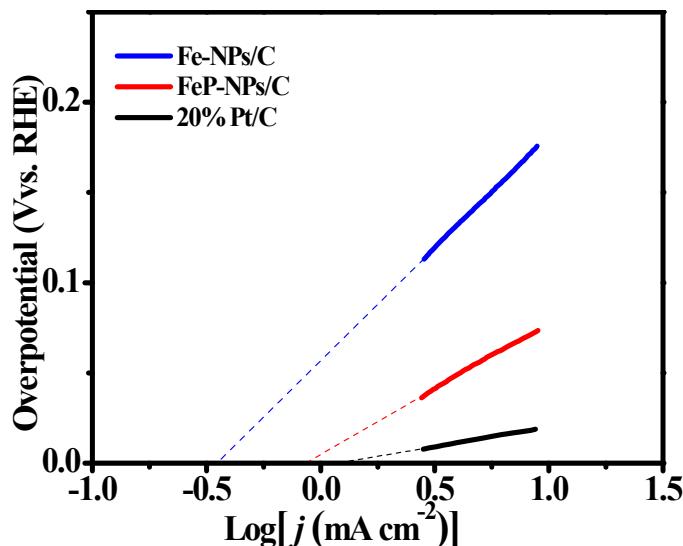
**Fig. S4.** (a) Nitrogen adsorption-desorption isotherms of Fe-NPs/C, (b) The BJH pore size distribution of the Fe-NPs/C calculated from the desorption branch of the  $\text{N}_2$  isotherm.

**Table S1.**  $\text{N}_2$  adsorption-desorption isotherms of synthetic materials.

|  | MIL-101(Fe) | Fe-NPs/C | FeP-NPs/C<br>(before acid washing) | FeP-NPs/C<br>(after acid washing) |
|--|-------------|----------|------------------------------------|-----------------------------------|
| BET surface area<br>( $\text{m}^2 \text{g}^{-1}$ ) | 2978.0      | 118.5    | 10.7                               | 114.3                             |
| BJH surface area<br>( $\text{m}^2 \text{g}^{-1}$ ) | 2613.2      | 63.6     | 8.5                                | 140.8                             |
| Pore Volume<br>( $\text{cm}^3 \text{g}^{-1}$ )     | 1.42        | 0.21     | 0.023                              | 0.42                              |
| Pore Size<br>(nm)                                  | 2.17        | 13.14    | 10.94                              | 11.81                             |



**Fig. S5.** Three-dimensional histograms of the corresponding overpotentials, when the current density was 1, 10, 20 and 50  $\text{mA cm}^{-2}$ , respectively.

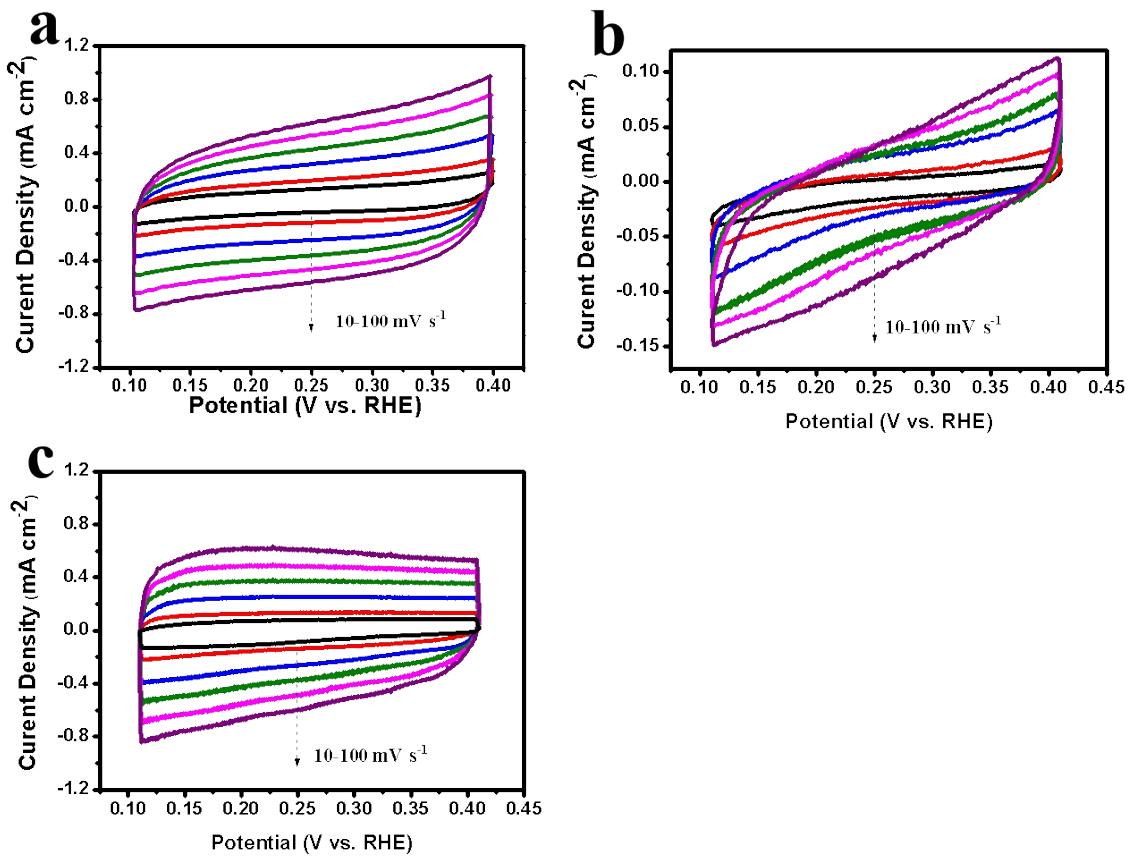


**Fig. S6.** The exchange current density ( $j_0$ ) calculated by the Tafel plots of the Fe-NPs/C, FeP-NPs/C and 20% Pt/C.

The  $j_0$  was calculated by using extrapolation methods. The corresponding  $j_0$  values for Fe-NPs/C, FeP-NPs/C and 20% Pt/C were calculated to be 0.357, 0.925 and 1.389  $\text{mA cm}^{-2}$ , respectively.

**Table S2.** Summary of HER performance of the reported catalysts.

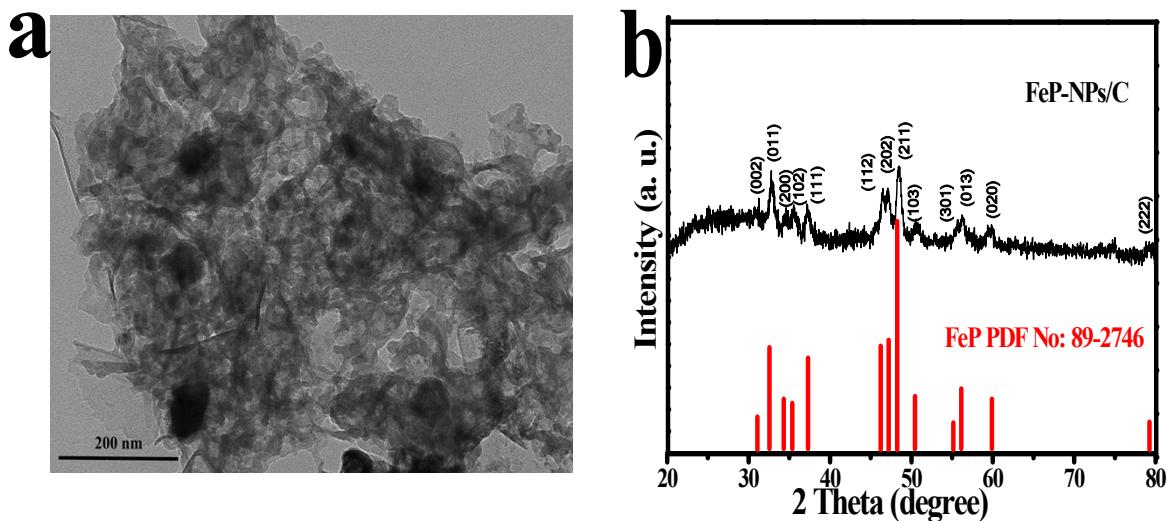
| Catalyst  | Mass density (mg cm <sup>-2</sup> ) | Onset overpotential η(mV) | Overpotential (@10 mA cm <sup>-2</sup> ) | Tafel slope (mV dec <sup>-1</sup> ) | Reference |
|---|-------------------------------------|---------------------------|--|-------------------------------------|-----------|
| (CoP) <sub>x</sub> -(FeP) <sub>1-x</sub>                    | 0.285                               | 15                        | 57                                       | 52                                  | [7]       |
| NiS nanoframe   | 1.00                                | --                        | 94                                       | 115                                 | [11]      |
| CoMoS <sub>3</sub>  | 0.5                                 | --                        | 171                                      | 59.9                                | [13]      |
| MoCx  | 0.8                                 | 25                        | 142                                      | 53                                  | [15]      |
| FeP film  | 1.50                                | 16                        | 84                                       | 48.5                                | [16]      |
| Fe <sub>2</sub> P   | 0.36                                | 40                        | --                                       | 49                                  | [18]      |
| Fe <sub>2</sub> P-ND/FG                                     | 0.41                                | --                        | 91                                       | 47                                  | [19]      |
| Porous Co Phosphide/phosphate film                          | 0.10                                | 35                        | 175@30 mA cm <sup>-2</sup>               | 53                                  | [20]      |
| HNDCM-Co/CoP  | --                                  | --                        | 135                                      | 64                                  | [21]      |
| Ni <sub>2</sub> P/Ti  | 2.00                                | 60                        | 138@20 mA cm <sup>-2</sup>               | 60                                  | [22]      |
| MoP@PC  | 0.41                                | 77                        | 153                                      | 66                                  | [23]      |
| Cu <sub>3</sub> P NAs                                       | 15.20                               | 62                        | 143                                      | 67                                  | [24]      |
| Cu <sub>3</sub> P@NPPC                                      | 0.29                                | --                        | 89                                       | 76                                  | [25]      |
| WP <sub>2</sub> SMPs  | 0.50                                | 54                        | 161                                      | 57                                  | [26]      |
| Hydrogenated FeP  | 0.72                                | --                        | 145                                      | 64                                  | [27]      |
| CFP-FeP HNA   | 3.80                                | --                        | 31                                       | 53                                  | [28]      |
| Carbon shell-coated FeP/C                                   | 0.44                                | --                        | 71                                       | 52                                  | [31]      |
| HM FeP@C  | 0.72                                | 25                        | 115                                      | 56                                  | [32]      |
| FePN Rs/VAGNs/CC  | 0.776                               | 19                        | 53                                       | 42                                  | [43]      |
| P-WN/Rgo  | 0.34                                | 46                        | 85                                       | 54                                  | [S1]      |
| FeP NR  | 0.20                                | 45                        | 120                                      | 55                                  | [S2]      |
| FeP nanotubes   | 1.60                                | 35                        | 88                                       | 35.5                                | [S3]      |
| Co-NR CNTs  | 0.28                                | 50                        | 260                                      | 69                                  | [S4]      |
| Mn-Co-P/Ti  | --                                  | --                        | 49                                       | 55                                  | [S5]      |
| Ni <sub>5</sub> P <sub>4</sub> -Ni <sub>2</sub> P nanosheet | 0.283                               | 54                        | 120                                      | 79.1                                | [S6]      |
| FeP-NPs/C   | 0.51                                | 23                        | 72                                       | 65                                  | This work |



**Fig. S7.** The cyclic voltammograms of (a) FeP-NPs/C, (b) bulk FeP and (c) Fe-NPs/C with the scan rates of 10, 20, 40, 60, 80 and 100  $\text{mV s}^{-1}$ , the potential range from 0.1 to 0.4 V vs. RHE.

**Table S3.** The fitting results of EIS spectra.

|           | $R_s$<br>( $\Omega$ ) | $R_{ct}$<br>( $\Omega$ ) | CPE1-P  | CPE1-T<br>( $\Omega^{-1} \text{cm}^{-2} \text{s}^{-n}$ ) |
|-----------|-----------------------|--------------------------|---------|--|
| FeP-NPs/C | 11.0                  | 25.6                     | 0.76563 | $3.235 \text{ e}^{-3}$                                   |
| Bulk FeP  | 8.5                   | 85.9                     | 0.67677 | $6.519 \text{ e}^{-5}$                                   |
| Fe-NPs/C  | 7.2                   | 139.4                    | 0.79130 | $1.788 \text{ e}^{-5}$                                   |



**Fig. S8.** (a) TEM image and (b) XRD pattern of FeP-NPs/C after stability test.

## References

- [S1] H. Yan, C. Tian, L. Wang, A. Wu, M. Meng, L. Zhao, H. Fu, *Angew. Chem., Int. Ed.* 2015, **54**, 6325-6329.
- [S2] H. Du, S. Gu, R. Liu, C. Li, *Int. J. Hydrogen Energy*, 2015, **40**, 14272-14278.
- [S3] Y. Yan, B. Xia, X. Ge, Z. Liu, A. Fisher, X. Wang, *Chemistry*, 2015, **21** 18062-18067.
- [S4] X. Zou, X. Huang, A. Goswami, P. Silva, B. R. Sathe, T. Asefa, *Angew. Chem., Int. Ed.*, 2014, **53**, 4372-4376.
- [S5] Y. Sun, L. Hang, Q. Shen, T. Zhang, H. Li, X. Zhang, X. Lyu, Y. Li, *Nanoscale*, 2017, **9**, 16674-16679.
- [S6] X. Wang, Y. V. Kolen'ko, X. Bao, K. Kovnir, L. Liu, *Angew. Chem. Int. Ed.* 2015, **54**, 8188-8192.