## Supplementary Information

For

## Free-sustaining Three-dimensional S235 Steel-based Porous Electrocatalyst for Highly Efficient and Durable Oxygen Evolution

Weijia Han<sup>1</sup>, Karsten Kuepper<sup>2</sup>, Peilong Hou<sup>1</sup>, Wajiha Akram<sup>1</sup>, Henning Eickmeier<sup>1</sup>,

Jörg Hardege<sup>3</sup>, Martin Steinhart<sup>1</sup>, and Helmut Schäfer<sup>\*1</sup>

1. Institute of Chemistry of New Materials and Center of Physics and Chemistry of New Materials, Universität Osnabrück, Barbarastrasse 7, 49076 Osnabrück, Germany

2. Department of Physics, Universität Osnabrück, Barbarastraße 7, 49069 Osnabrück, Germany

3. School of Environmental Sciences, Hull University, HU67RX, Hull, U.K.

\* corresponding author

Figure S1



Figure S1. The cross-section SEM of 3D S235-P steel. The average phosphorized layer is about 40  $\mu m.$ 





Figure S2. IR-corrected Tafel plots of 3D S235-P steel, S235-P-650 steel, S235-P-450 steel, and untreated S235 steel determined in 0.1 M KOH. Average voltage values for the Tafel plots were derived from 200 second chronopotentiometry scans at current densities 0.80, 1.48, 2.03, 2.67, 4.12, 4.98, 5.82, 7.07, 8.50, 9.98, 12.93, 16.36, and 20.34 mA cm<sup>-2</sup>. IR compensation was performed by taking in account the electrolyte resistance from EIS measurements (Figure 5).









Figure S3. High-resolution XPS patterns for 3D S235-P steel before and after electrolysis for 2000 s: Fe 2p, P 2p, and Mn 2p.

Figure S4





Figure S4. Cyclic voltammograms in the region of 0-0.10 V vs. RHE at various scan rates and the corresponding linear fitting of the capacitive currents vs. scan rates to estimate the  $C_{dl}$  (a) and (b) for 3D S235-P and (c) and (d) for S235; and the calculated  $C_{dl}$  values are shown in the insets.

## Figure S5



Figure S5. SEM images (a, b) of the 3D S235-P steel after long-term chronopotentiometric measurement, (c) the corresponding elemental mapping images and (d) XRD patterns.

## Figure S6



Figure S6. Raman spectrum of 3D S235-P steel after usage in OER testing.

| Catalysts   | Electrolyte   | η <sub>onset</sub><br>(mV) | Tafel<br>slope<br>(mV<br>dec <sup>-1</sup> ) | J <sub>geo</sub><br>(mA cm <sup>-</sup><br><sup>2</sup> ) | Loading<br>mass<br>(mg cm <sup>-</sup><br><sup>2</sup> ) | Ref.                                     |
|---|---------------|----------------------------|--|---|--|--|
| 3D S235-P   | 0.1 M<br>KOH  | 180                        | 76.3   | 10@ η =<br>295 mV   | 0.68   | This work                                |
| RuO <sub>2</sub>  | 0.1 M         | -                          | -  | 10@ η =<br>298 mV   | -  | J. Phys. Chem. Lett.<br>2012, 3, 399     |
| IrO <sub>2</sub>  | КОН           | -                          | -  | 10@ η =<br>288 mV   | -  |  |
| FeP NRs<br>on CP  | 1.0 M<br>KOH  | 290                        | 63.6   | 10@ η =<br>350 mV   | 0.7  | Chem. Commun., 2016, 52, 8711            |
| NiFeO <sub>x</sub> film   | 1.0 M<br>NaOH | -                          | -  | 10@η ><br>350 mV  | -  | J. Am. Chem. Soc. 2013, 135, 16977       |
| sea-urchin-like<br>(Co <sub>0.54</sub><br>Fe <sub>0.46</sub> ) <sub>2</sub> P | 0.1 M<br>KOH  | -                          | -  | 10@ η =<br>370 mV   | 0.2  | Angew. Chem. Int.<br>Ed. 2015, 127, 9778 |
| Fe <sub>1.1</sub> Mn <sub>0.9</sub> P<br>nanoparticles                        | 1.0 M<br>KOH  | -                          | 39   | $\begin{array}{c} 10@~\eta = \\ 350~mV \end{array}$       | 0.28   | Chem. Mater.<br>2017, 29, 3048           |
| NiFe LDHs<br>Nanosheets   | 1.0 M<br>KOH  | -                          | 40   | 10@η =<br>300 mV  | 0.07   | Nat. Commun.<br>2014, 5, 4477            |
| Ni <sub>30</sub> Fe <sub>7</sub> Co <sub>20</sub> Ce<br>43O <sub>x</sub>      | 1.0 M<br>NaOH | 270                        | 70   | 10@η =<br>310 mV  | -  | Energy Environ. Sci.<br>2014,7, 682      |
| Ni doped<br>FeOOH   | 0.1 M<br>KOH  | -                          | -  | $\begin{array}{l} 10@~\eta > \\ 340~mV \end{array}$       | -  | J. Mater. Chem. A, 2014, 2, 14957        |
| amorphous<br>FeNi oxides<br>nanospheres                                       | 1.0 M<br>KOH  | -                          | 48   | 10@η =<br>286 mV  | 0.1  | Angew. Chem. Int.<br>Ed. 2014, 53, 7547  |
| FeP@Au  | 1.0 M<br>KOH  | 250                        | 56.8   | 10@η =<br>320 mV  | -  | J. Mater. Chem. A, 2016, 4, 9750         |
| iron phosphide<br>nanotube  | 1.0 M<br>KOH  | 250                        | 43   | 10@η =<br>288 mV  | 1.6  | Chem. Eur.J.<br>2015, 21,18062           |
| Fe-Ni oxides  | 1.0 M<br>KOH  | -                          | 51   | 10@ η ><br>375 mV   | 1  | ACS Catal. 2012, 2, 1793                 |
| Nickel<br>Phosphide<br>nanoparticles  | 1.0 M<br>KOH  | -                          | 59   | 10@ η =<br>290 mV   | 0.14   | Energy Environ. Sci.,<br>2015, 8, 2347   |
| NiCo <sub>2.7</sub> (OH) <sub>X</sub><br>Amorphous<br>nanocages               | 1.0 M<br>KOH  | 250                        | 67   | 10@ η =<br>350 mV   | 0.2  | Adv. Energy Mater.<br>2015, 5, 1401880   |

Table S1. OER activities of the 3D S235-P steel and reported catalysts in alkaline condition.

| Ι                    | Π                          | III                                   | VI                        | VII                           |
|----------------------|----------------------------|---------------------------------------|---------------------------|-------------------------------|
| Mass<br>loss<br>[mg] | V (pH 7<br>buffer)<br>[ml] | Ion<br>concentration<br>(Electrolyte) | ∑detected<br>ions<br>[mg] | ∑detected<br>material<br>[mg] |
| 0.10                 | 400                        | 0.16 (Fe)<br>0.01 (Mn)                | 0.064 (Fe)<br>0.004 (Mn)  | 0.068                         |

Table S2. ICP OES analysis of the pH 7 electrolyte used for the long term chronopotentiometry measurements carried out for 40000 s at 2 mA/cm<sup>2</sup>. The values in column III and IV are **averaged values** representing the results from three test runs. Column I represents the average mass loss of the steel samples while carrying out the long term chronopotentiometry measurement.