

Supporting Information for  
**Co-doped CuO Nanoarray: An Efficient Oxygen Evolution  
Reaction Electrocatalyst with Enhanced Activity**

Xiaoli Xiong,<sup>1</sup> Chao You,<sup>1</sup> Zhiang Liu,<sup>3</sup> Abdullah M. Asiri,<sup>4</sup> and Xuping Sun<sup>2,\*</sup>

<sup>1</sup>College of Chemistry and Materials Science, Sichuan Normal University, Chengdu  
610068, Sichuan, China

<sup>2</sup>College of Chemistry, Sichuan University, Chengdu 610064, China

<sup>3</sup>College of Chemistry and Chemical Engineering, Qufu Normal University, Qufu  
273165, China

<sup>4</sup>Chemistry Department, Faculty of Science & Center of Excellence for Advanced  
Materials Research, King Abdulaziz University, P.O. Box 80203, Jeddah 21589,  
Saudi Arabia

\*E-mail: sunxp\_scu@hotmail.com

## Content

Experimental Section.....	S3-S5
<b>Figure S1.</b> EDX spectrum of Co-CuO NA/CF.....	S6
<b>Figure S2.</b> XPS survey spectrum for Co-CuO.....	S7
<b>Figure S3.</b> XPS spectra for CuO and CoO.....	S8
<b>Figure S4.</b> XRD and TEM analyses for Co-CuO after OER test.....	S9
<b>Figure S5.</b> N <sub>2</sub> adsorption/desorption isotherms for CuO and Co-CuO.....	S10
<b>Figure S6.</b> LSV curve normalized by BET surface area.....	S11
<b>Figure S7.</b> CVs and TOF curve.....	S12
<b>Table S1.</b> Comparison of OER performance.....	S13-S15

## Experimental Section

**Materials:** CF was purchased from Ailantian Advanced Technology Materials Co. Ltd (Dalian, China). NaOH,  $\text{RuCl}_3 \cdot 3\text{H}_2\text{O}$ , and  $\text{Co}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$  were purchased from Aladdin Ltd. (Shanghai, China). Hydrochloric acid (HCl) and ammonium persulfate (APS) with analytical grade were purchased from Tianjin Fuchen Chemical Reagent Factory. Nafion (5 wt%) was purchased from Sigma-Aldrich. All reagents were used as received. The water used throughout all experiments was purified through a Millipore system.

**Preparation of  $\text{Cu}(\text{OH})_2$  NA/CF and CuO NA/CF:** CF was firstly washed with HCl, water several times to remove the surface oxide. Then it was rapidly immersed into an aqueous solution with 0.92 g APS, 3 ml ammonia ( $14 \text{ mol L}^{-1}$ ) and 3.2 g NaOH at room temperature for 20 min. Following this, the  $\text{Cu}(\text{OH})_2$  NA/CF was dried at  $70^\circ\text{C}$  for 10 h in vacuum oven for use. To obtain CuO NA/CF,  $\text{Cu}(\text{OH})_2$  NA/CF was placed in the furnace, heated to  $300^\circ\text{C}$  under air atmospheres for 2 h.

**Preparation of Co-CuO NA/CF:** To obtain Co-CuO NA/CF, CuO NA/CF and 38 mL ethylene glycol with 1 mM  $\text{Co}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$  were placed to a 40 mL Teflon-lined stainless-steel autoclave and heated at  $120^\circ\text{C}$  for 2h, and the resulting material was then rinsed with deionized water for several times and then dried at  $60^\circ\text{C}$  for 12 h in vacuum oven.

**Electrochemical measurements:** Electrochemical measurements were performed with a CHI 760E electrochemical analyzer (CH Instruments, Inc., Shanghai) in a conventional three-electrode system. Graphite rod, Hg/HgO, and Co-Cu NA/CF were used as counter, reference and working electrodes, respectively. Overpotentials ( $\eta$ ) were calculated by the following equation:  $\eta = E(\text{RHE}) - 1.23 \text{ V}$ , where  $E(\text{RHE}) = E(\text{Hg}/\text{HgO}) + (0.098 + 0.059 \text{ pH}) \text{ V}$ . All experiments were carried out at room temperature (298 K).

**TOF calculation:** To calculate TOF, the surface concentration of active sites needs to be quantified by electrochemistry. we make a rough estimation of TOF for each active site using the following equation:

$$\text{TOF} = \text{JA}/4\text{F m} \quad (1)$$

Where J is current density ( $\text{A cm}^{-2}$ ) at defined overpotential during the LSV measurement in 1 M KOH; A is the geometric area of the electrode; 4 indicates the mole of electrons consumed for evolving one mole of  $\text{O}_2$  from water; F is the Faradic constant ( $96485 \text{ C mol}^{-1}$ ); m is the number of active sites (mol), which can be extracted from the linear relationship between the oxidation peak current and scan rate using the following equation:

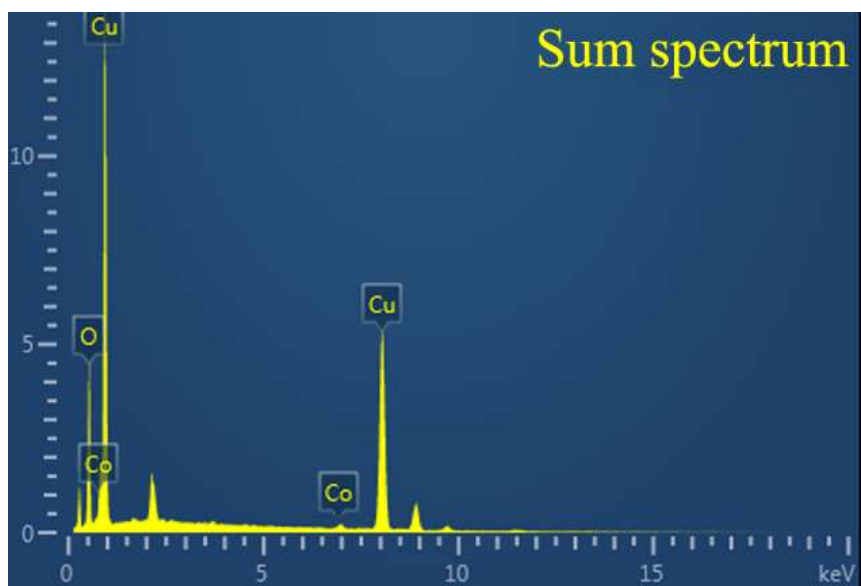
$$\text{Slope} = n^2\text{F}^2\text{m}/4\text{RT} \quad (2)$$

Where n is the number of electrons transferred; F is the Faradic constant; A is the surface area of the electrode; R and T are the ideal gas constant and the absolute temperature, respectively.

**FE determination:** The FE was calculated by comparing the amount of measured  $\text{O}_2$  generated by potentiostatic anodic electrolysis with calculated  $\text{O}_2$  (assuming 100% FE). GC analysis was carried out on GC-2014C (Shimadzu Co.) with thermal conductivity detector and nitrogen carrier gas. Pressure data during electrolysis were recorded using a CEM DT-8890 Differential Air Pressure Gauge Manometer Data Logger Meter Tester with a sampling interval of 1 point per second.

**Characterizations:** Powder XRD data were collected on Bruker D8 ADVANCE Diffractometer ( $\lambda=1.5418 \text{ \AA}$ ). SEM measurements were performed on a XL30 ESEM FEG scanning electron microscope at an accelerating voltage of 20 kV. TEM measurements were performed on a HITACHI H-8100 electron microscopy (Hitachi, Tokyo, Japan) with an accelerating voltage of 200 kV. XPS spectra were acquired on a Thermal ESCALAB 250 spectrometer using an Al  $\text{K}\alpha$  X-ray source (1486.6 eV photons). To determine the contents of  $\text{Co}^{2+}$  and  $\text{Cu}^{2+}$  by ICP-OES, the material was completely dissolved in 10 mL diluted hydrochloric acid (0.1 M) and then the solution was diluted to 50 mL by deionized water, which was analyzed by a Perkin Elmer 2000 DV ICP Optical Emission Spectrometer. The samples were collected from the films prior to the measurement and BET surface areas were measured by  $\text{N}_2$  adsorption and desorption at 77 K on a Quadrasorb SI-MP Analyser from

Quantachrome Instrument Company and analysed by means of computer using quadrasorb win software.



**Figure. S1** EDX spectrum of Co-CuO NA/CF.

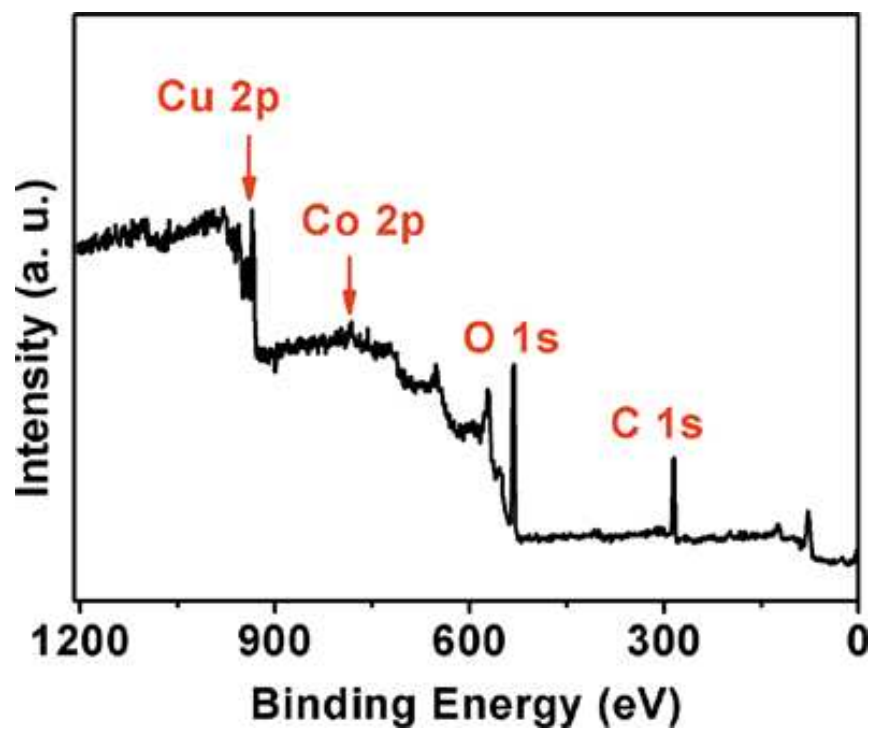
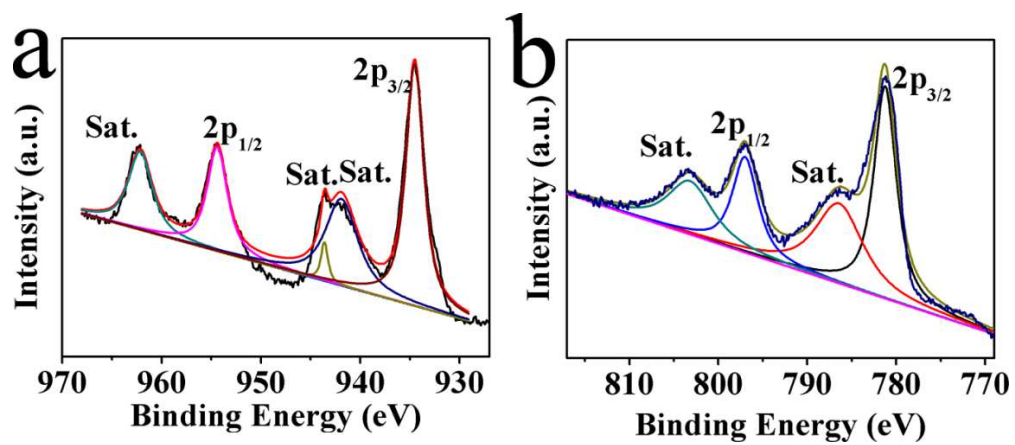
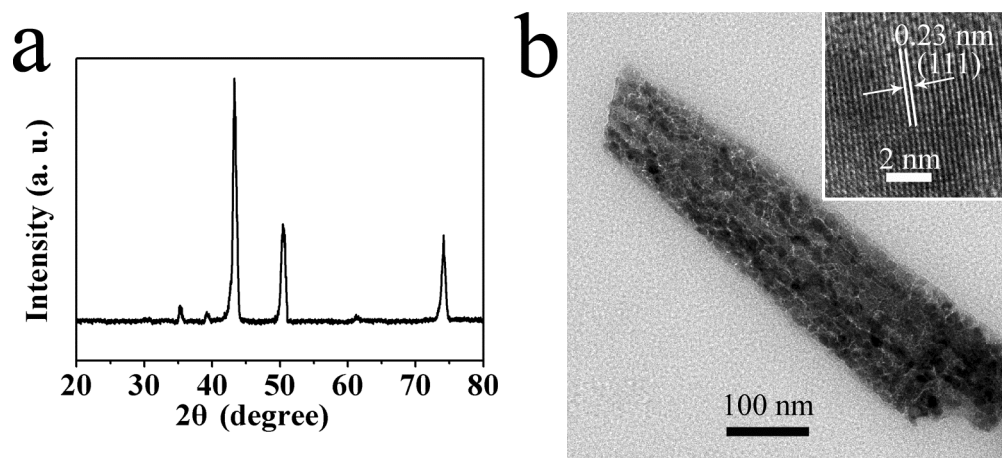


Figure S2. XPS survey spectrum for Co-CuO.

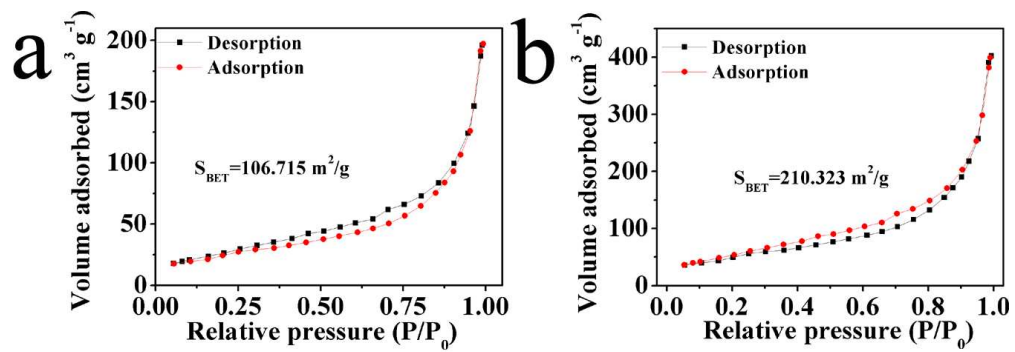


**Figure S3.** XPS spectra in the (a) Cu 2p region for CuO and (b) Co 2p region for CoO.

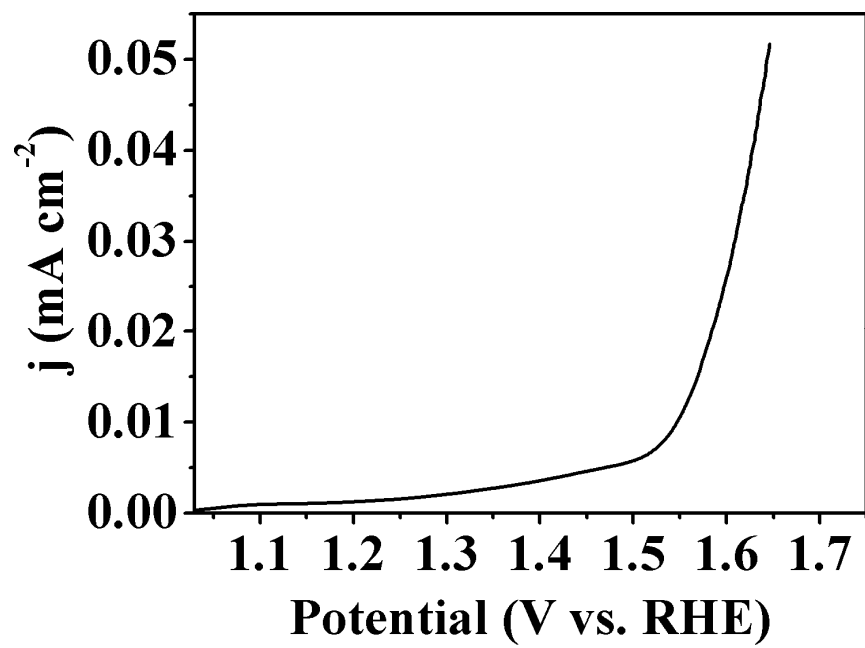




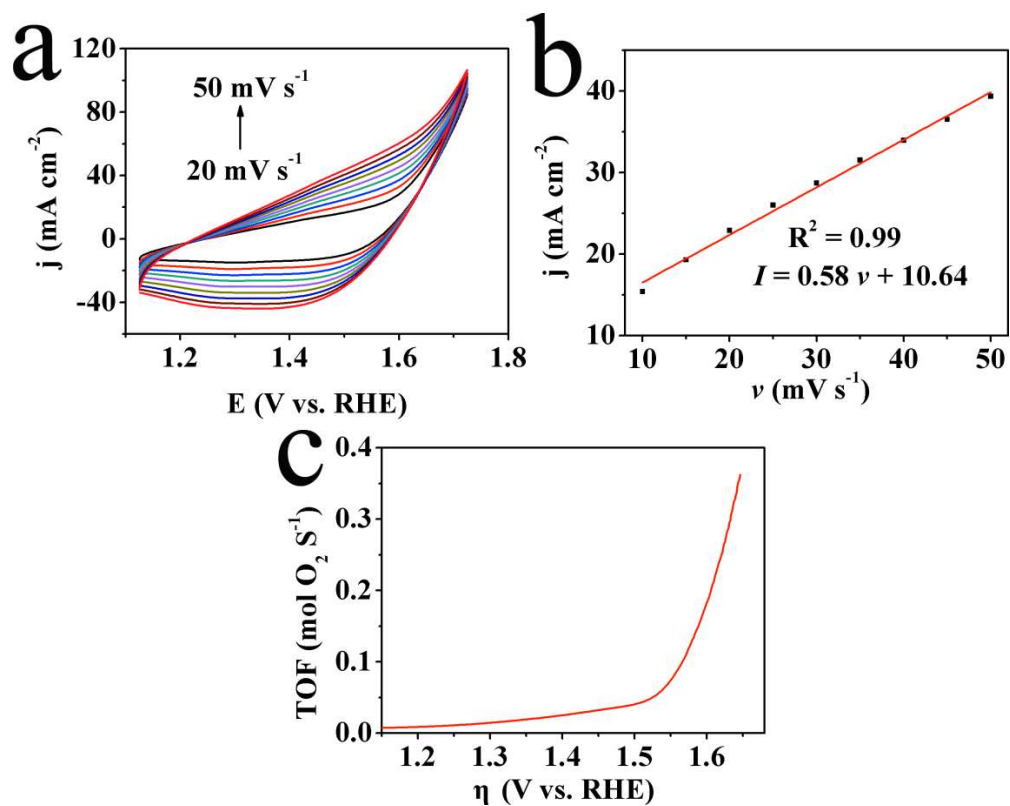
**Figure S4.** (a) XRD and (b) TEM analyses for Co-CuO after OER test.



**Figure S5.**  $\text{N}_2$  adsorption/desorption isotherms of (a) CuO and (b) Co-CuO.



**Figure S6.** LSV curve normalized by BET surface area for Co-CuO NA/CF.



**Figure S7.** (a) CVs of Co-CuO NA/CF at different scan rates in 1 M KOH. (b) Plot of oxidation peak current vs. scan rate for Co-CuO NA/CF. (c) The relationship between potentials and TOF recorded from Co-Cu NA/CF.

**Table S1.** Comparison of OER performance for Co-CuO NA/CF with other OER electrocatalysts in alkaline media.

Catalyst	$j$ (mA cm <sup>-2</sup> )	$\eta$ (mV)	Electrolyte	Ref.
Co-CuO NA/CF	50	299	1 M KOH	This work
	100	330	1 M KOH	
Cu <sub>3</sub> P NB/Cu NB	10	380	1 M KOH	1
Cu <sub>3</sub> P	50	412	0.1 M KOH	2
CuO <sub>x</sub>	50	707	0.1 M KOH	2
CoO <sub>x</sub> @CN	10	260	1 M KOH	3
Nitrogen-doped crumpled graphene CoO	10	340	1 M KOH	4
Cu <sub>x</sub> Co <sub>3-x</sub> O <sub>4</sub>	100	367	1 M KOH	5
Cu(OH) <sub>2</sub> @CCHH NW/CF	50	270	1 M KOH	6
Co-P	50	420	1 M KOH	7
Co-S	50	410	1 M KOH	8
ETC-Co <sub>0.5</sub> Fe <sub>0.5</sub> O	50	290	1 M KOH	9
Cu@NCNT/Co <sub>x</sub> O <sub>y</sub>	10	370	1 M KOH	10
Ir-Cu nanoframe structures	10	340	1 M KOH	11
NiCuP	10	292	1 M KOH	12

## References

- (1) Wei, S.; Qi, K.; Jin, Z.; Cao, J.; Zheng, W.; Chen, H.; Cui, X. One-Step Synthesis of a Self-Supported Copper Phosphide Nanobush for Overall Water Splitting. *ACS Omega* **2016**, *1*, 1367 - 1373, DOI 10.1021/acsomega.6b00366.
- (2) Hou, C.; Chen, Q.; Wang, C.; Liang, F.; Lin, Z.; Fu, W.; Chen, Y. Self-Supported Cedarlike Semimetallic Cu<sub>3</sub>P Nanoarrays as a 3D High-Performance Janus Electrode for Both Oxygen and Hydrogen Evolution under Basic Conditions. *ACS Appl. Mater. Interfaces* **2016**, *8*, 23037 - 23048, DOI 10.1021/acsami.6b06251.
- (3) Jin, H.; Wang, J.; Su, D.; Wei, Z.; Pang, Z.; Wang, Y. In Situ Cobalt - Cobalt oxide/N-doped Carbon Hybrids as Superior Bifunctional Electrocatalysts for Hydrogen and Oxygen Evolution. *J. Am. Chem. Soc.* **2015**, *137*, 2688 - 2694, DOI 10.1021/ja5127165.
- (4) Mao, S.; Wen, Z.; Huang, T.; Hou, Y.; Chen, J. High-Performance Bi-Functional Electrocatalysts of 3D Crumpled Graphene - Cobalt Oxide Nanohybrids for Oxygen Reduction and Evolution Reactions. *Energ. Environ. Sci.* **2014**, *7*, 609 - 616, DOI 10.1039/C3EE42696C.
- (5) Wu, X.; Scott, K. Cu<sub>x</sub>Co<sub>3-x</sub>O<sub>4</sub> (0 ≤ x < 1) Nanoparticles for Oxygen Evolution in High Performance Alkaline Exchange Membrane Water Electrolysers. *J. Mater. Chem.* **2011**, *21*, 12344 - 12351, DOI 10.1039/C1JM11312G.
- (6) Xie, L.; Tang, C.; Wang, K.; Du, G.; Asiri, A. M.; Sun, X. Cu(OH)<sub>2</sub>@CoCO<sub>3</sub>(OH)<sub>2</sub> · nH<sub>2</sub>O Core-Shell Heterostructure Nanowire Array: An Efficient 3D Anodic Catalyst for Oxygen Evolution and Methanol Electrooxidation. *Small* **2017**, *13*, 1602755, DOI 10.1002/smll.201602755.
- (7) Jiang, N.; You, B.; Sheng, M.; Sun, Y. Electrodeposited Cobalt - Phosphorous - Derived Films as Competent Bifunctional Catalysts for

- Overall Water Splitting. *Angew. Chem., Int. Ed.* **2015**, *54*, 6251 – 6254, DOI 10.1002/ange.201501616.
- (8) Liu, T.; Liang, Y.; Liu, Q.; Sun, X.; He, Y.; Asiri, A. M.; Electrodeposition of Cobalt-Sulfide Nanosheets Film as an Efficient Electrocatalyst for Oxygen Evolution reaction. *Electrochem. Commun.* **2015**, *60*, 92 – 96, DOI 10.1016/j.elecom.2015.08.011.
- (9) Chen, W.; Wang, H.; Li, Y.; Liu, Y.; Sun, J.; Lee, S.; Lee, J.; Cui, Y. In Situ Electrochemical Oxidation Tuning of Transition Metal Disulfides to Oxides for Enhanced Water Oxidation. *ACS Cent. Sci.* **2015**, *1*, 244 – 251, DOI 10.1021/acscentsci.5b00227.
- (10) Zhao, X.; Li, F.; Wang, R.; Seo, J. M.; Choi, H. J.; Jung, S. M.; Mahmood, J.; Jeon, I. Y.; Baek, J. B. Controlled Fabrication of Hierarchically Structured Nitrogen - Doped Carbon Nanotubes as a Highly Active Bifunctional Oxygen Electrocatalyst. *Adv. Funct. Mater.* **2017**, *27*, 1605717, DOI 10.1002/adfm.201605717.
- (11) Pei, J.; Mao, J.; Liang, X.; Chen, C.; Peng, Q.; Wang, D.; Li, Y. Ir - Cu Nanoframes: One-Pot Synthesis and Efficient Electrocatalysts for Oxygen Evolution Reaction. *Chem. Comm.* **2016**, *52*, 3793 – 3796, DOI 10.1039/C6CC00552G.
- (12) Wei, L.; Goh, K.; Birer, Ö.; Karahan, H. E.; Chang, J.; Zhai, S. A Hierarchically Porous Nickel - Copper Phosphide Nano-Foam for Efficient Electrochemical Splitting of Water. *Nanoscale* **2017**, *9*, 4401 – 4408, DOI 10.1039/C6NR09864A.