

Supporting Information

Mesoporous manganese-phthalocyanine based materials for electrochemical water oxidation via tailored templating

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Electrochemical water splitting on non-noble metals is of increasing importance for the future energy sector. Especially efficient catalysts for the demanding oxygen evolution reaction (OER) present a major challenge. As contribution to the field, tailored mesoporous hard-templated materials based on manganese-phthalocyanine were prepared. The preparation method proved to be crucial to achieve suitable physicochemical properties for high activity. The materials show overpotentials in RDE experiments between 490 and 590 mV at 10 mA/cm². This performance can be mainly attributed to efficient graphitization, high Mn dispersion together with a tailored oxidation state.

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1. Experimental Procedures

Materials

Tetraethylorthosilicate (TEOS) (99%), Pluronic P123 (99%), methanol (99%), ethanol (99.8%) Nafion® (5 wt.% in lower aliphatic alcohols containing 15-20% water) and NiCo₂O₄ (99%) were purchased from Aldrich. Manganese(II) phthalocyanine were obtained from Alfa Aesar. Hydrochloric acid (36 %) was purchased from ChemSolute. Potassium hydroxide and sodium hydroxide were obtained from Merck.

All chemicals used in the experiments showed analytical grade and were used without further purification.

Physicochemical Characterization

N₂-Physisorption was performed on an Asap 2000 from Micromeritics. The samples were heated for 24 hours at 300 °C and afterwards the measurement was performed at -196 °C. Inductively coupled plasma (ICP-OES) was executed by SPECTRO Analytical Instruments, Model SPECTROFLAME. Confocal Raman Microscopy images were obtained in a WITec Alpha 300R microscope, equipped with a 532 nm solid state laser. The pore structure of the samples was observed by STEM (Hitachi HD-2700 CS-corrected, 200 kV, Cold FEG, EDX Octane T Ultra W 100 mm² SDD TEAM-Software). XPS measurements were carried out in an UHV setup equipped with a Gamdata-Scienta SES 2002 analyzer. The base pressure in the measurement chamber was 5×10^{-10} mbar. Monochromatic Al K α (1486.6 eV; 14.5 kV; 30 mA) was used as incident radiation and a pass energy of 200 eV was chosen, resulting in an energy resolution better than 0.6 eV. Charging effects were compensated using a flood gun, and binding energies were calibrated by positioning the main C 1s peak at 284.5 eV which originates from carbon black. X-ray diffraction (XRD) was performed on a Siemens D5000 Radiation /wavelength: Cu K-alpha, 0.15418 nm. Thermogravimetric analysis (TGA) was performed on a STA 409 cell from Netzsch.

Electrochemical Characterization

Catalyst inks were prepared by dispersing the catalyst (5 mg/mL) in a mixture of milli-Q water (49 μ L), ethanol (49 μ L) and Nafion (2 μ L). The ink was shaken and sonicated for 15 min. 2.27 μ L of catalyst ink was pipetted onto the pre-cleaned glassy carbon rotating disk electrode (RDE) surface with a geometric area of 0.1134 cm², to form a catalyst film with a loading of 100 μ g cm⁻². The electrodes were polished using 3 μ m and 1 μ m polishing paper and 0.3 μ m and 0.05 μ m polishing paste, sonicated and raised in ethanol and milli-Q water before use. After the polymer film was deposited on the glassy carbon electrodes, it was dried at room temperature for 30 min.

Electrochemical measurements were performed in a glass cell using the conventional three electrode configuration at room temperature. The modified glassy carbon RDE was used as working electrode. A platinum wire and a Ag/AgCl (3 M KCl) electrode were used as the counter and the reference electrode, respectively, and 1 M KOH as electrolyte. The electrocatalytic activity was investigated by linear sweep voltammetry using an Autolab potentiostat (Metrohm) @ 0.01 V/s, 1600 rpm. Potentials were referenced to the reversible hydrogen electrode (RHE). Before recording any data, the catalysts were first subjected to continuous potential cycling (CV) until steady voltammograms were obtained (20 CVs @ 0.1 V/s). Electrochemical impedance spectroscopy (EIS), measured in the frequency range from 50 kHz to 10 Hz at open circuit potential (OCP) with an AC perturbation of 10 mV/s was used to determine the uncompensated resistance of the electrolyte. Long-term performance was investigated via continuous potential cycling (20 CVs @ 0.1 V/s); until steady voltammograms. EIS measurement was performed at open circuit potential (OCP). Stability measurements were obtained at applied current of 0.001134 A (10 mA/cm²) @ 1600 rpm. Cut off at 1.2 V vs Ag/AgCl/3M KCl.

2. Sample preparation

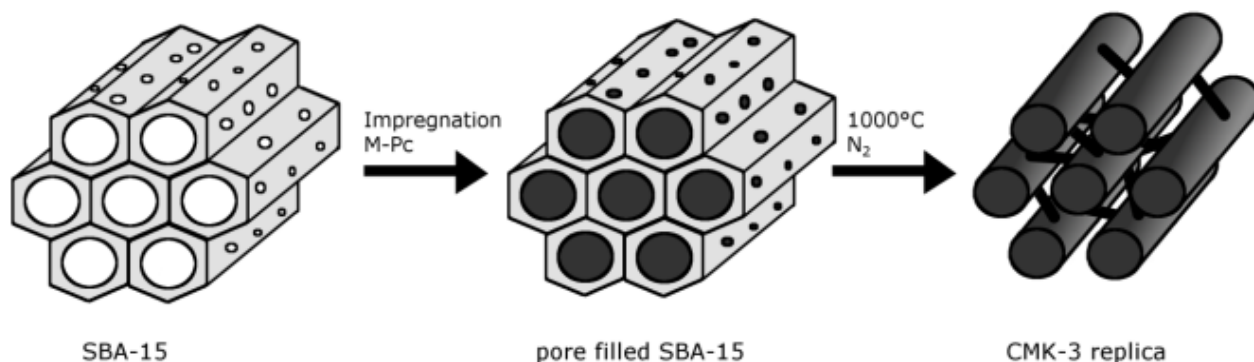
2.1. Synthesis of the template

SBA-15 materials were synthesized according to the procedure of Zhao *et al.*^[1] in order to use them as templates for the formation of nanostructured carbon. Ordered mesoporous silica templates were prepared using a surfactant EO₂₀PO₇₀EO₂₀ (P123), and TEOS as silica source. P123 (6.0 g) was completely dissolved in 2 M HCl (180 mL) overnight at room temperature. TEOS (12.6 mL) was added to the stirred mixture at 35 °C. The mixture was placed in the oven at 120 °C for 24 h. The white precipitates were filtered by vacuum filtration and washed twice with distilled water and twice with ethanol. The product was dried at 80 °C for 24 h and calcined at 550 °C for 6 h.

2.2. Synthesis of nanostructured carbon

Ordered mesoporous carbon materials (CMK-3) were formed using the same procedure as introduced by Ryoo *et al.*^[2] CMK-3 was synthesized with manganese phthalocyanine (MnPc) as a carbon source by replicating mesoporous silica SBA-15 (template). The pores of SBA-15 were filled with MnPc via different impregnation methods (2.2.1-2.2.3). The mixture was placed into an oven at 100 °C for 1 h, 350 °C for 1 h and subsequently at 1000 °C for 1 h under nitrogen atmosphere. To etch a silica template from the silica-Mn-phthalocyanine composite, the resulting black powder was treated with 5 M NaOH solution and kept at 100 °C for 24 h. The solution was then centrifuged at 6000 rpm for 15 minutes, followed by decantation of the supernatant solution.

The sediment was dispersed in distilled water. Centrifugation was repeated ten times to ensure a neutral pH of the supernatant solution. The silica removal step was repeated. The replica was dried at 100 °C and ordered mesoporous carbon materials were obtained (see Scheme 2).



Scheme S1. Schematic illustration of the synthesis of CMK 3 replica by using SBA 15 mesoporous silica materials: Impregnation of the metal precursor within the pores of the SBA 15 template. Carbonization under nitrogen atmosphere at 1000 °C for 1 h. Template removal with 5 M sodium hydroxide solution.

2.2.1 Grinding (solid/solid-impregnation)

SBA-15 (1.0 g) was added to MnPc (1.0 g) and both materials were mortared together until a homogeneous colored powder was formed.

2.2.2 Wet Impregnation

Typically, MnPc (1.0 g) was dissolved in ethanol (50 mL) and SBA-15 (1.0 g) was added. The mixture was heated up to 60 °C for 24 h and stirred until the solution turned colorless. The solvent was evaporated under reduced pressure.

2.2.3. Incipient Wetness Impregnation

SBA-15 (1.0 g) was impregnated with MnPc (1.0 g) dissolved in ethanol (2 mL). The metal solution was added to SBA 15 by dropping.

3. Characterization of the electrode material

Table S1. Physical properties of CMK-3 materials: Specific surface area ($S_{A\text{ BET}}$) was determined via BET method, total pore volume ($V_{P\text{ total}}$), average pore size distribution (D_p), metal loading of MnPc after carbonization and silica removal determined via ICP/OES (Mn_{ICP})

| Materials | $S_{A\text{ BET}}$ [m^2/g] | $V_{P\text{ total}}$ [cm^3/g] | D_p [nm] | Mn _{ICP} [wt.%] |
|--------------------|--|---|------------|--------------------------|
| CMK-3-Sucrose | 1480 | 1.28 | 4.9 | - |
| CMK-3-MnPc-WI | 598 | 0.63 | 4.8 | 7.8 |
| CMK-3-MnPc-IWI | 692 | 0.74 | 4.4 | 7.1 |
| CMK-3-MnPc-GR | 584 | 0.97 | 3.2 | 7.8 |
| Template free MnPc | 43 | 0.09 | - | 9.0 |

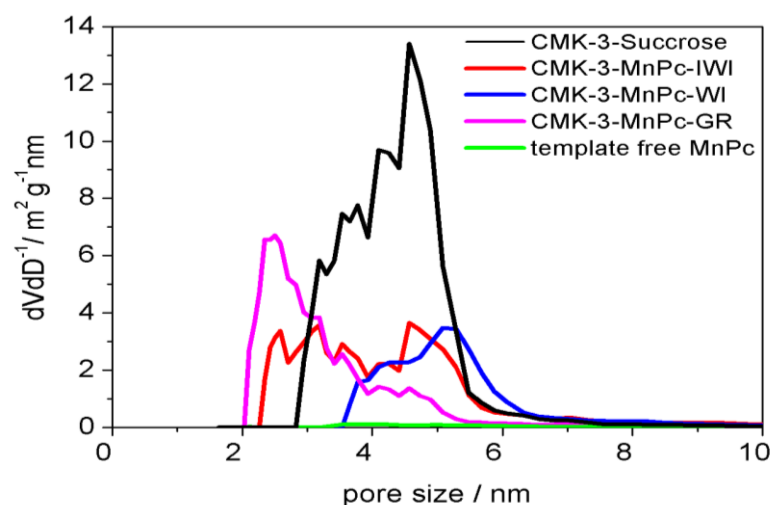


Figure S1. Pore size distribution of micro and mesopores calculated via DFT of CMK-3-Sucrose (black), CMK-3-MnPc-WI (blue), CMK-3-MnPc-IWI (red), CMK-3-MnPc-GR (magenta), template free MnPc (green).

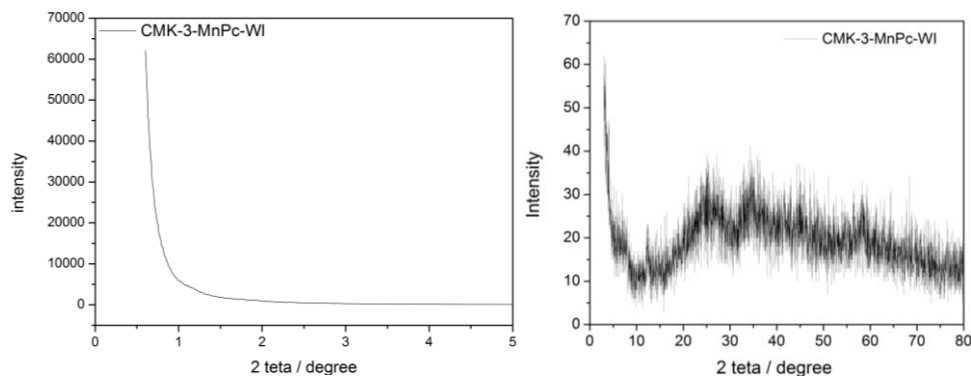


Figure S2. XRD spectra of CMK-3-MnPc-WI at small angle and wide angle range.

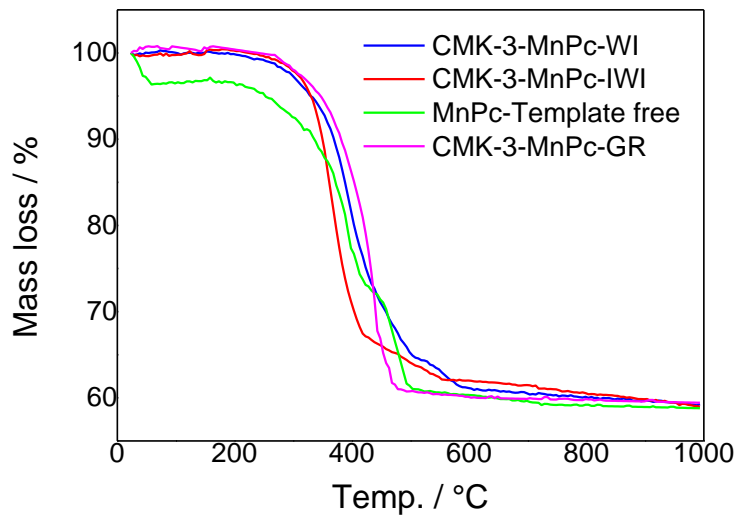


Figure S3. Thermogravimetric analysis of CMK-3-MnPc-WI (blue), CMK-3-MnPc-IWI (red), CMK-3-MnPc-GR (magenta), template free MnPc (green).

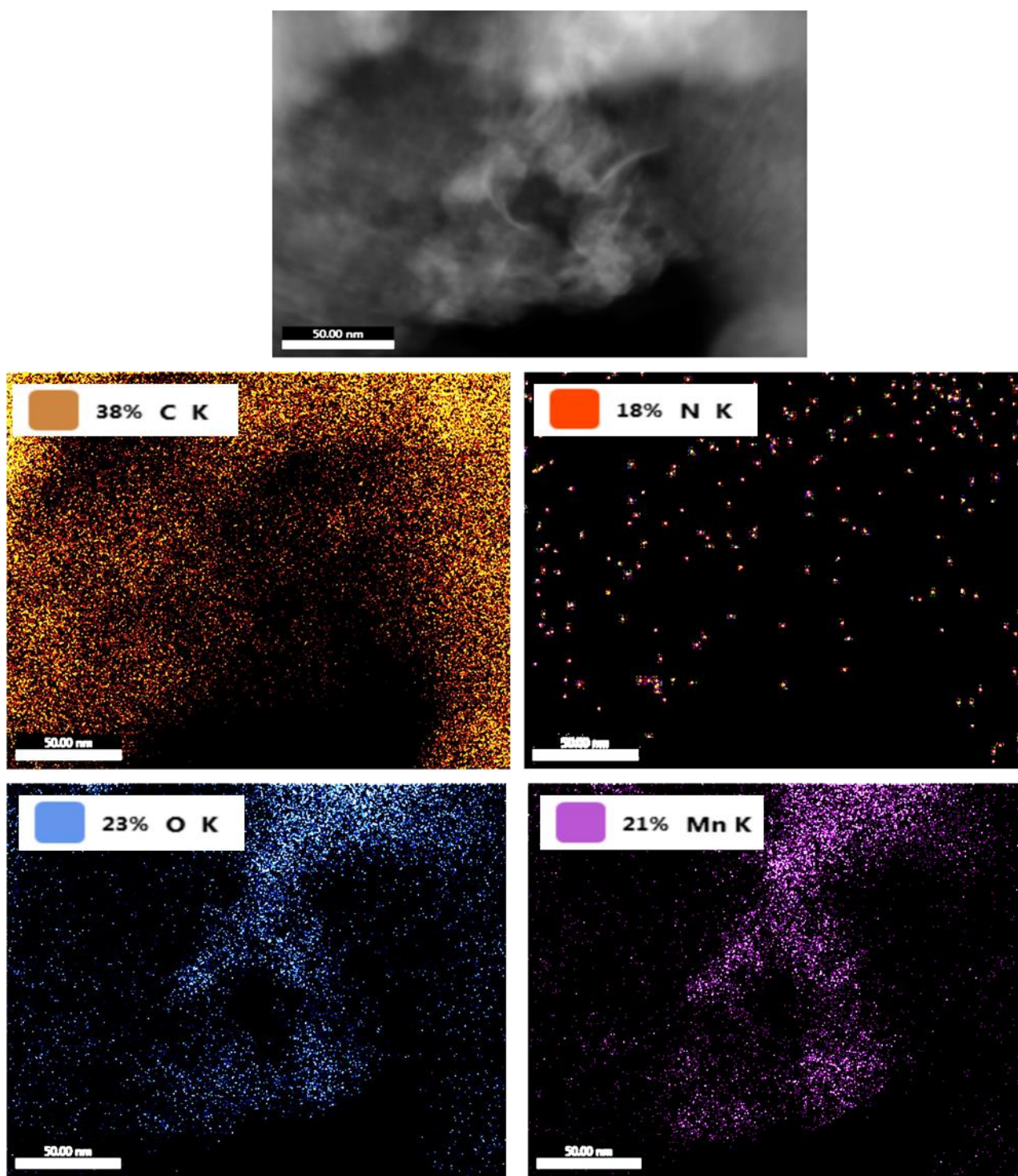


Figure S4. STEM elemental mapping analyses of carbon, oxygen, nitrogen and manganese of CMK-3-MnPc samples.

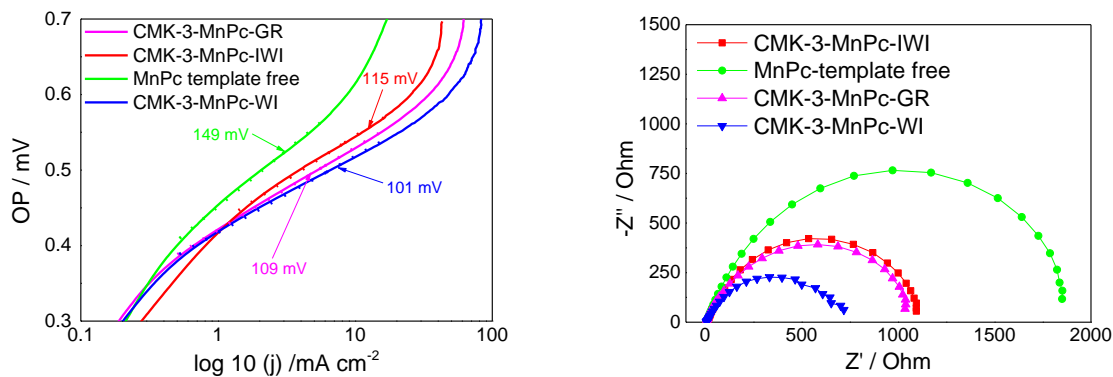


Figure S5. Determination of the Tafel plot (left) and the Nyquist plot (right) for CMK-3-MnPc-WI (blue), CMK-3-MnPc-IWI (red), CMK-3-MnPc-GR (magenta), template free MnPc (green).

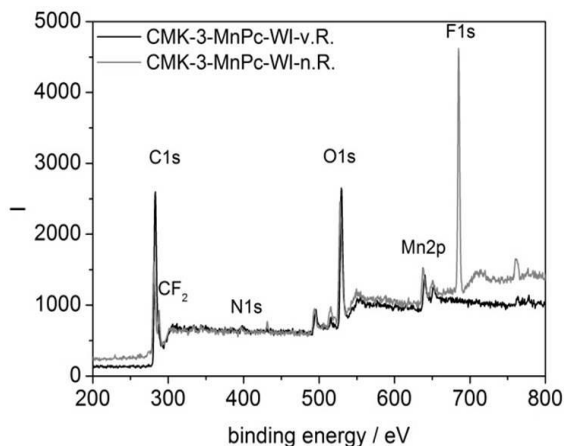


Figure S6. XPS spectra of the Wet impregnated material before (black) and after (grey) the electrochemical activity and stability tests.

1 References

- [1] D. Zhao, J. Feng, Q. Huo, N. Melosh, G. Fredrickson, B. Chmelka, G. Stucky, *Science* **1998**, 279, 548–52.
 [2] J. W. Grate, G. C. Frye in *Sensors Update, Vol. 2* (Eds.: H. Baltés, W. Göpel, J. Hesse), Wiley-VCH, Weinheim, **1996**, pp. 10-20.

2 Author Contribution

C. Broicher synthesized the materials, recorded and interpreted the electrochemical data and characterized the materials via N_2 -physisorption, elemental analysis, X-ray powder diffraction; J. Artz supported material synthesis and interpretation of the structural data; M. Drögeler and C. Stampfer measured Raman spectroscopy and supported the interpretation of the results; H. Antoni carried out XPS analyses and supported the interpretation of the results; D.M. Morales and S. Palkovits supported the electrochemical investigations and data interpretation; J. Artz, S. Palkovits and R. Palkovits designed the project, acquired funding and supervised the project; C. Broicher, S. Palkovits and R. Palkovits integrated the insight of the comprehensive data interpretation and wrote the manuscript draft; all authors discussed the results and commented on the manuscript.