Supporting information for

Ni-based heterogeneous catalyst from the designed molecular precursor for the efficient electrochemical water oxidation

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Experimental details

1. Materials and reagents

All synthetic manipulations were carried out using standard Schlenk techniques under an argon atmosphere. Methanol was dried upon boiling with magnesium methoxide followed by distillation. Dimethylformamide (DMF) was distilled twice under reduced pressure. Solvents were stored over molecular sieves (4 Å for DMF, 3 Å for methanol) under an argon atmosphere. Commercially available MoO_2Cl_2 (Aldrich) and KOCH₃ solution in methanol (~ 25%) (Aldrich) were used as recieved. Before use, KOCH₃ was diluted with methanol to the concentration *ca.* 0.8 - 1 M, which was specified by means of the acid-base titration. Anhydrous NiCl₂ was obtained by heating NiCl₂·6H₂O at 250⁰C *in vacuo* for 12 h.



Fig. S1. ORTEP representation of the molecular structure of [Ni₂Mo₂O₄(OCH₃)₈(CH₃OH)₂(C₃H₇NO)₂] (**Ni₂Mo₂**) (H atoms except those of hydroxo groups are omitted). Selected bond lengths (angstroms) and angles (deg) are as follows: Mo(1)-O(1) 1.7151(13), Mo(1)-O(2) 1.7044(13), Mo(1)-O(3) 2.0295(12), Mo(1)-O(4) 2.2314(12), Mo(1)-O(5) 1.9885(13), Mo(1)-O(6) 2.0905(12), Ni(1)-O(7) 2.0779(13), Ni(1)-O(3) 2.0472(12), Ni(1)-O(4) 2.0467(12), Ni(1)-O(7), O(1)-Mo(1)-O(2) 104.05(7), O(4)-Mo(1)-O(6) 73.24(4), O(5)-Mo(1)-O(6) 79.88(5), O(4A)-Ni(1)-Mo(6A) 78.10(5), O(3)-Ni(1)-O(4) 77.77(5).

Table S1. Crystallographic data for Ni₂Mo₂.

Formula	$C_{16}H_{46}Mo_2N_2Ni_2O_{16}$				
Formula weight	831.85				
Crystal colour	light green				
Crystal size, mm	0.32 x 0.38 x 0.40				
Т, К	120				
Crystal system	monoclinic				
Space group	P2 ₁ /n				
Z / Z'	2 / 0.5				
a, Å	12.0683(6)				
b, Å	10.1464(5)				
c, Å	12.6315(6)				
β, °	91.8930(10)				
V, Å ³	1545.88(13)				
d _{calc} , g cm ⁻³	1.787				
Radiation type	ΜοΚα (λ =0.71072 Å)				
μ , mm ⁻¹	2.059				
2θ _{max} , °	60				
Refls. collected / independent	20049 / 4500				
Observed refls. [I>2 σ (I)]	4001				
R ₁	0.0217				
wR ₂	0.0522				
GOF	1.040				
Residual density, e Å ⁻³ (d_{min}/d_{max})	-0.47 / 0.51				

2. Instrumentation

The infrared spectra were measured on solid samples using a Perkin Elmer Spectrum 100 Fourier Transform infrared spectrometer.

UV-Vis spectra were recorded using a HP 8451A DIODE ARRAY Spectrophotometer.

X-ray crystal data collection for sample Ni₂Mo₂ was performed on a Bruker APEX DUO diffractometer, equipped with Apex II CCD detector. Frames were integrated using the Bruker SAINT software package [1] by a narrow-frame algorithm. A semi-empirical absorption correction was applied with the SADABS [2] program using intensity data of equivalent reflections. The structures were solved by direct methods and refined by the fullmatrix least-squares technique against F^{2}_{hkl} in anisotropic approximation with SHELX [3] software package. Hydrogen atom of coordinated methanol moiety was found from difference Fourier synthesis and refined in isotropic approximation. The positions of other hydrogen atoms were calculated, and they were refined in a riding model with $U_{iso}(H) = 1.5U_{eq}(C_m)$ and $1.2U_{eq}(C_i)$, where $U_{eq}(C_m)$ and $U_{eq}(C_i)$ are respectively the equivalent thermal parameters of the methyl and all other carbon atoms to which corresponding H atoms are bonded. Detailed crystallographic information is given in Table S1. Crystallographic data have been deposited to the Cambridge Crystallographic Data Center, CCDC number 1473442. Copies of the data can be obtained free of charge via http://www.ccdc.cam.ac.uk/data request/cif, or by e-mailing data request@ccdc.cam.ac.uk, or by contacting The Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: +44(0)1223-336033.

Electron microscopy images were recorded using Hitachi SU8000 field-emission scanning electron microscope equipped with Oxford Instruments X-Max EDX detector. Images were acquired in a secondary electron mode with accelerating voltages 2 and 15 kV.

X-ray photoelectron spectroscopy (XPS) of the as-deposited **Ni₂Mo₂** and the catalyst film obtained upon preconditioning of the as-deposited **Ni₂Mo₂** (treatment with base, potential cycling and 30 min electrolysis in 1M NaOH at 2 mA cm⁻²) were carried out using a KRATOS AXIS ULTRA DLD spectrometer (Kratos Analytical Ltd., United Kingdom). The probed area for each sample was 300 x 700 μ m², and the probing depth was 1–2 nm. Monochromatic X-rays were generated by an Al K α source (1486.6 eV), energy resolution 0.6 eV. Binding energies of XPS spectra were calibrated against the C 1s peak of the adventitious carbon (284.8 eV) as an internal standard.

All electrochemical measurements were carried out at room temperature using Autolab PGSTAT 302 N or Elins P30I potentiostats controlled by Nova or PS_Pack software,

respectively, in a single-compartment cell using conventional three-electrode setup. Prior measurements, reaction vessels were degassed and purged with argon. Various Ni₂Mo₂derived thin film-coated glassy carbon (GC), pyrolytic carbon (PC) and ITO-coated glass electrodes were prepared, as described below, and used as working electrodes. Saturated silver chloride Ag/AgCl, KCl(sat.) [EAg/AgCl, KCl(sat.) = 0.197 V vs. NHE] or saturated calomel Hg/Hg₂Cl₂, KCl(sat.) [$E_{Hg/Hg_2Cl_2, KCl(sat.)} = 0.241$ V vs. NHE] electrodes were used as reference electrodes and a platinum mesh was employed as a counter electrode. Potentials are reported against RHE, recalculations were performed using the Nernst equation: E (V vs. RHE) = E (V vs. Ag/AgCl, KCl (sat.)) + 0.197 + (0.059 × pH) or E (V vs. RHE) = E (V vs. Hg/Hg₂Cl₂, KCl (sat.)) + 0.241 + (0.059 × pH). Cyclic voltammetry (CV) and linear sweep voltammetry (LSV) were automatically corrected for IR drop using Nova software. Chronopotentiometry measurements were manually corrected for IR drop. Electrical Impedance Spectroscopy (EIS) was used to determine R value which was typically in the range 10-15 Ohm for GC and PC electrodes and 20-25 Ohm for ITO-glass in 1 M NaOH electrolyte solution and 140-160 Ohm for PC electrodes in 0.1 M sodium borate solution. Electrochemical capacitance was determined using cyclic voltammetry (CV) measurements in a potential range where there is a non-Faradaic current response (1.0 - 1.2 V vs RHE). The electrochemically active surface areas (ECSA) values determined from these measurements are order of magnitude approximations for rough comparison of electroactive surface areas.

3. Electrode preparation

Glassy carbon (GC) electrodes (Sigradur® G) with a diameter of 3 mm or pyrolytic carbon (PC) electrodes (Volta) with a diameter of 3 mm were polished consequently with alpha alumina powders of decreasing size suspended in distilled water finishing with 0.05 micron grain size. After each polishing step, the electrodes were thoroughly rinsed with bidistilled water. Then the electrodes were ultrasonicated consequently in bidistilled water and absolute ethanol for 10 seconds each, and dried with compressed air. Subsequently, the polished GC electrodes were pretreated electrochemically as described in ref. [4]. The bare working electrode underwent 20 CV cycles at a potential window of 0.5 to 1.9 V vs. RHE at a scan rate of 100 mV s⁻¹ in 1 M NaOH. Finally, the pretreated electrode was rinsed with absolute ethanol and dried with compressed air. No electrochemical pretreatment was performed for the PC electrodes. Solution of Ni₂Mo₂ in methanol was then drop-casted portionwise on an electrode surface using microsyringe (approximate volume: 40 μ L), and the solvent was allowed to evaporate at room temperature in air. The catalyst loadings were 1.43 mg cm⁻²

(0.32 mg cm⁻² based on active mass in form of nickel(II) hydroxide Ni(OH)₂). Dried film was covered with drop of bidistilled water to facilitate hydrolysis of Ni_2Mo_2 . Thin film was then covered with drop of 1 M NaOH solution and was left to dry overnight in air.

ITO-coated glass (Lumtec, resistance 4-6 Ω sq⁻¹, 0.7 mm thickness) sheets (2.5 × 7.5 cm²) were cut into 2.5 × 0.5 cm² slides and were cleaned by consequent ultrasonication in acetone, bidistilled water and finally in isopropanol for 5 min each. 0.5 × 0.5 cm² area at one end of the slide was used for the deposition of the film. In order to define the deposition area and to avoid the spreading of the solvent, the other side of the glass slide was covered with a scotch tape. Deposition was performed by drop-casting the solution of **Ni₂Mo₂** in methanol using microsyringe (approximate volume: 150 µL). The solvent was allowed to evaporate at room temperature in air. The catalyst loadings were 1.73 mg cm⁻² (0.39 mg cm⁻² based on active mass in form of nickel(II) hydroxide Ni(OH)₂). Once the solvent evaporated, the scotch tape was removed and the central area of the electrode was covered with epoxy glue leaving only the deposition area and the opposite side (0.7 × 0.5 cm²) of the glass slide uncovered. The opposite end of the glass slide was used to set the electric contact using the platinum wire fixed in a custom-made Teflon holder (see Fig. S2). Casted film was then hydrolyzed and treated with 1 M NaOH analogously to the pretreatment of GC/PC electrodes.

Prior LSV or chronopotentiometry measurements, working electrode was cycled in 1 M NaOH in a potential window of 1 to 1.75 V vs. RHE at a scan rate of 100 mV/s until the currents stabilize.



Fig. S2. Photograph image of ITO-coated glass electrode covered with Ni₂Mo₂-derived film.

4. Additional experimental data



Fig. S3. (a) FE-SEM images of two distinct sections of the Ni_{cat} film deposited on a glassy carbon substrate, highlighting the porous, foam-like structure of the deposit.



Fig. S4. Polarization curves for the electrodes covered with Nicat film and for the corresponding blank electrodes.



Fig. S5. CV scans recorded at 50 mV s⁻¹ for the Ni_{cat} | PC electrodes before and after 3 h and 6 h electrolysis at constant current density of J = 10 mA cm⁻².



Fig. S6. (a) Galvanostatic curves of $Ni_{cat}|GC$ electrodes in 1 M NaOH, pH 13.6 at a current density of J = 2 mA cm⁻². Arrows indicate the points when the electrolysis was aborted and O₂ bubbles were mechanically removed from the electrode surface. (b) CV scans recorded at 50 mV s⁻¹ for the Ni_{cat} | GC electrodes before and after 2 h electrolysis at constant current density of J = 2 mA cm⁻².



Fig. S7. (a) Representative CV scans recorded at 50 mV s⁻¹ for Ni_{cat} deposited on different conducting substrates.



Fig. S8. Portion of the XPS spectrum of the Ni_{cat} sample deposited on indium-tin oxide coated glass demonstrating absence of the Mo signals.

Table S2.	Characteristics of different	water-oxidizing electrodes	containing Ni_{cat} as an active
layer ^a .			

Conducting substrate	η@10mA cm ⁻² , V ^b	Roughness factor ^c
GC	0.32 - 0.42	900 ± 700
PC	0.32 - 0.36	230 ± 170
ITO	0.41 - 0.45	340 ± 160

^a All data are obtained from the measurements for 3-7 different electrodes. η @10mA cm⁻² were determined either from the LSV scans recorded at 2 mV s⁻¹ or from the anodic traces of the CV scans recorded at 10 mV s⁻¹. Results are presented in form of the intervals of values. 1 M NaOH was used as an electrolyte. ^b Overpotential (η) required to achieve a current density of J = 10 mA cm⁻². ^c Roughness factor (RF) calculated using the equation RF = C_{DL}·S⁻¹·C_{sp}⁻¹, where C_{DL} is a double layer capacitance determined from CV measurements, S is a geometrical surface area of the electrode (0.0707 cm⁻² for GC and PC electrodes, 0.25 cm⁻² for ITO-coated glass electrodes), C_{sp} is an average specific capacitance of the flat metal electrode (0.040 mF cm⁻² [5]).

Table S3. Comparison of the catalytic performance of Ni_{Cat} to some of the most active Nibased water-oxidizing catalysts reported to date excluding those deposited on 3D conducting substrates.

Catalyst/catalyst precursor ^a	Loading (mg cm ⁻²)	Conducting substrate	Electrolyte	η@10mA cm ⁻² , V ^b	Reference
NiO _x /NiOOH (from Ni-Mo alkoxide) [Ni cat]	0.32 °	GC (or pyrolytic carbon)	1 M NaOH	~ 0.32	This study
NiFe-LDH with intercalated MoO4 ²⁻	0.28	GC	1 M KOH	0.28	[6]
Ni ₂ P nanoparticles	0.14	GC	1 M KOH	0.29	[7]
NiOx	~ 0.02 - 0.05	Au / QC d	0.5 M KOH	0.32	[8]
NiFe-LDH	0.2	GC	1 M KOH	~ 0.32	[9]
Ni ₂ P nanowires	0.14	GC	1 M KOH	0.33	[7]
α-Ni(OH)2	~ 0.2	GC	0.1 M KOH	0.33	[10]
NiFeOx	-	GC	1 M NaOH	0.34	[11]
NiMoFeOx	-	GC	1 M NaOH	0.34	[11]
Li _{1.03} Ni _{0.66} Co _{0.21} Fe _{0.10} O _{1.95}	0.128	GC	0.1 M KOH	~ 0.37	[12]
NiCoOx	-	GC	1 M NaOH	0.38	[11]
Ni ₂ P nanowires	~ 0.1	FTO	1 M KOH	~ 0.40	[13]

BaNiO ₃	0.295	GC	0.1 M KOH	~ 0.41	[14]
NiMn ₃ O _x	-	GC	0.1 M KOH	0.42	[15]
β-Ni(OH) ₂	~ 0.2	GC	0.1 M KOH	0.44	[10]
Ni ₂ P nanoparticles	~ 0.1	FTO	1 M KOH	~ 0.50	[13]

^a Formulas are generally presented according to author's designations and may not reflect the actual stoichiometry of the catalyst/precursor; for detailed information, reader is referred to original papers. ^b Overpotential (η) required to achieve a current density of J = 10 mA cm⁻². ^c Based on active mass in form of Ni(OH)₂. ^d QC – quartz crystal.

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