



Kolloquium des Wilhelm-Ostwald-Instituts

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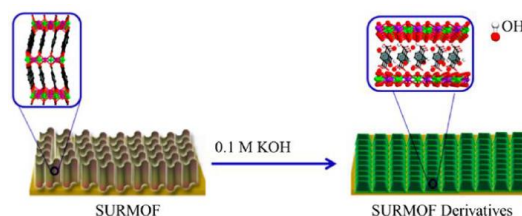
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Surface Mounted Metal-Organic Frameworks

Abstract

Metal-Organic Frameworks (MOFs) are crystalline and porous coordination network materials which are composed of metal ion building units connected by organic linkers via coordination bonds. MOFs feature a wide range of fascinating structures, and offer unique opportunities of molecular materials design and a huge parameter space of fine tuning of chemical and physical properties. Applications of MOF include energy, environment, health and information technologies. We pioneered MOF integration to devices by MOF thin film deposition and selective positioning to substrate surfaces.^[1] Within the past decade, surface anchored MOF (SURMOF) research has seen a tremendous evolution.^[2-5] In the first part of the lecture, this development is summarized.

In the second part of the lecture a novel perspective of SURMOF-derived materials is presented.^[6-9] Unprecedented catalyst mass specific activity and stability in the oxygen evolution reaction (OER), a key step in electrocatalytic water splitting were discovered. The NiCo hydroxide materials, which were derived from NiCo-BDC SURMOFs on macro- and microelectrode substrates feature a mass activity of $\sim 2.5 \text{ kA}\cdot\text{g}^{-1}$ at the overpotential of 300 mV, which is superior to benchmarked electrocatalysts. The excellent morphology of the SURMOF-derived ultrathin electrocatalyst coating led to a high exposure of the most active Ni and Co sites.^[6]



The performance can be further improved by a lattice strain modulation approach. NiFe-BDC SURMOF derivatives were obtained reaching a current density of $200 \text{ mA}\cdot\text{cm}^{-2}$ at a small overpotential of 210 mV, and long-term stability of over 120 h at a current density of $500 \text{ mA}\cdot\text{cm}^{-2}$. This bi-functional catalyst for OER and ORR features a very narrow overpotential window of 0.68 V in 0.1 M KOH, in which the mass loading was two orders of magnitude lower than benchmark electrocatalysts.^[7,8] Finally, starting-out with hetero-structured Ni/Fe-BNC SURMOFs the specific reconstruction and self-optimization process yields a further rise of mass activity close to $3 \text{ kA}\cdot\text{g}^{-1}$ at 300 mV overpotential.^[9]

References.

[1] Surface-Mounted Metal–Organic Frameworks: Past, Present, and Future Perspectives, A. L. Semrau, et al., *Langmuir* **2021**, 37(23), 6847–6863. – [2] S. Hermes, et al., "Selective Nucleation and Growth of Metal–Organic Open Framework Thin Films on Patterned COOH/CF₃-Terminated Self-Assembled Monolayers on Au(111)", *J. Am. Chem. Soc.* **2005**, 127, 13744–13745. – [3] A. Bétard, et al., „Metal–Organic Frameworks Thin Films: From Fundamentals to Applications“, *Chem. Rev.* **2012**, 112, 1055–1083. – [4] I. Stassen, et al., “An updated roadmap for the integration of metal– organic frameworks with electronic devices and chemical sensors,” *Chem. Soc. Rev.* **2017**, 46, 3185–3241. – [5] M. Tu, et al., “Direct X-ray and electron-beam lithography of halogenated zeolitic imidazolate frameworks”, *Nature Materials* **2021**, 20, 93–99. – [6] J. Liu, et al., “Recent approaches to design electrocatalysts based on metal–organic frameworks and their derivatives”, *Chemistry, Asian J.* **2019**, 14, 3474–3501. – [7] W. Li, et al., „Unprecedented high oxygen evolution activity of electrocatalysts derived from surface-mounted metal–organic frameworks“, *J. Am. Chem. Soc.* **2019**, 141, 5926–5933. – [8] W.-J. Li, et al., “Advanced Bifunctional Oxygen Reduction and Evolution Electrocatalyst Derived from Surface-Mounted Metal–Organic Frameworks”, *Angew. Chem. Int. Ed.* **2020**, 59, 5837–5843. – [9] S. Hou, et al., Metamorphosis of Heterostructured Surface-Mounted Metal–Organic Frameworks Yielding Record Oxygen Evolution Mass Activities, *Adv. Mater.* **2021**, 33, 2103218.