

Abstract

Green hydrogen produced from fossil-free resources is considered a key game changer in the search for solutions enabling the energy transition. In this context the development of hydrogen production technologies like electrolysis is strongly driven by the two main criteria: sustainability and economy of scale. Over the past decades, various technological achievements have resulted in a reduction of costs, which has significantly improved the economic potential of hydrogen produced by water electrolysis. Especially in the field of material development, great effort was devoted to modify nanostructures of state-of-the-art precious metal-based catalyst materials and to replace them with abundant cost-effective catalysts accelerating sluggish water splitting reactions.

This thesis describes the **molecule-to-advanced material** value chain with a special focus on chemically tailored molecular precursors. Within these studies, synthetic approaches starting from new bidentate ligand systems based on nitrogen-oxygen (–N–O–) and nitrogen-sulfur (–N–S–) donor systems were investigated in terms of their chelating properties and decomposition patterns. Within the precursor approaches, the role of here developed ligand classes on the molecular structure and their thermal properties were evaluated. A heteroleptic precursor concept based on neutral and anionic ligands in Cu(I) precursor molecules was established and investigated regarding their stability, volatility and thermal decomposition. The new complexes were investigated by nuclear magnetic resonance (NMR) spectroscopy and electron ionization mass spectrometry (EI MS). The representative Cu(I) precursor [(COD)Cu(TFB-TFEA)] offered high volatility ($T_{\text{sublimation}} = 80\text{ °C}$, $p = 10^{-2}\text{ mbar}$) and sufficient stability in the gas phase and a defined thermal decomposition behavior revealing an intramolecular ligand elimination cascade. Thermal and plasma-enhanced CVD experiments demonstrated the suitability of the copper compound for deposition of copper(0) and copper(I) oxide films with high molecule-to-material conversion efficiency that could be converted into crystalline copper(II) oxide upon heat treatment at $T_{\text{annealing}} = 500\text{ °C}$, which were characterized regarding their crystallinity (X-ray diffraction, XRD), composition X-ray photoelectron spectroscopy, XPS), morphology (scanning electron microscopy, SEM), transparency (UV-Vis spectroscopy) and electrical measurements to reveal transparent and semiconducting properties of as-deposited metallic copper ultra thin films.

Iridium(I) precursors [(COD)Ir(N[^]O)] and [(CO)₂Ir(N[^]O)] (N[^]O = 3-(thiazol-2-yl)-1,1,1-trifluoropropen-2-olate, ThTFP; N-(4,4,4-trifluorobut-1-en-3-on)-6,6,6-trifluoroethylamine, TFB-TFEA) were obtained in high yields (up to 96%) and offered high volatility ($T_{\text{subl.}} = 30\text{ °C}$,

$p = 10^{-2}$ mbar). They were investigated in solution by 1D and 2D NMR and UV-Vis spectroscopy, and in the solid-state by single-crystal X-ray diffraction, elemental analysis and Fourier Transform Infrared (FT-IR) spectroscopy and subsequently in the gas phase by EI MS spectrometry. The thermogravimetric studies and CVD experiments revealed the clean decomposition of Ir(I) precursors into Ir-based nanoparticulate thin films that was evaluated for different gas phase methods (MOCVD, PECVD and ALD). Thin films were characterized regarding their crystallinity (XRD), composition (XPS) and morphology (SEM). The deposited metallic and oxidic iridium thin films on various substrate materials were characterized towards their catalytic properties in a bilayered ($\text{IrO}_x @ \alpha\text{-Fe}_2\text{O}_3$ and $\text{IrO}_x @ \text{TiO}_2$) photoelectrochemical setup to evaluate oxygen evolution reaction (OER, $2 \text{H}_2\text{O} + 4 \text{h}^+ \rightarrow \text{O}_2 + 4 \text{H}^+$) and, furthermore, oxygen reduction reaction (ORR, $\text{O}_2 + 4 \text{H}^+ + 4 \text{e}^- \rightarrow 2 \text{H}_2\text{O}$) performance of as-deposited composites. Finally, water splitting by solar irradiation was achieved without external bias through incorporation of Ir-based electrodes in tandem PV-EC devices.

In a new approach to obtain metal sulfides novel sulfur-based ligand systems were evaluated for the targeted precursor synthesis of homoleptic $3d$ (Fe^{2+} , Co^{2+} , Ni^{2+} , Cu^{2+} and Zn^{2+}), $4d$ (Pd^{2+}) and main group elements (In^{3+} and Sn^{2+}) in order to demonstrate the applicability of sulfur-based precursors for the selective metal sulfide synthesis via gas phase methods. Homoleptic $[\text{M}(\text{N}^{\wedge}\text{S})_x]$ ($x = 2, 3$; $\text{N}^{\wedge}\text{S} = 3\text{-(dimethylloxazol-2-yl)-1,1,1-trifluoropropen-2-thiolate}$, DMOTFPT; $N\text{-(4,4,4-trifluorobut-1-en-3-thione)-tert-butylamine}$, TFBT-TBA) precursor molecules were comparatively characterized by single-crystal X-ray diffraction analysis and thermogravimetric experiments to reveal the formation of Co_9S_8 , Ni_3S_2 and SnS_2 . MOCVD experiments confirmed the formation of metal sulfides that were investigated towards phase composition (XRD) and morphology (SEM). Finally, nickel sulfide thin films were electrochemically investigated in a PEC setup as electrocatalysts for oxygen evolution reaction. The results described in this thesis enrich the possibilities for the replacement of precious metals as state-of-the-art OER materials. In addition, the synthetic chemical concepts that have been developed with respect to controlled materials synthesis, clearly demonstrated the influence of the molecular structure on the phase composition and chemical purity of the final catalytic material.