**Understanding the formation and dynamic nature of non-noble-metal oxide co-catalysts for photocatalytic water splitting reactions**

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Photocatalytic water splitting has been recognised by the community as a promising way to produce molecular H2 from abundant water. The reaction of water splitting is, however, a rather challenging one and requires careful design of the catalytic sites for both, water oxidation (OER) and hydrogen evolution (HER), in order to become a viable alternative to existing ways of H2 generation. The currently most efficient co-catalysts for the photocatalytic reduction and oxidation of water are Pt and Pd as well as IrO2 and RuO2, respectively: all are expensive materials based on rare noble metals.To achieve large scale industrial application, the development of new co-catalysts based on cheap and widely available elements remains an important issue.

In this work [1], we systematically investigated a set of oxide-based co-catalysts featuring Mn, Cu, Co, Fe and Ni prepared using a common wet impregnation – thermal decomposition route directly on TiO2 nanoparticles, used here as a model photoactive substrate (Figure 1a). We carefully characterized the systems with a combination of TGA, *in situ* XRD (Figure 1d), ATR-FTIR, Raman, PL and XPS as well as tested all generated MOx-TiO2 composites towards sacrificial HER and OER reactions using our home-built photocatalytic reactors with *in situ* data collection

Combined spectroscopic and structual analyses revealed strong differences in thermal evolution of the pure M(acac)x compared to impregnated M(acac)x-TiO2 samples where the M precursor underwent decomposition at substantially lower temperatures, via different mechanism and often resulted in the formation of otherwise unstable MOx species. The final state of the co-catalyst nanoparticles, however, could be controlled by optimizing the calicnation conditions. Further SEM and TEM analyses along with EDX mappings confirmed the morphology of the generated MOx-TiO2 samples featuring small (2-5 nm) amorphous MOx co-catalysts nanoparticles decorating the TiO2 surface (Figure 1b), while spectroscopic methods provided in-depth information about the interactions between the composite components.

Finally, our water splitting tests indicated the dynamic nature of the NiOx-TiO2 and CuOx-TiO2 composites – both active towards HER – that undergo reversable *in situ* reduction during the photocatalytic cycle (Figure 1c). On the other hand, we found that FeOx-TiO2 and CoOx-TiO2 composites exhibited the highest OER activity compared to the bare TiO2, while XPS data of the samples after reaction indicated that partial oxidation of M species took place during the course of the photocatalytic experiments.

This contribution provides a systematic study on the specifics of the wet chemistry-based synthesis of small MO*x* NPs directly onto the surface of TiO2, which can be expanded to other inorganic substrates, and thus will be of interest to the broad audience of materials scientists and chemical engeneers.



**References**

1. Schubert, J., Popovic J., Haselmann G., Nandan S., Wang J., Giesriegl A., Cherevan A. and Eder D. (2019). Immobilization of Co, Mn, Ni and Fe oxide co-catalysts on TiO2 for photocatalytic water splitting reactions. J. Mater. Chem. A, 7, 18568–18579.