5th live session of **Focus Materialchemie** – Wednesday, **03.05.2023** 16:00 – @ **Seminarraum Lehar 01** (TU-Wien, Getreidemarkt 9, BC, OG. 01, room A46) – join us on **ZOOM** (ID: 983 0066 2349)

Elucidating the formation and active state of Cu and Ni co-catalysts for photocatalytic hydrogen evolution

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Design of active and selective co-catalysts constitutes one of the major challenges in developing heterogeneous photocatalysts for energy conversion applications. This work provides a comprehensive insight into thermally induced bottom-up generation, transformation and hydrogen generating mechanism of promising Cu and Ni based co-catalysts. We show how the photocatalytic activity is affected by different calcination temperature, leading to a decreased hydrogen generation by increasing temperature. Supported by DFT modeling, a combined assessment using Raman spectroscopy, FTIR, DRS, HRTEM, XRD, XPS, UPS and TXRF, our data suggest that low temperature (< 200 °C) treatments facilitate optimal electronic communication of the Cu and Ni species to the TiO_2, which allows for a more efficient charge utilization and yields maximum HER rates. In contrast, higher temperatures (> 200 °C) do not affect the oxidation state of Cu and Ni, but rather facilitate a gradual increase of the coordination strength of the metals with the TiO_2 surface and sub-surface. The stronger chemisorbed and sub-surface diffusion of Ni and Cu, leads to the introduction of new defect states and marks the drop in HER performance. This work examines the variety of electronic and structural effects that are in control of photocatalytic activity of similar co-catalyst loaded semiconductor photocatalysts and will, thus be relevant to the development of other advanced photocatalysts.