

Formic acid photoelectroreforming on bismuth vanadate based catalysts

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Hydrogen storage materials are a key factor in implementation of a sustainable hydrogen economy.^[1] Among many options, liquid organic hydrogen storage (LOHC) materials are of high interest due to their easy handling and implementation to existing infrastructure. A possible candidate for LOHC is formic acid (FA), a low toxicity, water miscible compound that can also be found in nature.^[2] Furthermore, a key advantage is the possibility of implementing a carbon neutral cycle by coupling carbon dioxide (CO₂) reduction to FA with selective FA oxidation to CO₂.^[3]

For the oxidative part of aforementioned cycle, most research up to now has focused on FA photoreforming over titanium dioxide (TiO₂)^[4], a UV absorbing semiconductor, but little effort has been made to implement a semiconductor with absorption in the visible light range, such as bismuth vanadate (BiVO₄), which recently has gained attention due to its capabilities for oxygen evolution reaction.^[5] This thesis focuses on utilisation of BiVO₄ as a photocatalyst under applied external potential.

Preliminary experiments were conducted in search of metal co-catalysts for support of the photocatalytic reaction on TiO₂. The same metal co-catalysts were then introduced to BiVO₄ based samples for use under photoelectrocatalytic conditions.

It was found, that both copper (Cu) and (Ni) were suitable for selective photoreforming of FA to CO₂ over TiO₂ under UV illumination (365 nm). Furthermore, BiVO₄ showed to be a selective catalyst for the oxidation of FA to CO₂ under photocatalytic conditions (solar spectrum) with applied external potential of 0.4 V vs. reversible hydrogen electrode (RHE). It was then examined, if Cu and Ni were also applicable as co-catalysts on BiVO₄ under photoelectric conditions. While addition of Copper co-catalyst to BiVO₄ lead to unstable material, introduction of Ni as a co-catalyst was successful, showing promising results for the reduction of required energy for photoelectric oxidation of FA over BiVO₄.

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