

Title of Project: *Mass- and charge-transport in hybrid organic/inorganic photocatalyst systems (SNPs@LDHs) – a high-throughput approach.*

Co-supervisor 1: Dr. Michael J. Bojdys, Humboldt Universität zu Berlin

Co-supervisor 2: Prof. Dr. Arne Thomas, Technische Universität Berlin

1. Abstract

The question of “*What constitutes an **ideal heterogeneous photocatalysts for water splitting?***” is of paramount importance for a truly sustainable hydrogen economy. In practice, however, only one half-reaction (proton reduction) occurs preferentially, because the four-hole water oxidation is sluggish in comparison to spontaneous electron–hole recombination within the catalyst. Organic systems such as sulphur- and nitrogen-containing porous polymers (SNPs) are efficient photocatalysts for hydrogen evolution from water (HER), while inorganic materials like layered double hydroxides (LDH) are oxygen evolution photocatalysts (OER). This project will develop the next-generation overall photocatalysts by coating LDH-OER-photocatalysts with SNP-HER-photocatalysts. The resulting hybrid organic/inorganic systems grow as intimately fused, bulk heterojunctions that not only enable efficient mass-transport but also promote electron transport between the OER- and HER-phase thanks to the overall π -conjugation of the organic catalyst-coating.

2. Extended version of the project

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i. Overall goal of the project

This project combines the expertise of two very unique labs from the HU (IRIS Adlershof) and the TU (UniSysCat) in organic and inorganic functional nanomaterial design and study of effects at interfaces. We will create and analyse a library of organic donor-acceptor photocatalysts with suitable bandgaps from the family of sulphur- and nitrogen-containing porous polymers (SNPs) grown on-top of inorganic oxygen evolution catalysts from the family of layered double hydroxides (LDHs). The SNPs@LDHs materials will have systematic variations of the donor-acceptor motifs in the organic part and of the composition in the inorganic part.

ii. State of the art

Overall water splitting using noble-metal free catalysts is a key technology to a truly sustainable hydrogen-based energy economy, yet, it has eluded cross-disciplinary efforts of chemists, physicists and engineers.¹ Until very recently, only two publications from the Thomas group (UniSysCat) and the Bojdys group (IRIS Adlershof) explored donor-acceptor interactions in polymer photocatalysts,² e.g. in highly modular sulphur- and nitrogen-containing porous polymers (SNPs).³ SNPs combine strong donor-acceptor interactions and an overall conjugated, porous polymer framework. This enables them to achieve outstanding performance in photocatalytic hydrogen evolution (HER) from water with rates of up to 3200 $\mu\text{mol h}^{-1} \text{g}^{-1}$ at excellent apparent quantum yields of 4.5%. On the inorganic end, layered double hydroxide (LDH) can be obtained with different Zn/metal atomic ratios (from 4:2 to 4:0.25; M: Ti, Ce, Cr, Al) with relative ease by changing of the molar ratio of starting salts during synthesis. The Thomas group (*UniSysCat*) has expertise in the synthesis and characterization of metal oxides and LDH-type materials and their application in energy conversion as well as catalysis.⁴ These LDH materials have extremely high apparent quantum yields for oxygen generation (OER) in photocatalytic water splitting of between 12.2% and 60.9%. However, milling, mixing or any other physical combination of such HER and OER catalysts never resulted in any convincing overall water splitting materials. Surface-assisted growth of one organic phase on-top of an other organic/inorganic phase may create a more intimate and more efficient heterojunction, e.g. in van der Waals heterostructures. The Bojdys group pioneered macroscopic films of 2D/3D organic polymers grown via a twinned mechanism – first the 2D crystalline organic framework, then the 3D polymer. The two organic phases form an efficient type I heterojunction that facilitates electron transfer to such a degree that photocatalytic evolution of hydrogen gas from water becomes possible entirely without the need for any noble metal co-catalyst.⁵ With the advent of accelerated discovery of organic polymer photocatalysts, the Bojdys group proposes to extend this robot-assisted approach to the search of the optimal hybrid organic/inorganic photocatalyst (SNPs@LDHs).

iii. Specific aims and how they may be reached

In the first work package of the project, the applicant will synthesise a library of binary layered double hydroxides (LDHs), ZnCr, CoAl, and ZnAl with Zn/metal atomic ratios (from 4:2 to 4:0.25) [WP1, Thomas TU]. A parallel library of LDHs will be doped with Pd-nanoparticles, since a Pd⁰/LDH hybrid, can activate Heck, Suzuki, Sonogashira and Stille coupling reactions. LDH materials with and without Pd and with various morphologies (powders, platelets, particles, rods), will act as the catalytically active surfaces to be coated by organic donor-acceptor polymers (SNPs) [WP2, Bojdys HU]. The family of SNPs combines two important features for heterogeneous photocatalysts: an open pore-structure and a highly modular, π -conjugated backbone. In particular, the modularity of the bridge-units enables us to vary the sulphur content in a very controlled way, and hence to achieve materials with a range of optical band gaps (from 1.67 to 2.58 eV) that are in the window of interest for the

hydrogen evolution reaction (HER) from water. Suitable C_2 and C_3 symmetric thiophene-based electron acceptors (thienothiophene (TT), bithiophene (BT), benzotrithiophene (BTT), and naphthodithiophene (NDT)) are coupled with C_3 symmetric triazine (C_3N_3) containing electron acceptors using Pd-catalysed Stille coupling. Also, Glaser-type couplings of $C\equiv C-H$ or $C\equiv C-TMS$ using Lewis acidic interfaces (LDH/metals) has been reported by the Bojdys group, and will make excellent use of Pd-free LDHs prepared previously. Different combinations of donor-acceptor tectons, and Pd-containing and Pd-free LDHs will be reacted together in a high-throughput (HT) robot-assisted approach using the Chemspeed ASW2000 synthetic station situated at IRIS Adlershof [WP3, Bojdys HU]. Different combinations of porous, organic HER catalysts and inorganic OER catalysts pose a challenge for detailed investigations of bulk properties and give rise to the opportunity to carry out computational predictions/post-rationalisations (possible coop. within UniSysCat, P. Saalfrank, or its partner network, ICDC/L. Gagliardi, or IRIS Adlershof/C. Cocchi).

The resulting SNPs@LDHs materials will be characterised in an HT approach using autosampler-enabled FT-IR (IRIS Adlershof, end group analysis). Gas adsorption (N_2) studies will be performed at both institutions to ensure no analytical bottlenecks are created (Thomas TU Berlin, Bojdys HU Berlin). IRIS Adlershof and UniSysCat are uniquely positioned to study surface phenomena of the obtained SNPs@LDHs, using e.g. XPS (N. Koch, HU, Roldan, FHI), XAFS (Dau, FUB), time-resolved spectroscopies (van de Krol, HZB) and surface enhanced Raman (Raabe, HU, Weidinger, TU Dresden) as-well-as a number of setups within the Bojdys group to probe the conductivity of monolithic- and powder-samples. Phase-behaviour of the organic/inorganic hybrid materials will be investigated at IRIS Adlershof (Ch.T. Koch, HU). Fully characterised and selected samples will be tested in overall water splitting [WP5, Thomas, coop. Schomäcker, TUB]. Hard-to-predict composite effect of SNP@LDH hybrids will likewise be tested in photocatalytic CO_2 reduction [WP5, Thomas].

The co-PIs have conducted research at the highest scientific levels in the past and they have established facilities, equipment and the scientific networks necessary to continue to do so in the context of this project. High-throughput synthesis of organic SNP-precursors and their analysis can be carried out at the bojdysLAB, while library design of LDHs will be carried out at the Thomas group. The here-proposed project methodology prepared will initiate extensive collaborative research in the UniSysCat and IRIS networks, in particular since the high-throughput, combinatorial approach to materials discovery yields itself to cross-disciplinary problems not only of the chemistry community, but also of physics, engineering and computational materials design.

