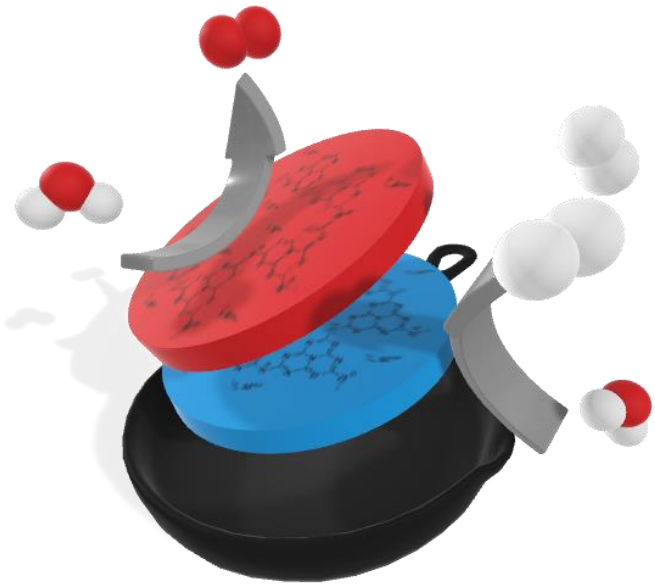
Abstract:

Title of Project: Interfacial catalysts for overall water splitting (InterCat)

Co-supervisor 1: Prof. Dr. Arne Thomas, Technische Universität Berlin

Co-supervisor 2: Prof. Dr. Michael J. Bojdys, Humboldt-Universität zu Berlin

A sought-after alternative for finite fossil fuels is direct water splitting using a semiconductor photocatalyst with visible light to produce hydrogen, thus converting sunlight into storable and transportable energy. Methods to produce potential catalysts for efficient overall water splitting currently yield materials as insoluble powders with small poly-crystalline domains, grain boundaries and inhomogeneities, which cannot be implemented into macroscopic devices. Using ionothermal synthesis at the liquid-solid interface, we propose to combine two layered, π-conjugated hybrid polymer catalysts – based on poly(heptazine imide) and poly(triazine imide) – into one free-standing, intimately interfacing device that is able to spatially separate the underlying redox-reactions thus capable of overall water splitting.



Extended description version of the project:

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1. 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 sets of polymer-supported hybrid catalyst systems – based on carbon nitride polymers – that are individually able of oxygen evolution (OER) and hydrogen evolution (HER) from water. Then we will combine them via interfacial growth into free-standing, spatially separated and intimately interfacing devices capable of overall water splitting.

2. State of the art

Water splitting using photo- and electroactive organic materials is a key technology to a truly sustainable hydrogen-based energy economy, as it offers to reduce or to replace environmentally damaging and unsustainably sourced metals that are widely used in inorganic catalysts.[1] However, to this day, no metal-free material that is capable of overall water splitting with practical efficiencies has been achieved. Most of these organic systems suffer from structural disorder, as conventional covalent organic materials nucleate and grow in solvent mixtures and precipitate exclusively as insoluble powders with small (up to µm-sized), poly-crystalline domains, which cannot be implemented into macroscopic devices. We have shown previously that polymerisation at the liquid-solid interface produces organic materials (triazin-based graphitic carbon nitride (TGCN)) of unparalleled crystalline order.[2] A continuous band structure and macroscopic charge transport is possible in such organic materials because of the optimal alignment of π-conjugated building blocks.[3] TGCNs as well as related poly(heptazine imides) (PHI)[4] and poly(triazine imides) (PTI),[5] are therefore currently examined in our groups owing to their notable semiconducting and (photo)catalytic properties (**Fig. 1**). These CN-materials are prepared by thermal treatment of nitrogen-rich molecules in eutectic salt melts, such as LiX and KX (X=Cl or Br). We have recently shown that PHIs and PTIs can serve as host and matrix for transition metal cations and that the nature and amount of the metal species is strongly influencing their optoelectronic properties and photocatalytic performance.[4] These properties as well as the possibilities to deposited well-defined films on substrates should enable the preparation of hybrid layered catalysts with an intimate interface between OER and HER active layers, finally producing a Z-scheme catalyst for overall water splitting. Integration of HER/OER catalysts into devices is desirable to spatially separate the evolving gases (O_2 and H_2) for reasons of usability and safety.

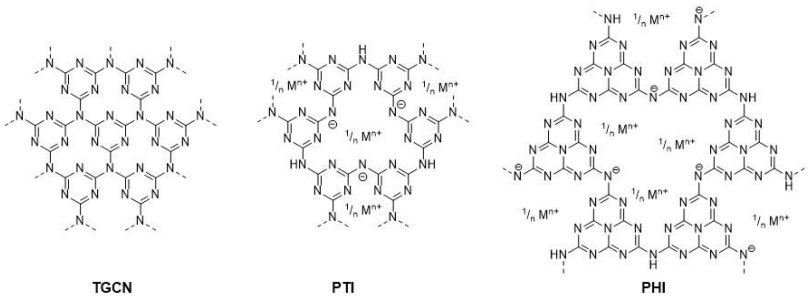

Figure 1: Chemical structures of TGCN, PTI, PHI

3. Specific aims and how they may be reached:

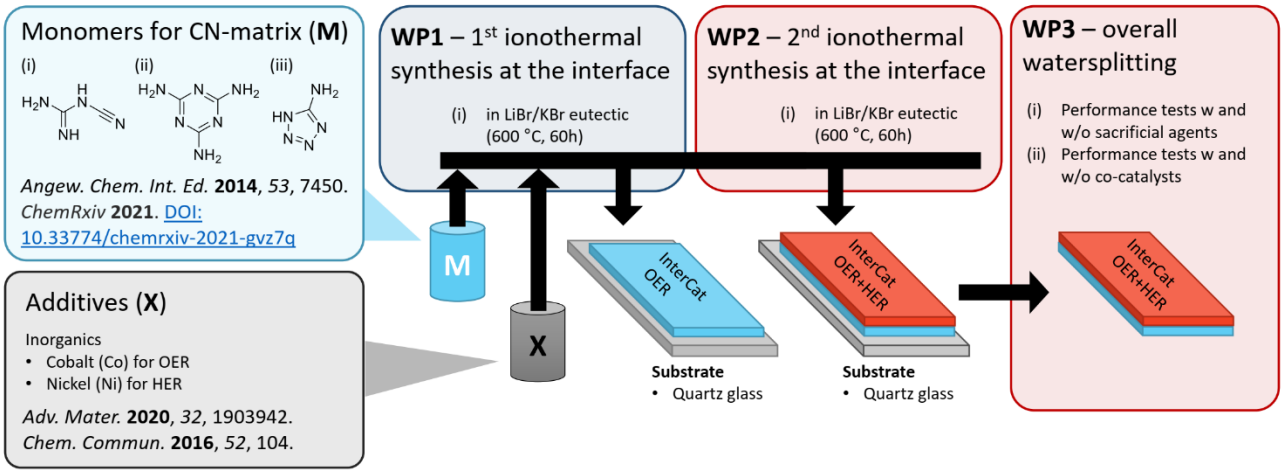

Figure 2. Proposed workflow for InterCat project.

We propose to interface two layered, π-conjugated hybrid polymer catalysts – based on TGCN, PTI and PHI – into one operational device capable of overall water splitting.

Thermodynamically stable, large single-crystalline structures from layered HER and OER catalysts will be achieved by sequential ionothermal synthesis of carbon nitride frameworks on interfaces.
The **proposed workflow of the InterCat project** is shown in Fig. 2. Ionothermal synthesis of N-rich monomers (M) in presence of inorganic additives (Co salts) in presence of a substrate will yield CN-polymer layers active for OER. A second polymerization step in the presence of another inorganic additive (Ni salt) will then generate an InterCat material composite set-up for OER and HER. Finally, by removing the substrate (either by etching or by physical delamination) a **free-standing, spatially separated and intimately interfacing device capable of simultaneous OER/HER** will be produced. The active solid substrate plays three roles in the InterCat process: it acts (i) as a **physical template** for the polymer film, (ii) as a an **adressable, synthetic platform** that allows transfer of InterCat materials between reaction environments, and (iii) as an **optically transparent substrate** for *e.g.* spectroscopic analysis and device integration.
Beside the analytical tools available in the groups of the applicants (XRD/XPS/IR/UV/TGA/Gas-Sorption) the structure and photophysical properties of bulk CN-polymers have been already investigated together with the UniSysCat groups of Bittl/Teutloff (EPR), van de Kroel (UPS/Transient spectroscopies), Kanngießer (XAS) and Antonietti (SEM/TEM), Schlögl (HR-TEM) as well as other groups from IRIS Adlershof and in the Berlin area, e.g. Oschkinat/Chow (NMR), Lu (Kryo-TEM), Raabe (AFM), N. Koch (XPS/UPS), C. Koch (cryoTEM, SEM, EDX). Computational predictions on optoelectronic properties of related materials has been conducted by P. Saalfrank (UniSysCat) and C. Cocchi (IRIS). For further studies, IRIS Adlershof and UniSysCat are uniquely positioned to study surface phenomena of the obtained InterCats, 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. Photocatalytic tests will be carried out in the group of R. Schomäcker and with a newly acquired fully integrated photocatalytic setup in the Thomas group, suitable for HER/OER/overall water splitting and CO2RR.