Maria Wächtler

Insights into Semiconductor Nanocrystal-Based Light-Driven Catalysis – Linking Charge-Carrier Dynamics and Activity

Building on the groundbreaking pioneering work of the Nobel Prize Winners Bawendi, Brus, and Yekimov, a large variety of routes to produce colloidal nanocrystals with exceptional control over size, crystallinity, shape, surface properties and composition have been established, enabling the design of materials with tunable chemical, physical, electrical, and optical properties [1, 2]. Quantum dots are one famous member of this material class offering strong light absorption and bright narrowband emission both tunable across the visible and infrared spectral range via crystal size. More complex nanocrystal heterostructures combining domains of different semiconductor materials enable to gain control over localization of charge carriers in the structures by relative alignment of valence and conduction band states. This wave function engineering concept can be utilized to generate structures supporting, e.g., either radiative processes or separation of charge carriers, and the design of nanocrystals fitting to a target application. Nowadays, colloidal nanocrystals are researched for applications for illumination, in displays, as sensors, in communication and information technology, biology and medicine; but also for light-harvesting, e.g. in next generation photovoltaics, and for light-driven catalysis.

The development of approaches for direct capturing and storing the energy of sunlight in chemical bonds of a fuel, e.g., molecular hydrogen, offering a clean, sustainable, and abundant source of energy is a long-standing challenge. Inspired by the successful UV light-activated splitting of water with TiO_2 [3] and the first demonstration of the capability of microcrystalline CdS particles functionalized with Pt and RuO_2 to activate water for splitting in to hydrogen and oxygen upon irradiation with visible light [4], colloidal semiconductor nanocrystals gained more and more attention for application in not just splitting water, but solar-driven redox-catalysis in general [5, 6]. The key features supporting this development are the tunability of the absorption within the visible spectral range and of redox potentials via, e.g. dimensions of the nanocrystal. Nevertheless, in the context of light-driven catalysis, the absorption of light resulting in the generation of an electron-hole pair, an exciton,

in the nanocrystals is only the very first step. Equally important is to achieve a high photon-conversion yield. In this respect the fate of the charge carriers generated upon excitation is important. The charge carrier transfer to reactive sites at the surface or to cocatalysts deposited at the surface of the particles competes with nanocrystal intrinsic relaxation processes involving charge-carrier trapping, radiative and non-radiative recombination. All these processes are sensitive to the structure of the particles at hand, e.g. composition, crystallinity, shape and dimensions of the semiconductor particles, the nature of cocatalysts and the type of surface ligands. Hence, to push forward the development of functional materials based on semiconductor nanocrystals for application in light-driven catalysis, the function immanent exciton and charge-separation/recombination dynamics in relation to structural parameters and how these translates into activity needs to be understood.

In my research group, we strive to reveal the connections between structure, charge-carrier dynamics, and the targeted function by applying a combination of time-resolved transient absorption and photoluminescence spectroscopy. Analysis of photoluminescence spectra, the quantum yields and lifetimes delivers information on processes competing with the formation of the emitting lowest excitonic state. This can be the population of trap states, sometimes leading to a characteristic trap state emission, impacting quantum yields and lifetimes for photoluminescence from the band edge states; but also charge carrier transfer processes, both of holes and electrons to any type of acceptor, hence also charge carrier shuttles or reaction centers relevant for a catalytic reaction. Time-resolved transient absorption spectroscopy applied with fs temporal resolution can give insights into the fast relaxation towards the lowest band edge state, and any type of process competing with it, e.g. transfer of an electron from the conduction band state manifold to an electron acceptor. Extended to the ns-ms time range also information on recombination processes can be collected.

A lead structure, which accompanied our research during the past years, are dot-in-rod heteronanostructures, especially CdSe@CdS nanorods. These particles, consisting of a CdSe quantum dot enclosed in a rod-shaped CdS shell, gained a lot of interest over the past decade as sensitizers for the light-driven water-reduction half reaction producing hydrogen from water. Coupled with potential metal nanoparticles as cocatalysts, which can be selectively grown at a certain position, e.g., one tip of the rods, such nanostructures are reported to be able

Prof. Dr. Maria Wächtler
Rheinland-Pfälzische Technische Universität Kaiserslautern-Landau
Fachbereich Chemie
Erwin-Schrödinger-Straße 52, 67663 Kaiserslautern
maria.waechtler@chem.rptu.de

to show high quantum yields of photon-to-hydrogen conversion [7]. Very roughly summarized, the light-induced processes, which need to occur leading to activity, are the transfer of electrons to the cocatalyst, where they are available to reduce protons, while holes localize in the CdSe seed and are quenched by a present sacrificial electron donor (Figure 1A).

In our earliest work in this field, we focused on the impact of composition and morphology of the metal particles as cocatalyst on the charge-separation step at the nanosized semiconductor/metal interface. Both, composition [8] and size [9] can severely impact the photon-to-hydrogen conversion efficiency, which could be related to either efficiency of the transfer of charges to the cocatalyst, or the subsequent reaction occurring at the metal surface. An interesting finding for a series of Ni-tipped nanorods was the appearance of an optimal metal tip size showing superior photon-to-hydrogen conversion (Figure 1C). Applying time-resolved transient absorption and photoluminescence spectroscopy, we were able to relate this effect directly to the efficiency of charge separation at the semiconductor/metal interface [9]. We observed an optimum for the formation of the charge separated state at the tip size of the highest activity. We discussed the appearance of this optimum based on a model comprising two opposing trends: a size dependent Coulomb blockade decreasing with increasing size and another type of barrier growing in with size, which we called, in line with often used terminology, Schottky barrier. One should be aware, that it is highly debatable, whether a Schottky barrier could form at the scales of these structures and there is need for a more detailed investigation of the properties of such nanoscale interfaces and the source of size dependent barriers appearing [10].

Surprisingly, in this series of nanorods with Ni-tips with varying size, though the efficiency of charge separation varied, the observed time constants for charge separation were unaffected. We related this observation to the necessity of migration of charge carriers towards the semiconductor/metal interface re-

gion preceding the actual interface crossing step due to the significant length of the nanorods (40-50 nm). If this migration process is slow compared to the actual interface crossing step, it will determine the observed timescale for charge transfer. Only recently we were able to supply further proof for this hypothesis and observe nanorod length dependent charge transfer times, increasing with the square of the length of the nanorods, in agreement with charge carrier diffusion towards the semiconductor/metal interface [11]. Hence, charge-carrier migration between the region of exciton generation and the separating interface needs to be taken into account even on such short scales of 10s of nm.

Besides the transfer of electrons to the cocatalyst, a key step in these heterostructures turned out to be hole localization in the CdSe seed which enables the formation of long-lived charge separation in the order of 20 µs due to long-range spatial separation of electron and hole [8], supporting charge accumulation at the catalytic reaction centers necessary to drive multi-electron redox reactions. This hole localization in the seed is in competition with trapping processes of holes at surface defect sites (Figure 1B). We were able to show that by choice of the surface ligand we can achieve 100% hole localization efficiency in the seed with poly(ethylene imine) (PEI) ligands while for the usually used mercaptoundecanoic acid (MUA) ligands only 50% hole localization in the seed is observed [12]. The amines in PEI can saturate and remove surface traps to a wide extent, while MUA ligands binding via thiol groups to the surface are source of hole traps at the surface. This can be an explanation for the higher efficiency for photon-to-hydrogen conversion observed for PEI coated metal tipped nanorods compared to MUA capped systems [13] and emphasizes the importance to also carefully consider the design of surface properties for optimized systems.

So far, we have only considered transfer of electrons from conduction band states towards catalysts to drive a reduction reaction, in our case proton reduction for hydrogen evolution. But what about the holes. Efficient removal of holes from the valence band states is of utmost importance to prevent oxidation of the nanocrystal and ensure long-term stability. Further, it impacts overall efficiency, as it contributes to suppressing electron-hole recombination which is detrimental for the photon-conversion yield. In model systems for hydrogen evolution, hole removal is at the current state usually achieved by adding sacrificial agents, e.g. MeOH, which are consumed during the reaction. Long-term goal needs to be to link a useful oxidation reaction. In a full water-splitting scheme, this would be the oxidation of water to oxygen. To realize this a number of challenges need to be addressed which can not be discussed here in detail and I only want to give two current examples. One starting point is that in the design of nanocrystals also the hole extraction process needs to be optimized. As beneficial the hole localization in the CdSe seed in the CdSe@CdS nanorods might be for driving light-driven reduction reactions, the CdS shell presents a barrier for hole extraction from the system. In this case careful adjustment of the shell width can lead to structures still showing the beneficial hole localizing properties, combined with efficient hole extraction [14]. A first step towards substitution of the sacrificial agent by an oxidation catalyst was demonstrated by combining metal-tipped
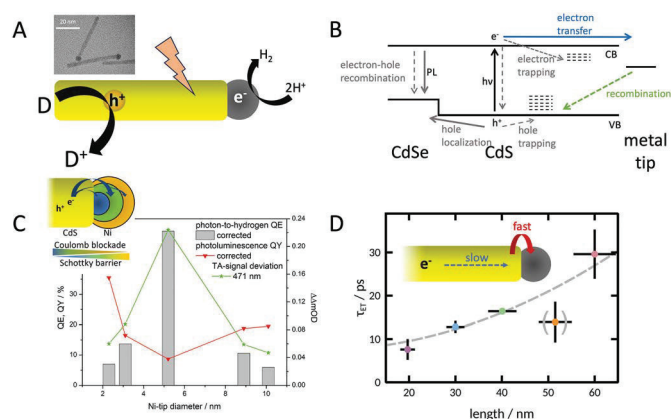

Fig. 1: A) Illustration of light-driven hydrogen evolution using metal-tipped CdSe@CdS nanorods (D represents sacrificial electron donor) and **B)** summary of competing exciton relaxation and charge-carrier transfer processes following excitation of a metal-tipped dot-in-rod system in absence of sacrificial donor. **C)** Size dependent photon-to-hydrogen conversion efficiency vs. photoluminescence quantum yields and extent of formation a characteristic spectroscopic feature indicating charge separation as measure for charge-separation efficiency at the semiconductor metal interface [9]. **D)** Time constants for charge transfer to the metal tip in dependence of rod length [13].

CdSe@CdS nanorods with molecular metallocorroles suitable for catalyzing water oxidation, using redox species as a charge transfer shuttle. The hybrid system supports long-term hydrogen production in the absence of sacrificial hole scavengers, with efficiencies as high as 17 % and impressive turnover number at the corrole center of around 300,000 [15].

The last examples illustrate that although model studies for light-driven reduction reactions impressively prove the potential of these CdSe@CdS dot-in-rod structures for light-driven redox catalysis, it is still a long way to go to achieve a real sustainable process, which could also be used at large scales. Also considering the understanding of charge-carrier dynamics we should be aware that the presented studies are discussing the transfer of only one charge carriers. In future investigations we will also take into consideration that multiple charges need to be transferred between the excited nanocrystal and cocatalysts. We will establish spectroscopic schemes allowing to investigate stepwise multielectron transfer processes, but also explore the possibility of simultaneous transfer of several charge carriers from nanocrystals hosting several excitations, so called multiexcitons.

Acknowledgement

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Prof. Dr. Maria Wächtler

Maria Wächtler studied Chemistry at the Friedrich Schiller University in Jena where she also received her PhD in 2013. After a postdoctoral period at Leibniz Institute of Photonic Technology Jena, she was appointed head of work group Ultrafast Spectroscopy in the department Functional Interfaces at Leibniz-IPHT in 2015 and in 2020 founded the work group Quantum Confined Nanostructures. Since 2022 she is professor for Physical Chemistry at RPTU Kaiserslautern-Landau and member of the state research center OPTIMAS. The research focus of her group is on the design of photoactive functional hybrid materials based on colloidal semiconductor nanocrystals, e.g. quantum dots or nanorods, and the investigation of function determining interactions and the characterization of light-driven processes by (time-resolved) spectroscopy. The investigated systems are designed with the purpose to be part of assemblies for the application in light-driven catalysis, e.g. for hydrogen generation from water, as materials for application with non-linear optical properties or for sensor applications.