

Improving Photocatalytic Activity through Electrostatic Self-Assembly: Polyelectrolyte Assemblies for Light Energy Conversion

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Inspired by natural systems where assemblies perform efficient photosynthesis, it is of great interest to form synthetic nanostructures based on non-covalent interactions that bear great potential in solar energy conversion, including H₂ generation and energy storage. Nanoscale structures showing high efficiency in photocatalysis are of particular importance for light energy conversion.

In this contribution, new types of catalytically active and stimuli responsive nanostructures will be presented. Self-assembled structures are formed from polymeric templates based on different interaction forces, including electrostatic interaction, halogen bonding, hydrogen bonding and π - π stacking in aqueous solution at pH values ranging from acidic to basic conditions. Assemblies include organic macroions and multivalent organic or inorganic counterions, such as anionic polyoxometalates (POM) or porphyrins acting as both: building blocks for structure formation and photosensitizer, representing a key to versatile and catalytically efficient self-assembled systems. While polyoxometalates show excellent redox properties, porphyrins are potential candidates for light energy conversion due to their absorption properties in the visible wavelength range. Hence, through a combination the structures presented may be tuned for desired applications in the field of solar energy conversion.

Detailed structural characterization and possible applications of the catalytically active polymer structures will be discussed. While aggregate sizes are studied using light scattering and SANS, interaction of the components is investigated using isothermal titration calorimetry (ITC), UV/Vis spectroscopy, ζ -potential and NMR. In particular, the porphyrin- and dye-photosensitized methyl viologen reduction, representing an important step towards H₂ generation, is investigated as a model reaction revealing a substantially increased catalytic activity of the self-assembled structure as compared to the building blocks only. Experiments reveal a selectivity in which porphyrins show different photocatalytic performance depending on their molecular structure and resulting interaction forces. Additionally, a strong dependence of the catalytic activity on the applied ratio of photosensitizer to polymer as well as the pH of the solution is found.

Electrostatic self-assembly of polyelectrolytes and polyoxometalates leads to size-tunable nanostructures showing modified photocatalytic activity with regard to dye degradation processes as model reaction. Further, based on the redox properties of polyoxometalates the formation and stabilization of metal nanoparticles in ternary self-assembled structures is discussed as those structures may represent potential candidates for water splitting systems.

With that, a great variety of structures with the capability of using visible light for photocatalysis will be presented, demonstrating the importance of the concept of self-assembly for solar energy conversion.

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