

Nanochannels for supramolecular organization of photoactive guests

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Structurally organized and functionally integrated artificial systems that are capable of elaborating the energy and information input of photons to perform functions such as processing and storing information, sensing microscopic environment on a nanoscale level or transforming and storing solar energy, are fascinating topics of modern photochemistry [1]. One-dimensional channel materials, such as zeolites and mesoporous silicas, are very attractive hosts for the preparation and investigation of hierarchically organized structures, presenting a successive ordering from the molecular up to macroscopic scale; thus highlighting the relationship between molecular arrangements and macroscopic properties [2,3].

The focus is on photocatalytically active layers that have been built by incorporating organic dyes, metal cations and clusters into one-dimensional nanochannel materials.

Integrating photochemically active substances into zeolite monolayers coated on an electrode and taking advantage of intrazeolite processes for designing a reversible electrode for photocatalytic water oxidation will be discussed. It has been shown that a thin silver chloride layer deposited on a conducting support photocatalyzes the oxidation of water to O₂ in the presence of an excess of silver ions. The light sensitivity in the visible part of the spectrum is due to self-sensitization caused by reduced silver species. To test the water splitting capability, AgCl photoanodes were combined with an amorphous silicon solar cell. The AgCl layer was employed in the anodic part of a photoelectrochemical setup consisting of two separate compartments. A platinum electrode and an amorphous silicon solar cell were used in the cathodic part. Illumination of the AgCl photoanode and the amorphous Si solar cell led to photoelectrochemical water splitting to O₂ and H₂. In other yet preliminary experiments we prepared zeolite monolayers on conducting surfaces like gold coated glass and gold foil. For the preparation of the monolayers, cubic crystals of zeolite A and disc-shaped crystals of zeolite L were used. The zeolites were linked to the gold surface by means of a thiolalkoxysilane as molecular linker. The monolayers were then modified with Ag⁺ and AgCl. The so prepared AgCl/Ag⁺-zeolite photo-anodes showed an increased water oxidation capability.[4] We have good reasons to assume that utilization of dense, high quality zeolite L monolayers, consisting of disc shaped crystals with a length of about 100 nm, well attached with their base on a gold electrode, will lead to a considerable improvement of these photoanodes for water oxidation.

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