

Zeolite A and zeolite L monolayers modified with AgCl as photocatalyst for water oxidation to O₂

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The appealing features of zeolite A and zeolite L tempted us to prepare zeolite monolayers on conducting surfaces like gold coated glass and gold foil. For the preparation of the monolayers, cubic crystals of zeolite A, disc-shaped and cylindrical crystals of zeolite L were used. The zeolites were linked to the gold surface by means of a thiolalkoxysilane as molecular linker. Afterwards, the monolayers were used as back support for AgCl, a photocatalyst used in water oxidation and water splitting experiments. All AgCl photoanodes modified with a zeolite monolayer on the back showed an increased water oxidation capability.

Introduction

Classical zeolites are crystalline aluminosilicates, consisting of an anionic framework and charge-compensating cations.^{1,2} The primary building units of the framework are SiO₄ and AlO₄ tetrahedra. The framework is built up by corner-sharing TO₄ tetrahedra (T = Si, Al) leading to materials featuring defined channels and cavities. These empty intracrystalline spaces are on the nanometre scale and are termed as micropores³ or nanopores (smaller than 2 nm). The presence of aluminium results in a negative charge of the framework, which is compensated by protons or cations inside the cavities of the framework. Additional water molecules can also be present in the cavities under ambient conditions.

Zeolites are used in a broad field of applications. Due to their ion exchange capability they can act as water softeners or be used for the removal of pollutants, and their well defined cavities allow size-selective reactions, for example in catalysis.⁴ Zeolites are also being used for cooling application, like cooling beverages.⁵ It is possible to accommodate photoactive guests within the cavities created by the rigid framework. The photoactive guests can be an organic photosensitizer, an inorganic semiconductor or a combination of both. The combination of a zeolite host and photoactive sites renders solid photocatalysts in which the high surface area and the adsorbent capacity provided by zeolites cooperate to increase the efficiency of the photocatalytic process. In addition, the zeolite pores define a compartmentalized space in which multi-component systems can be assembled by a stepwise procedure. Other positive effects derived from the encapsulation of a guest inside zeolites are a higher photostability of the sensitizer, the observation of quantum size effects for semiconductor clusters and a favourable polar environment for photoinduced electron transfer. Being transparent in the UV/Vis/NIR makes zeolites ideal host materials for supramolecular organization of different kinds of molecules, clusters, and metal complexes.^{6,7} Other recent research reports show the usage of zeolites for

applications such as biocompatible surface for enzyme immobilization,⁸ as host for PbS quantum dots showing very high third-order nonlinear optical activities,⁹ as host for TiO₂ as photoactive semiconductor as a novel concept for photovoltaic cells,¹⁰ and in drug delivery studies.¹¹

Zeolite A and zeolite L

Zeolite A and zeolite L are for our research group of particular interest due their versatile structural features for the encapsulation of photoactive guests and their related studies.⁷ The stoichiometry of zeolite A with sodium as monovalent cation is Na₁₂[Al₁₂Si₁₂O₄₈]·27H₂O.^{1,2} The framework of zeolite A is assembled by linking together TO₄ primary building units *via* oxygen bridges resulting in a larger building unit called a β cage or sodalite cage. Eight β cages are linked together over 4-membered rings (counting only T positions), resulting in a larger cavity called an α cage. The α cage has an opening of 4.1 Å and an outer diameter of 12.3 Å.

We have been extensively exploring the research area in which zeolite A can be used as a host material for accommodating inorganic guests such as metal and semiconductor clusters.¹² Ag₂S–zeolite A host–guest systems show fascinating optical properties. It was found that these materials emit visible light when they are irradiated with UV light. The colour of the emitted light depends on the size of the silver sulfide clusters. Ag₂S monomers emit green light, while the colour of the emission of the Ag₄S₂ dimers is orange. Another surprising discovery was that silver sulfide clusters inside zeolite A crystals exhibit luminescence thermochromism in the presence of K⁺ co-cations.¹³

The stoichiometry of zeolite L with sodium and potassium as monovalent cations is Na₃K₆[Al₉Si₂₇O₇₂]·21H₂O.^{1,2} The framework is assembled by linking together TO₄ primary building units *via* oxygen bridges resulting in a larger building unit called a cancrinite cage. These units are linked together over 6-membered rings (counting only T positions) building columns along the *c*-direction of the crystal. These columns are interconnected giving rise to a 12-membered ring arrangement. As a consequence, zeolite L has a one-dimensional channel

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