



DEVELOPMENT OF LUMINESCENT SOLAR CONCENTRATORS

MOLECULAR ALIGNMENT CHIPS

Annual Report 2013

Author and Co-Authors	Dominik Brühwiler, Michael J. Reber
Institution / Company	Institute of Chemistry and Biological Chemistry Zurich University of Applied Sciences (ZHAW)
Address	Einsiedlerstrasse 31, CH-8820 Wädenswil
Telephone, E-mail, Homepage	058 934 5543, dominik.bruehwiler@zhaw.ch
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ABSTRACT

The project aims to develop methods for the synthesis of arrays of silica nanochannels with disc-shaped morphology and tunable pore size. These so-called Molecular Alignment Chips (MACs) are promising host materials for the supramolecular organization of guests. The project investigates several applications of MACs with a focus on light-harvesting systems such as luminescent solar concentrators (LSCs). The fundamental project objectives concern the synthesis of MACs with well-defined particle morphology and tunable nanochannel diameter. Host materials of this kind provide a platform for the alignment of any desired guest species. In the field of LSCs, this ultimately opens possibilities for increasing the trapping efficiency and for reducing self-absorption losses.

Introduction / Project Goals

The project builds on our recent work on the synthesis and functionalization of mesoporous silica [1]. Representing the mesoporous counterpart of zeolites with one-dimensional channel systems, arrays of silica nanochannels (ASNCs) are of particular interest [2]. The fundamental project objectives concern the synthesis of disc-shaped ASNCs, so called Molecular Alignment Chips (MACs), and the fine tuning of the pore size of these materials. In a later stage of the project, the alignment of dyes in MACs will be studied.

Artificial light-harvesting systems constitute an essential part of solar energy research. A potential application of dye-loaded MACs is found in the field of luminescent solar concentrators (LSCs). A classical LSC consists of a transparent plate (plastic or glass) containing luminescent centers. Light enters the face of the plate and is partially absorbed and reemitted by these centers. A fraction of the luminescent light is trapped by total internal reflection and guided to the edges of the plate where it can be converted to electricity by a solar cell. As the edge area of the plate is much smaller than the face area, the LSC operates as a concentrator of light [3]. Despite the fact that this concept has been studied since the 1970's, no commercial application of LSCs in solar energy conversion devices has been developed. Dyes suitable for the application in LSCs feature an overlap between their absorption and fluorescence spectra, causing self-absorption and a decrease in optical efficiency [4]. Self-absorption has been recognized as the main problem in LSCs and research activities towards solving this problem have increased [3].

Recent work has shown that the trapping efficiency of LSCs can be increased by vertical alignment of the dyes, as this leads to preferential emission into waveguide modes [5]. Nanoporous hosts with one-dimensional channel systems are ideal for this purpose. Extending the high level of organization provided by a single nanoporous particle to the macroscopic scale requires particles with regular morphology and defined channel orientation.

General Concepts

The idea of using MACs to align dye molecules in LSCs is based on the ZeoFRET[®] concept [6]. ZeoFRET[®] materials are host-guest systems that exploit the alignment of dye molecules in the one-dimensional channels of zeolite L. Donor dyes absorb the incoming light and transfer the electronic excitation energy via FRET (Förster Resonance Energy Transfer) to acceptor dyes. A large donor/acceptor ratio reduces the self-absorption losses in the LSCs, because the emission of the acceptor dyes cannot be absorbed by the donor dyes (Figure 1). Zeolite L is used as a host material to fabricate ZeoFRET[®]. As the pore diameter of zeolite L is set at 0.71 nm, the choice of guest molecules is limited. MACs can extend the range of implementable dye molecules by providing means to adapt the pore diameter to the dimensions of the guest.

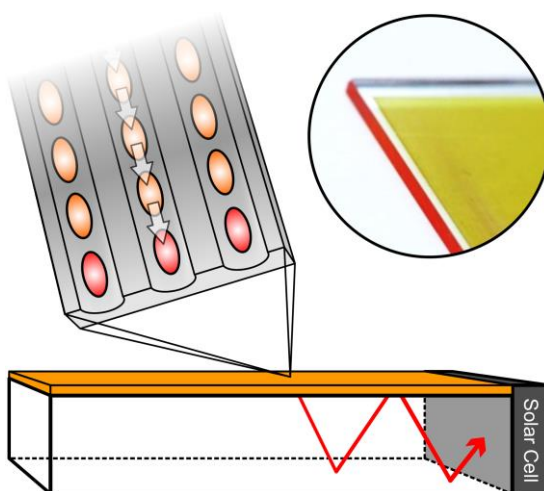


Figure 1. Luminescent solar concentrator based on a host-guest material as the active component in a thin polymer film on a waveguide. Dye molecules are aligned in the nanochannels of the host and harvest light by a FRET mechanism. Self-absorption of the emitted light is reduced by a well-selected combination of donor and acceptor dyes.

Results

A narrow pore size distribution (PSD) is an important prerequisite for the alignment of dye molecules in nanochannels. An extremely narrow PSD can be obtained with MCM-41 type materials [7], but the morphology of the particles is irregular (Figure 2). Contrary to classical MCM-41 type materials, ASNCs feature a hexagonal morphology with a defined direction of the nanochannels along the long axis of the particles. ASNCs with a narrow PSD can be obtained (Figure 2) [2], but tuning the pore size of ASNCs by adjusting the synthesis parameters (temperature, concentration of reactants, duration) has been unsuccessful. We have therefore started to develop procedures based on the postsynthetic deposition of silica layers that yield mesoporous silica with smaller pore sizes. Figure 2 (left) shows an example of a stepwise pore size reduction of a MCM-41 type material by a liquid phase deposition technique. We have also built a fully automated CVD setup that allows for a well-controlled solventless deposition of silica layers.

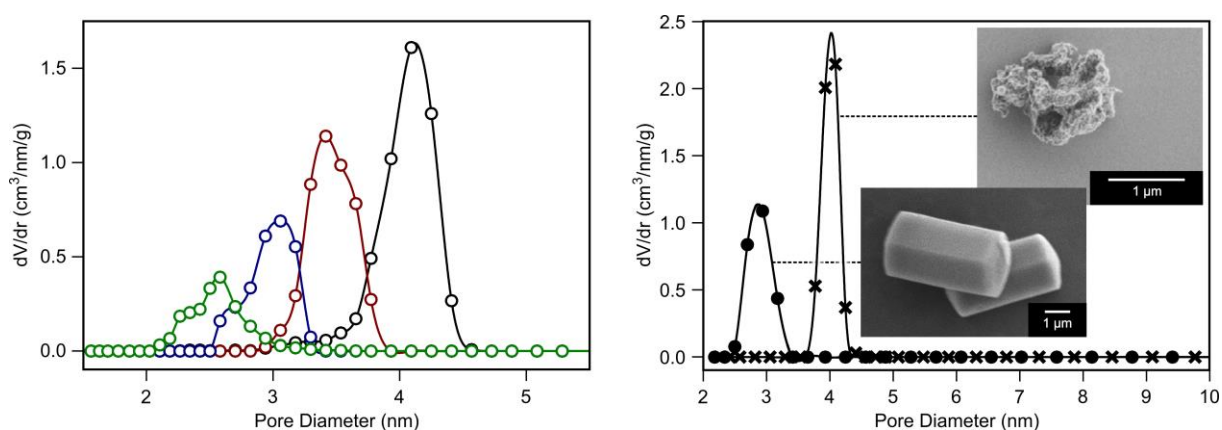


Figure 2. Left: Stepwise pore size reduction of a MCM-41 type material by liquid phase deposition of silica layers. Right: Pore size distributions and scanning electron microscopy images of mesoporous silica MCM-41 (crosses) and ASNCs (dots).

Particle morphology is a key topic in the development of MACs. The aspect ratio (length/diameter) of ASNCs is larger than one (Figure 3, left). Our goal is to significantly reduce the aspect ratio, thereby enabling orientation of the channels perpendicular to a surface by means of simple monolayer deposition techniques. We have recently started to study the influence of temperature, reactant concentration, co-solvents, and co-surfactants on the aspect ratio of ASNCs. First results are promising and show a substantial decrease of the aspect ratio (Figure 3, right).

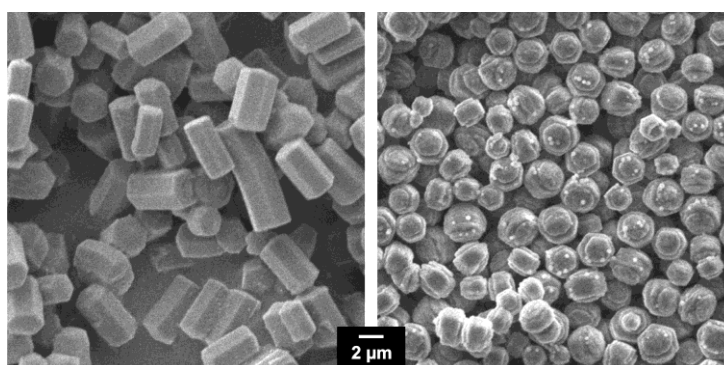


Figure 3. Scanning electron microscopy images of conventional ASNCs (left) and ASNCs with reduced aspect ratio (right). A single particle consists of approximately 200'000 nanochannels.

The alignment of dye molecules in the nanochannels requires full accessibility of the pores. Confocal laser scanning microscopy is employed to check for potential pore blocking effects. The coupling of the host-guest composites to waveguides is accomplished by adding the composites to a poly(methyl methacrylate) solution and subsequent casting onto the waveguide.

Assessment 2013 and Outlook 2014

The first phase of the project has primarily focused on the synthesis of the host materials. Methods were developed that allow a stepwise postsynthetic reduction of the pore size. In addition to liquid and gas phase deposition techniques, pore size tuning by pseudomorphic transformation will be investigated in 2014. Adjusting the aspect ratio of ASNCs has proven to be difficult, particularly regarding the generation of flat particle surfaces. First results show, however, that the aspect ratio can be reduced substantially by the addition of co-surfactants. This result is particularly significant regarding the vertical alignment of dyes (and thus of the electronic transition dipole moments) in luminescent solar concentrators.

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