

Dynamic and Reversible Organization of Zeolite L Crystals Induced by Holographic Optical Tweezers

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Porous materials based on aluminosilicate such as zeolite L have proven to be very versatile hosts for supramolecular organization of various molecular guest species.^[1–3] When loaded with organic dyes, metal clusters or complexes,^[4] they exhibit fascinating optical properties which make them very desirable in various applications including light harvesting antenna materials,^[1] luminescent labels for imaging purposes^[5] or even for bio-medical applications.^[6]

Zeolite L features parallel, one dimensional and hexagonally arranged channels that lead to supramolecular organization of the guests in the channels. Size and aspect ratio of zeolite L can be tuned over a wide range, enabling shapes from cylindrical to disc-like.^[7] These hosts in turn can be themselves arranged on a larger scale, thus extending ordering from molecular to macroscopic scale and leading to hierarchical supramolecular organization.^[3,8–12]

This hierarchical organization can lead to materials with exciting properties, such as mono-directional transfer of electronic excitation energy or coherent emission of stimulated radiation.^[8,9,13] However, most methods available for patterning and assembling of zeolite L crystals are limited to the arrangement of large quantities of crystals on large area substrates by either chemical means or physisorption.^[8–9,14–20] The main drawback of these approaches is the lack of any fine control over positioning for small numbers of selected single crystals, thus preventing the formation of complex patterns on a small scale.

The idea of this work is therefore to achieve hierarchical supramolecular organization by using optical trapping for highly ordered arrangements of a defined number of zeolite L hosts. We demonstrate for the first time the use of holographic optical tweezers for the realization of dynamic geometric patterns composed of single zeolite L crystals that can be modified and rearranged in real-time. This novel approach enables precise organization of zeolites into well defined structures not only for microscopic and spectroscopic studies but also for potential applications in the fields of microfluidic devices, biochemical nanosensors or small scale optical elements.

Optical trapping of single transparent spherical objects by means of a the light gradient forces of a tightly focused laser

beam has been known since more than two decades and is commonly called *optical tweezers*.^[21] Although it seems obvious to trap single zeolite L crystals and position them by means of single optical tweezers, only very few publications on trapping zeolites are available,^[22] and none of them is discussing optical trapping as a means of controlling single synthetically made zeolite L crystals in position and orientation, nor subsequently using them as building blocks for ordered assemblies. For the independent control of multiple zeolite L crystals, the concept of optical tweezers has to be expanded.^[23–26] One of the most flexible approaches are *holographic optical tweezers* (HOT), where the light field is tailored with diffractive optical elements (DOE) such that a number of spatially arranged optical traps is generated.^[26] It is this approach that we employ in our work to obtain dynamic patterning and reversible organization of zeolite L based on individual control of single crystals.

The experimental setup of our HOT system is sketched in Figure 1 and described in detail in the experimental section. It consists of a commercially available inverted fluorescence microscope with integrated, in-house developed HOT. The key features are a near infrared ($\lambda = 1064$ nm) laser and a computer addressable spatial light modulator (SLM) which is used as the DOE.^[27–30] For comparison we use a second setup having the same optical characteristics, but with a green ($\lambda = 532$ nm) laser light source.

The construction of complex assemblies on the single crystal level requires precise control of the position of each particle. To demonstrate the capability of optical control, empty and dye-loaded (DXP) zeolite L crystals with diameters of roughly 1 μm and lengths of 1 μm and 3 μm , respectively, were used. As these crystal types are commonly employed in literature,^[3,12,31,32] the results described here can be directly transferred to existing systems. The most important observation is that both types of crystals are successfully trapped three-dimensionally at the position of the laser focus. Within the trap, the cylinder axis of the crystals aligns parallel to the optical axis of the trap, such that one always sees the circular top or bottom of the cylinders. This clear preferential direction is worth mentioning in the case of the 1 μm long crystals as their aspect ratio is almost one.^[33] A likely explanation is that the nano channels running parallel to the cylinder axis interact with the laser light such that the asymmetry of the crystals is effectively increased. Trapped crystals are confined except for a slight vibration due to Brownian motion and the amplitude of the vibration depends on the depth of the trapping potential.^[34] No difference was found between the behavior of empty and dye-loaded zeolite L crystals as DXP is not excited at $\lambda = 1064$ nm and thus the crystals are similarly transparent. The important conclusion is that not only empty

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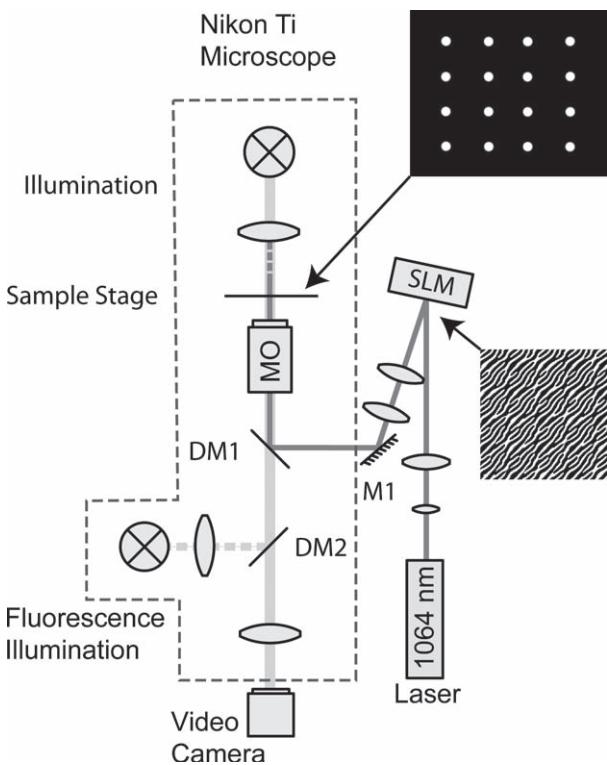


Figure 1. Sketch of the optical setup; for details see experimental section. DM1, DM2: dichroic mirrors; MO: microscope objective; M1: Mirror. Insets indicate one possible phase structure on the SLM and the resulting geometry of optical traps in the sample plane.

but also loaded crystals can be trapped optically as long as the guest species does not interact with the trapping laser light.

Once a crystal is trapped, there are two ways to position it in space. Either the whole sample is moved with the microscope translation stage, or the phase pattern on the SLM is slightly modified so that the focus is repositioned in the transversal plane or axially, respectively.^[27] Both approaches allow almost arbitrary positioning of a single crystal within the sample chamber and thus are the basis for complex assemblies, but modifying the phase pattern is the more versatile way with respect to the desired independent control of multiple particles and thus is our method of choice.

For the construction of arbitrary three dimensional assemblies, full orientational control of the constituents is required. Rotating the crystals into lateral position is also important to access information about the loading of the nano channels.^[12,31,32] As these channels run parallel to the cylinder axis, lateral observation of the whole crystal is required, e.g. to be able to investigate the loading distribution or spatial behavior along the channels. One obvious approach to rotate elongated objects is to press them against a surface and move them slightly until they turn.^[35] This approach, however, is limited as it requires a suitable surface and does not work well with cylinders without clear elongation. We thus aimed for rotational control solely by optical means.^[36–40] Our approach consists of multiple traps that provide an asymmetric potential and enable defined rotation. **Figure 2a** shows the scheme of two traps of equal power with a spacing of approximately 1.5–2.0 μm that was successfully used

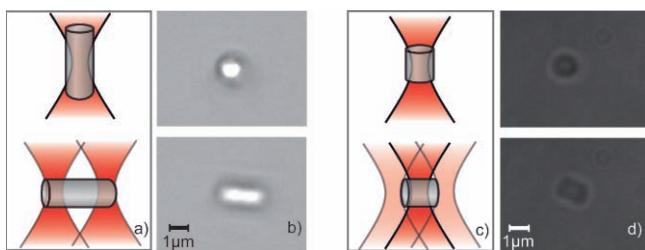


Figure 2. Geometry used to trap zeolite L crystals laterally a) and corresponding experimental images b). More sophisticated rotational control is required if crystals without clear elongation are used (c,d).

to rotate distinctly elongated crystals by 90 degrees with respect to the optical axis. In this configuration, trapping in lateral position is stable (Figure 2b) and the crystals remain in the rotated position as long as desired. In contrast, the 1 μm crystals cannot be rotated with this simple configuration as their aspect ratio is too close to one. Figure 2c shows the advanced scheme of three traps of different power that was successfully used to rotate the 1 μm crystals in a controlled way. It is composed of a strong central trap to define the lateral and axial position and two weaker side traps to induce the rotation. With this scheme we achieved rotation into the lateral position, but having a relatively small degree of asymmetry, the crystals tend to turn back and forth every few seconds. The reason for this instability is the interplay between the trapping potential and stochastic translational and rotational Brownian motion. If long-term stable trapping in lateral position is desired for crystals with an aspect ratio close to one, the viscosity of the surrounding medium has to be increased. Using a mixture of 50% water and 50% glycerol, resulting in a viscosity increase by a factor of 6.0 compared to pure water,^[41] stable trapping in the lateral position is achieved (Figure 2d).

Having developed the schemes to trap and fully control one zeolite L crystal, it is crucial to have reservoirs with a high density of crystals that can be used as building blocks to assemble structures at locations with low crystal density. We suggest a simple and very efficient solution that implies the use of the large laser power of the trap itself to provide the necessary gradient of particle density. For this purpose, we choose the laser wavelength such that the DXP dye is excited ($\lambda = 532$ nm), resulting in a complete change in the response of the trap. At this wavelength the dye-loaded crystals absorb energy from the laser beam and are no longer confined in the focus but avoid it. This energy transfer is utilized to efficiently gather large numbers of crystals at a defined position with micrometer resolution. To start the gathering process a seed is needed, e.g. a crystal that is incidentally adhered to the surface and cannot avoid the laser beam and generates a strong local heat source when exposed. In the typical geometry of a small sample volume between an object slide and a cover slip and with gravity orthogonal to these surfaces, the temperature gradient induces convective flows in the form of convection rolls^[42] as sketched in **Figure 3**. The convection rolls transport large numbers of crystals towards the laser focus, thereby enhancing the heat production and transport process. Thousands of zeolite L crystals can be gathered in one spot within a couple of seconds, leading to strong spatial gradients of particle density. The areas of high density

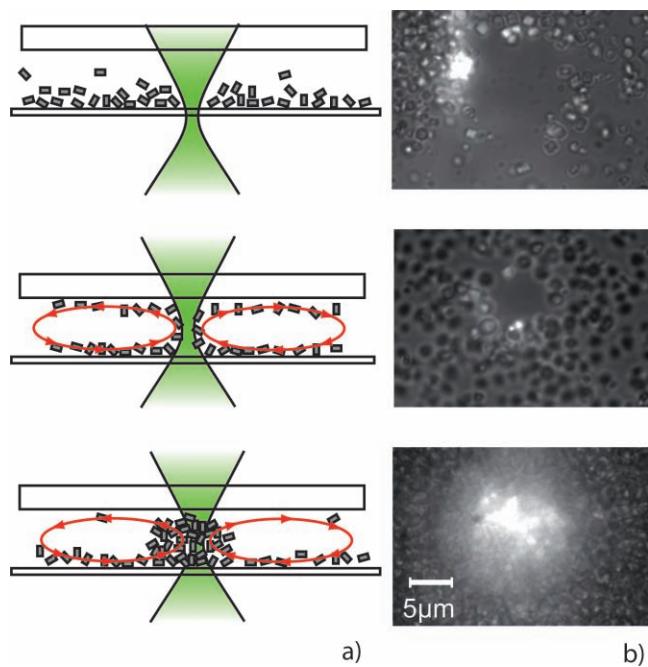


Figure 3. Laser induced convection rolls in a sample containing DXP-loaded zeolite L crystals.

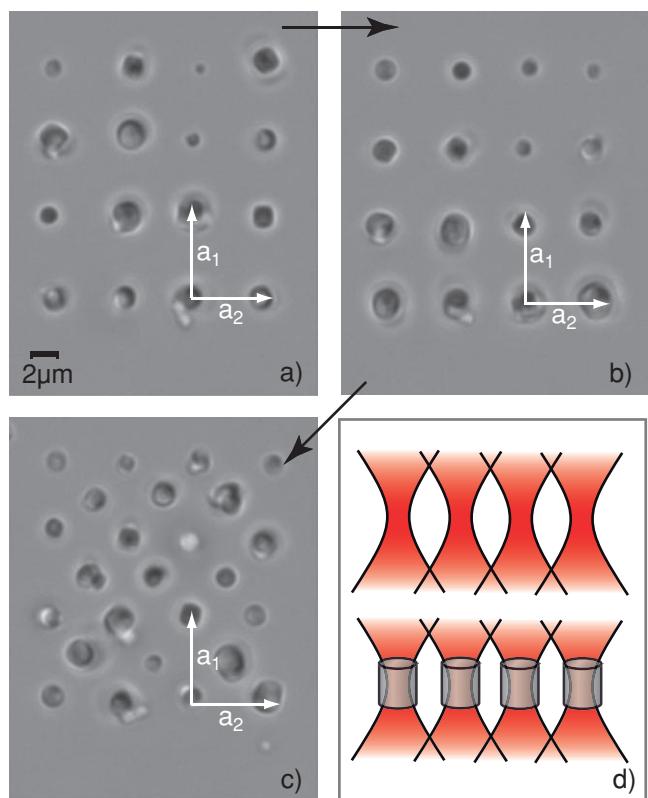


Figure 4. Rectangular Bravais lattice of three dimensionally trapped zeolite L crystals a). The crystals are ordered by size b) and then the lattice is reconfigured into a centered rectangular lattice c). The geometry of multiple traps is shown in d).

are perfect reservoirs of spare crystals that can be trapped and transported to the areas of low density, where they can be assembled without being disturbed by interfering crystals.

With the tool of optical control of single zeolite L crystals and the availability of adequate reservoirs, it becomes possible to assemble static patterns of arbitrary configuration by a sequential step-by-step arrangement. This approach, however, requires arranging the crystals on a surface, as only one crystal is confined in the optical trap and all others would disperse if they are not adhered. HOT on the other hand enable multiple traps simultaneously in an arbitrary configuration that can be adjusted dynamically and it becomes possible to trap and control multiple crystals at the same time. The trapping geometry sketched in Figure 4d is used to trap 16 zeolite L crystals in a 4×4 array (Figure 4a). All 16 crystals are trapped simultaneously in all three dimensions and are not supported by any surface. Only the top (object slide) and bottom (cover slip) margins of the sample chamber limit the range of translation in axial direction. The array represents one example of a large variety of possible multiple trap configurations. Almost any arbitrary pattern of up to hundreds^[28] of zeolite L crystals can be achieved. Although static organization with HOT already allows controlled arrangements that can not be achieved by other means, it is important to note that all particles can be controlled interactively and independently from each other. To demonstrate this unique feature of dynamic reorganization, we ordered the zeolites in the by size. Figure 4b shows the crystals with increasing size from the top right to the bottom left. Furthermore, the complexity of the pattern can be increased dynamically by adding or removing crystals and thereby the packing density and the nature of organization can be specified. We demonstrate this feature by transforming the rectangular Bravais lattice shown in Figure 4b into a centered rectangular lattice. Therefore, we filled the geometrically relevant positions in the 4×4 array by capturing additional crystals of different sizes from a reservoir. Figure 4c shows the result with 25 crystals trapped simultaneously in a centered rectangular lattice, highlighting the flexibility of the dynamic organization. The organization process is fully reversible as long as the crystals are not intentionally fixated, e.g. by adhering them to a surface.

In conclusion, we have demonstrated that HOT are a powerful and versatile tool to control and organize zeolite L crystals in defined configurations within sub micrometer precision. Up to a few hundred crystals can be trapped simultaneously and organized in arbitrary patterns. The method offers new opportunities to create highly ordered assemblies of individually selected zeolite L crystals in space and on diverse substrates. Additionally, it can be used to hold and orient crystals in microfluidic devices. Moreover, the dynamic nature of the technique allows adapting organized structures to different needs either by rearranging crystals or by changing fundamental organizational structures by adding or removing crystals. We expect that this method opens a paradigm shift in the creation of hierarchically ordered structures – from unspecific chemical to particle-oriented optical trapping techniques that allow complete control of each single host in a large arrangement. This in turn will pave the way to the realization of novel optical devices such as micro sensor arrays, or for the study of optical processes occurring inside or at the interface of single dye-loaded zeolite L crystals.

Experimental Section

Preparation of zeolite L: Zeolite L crystals with a diameter of roughly 1 µm and lengths of 1 µm and 3 µm were synthesized according to reported procedures.^[7] The zeolites were subjected to an ion exchange process with an aqueous 1.0 M KNO₃ solution for 3 h. The K⁺ exchanged material was then washed three times with doubly distilled water to remove excess salt.

Loading of the crystals with DXP (N,N'-bis(2,6-dimethyl phenyl)-3,4:9,10-perylene tetracarboxylic diimide) was carried out by means of gas phase adsorption. 100 mg of potassium exchanged zeolite L was mixed with 1.35 mg of pure dye (corresponding to 0.06 dye molecules per unit cell) in a glass ampoule. The mixture was dried on a high vacuum line for 6 h at 5×10^{-6} mbar before sealing it. Insertion then took place in a rotating oven at $T = 270^\circ\text{C}$ for 48 h. The dye-loaded material was washed several times with 15 mL portions of 1-butanol to ensure removal of dyes adsorbed on the external surface.

Optical setup: The apparatus is based on a Nikon Ti inverted fluorescence microscope with a motorized x/y-translation stage and piezo-driven focus control. Near infrared HOT are integrated into the system. A 2.5 Watt Nd:YVO₄ laser, emitting at $\lambda = 1064\text{ nm}$ illuminates a phase-only spatial light modulator (SLM) that acts as a DOE. The SLM is a Pluto LCOS micro display from Holoeye Photonics AG with a resolution of 1920 \times 1080 pixels and phase modulation over the full 2π range. By means of a Gerchberg-Saxton algorithm or, alternatively, a superposition of Fresnel lenses and diffraction gratings,^[27,28,30] the phase pattern corresponding to the desired optical trapping configuration is calculated and displayed on the SLM which is imaged onto the back aperture of the high numerical aperture microscope objective (MO, 100x magnification, NA = 1.49). The pre-structured light field is focused through the MO, generating the desired traps in the sample plane of the microscope. A dichroic mirror (DM1) is used to separate the illumination from the laser beam path by their different wavelengths. A second dichroic mirror (DM2) reflects the fluorescence excitation light to illuminate the sample through the MO. This setup enables simultaneous use of fluorescence microscopy and optical tweezers. A second, similar setup was implemented, the main difference being the trapping laser wavelength of $\lambda = 532\text{ nm}$.

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