Optical control and dynamic patterning of zeolites

Mike Woerdemann*[a], Christina Alpmann[a], Florian Hörner[a], André Devaux[b], Luisa De Cola[b], Cornelia Denz[a]
[a] Institut für Angewandte Physik, Westfälische Wilhelms-Universität Münster, Corrensstraße 2, 48149 Münster, Germany; [b] Physikalisches Institut and Center for Nanotechnologie, Heisenbergstraße 11, 48149 Münster (Germany)

ABSTRACT

Zeolite crystals have a wide use as model systems for artificial light harvesting systems, as nano-containers for supramolecular organization or as building blocks for 1D and 2D assemblies of several crystals.

In particular the assembly of zeolite L crystals with the aim to bridge the gap between the nano- and the macroscopic world has been a focus of research during the last years. However, almost all available approaches to order, assemble and pattern Zeolite L are restricted to large amounts of crystals. Although these approaches have proven to be powerful for many applications, but they have only limited control over positioning or orientation of single crystals and are lacking if patterns or structures are required which are composed of a few or up to a few hundred individual crystals.

We demonstrate here that holographic optical tweezers are a powerful and versatile instrument to control zeolite L on the single crystal level. It is shown that full three-dimensional positioning, including rotational control, of any zeolite L crystal can be achieved. Finally, we demonstrate fully reversible, dynamic patterning of a multitude of individually controlled zeolite L crystals.

Keywords: zeolites, optical trapping, supramolecular organization, holographic optical tweezers

1. INTRODUCTION

Organization – from the molecular up to the macroscopic scale – is of highest importance not only for a deep understanding of the principles and interactions of the underlying constituents, but also to design and engineer tailored micro- and nanoscale materials with defined properties. Hierarchically organized structures are believed to be the key to the design of novel, functional organic, inorganic, and biomaterials with defined and tailored properties that exploit the strong relationship between molecular arrangements and macroscopic properties [1, 2, 3].

The first level of supramolecular organization with ordering lengths up to a few micrometer can be – and is commonly – reached by means of porous materials, where molecules assemble themselves into highly ordered states [4]. A most versatile and for this reason common choice as porous host-guest systems are zeolite-type structures [5]. The final level of supramolecular organization that extends the ordering to the macroscopic scale is significantly less understood. Various different approaches are employed that can be roughly classified into schemes based on pre-structured surfaces or micro contact printing [6] (top down) or self-assembly of the hosts (bottom up), respectively [2].

Both types of approaches have led to structures and materials with promising and exciting properties, but both are limited in the very fundamental way that they allow for (almost) no control on the individual single host, but always work on the ensemble level. We believe that this fundamental restriction is the main reason that so far hierarchically organized structures are limited to homotypic or relatively simple heterotypic examples and that the organized structures have found only relatively few applications compared to the quantity of proposed methods.

*woerde@wwu.de; phone +49 (0)251 83-33518

Optical Trapping and Optical Micromanipulation VII, edited by Kishan Dholakia, Gabriel C. Spalding,
Proc. of SPIE Vol. 7762, 77622E · © 2010 SPIE · CCC code: 0277-786X/10/$18 · doi: 10.1117/12.863610

In our contribution we circumvent this restriction by an approach that goes far beyond the borders of ensemble-based methods by providing full control on every individual host. The obvious – though important – impact of this new generation of supramolecular organization is that every single host can be selected for its individual microscopic properties. Thereby, structures can be fine tuned by a strict selection of hosts with e.g. a narrow size distribution or well-defined morphology.

The tools we propose and utilize to achieve this high level of control are holographic optical tweezers (HOT), where transfer of momentum from laser light to matter is used to confine single and multiple hosts with full control on every particle. Moreover, HOT not only allows supramolecular organization on a single particle level, but provide further unique features: the structure can be built interactively while the progress is observed through an optical microscope, the control is very precise and dynamic, and – most importantly – there is no need for elaborate pre-treatment of a surface or the hosts.

We chose as a porous host system zeolite-type structures. Among them, zeolite L is a well known material which can be synthesized in a broad size and aspect ratio range. It is therefore ideally suited to demonstrate the versatility of our technique.

2. ZEOLITE L

Zeolites are microporous materials that are well suited as hosts for various guest species that can occupy the cavities and are organized by the geometrical constraints imposed by the host. In particular zeolite L crystals are a good choice due to their well established synthesis methods allowing for a wide range of aspect ratios and sizes from 30nm to 10.000 nm [4]. Zeolite L have a cylindrical shape and feature a system of strictly parallel one dimensional channels that run along the cylinder axis. The distance between neighboring channels is 1.84 nm, the diameter varies along the channel between 0.71 nm at the pore opening and 1.26 nm in the largest place. These geometrical constraints enable extremely high concentrations of supramolecularly organized guests that often behave as monomers. When loaded with organic dyes, metal clusters or complexes [5], zeolite L host-guest materials have fascinating optical properties which make them very desirable in various applications including light harvesting antenna materials [7], luminescent labels for imaging purposes [8, 9] or even for bio-medical applications [10]. These hosts can be themselves arranged on a larger scale, thus extending ordering from molecular to macroscopic scale and leading to hierarchical supramolecular organization [4, 11, 12, 13, 14, 15].

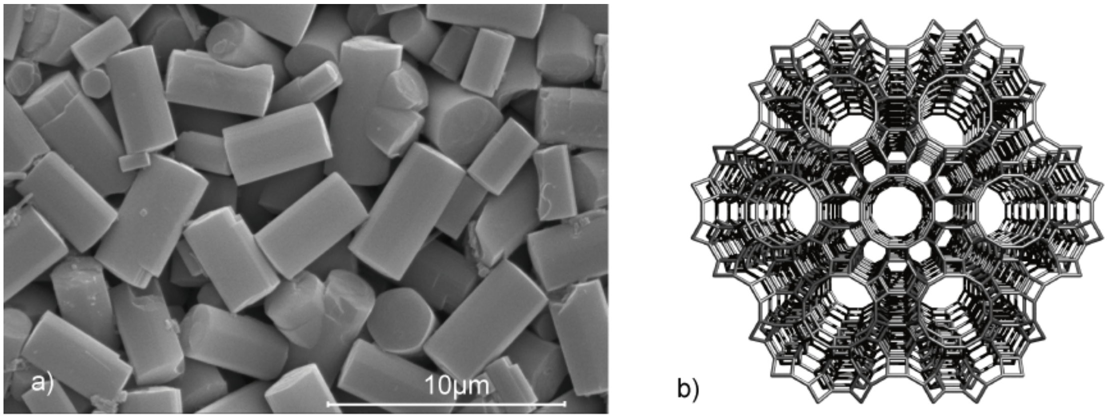

Figure 1. a) SEM image of zeolite L. b) Scheme of the zeolite L framework

Zeolite L crystals used for this study were synthesized with a diameter of roughly 1 µm and lengths of 1 µm and 3 µm according to procedures reported in [16, 17]. The zeolites were subjected to an ion exchange process with an aqueous 1.0 M KNO_3 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-perylentetracarboxylic 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 °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.

3. OPTICAL SETUP

Trapping and organization of Zeolite L is done with holographic optical tweezers [18, 19]. We chose a wavelength of $\lambda = 1064$ nm as this wavelength does not interact with most of the guest loaded zeolite L materials that we intent to investigate. A Nd:YVO$_4$ laser provides a well defined TEM$_{00}$ ($M^2 < 1.2$) beam with a maximum power of $P_{max} = 2.5$ W. A combination of a half wave plate and a polarizing beam splitter acts as a variable attenuator, allowing for powers P ($0 < P < P_{max}$) to be used, depending on the actual requirements. The laser beam is expanded and illuminates a high resolution phase only spatial light modulator (SLM, Holoeye Photonics "Pluto", 1920 x 1080 pixels, full 2π phase range at $\lambda = 1064$ nm), which acts as the diffractive optical element (DOE). Being structured by the DOE, the beam is relayed by two lenses and guided into a microscope such that the SLM plane is imaged onto the back focal plane of the microscope objective (MO, M=100x, NA = 1.49). The MO performs an optical Fourier transformation, resulting in the desired trapping pattern in its front focal plane which also is the observation plane of the microscope. We chose a commercially available microscope (Nikon Ti Eclipse) with integrated fluorescence illumination, high precision translation stage, piezo driven focus control and external phase contrast. Integration of HOT is supported by an additional stage of the microscope that contains the dichroic mirror (high reflectivity at $\lambda = 1064$ nm, high transmission in the VIS regime) mounted in a revolver. By this means, HOT can be used and also disabled completely independently from the mode of observation and, for example, fluorescence observation can be used together with optical trapping. Video data is captured with different cameras, including a high speed CMOS device (Photon Phocus, MV2-D1280, 488 fps at full resolution) and a highly sensitive CCD device (PCO, Pixelfly qe, quantum efficiency > 60 %). The phase holograms of the DOE are calculated by either iterative Fourier transformation algorithms [20] or a superposition of diffraction gratings and Fresnel lenses [21]. Using interactive software with graphics board aided calculation, positioning of many traps in real-time is possible [22]. For some specific application, line traps are used. The corresponding holograms are calculated by the phase-shape hologram method [23].

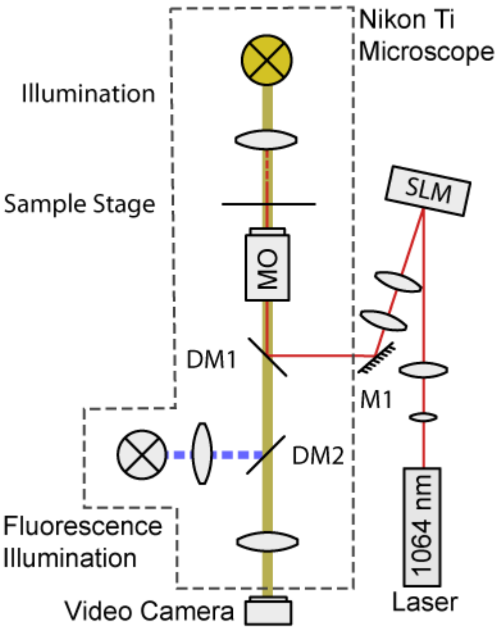

Figure 2: Integration of HOT into a commercial microscope.

4. TRAPPING AND ORGANIZATION OF ZEOLITE L

A fundamental question is if zeolites can be trapped at all by means of optical tweezers. Zeolite L are transparent, have a cylindrical shape and a refractive index between 1.4 and 1.5 [4]. Thus it should be simple to trap them as was successfully demonstrated with similar geometrical objects [24]. On the other hand, Zeolite L features a strongly periodic fine structure with dimensions of a few nanometers in lateral direction and many tens to thousands of nanometers in the axial direction. It seems likely that there is some significant interaction between this structure and the laser trapping light, which itself has a nontrivial shape close to the focus.

Our experiments show that it is possible to trap zeolite L in an optical trap [19]. The 1 µm long crystals as well as the 3 µm long crystals are trapped in a stable way and align with their cylinder axis along the beam axis. Figure 3 shows an example of an array of 4 x 4 zeolite L crystals trapped in a rectangular pattern. The pattern is trapped three dimensionally, i.e. not supported by any surface. This example already demonstrates hierarchical organization.

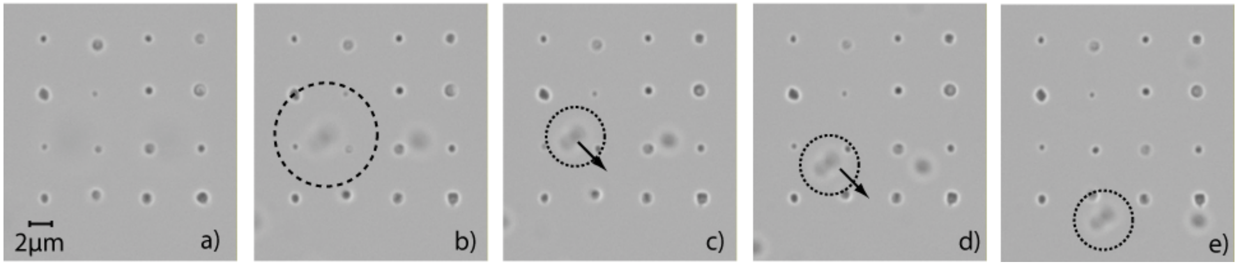

Figure 3: A rectangular pattern of 1 µm long zeolite L is trapped three dimensionally. This is demonstrated by an axial shift of the sample (a->b->c) and a transversal shift (c->d->e). The dashed circle indicates the lateral position and axial position (diameter of the circle) of an adhered reference particle.

HOT, however enable a kind of organization that goes far beyond simple, static patterns. The computational power of current graphic boards allows for interactive, fully dynamic and reversible organization of selected hosts. To demonstrate this feature we have arranged 16 zeolite L hosts in a rectangular pattern and sorted them by size. We then change the pattern interactively by adding additional hosts. The initial and the final configuration of traps are depicted in Figure 4 a) and b), respectively. Figure 4 c) and d) show the corresponding patterns of zeolite L crystals from the 1 µm batch that are reorganized from a rectangular lattice into a centered rectangular lattice.

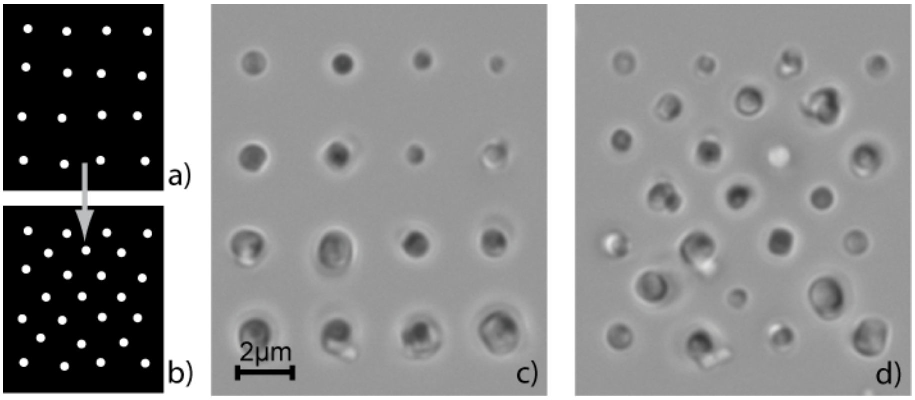

Figure 4. Dynamic reorganization of a rectangular into a centered rectangular lattice. a,b) Initial and final trap configuration. c,d) Corresponding pattern of zeolite L from the 1 µm batch with a broad size distribution.

For the vision of arbitrary, three dimensional structures of molecular hosts, not only position control is important, but also precise control of the orientation of single hosts. Rotating the 1 µm crystals without clear elongation requires a more sophisticated approach and is described elsewhere [19]. Clearly elongated crystals, however, can be rotated in a relatively simple way. One way for full rotational control is the use of a two trap scheme, where both traps act as handles at the poles of the cylindrical zeolite L crystal and by this means exert the required torque [25, 26]. In Figure 5a) a 3 µm zeolite L is shown in its usual, axial trapping position, just before it is rotated into lateral position 4b). With this method, the crystal can be orientated arbitrarily. If only lateral trapping is required, but no intermediate orientation, also line traps can be used. Figure 5c) and d) show a zeolite L crystal trapped in a line trap that was generated by phase-shape holography [23]. This method yields line traps that can provide the necessary axial gradient forces to confine particles in all three dimensions. This is in contrast to line traps that are generated with one dimensional Fresnel lenses, where the strong astigmatism usually makes three dimensional trapping impossible. Line traps enable organization of zeolite L hosts that is somewhere between a classical top-down approach and individual control of single hosts. The line trap defines a one-dimensional optical potential well that enables multiple zeolites to align in a chain of hosts. The rough shape of the organizational structure is defined by the line trap and individual hosts can be preselected to some extent, but the actual assembly is done by interplay between optical potential and geometry of the hosts. Figure 5e) demonstrates a chain of laterally aligned zeolites out of the 1 µm batch with a broad size distribution. The chain is not trapped three dimensionally, but axially supported by the glass cover slip.

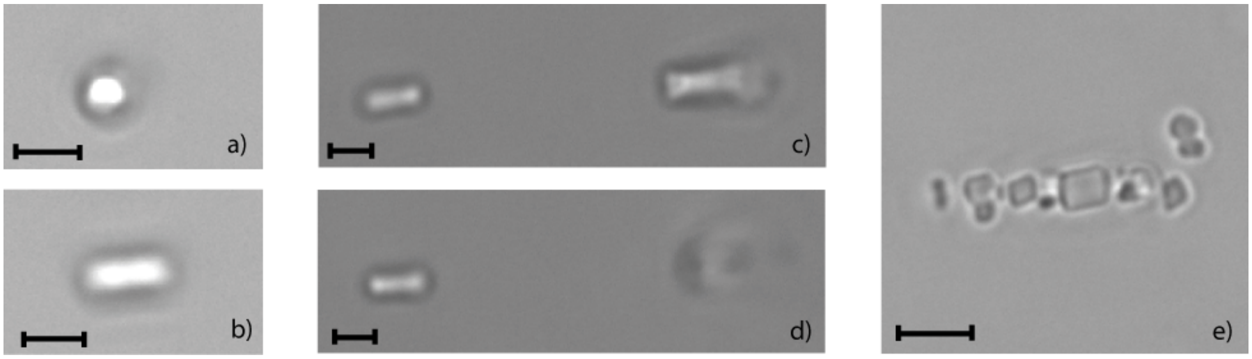

Figure 5: Lateral trapping of zeolite L. a) A 3 µm zeolite crystal in its natural, axial trapping position. b) The same crystal is rotated in lateral position by means of an additional trap. c) One 3 µm zeolite is trapped in a line trap (left) and another is moving freely. d) After an axial motion of the sample, the trapped zeolite remains in focus. e) Chain of nominally 1µm zeolite crystals, aligned along a line trap. Scale bars correspond to 2 µm.

The orientational control of individual zeolite L hosts can be combined with the translational control inherent to HOT and the possibility to manipulate multiple particles simultaneously. This degree of control is the basis for complex structures that allow for the desired degree of organization. As an example, a structure of 7 individually selected zeolite L hosts is trapped in a ring-like structure. The hosts are loaded with DXP as a guest species. 5 hosts are trapped laterally, the two remaining hosts are intentionally trapped in axial position (Figure 6a). The guest species does not interfere with the trapping process, as the excitation wavelength of DXP is far below $\lambda = 1064$ nm. The created structure can be observed with fluorescence microscopy without interfering the trapping as demonstrated in Figure 6b.

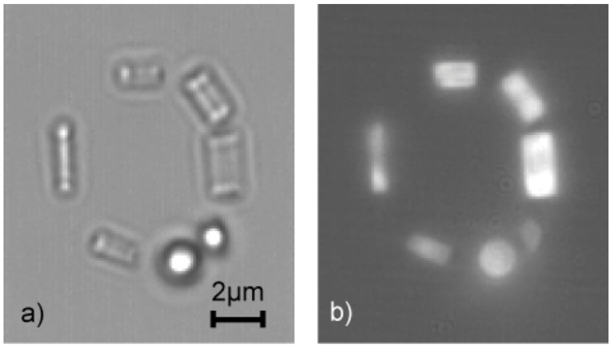

Figure 6: Structure of 7 zeolite L crystals, organized in a ring structure. 5 crystals are trapped laterally, 2 axially. a) Bright field image. b) The DXP load of the crystal is excited and fluorescence is observed.

In conclusion we have shown that HOT are versatile tools to achieve full, i.e. translational and orientational control of individual zeolite L crystals. These crystals can serve as hosts for various guest species and themselves be arranged and patterned with HOT. This HOT induced process of hierarchical supramolecular organization is fully dynamic and reversible and enables interactive, individual control of single particles for a larger number of confined hosts.

With control on the single crystal level, in principle every conceivable three dimensional structure with arbitrary degree of complexity can be constructed “from the scratch”. By this method, novel, functional materials could be tailored with properties that were not accessible before.

Acknowledgement: This work was supported by the Deutsche Forschungsgemeinschaft in the frame of the German-Chinese transregional research project TRR 61.

REFERENCES

[1] P. D. Yang, T. Deng, D. Y. Zhao, P. Y. Feng, D. Pine, B. F. Chmelka, G. M. Whitesides, and G. D. Stucky, “Hierarchically ordered oxides” *Science*, 282, 2244–2246 (1998).

[2] D. R. Walt, “Nanomaterials - top-to-bottom functional design” *Nature Materials*, 1, 17–18 (2002).

[3] A. Boker, Y. Lin, K. Chiapperini, R. Horowitz, M. Thompson, V. Carreon, T. Xu, C. Abetz, H. Skaff, A. D. Dinsmore, T. Emrick, and T. P. Russell, ”Hierarchical nanoparticle assemblies formed by decorating breath figures” *Nature Materials*, 3, 302–306 (2004).

[4] G. Calzaferri and A. Devaux, [Supramolecular Effects in Photochemical and Photophysical Processes] John Wiley & Sons, Inc. New Jersey, in press (2010).

[5] D. Bruhwiler and G. Calzaferri, “Molecular sieves as host materials for supramolecular organization” *Micropor. Mesopor. Mater.*, 72, 1–23 (2004).

[6] F. Cucinotta, Z. Popovic, E. A. Weiss, G. M. Whitesides, and L. De Cola, “Microcontact transfer printing of zeolite monolayers” *Adv. Mat.*, 21, 1142–1145 (2009).

[7] G. Calzaferri and K. Lutkouskaya, “Mimicking the antenna system of green plants” *Photochem. Photobiol. Sci.*, 7, 879–910 (2008).

[8] M. Tsotsalas, M. Busby, E. Gianolio, S. Aime, and L. De Cola, “Functionalized nanocontainers as dual magnetic and optical probes for molecular imaging applications” *Chem. Mater.*, 20, 5888–5893 (2008).

[9] M. M. Tsotsalas, K. Kopka, G. Luppi, S. Wagner, M. P. Law, M. Schafers, and L. De Cola, “Encapsulating in-111 in nanocontainers for scintigraphic imaging: Synthesis, characterization, and in vivo biodistribution” *Acs Nano*, 4, 342–348 (2010).

[10] C. A. Strassert, M. Otter, R. Q. Albuquerque, A. Hone, Y. Vida, B. Maier, and L. De Cola, “Photoactive hybrid nanomaterial for targeting, labeling, and killing antibiotic-resistant bacteria” *Angew. Chem. Int. Ed.*, 48, 7928–7931 (2009).

[11] A. Z. Ruiz, H. R. Li, and G. Calzaferri, “Organizing supramolecular functional dye-zeolite crystals” *Angew. Chem. Int. Ed.*, 45, 5282–5287 (2006).

[12] C. Leiggener and G. Calzaferri, “Monolayers of zeolite a containing luminescent silver sulfide clusters” *Chemphyschem*, 5, 1593–1596 (2004).

[13] Z. Popovic, M. Otter, G. Calzaferri, and L. De Cola, “Self-assembling living systems with functional nanomaterials” *Angew. Chem. Int. Ed.*, 46, 6188–6191 (2007).

[14] S. Suarez, A. Devaux, J. Banuelos, O. Bossart, A. Kunzmann, and G. Calzaferri, “Transparent zeolite-polymer hybrid materials with adaptable properties” *Adv. Funct. Mater.*, 17, 2298–2306 (2007).

[15] Z. Popovic, M. Busby, S. Huber, G. Calzaferri, and L. De Cola, “Assembling micro crystals through cooperative coordinative interactions” *Angew. Chem. Int. Ed.*, 46, 8898–8902 (2007).

[16] S. Megelski and G. Calzaferri, “Tuning the size and shape of zeolite l-based inorganic-organic host-guest composites for optical antenna systems” *Adv. Funct. Mater*, 11, 277–286 (2001).

[17] A. Zabala Ruiz, D. Brühwiler, L.-Q. Dieu, and G. Calzaferri, [Materials Syntheses, A practical Guide] Springer, Wien (2008).

[18] J. E. Curtis, B. A. Koss, and D. G. Grier, “Dynamic holographic optical tweezers” *Opt. Commun.*, 207, 169–175 (2002).

[19] M. Woerdemann, S. Gläsener, F. Hörner, A. Devaux, L. De Cola, and C. Denz, “Dynamic and reversible organization of zeolite l crystals induced by holographic optical tweezers” *Adv. Mater.*, in press, 2010.

[20] R. Gerchberg and W. Saxton, “A practical algorithm for determination of phase from image and diffraction plane pictures” *Optik*, 35, 237–246 (1972).

[21] J. E. Curtis, C. H. J. Schmitz, and J. P. Spatz, “Symmetry dependence of holograms for optical trapping” *Opt. Lett.*, 30, 2086–2088 (2005).

[22] J. Leach, K. Wulff, G. Sinclair, P. Jordan, J. Courtial, L. Thomson, G. Gibson, K. Karunwi, J. Cooper, Z. J. Laczik, and M. Padgett, “Interactive approach to optical tweezers control” *Appl. Opt.*, 45, 897–903 (2006).

[23] Y. Roichman and D. G. Grier, “Projecting extended optical traps with shape-phase holography” *Opt. Lett.*, 31, 1675–1677 (2006).

[24] R. C. Gauthier, M. Ashman, and C. P. Grover, “Experimental confirmation of the optical-trapping properties of cylindrical objects” *Appl. Opt.*, 38, 4861–4869 (1999).

[25] Stephen H. Simpson, and Simon Hanna. “Holographic optical trapping of microrods and nanowires”. *J. Opt. Soc. Am. A*, 27, 1255–1264 (2010).

[26] F. Hörner, M. Woerdemann, S. Müller, B. Maier, and C. Denz, “Full 3d translational and rotational optical control of multiple rod-shaped bacteria” *J. Biophoton.*, 3, 468–475 (2010).