Nanoassembled dynamic optical waveguides and sensors based on zeolite L nanocontainers

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ABSTRACT

Although optical functional devices as waveguides and sensors are of utmost importance for metrology on the nano scale, the micro-and nano-assembly by optical means of functional materials to create such optical elements has yet not been considered. In the last years, an elegant strategy based on holographic optical tweezers (HOT) has been developed to design and fabricate permanent and dynamic three-dimensional micro- and nanostructures based on functional nanocontainers as building blocks. Nanocontainers that exhibit stable and ordered voids to hierarchically organize guest materials are especially attractive. Zeolite L are a type of porous micro-sized crystals which features a high number of strictly one-dimensional, parallel aligned nanochannels. They are highly interesting as building blocks of functional nano-and microsystems due to their potential as nanocontainers to accommodate various different guest molecules and to assemble them in specific configurations. For instance, based on zeolite L crystals, microscopic polarization sensors and chains of several microcrystals for hierarchical supramolecular organization have been realized. Here, we demonstrate the ability of nanocontainers in general, and zeolite L crystals in particular to represent the basic constituent of optical functional microsystems. We show that the capability of HOT to manipulate multitude of non-spherical microparticles in three dimensions can be exploited for the investigation of zeolite L nanocontainers as dynamic optical waveguides. Moreover, we implement as additional elements dye-loaded zeolite L to sense the guiding features of these novel waveguides with high spatial precision and microspheres to enhance the light coupling into the zeolite L waveguides. With this elaborated approach of using nanocontainers as tailored building blocks for functional optical systems a new era of bricking optical components in a lego-like style becomes feasible.

Keywords: zeolite L crystal, holographic optical tweezers, nanocontainers, optical micro/nano assembly, optical waveguides

1. INTRODUCTION

Combination of biological or engineered soft materials in the micro-and nanoscale with advanced optical manipulation techniques is a promising strategy towards the design and fabrication of novel microsystems with specifically defined functionalities for applications in biomedicine and microfluidics. For instance, optically manipulated needle-shaped diatoms have been used for cell surface probing and imaging, while a large number of light-driven complex-shaped microrotors and optically patterned structures of motile bacteria have been applied for defined microflow induction. In addition, three-dimensional optically maneuvered two-photon polymerized microstructures have been proposed as tools and motors driven by light, or as light-deflecting guides for targeted-light delivery. These free-standing optically controlled guiding elements can achieve high numerical apertures and strong light guiding due to the high refractive index difference relative to the surrounding medium. In this respect, it is of high interest to implement novel materials which can deliver specific functionalities, on the one hand, by ordering them in certain hierarchical configurations and, on the other hand, by tailoring their optical properties. In contrast to soft matter that may be subject to alteration or disintegration, which may be desired in biomedical applications, but are disadvantageous in optical sensing or processing, hybrid guest-host materials with a rigid crystalline host matrix and the potential to stably accommodate soft host materials are ideally suited in the micro-and nano-assembly realization of functional devices.
Zeolite L is a type of porous micro-sized crystal that fulfills these requirements ideally. They feature a high number of strictly one-dimensional aligned nanochannels across the whole crystal axis. Thus, they are highly interesting building blocks because by accommodating different guest molecules within their nanopores, they can achieve specific photonic functionalities. In particular, if loaded with organic dyes, the organizational confinement exerted by the pore dimensions enhances the emissive properties of the molecular guests, leading to materials that can be used as effective light harvesting antenna systems, luminescent labels for imaging, or for bio-medical applications, to mention a few. In turn, the crystals themselves may also be hierarchically arranged on a larger scale, extending the ordering from the molecular to the macroscopic scale and leading to systems with exciting properties. An elegant strategy to realize this ordering on different scales is the use of holographic optical tweezers (HOT), which has been developed for the construction of sophisticated microstructures based on zeolite L crystals. The full three-dimensional control over each individual constituent of this micro-optomechanical approach can be applied to create permanent two-and-three-dimensional microstructures on surfaces as well as dynamic structures, as e.g. microscopic polarization sensors, chains of several microcrystals for hierarchical supramolecular organization, and bio-hybrid micro-robots.

In this work, we extend this concept and dynamically arrange empty zeolite L crystals with HOT to demonstrate their capability to guide light when dispersed in media with lower refractive index. We characterize the optical properties of the zeolite L waveguides for guiding the light emitted by classical optical fibers, and demonstrate control of direction of propagation of the light beam by steering the waveguide. Finally, dye-loaded zeolite L crystals are optically placed at the zeolite L waveguide output to detect the emitted light with high spatial precision and we discuss the implementation of optically controlled microspheres as an advantageous approach for the effective enhancement of light coupling into the zeolite L waveguide.

2. OPTICAL CONTROL OF ZEOLITE L WAVEGUIDES

2.1 Optical setup

The unique capability of HOT to dynamically control multiple non-spherical microparticles was exploited for the investigation and use of zeolite L nanocontainers as waveguides. Figure 1a depicts the schematic of the optical configuration that was used to perform the experiments. Trapping and organization of zeolite L crystals was achieved with a holographic optical tweezers system that was implemented on a commercial inverted fluorescence microscope (Eclipse Ti, Nikon). The principles of HOT are described in detail elsewhere, so that only a brief explanation of the HOT system is described below. The light source used for optical trapping and organization of zeolite L nanocontainers was a Nd:YVO4 laser (Smart Laser Systems, \( \lambda_{\text{HOT}} = 1064 \text{ nm} \), \( P_{\text{max}} = 2.5 \text{ W} \), \( \text{TEM}_{\text{00}} \) (\( M^2 < 1.2 \))) in order to avoid interaction with the excitation wavelength of the guest dye molecules that were loaded into the nanochannels of the zeolite L crystals (see Chapter 3.2). A high resolution phase-only spatial light modulator (SLM) (Holoeye, Pluto, 1920x1080 pixels, full \( 2\pi \) phase range at \( \lambda = 1064 \text{ nm} \)), was used together with a custom-made software and Camera 1 (PCO, Pixelfly qe) to modulate the laser beam and to tailor the desired trapping pattern in the front focal plane of a high numerical aperture microscope objective (MO1, Nikon Apo TIRF, 100x/1.49 oil-immersion). Depending on the actual requirements, different devices, including a high speed CMOS device (Photon Phocus, MV2-D1280) and a CCD device (The Imaging Source DMK 41BU02), were used for video data acquisition in Camera 2. The zeolite L nanocontainers were observed using the white light illumination of the inverted microscope for conventional bright field imaging. An optional band pass emission filter (F) was placed in the optical path between the sample and the cameras to filter the emission of the optical fiber and to detect the fluorescent signal emission of dye-loaded zeolite L crystals.
Figure 1. a) Schematic of the combined HOT system used for zeolite L optical trapping and the optical fiber system used for investigation of wave guiding properties of zeolite L crystals. λ/2: rotatable half wave plate, PBS: polarizing beam splitter, SH: shutter, MO: microscope objective, L: lens, SLM: spatial light modulator, M: mirror, DM: dichroic mirror, WS: white light source; CL: condenser lens, F: bandpass emission optical filter, SM: single mode optical fiber, BS: non-polarizing beam splitter, TL: tube lens. b) Schematic (not in scale) of the sample configuration for investigation of zeolite L waveguides.

For the investigation of the light guiding properties of zeolite L nanocontainers, the light of a frequency-doubled Nd:YAG laser (Coherent, Compass 100, λ_{fiber} = 532 nm; max. output power 100 mW) was coupled into a single mode optical fiber (460HP, Ø cladding=125 µm, mean field diameter (MFD) = 3.5 µm @ λ = 515 nm, Thorlabs). The fiber end was stripped, cleaved and fixed to the microscope glass slide. The power of the Gaussian output beam was set to few microwatts (= 10 µW) so that the green light beam exerted a negligible force over the particles in comparison with the optical trapping laser.

2.2 Preparation and optical control of zeolite L crystals

Zeolite L crystals used in this study were synthesized with an approximate diameter of 1-1.5 µm and length of 3-4 µm, according to procedures reported in literature 25, 26. The particular aspect ratio was chosen to tailor zeolite L crystals as micro-sized waveguides where the light wave is able to propagate a few wavelengths before exiting the crystal. In addition, zeolite L crystals featuring a strong asymmetry are easier to be fully controlled in three dimensions with HOT 19,24. In our experiments, we used dye-free zeolite L crystals for the study of light guiding (zeolite L waveguides) while pyronine-loaded zeolite L crystals (zeolite L sensors) were used for detection of frequency-doubled Nd:YAG laser light.

After fabrication, the zeolite L crystals were suspended in distilled water with 1% of a non-sticking surfactant (Tween 20), and optically trapped with the optical setup described above (Figure 1a). Clearly elongated materials, as the one we used, are inherently aligned along the z-axis of an optical single trap configuration, but can be rotated in a relatively simple way by a two trap scheme, where both traps act as handles at the poles of the material in order to exert the required torque for rotation (Figure 1b)19. In general, in our experiments, zeolite L waveguides were optically oriented perpendicular to the z-axis, and placed along the axis of the optical fiber with a distance fiber-zeolite of 5-10 µm. Zeolite L sensors were optically trapped with single optical tweezers and thereby oriented vertically along the z-axis.
3. ZEOLITE L WAVEGUIDES AND SENSORS

3.1 Characterization of the optical properties of zeolite L waveguides

A fundamental question that arises when using zeolite L crystals as waveguides is to characterize the typical properties that are used for optical fibers, as e.g. the numerical aperture $NA_{\text{zeolite}}$ and the normalized frequency or $V$ number. Assuming that the cylindrical zeolite L crystal acts as the core and the surrounding medium as the effective cladding of the waveguide, a theoretical estimation of these parameters can be calculated by using their usual definitions:

$$NA_{\text{zeolite}} = n_{\text{medium}} \cdot \sin \alpha_{\text{max}} = \sqrt{n_{\text{zeolite}}^2 - n_{\text{medium}}^2}$$

and

$$V_{\text{zeolite}} = \frac{\pi d_{\text{zeolite}}}{\lambda_0} \cdot NA_{\text{zeolite}}$$

where $\alpha_{\text{max}}$ is the half-angle of the cone of light entering (or exiting) the waveguide, $d_{\text{zeolite}}$ is the zeolite’s diameter and $\lambda_0$ is the wavelength in vacuum of the light beam that is launched into the zeolite L crystal. In our experiments, we used cylindrical zeolite L crystals with a diameter $d_{\text{zeolite}} \approx 1.5 \, \mu m$ and the wavelength of the beam launched on zeolite L micro-waveguides was $\lambda_0 = 532 \, \text{nm}$. Zeolite L crystals have a refractive index $n_{\text{zeolite}}$ between 1.4 and 1.5, which depends on the optical properties of the different guest molecules loaded within their nanopores. This range of values gives a rough estimate of the numerical aperture of a zeolite L waveguide to $0.44 < NA_{\text{theo.}} < 0.69$, and the normalized parameter $3.9 < V_{\text{theo.}} < 6.1$, which in any case indicates that at these conditions zeolite L crystals support more than one propagation mode.

A straightforward way to measure experimentally the numerical aperture of a zeolite L waveguide $NA_{\text{exp.}}$ is to arrange a horizontally oriented zeolite L with HOT in front of the core of the single-mode optical fiber in order to launch the output Gaussian beam onto the front facet of the zeolite L waveguide. Figure 3a shows an example of a zeolite L waveguide located in front of the optical fiber output. The vertical line at the left of the zeolite L crystal indicates the beam width of the Gaussian beam at this position while the dashed line indicates the axis of the optical fiber core. The cone of light emitted by the zeolite L waveguide has an approximate angle $\alpha_{\text{max}} = 23 \pm 3^\circ$, giving an experimental value of $NA_{\text{exp.}} = 0.52 \pm 0.06$ and $V = 5.13 \pm 0.19$.

In addition, the full rotational control of elongated particles using HOT can be exploited to control the direction of propagation of the light exiting the zeolite L waveguide. Figure 3b shows as an example that optical rotation of the zeolite L crystals by $22^\circ$ with respect to the optical fiber axis allows redirecting the emitted light sideways. When the crystal is rotated by an angle higher than the acceptance angle for light guiding, the crystal cannot longer be considered as waveguide, but causes complex light scattering at the interface. Figure 3c show the light scattering profile that was created when the crystal was rotated by $43^\circ$ with respect to the optical fiber axis.
3.2 Enhancement of light coupling into the zeolite L waveguide

If a light beam with a width larger than the diameter of the zeolite L waveguide is incident on it, the aperture is over-filled, and thus coupling losses are increased. For a higher efficient light coupling, the beam width of the incoming beam needs to be reduced by a focusing element, as e.g. tapered lens fibers, especially abruptly tapered fibers or microspheres embedded in hollow waveguides. In this paper, we realize an alternative approach by which we optically place silica microspheres with HOT at the output of the optical fiber which serve as the focusing element that adapts the beam diameter on the front surface of the zeolite L waveguide. The focal length $f_{\text{sphere}}$ of a microsphere can be determined by:

$$f_{\text{sphere}} = \frac{n_{\text{sphere}} \cdot d_{\text{sphere}}}{4 \cdot \left( \frac{n_{\text{sphere}}}{n_{\text{medium}}} - 1 \right)}$$

where $d_{\text{sphere}}$ is the diameter of the microsphere particle, and $n_{\text{sphere}}$ and $n_{\text{medium}}$ are the refractive indices of the microsphere particle and the medium, respectively. Our experiments were performed in distilled water, and we used silica SiO$_2$ microspheres with a diameter $d_{\text{sphere}} \approx 6.2 \pm 0.6$ µm and refractive index $n_{\text{sphere}} \approx 1.43$, resulting in a theoretical estimation of $f_{\text{SiO}_2-\text{microsphere}} = 17.4 \pm 1.7$ µm. In order to determine experimentally the distance at which the light refracted by the microsphere was focused, a zeolite L-based sensor was optically moved along the direction of light propagation, while the focusing silica microsphere was placed with a second optical trap directly in front of the end of the cleaved optical fiber (Figure 3a-c). The maximal fluorescence signal emitted by the zeolite L sensor could be used to determine the position with respect the center of the sphere at which the light of the optical fiber was focused by the silica microsphere within sub-micrometer precision: $f_{\text{SiO}_2-\text{microsphere}}^{\text{exp.}} = 19.1 \pm 0.8$ µm.

To demonstrate the enhancement in coupling efficiency with the microsphere with respect to the situation without using any focusing element, we positioned first a slightly tilted zeolite L waveguide with its front facet at a distance $f_{\text{sphere}} + d_{\text{sphere}} / 2$ on the axis of the optical fiber, while a zeolite L sensor was placed at the end facet of the zeolite L waveguide (Figure 3d). Then, by optically placing a SiO$_2$ microsphere at the output of the optical fiber, the enhancement of the light coupling into the waveguide is shown by the increased light emission of the pyronine-loaded zeolite L sensor. In addition, the axial and lateral position of the focusing microsphere can be further finely controlled with HOT with nanometer precision in order to maximize the light coupling into the entrance of the zeolite L waveguide. The difference of intensity of the fluorescence signal for the cases without (Figure 3d) and with the optically controlled focusing microsphere (Figure 3e) indicates an enhancement factor of 2, which demonstrates that optically nano-adjustable microspheres can be used as operative building blocks for the efficient launching of light into the zeolite L waveguide.
4. SUMMARY AND CONCLUSION

In this work, we have presented a novel method to investigate and assemble building blocks of zeolite L nanocontainers which are used as optical waveguides. We characterized the optical light guiding properties of zeolite L waveguides in aqueous medium by the experimental determination of the numerical aperture and normalized frequency of the zeolite L waveguide and found that these free-standing waveguides support in principle more than one propagation mode, and thus achieve strong light guiding. We demonstrated that these cylindrical micro-waveguides can be optically steered with holographic optical tweezers in order to control the direction of propagation of the illuminating light beam. Moreover, we exploited the capability of simultaneous manipulation of multiple microparticles with HOT in order to implement additional optically controlled building blocks as dye-loaded zeolite crystals for light detection, and silica microspheres for the enhancement of the light coupling at the zeolite L waveguide entrance. We believe that the exploitation of zeolite L nanocontainers as tailored building blocks with custom optical properties paves the way for the design and fabrication of novel microsystems where the micro- and nanoassembly of these elements can be used for the realization of modules for light guiding with specific functionalities.

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REFERENCES