

Visualizing single-probe diffusion in well-defined pore structures

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Introduction

Mass transport is a crucial aspect in heterogeneous catalysis as it can influence activity, selectivity, and the overall lifespan of a catalyst. Therefore, providing a better understanding of the molecular motion in a catalyst's pore space is of utmost importance for a more rational design of solid catalysts. Traditional diffusion experiments rely on bulk analytical measurements, which ignore the heterogeneity of diffusant behavior caused by host-probe interactions [1]. One way to unravel these diffusion heterogeneities, is localizing fluorescent probes over time with super-resolution fluorescence microscopy leading to probe trajectories. These can then be used to obtain information about the local pore geometry and composition as well as how these properties relate to the diffusion coefficient of individual probes. In previous work, we had successfully tracked single fluorophores inside fluid catalytic cracking (FCC) particles, shedding light on the ensemble-free diffusion behavior under confinement [2]. However, the pore space of each catalyst is extremely complex and, in many cases unknown, which severely complicates relating tracks to a probe's diffusion properties, the local pore geometries, and/or the host material's composition. To tackle this problem, we propose a stepwise bottom-up approach in which single diffusants are first traced over time in a well-defined model structure, where both composition and geometry are known. This will allow us to determine the diffusion properties of the used probes. Based on that knowledge, more complex pore space geometries can be explored in a more quantitative fashion.

Materials and Methods

A silica microfluidic device consisting of two microchannels connected by an array of nanoslits (Figure 1a), was fabricated using photolithography and wet etching. The device was loaded with a solution containing fluorescent probes (PEG coated quantum dots, 20 nm diameter) that were individually traced while moving inside the nanoslits (Figure 1b). The pH of the system as well as slit depth were varied in order to study their effects on diffusion and adsorption behavior.

Results

The adsorption could behavior be tuned by varying the pH of the system. As the pH decreased, more and longer adsorption events (Figure 1c) took place, leading to lower effective diffusion coefficients (Figure 1d). With this possibility to tune the system we have managed to (a) prevent adsorption entirely, (b) increase it and (c) to prevent diffusion entirely within the same confinement geometry. On the other hand, varying the slit depth at high pH did not seem to have a significant effect on the adsorption and diffusion behavior.

Discussion and conclusion

With growing pH, both probes and pore walls become increasingly negatively charged causing repulsion. Conversely, as the pH decreases, negative charge of the surfaces becomes weaker, and more adsorption takes place. The wall particle interactions caused by the change in pH in the system seem to be more important for mass transport than the pore and probe sizes.

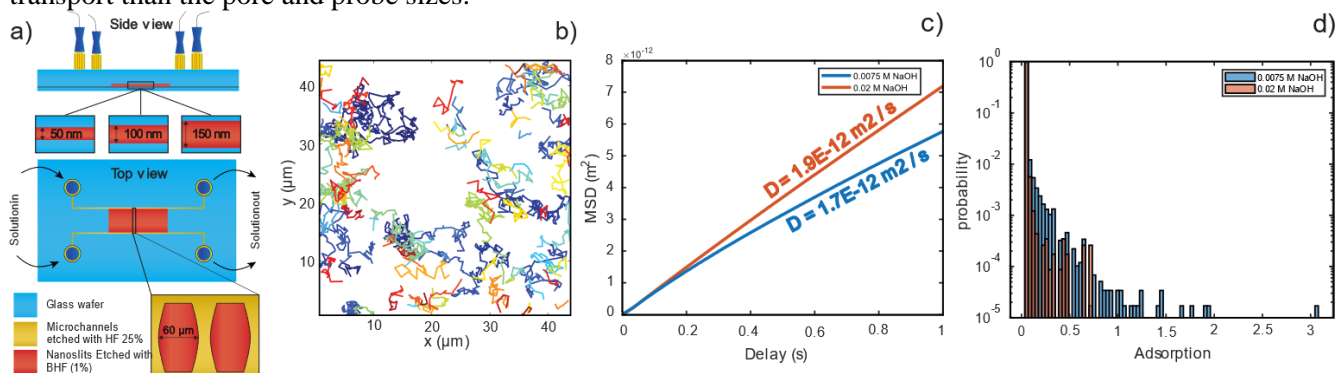


Figure 1: Schematic of the developed microfluidic device. b) Quantum dot tracks recorded over five seconds. c) Histogram of adsorption event duration within 50 nm slits with varying NaOH concentrations. d) Population-average MSD curves and corresponding effective diffusion coefficients within 50 nm slits with varying NaOH concentrations.

References

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