



Short communication

Molecular transport properties of ZIF-8 thin films in aqueous environments: The critical role of intergrain mesoporosity as diffusional pathway

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ABSTRACT

We report here the first use of electrochemical tools to quantify molecular transport from aqueous solutions into ZIF-8 MOF thin films. Our experimental findings reveal that molecular transport through ZIF-8 films in aqueous environments is purely dominated by solvent-filled intergrain mesoporosity and exhibits two well-defined transport regimes.

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1. Introduction

Metal-organic frameworks (MOFs) represent one of the most exciting research areas in modern materials science [1–7]. In recent years research on MOFs has extended from bulk synthesis, to thin film engineering, to the microscopic study of molecular dynamics and structure (i.e., the molecular level understanding of these systems) [8,9]. Particularly, the generation and use of thin films of MOFs has attracted significant attention due to their integration in chemical sensors, catalysts, and also optical devices [10–13]. These materials represent a versatile class of crystalline hybrid inorganic–organic solids exhibiting wide structural diversity with pore sizes ranging from a few angstroms to several nanometres and specific surface areas exceeding that of traditional adsorbents. These features have made MOFs the focal point of many studies focussed on their adsorption properties. However, their performance for practical capture, storage and release applications critically depends on the diffusion and interaction of probe molecules in the MOF environment. For instance, in most applications of MOFs

it is crucial to rely on quantitative information on diffusion of guest molecules within the host framework. While there has been considerable progress in recent years with regard to the understanding of molecular transport through MOFs in gas phase systems [14], very little is known about diffusion of molecules through solvent-filled MOFs [15]. This lack of information is even more striking in the context of molecular transport through intergrain voids in MOF thin films with hierarchical porosity. This aspect is particularly relevant in view of the potential applications of MOFs in liquid-phase separation [16], biocompatible materials for drug delivery [17,18], and chemical sensing [19]. For the use of MOFs as catalysts [20], hierarchical intercrystalline porosity is one of the most important aspects since it determines to a large extent the accessibility of reactive sites and the speed at which reactants can reach these sites within the porous structure [21]. In this regard, Sanchez, Serre, and co-workers [22–24], developed an interesting strategy to fabricate MOF thin films by assembly of colloidal MOF particles onto solid surfaces. A most appealing aspect of this strategy is the control over intergrain mesoporosity that, in turn, enables easier diffusion of analytes into the film. Formation of MOF thin films displaying hierarchical porosity [25,26] can also be attained by the method of seeding and secondary growth. This strategy relies on the impregnation of the substrate surface with an

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aged precursor solution containing the MOF seeds and permits separate control of MOF nucleation and growth steps. As a result, sequential impregnation steps enable the layer-by-layer formation of thick MOF films displaying mesoporous intercrystalline voids [27].

When considering solvent-filled MOFs in thin film formats, the elucidation of molecular transport mechanisms through mesoporous spaces and the concomitant estimation of diffusivities are increasingly important in the up-and-coming electrochemical applications of these materials [28]. It has long been considered that molecular transport through MOFs can be described as a simple Fickian diffusion. However, this vision changed after Grzybowski and co-workers demonstrated that considering a pure diffusion approach is a gross oversimplification and suggested that surface-governed processes are operative [29]. Taking into account these notions and being aware of the critical role of intergrain porosity in defining the molecular transport characteristics of MOF thin films we took this new paradigm one step further by exploring the use of electrochemical techniques to unravel the mechanisms governing the diffusion of molecules through intergranular voids in solvent-filled, hierarchically porous MOFs at the solid–liquid interface. The diversity of methodological approaches to quantify the molecular transport in MOFs is of varied complexity and applicability.

Among the techniques used quasi-elastic neutron scattering (QENS) [30], pulsed field gradient nuclear magnetic resonance (PFG NMR) [31], fluorescence correlation spectroscopy (FCS) [29], and quartz crystal microbalance (QCM) [32], can be mentioned.

Within the context of matching science to application, the use of electrochemical tools offers the possibility of exploring the inner environment of the porous material, studying transient transport processes, and estimating diffusion coefficients through simple experiments using readily available equipment [33,34].

The aims of the research presented herein are three-fold: to introduce a simple method to study the diffusion of probe molecules through solvent-filled MOF thin films, to elucidate the mechanisms that govern molecular transport through intergrain mesoporosity in MOFs, and to estimate the diffusivity of probe molecules permeating through solvent-filled MOF layers. To meet these goals, we exploited the versatility of electrochemistry to detect the diffusion of redox-active tracers (excluded from micropores) permeating through the MOF film and reaching a conductive substrate.

2. Experimental

2.1. Synthesis of ZIF-8 thin films

ZIF-8 films were synthesized over chemically modified ITO coated glass (Delta Technologies) using methanolic solutions of precursors according to previously published procedure [35,36]. Briefly, it consists of the following steps: i) clean ITO coated glass substrates were treated with APTES/Toluene solution at 110 °C for 2 h (0.2 mM APTES in 10 mL Toluene), then rinsed, and heated at 100 °C for 10 min, ii) modified ITO substrates were immersed in a fresh mixture of $\text{Zn}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ (25 mM) + 2-methyl-imidazole (50 mM) stock solutions for 40 min at room temperature, iii) substrates were then rinsed with fresh methanol and dried with N_2 prior to the next cycle. Films grown under these conditions were reported to increase ≈ 65 nm per cycle. APTES forms a self assembled monolayer that acts as an initiator of the enhanced heterogeneous nucleation process (via Zn^{2+} ion coordination). The samples were dried at moderate temperatures (50 °C) before use. Characterization of films obtained confirming the presence of ZIF-8 was performed via Scanning Electron Microscopy, ATR-FTIR, water contact angle, X-ray diffraction and Nitrogen adsorption isotherms,

and is given in [Supplementary Material](#). Fig. 1 shows a comparison of the diffractogram obtained for the different materials synthesized.

2.2. Water uptake via quartz crystal microbalance (QCM)

Experiments for determining water uptake of ZIF-8 films were carried using a flow cell Quartz Crystal Microbalance (QCM200 Stanford Research Systems) setup. For each experiment, the MOF films were grown in situ following the same procedure as described above, in such way that the weight of ZIF-8 per unit area was a known parameter, and thus water uptake could be normalized. The flow cell was equilibrated with dry N_2 at a flow rate of 30 mL/min and then treated with water saturated N_2 . Water saturated N_2 flow was achieved by directing dry N_2 through a bubbler at a flow rate of 30 mL/min. The bubbler was filled with deionized water and N_2 bubbles were forced to flow through. Water saturated N_2 flow was established, and weight increment was followed on the QCM until a plateau was reached (i.e., saturation of the film adsorption capacity), see [Supplementary Material](#) for more details on the setup.

2.3. Cyclic voltammetry experiments

Cyclic voltammetry experiments were carried out using a potentiostat Reference 600 from Gamry, with a three-electrode setup. Ag/AgCl and Pt wire were used as reference electrode and counter electrodes, respectively. In all the electrochemical experiments 1 mM $\text{Fe}(\text{CN})_6^{3-}/\text{Fe}(\text{CN})_6^{4-}$ + 100 mM KCl solutions were used.

3. Results and discussion

Zeolitic imidazolate framework (ZIF)-8 films were successfully synthesized over indium tin oxide (ITO)-coated supports at room temperature from stoichiometric methanolic precursor solutions using sequential one-pot procedure (see [Supplementary Material](#) for XRD characterization). The intercrystalline molecular transport through the MOF thin films was electrochemically probed using electroactive $\text{Fe}(\text{CN})_6^{3-}$ species diffusing across films of

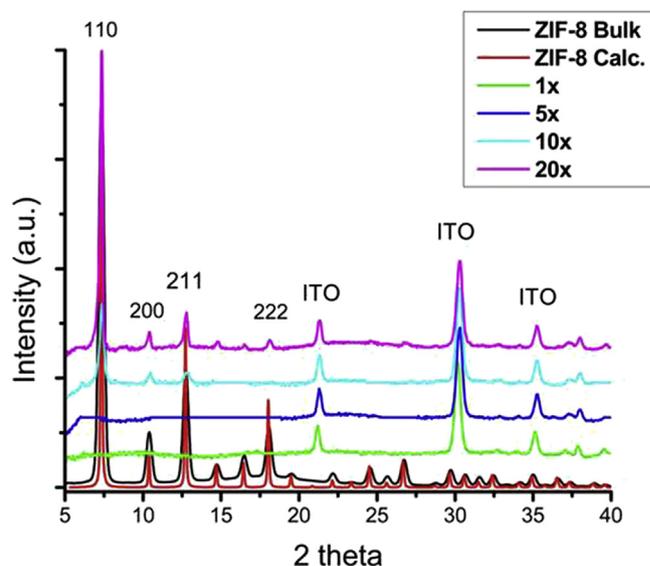


Fig. 1. XRD corresponding to the various ZIF-8 films synthesized over ITO substrates. Both calculated and experimentally obtained ZIF-8 bulk material diffractograms are also displayed for comparison.

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