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Supersonic cold spraying for zeolitic metal–organic framework films

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HIGHLIGHTS

- Zeolitic metal–organic framework (ZIF-8) films were deposited by supersonic spraying.
- This supersonic spray method produced textured crystalline films on copper and glass substrates.
- Addition of high-boiling-point solvents in ZIF-8 pores resulted in preferred crystal orientations.
- The produced films are microstructurally compact and strongly adherent to substrates.

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ABSTRACT

We describe the first use of high-rate supersonic spray coating to deposit thin films of ZIF-8, a zeolitic metal–organic framework (MOF), adopting a sodalite architecture. This cold-spray technique is versatile and scalable, with tunable processing parameters capable of generating either a textured crystalline film or a randomly oriented polycrystalline coating on both metallic and non-metallic substrates. We provide evidence that guest occupancy by organic solvents (dimethylformamide, dimethylacetamide, and dimethylsulfoxide) in the sodalite cage of ZIF-8 structurally stabilizes the framework against high-velocity impact, resulting in the preferred orientations observed. Moreover, we show that amorphous ZIF-8 films can be straightforwardly obtained at high air pressure exceeding 7 bars in which the particle velocity is ~500 m/s. It is anticipated that this high-throughput approach can be adapted to fabricate microstructurally compact and strongly adhered ZIF-8 films.

1. Introduction

Metal–organic frameworks (MOFs) are extensively studied as a new class of multifunctional materials in materials science and chemistry [1]. In MOFs, metal atoms are coordinated with organic ligands to form diverse crystalline 3D frameworks. The structures of MOFs can be dense or porous; MOFs of specific structures can be used in many applications such as gas separation, sensing, catalysis, optoelectronics, and magnetism [2–4]. Zeolitic imidazolate frameworks (ZIFs) [5] comprise an important subclass of MOFs closely related to zeolitic silica polymorphs as per their chemical bonding (Si—O—Si); [6] they typically consist of divalent metal cations (e.g., M = Zn^{2+}, Co^{2+}) solely coordinated by the nitrogen atoms of the imidazolate (Im) bridging ligand (M-Im-M), forming microporous crystalline lattices. In the ZIF family, ZIF-8 contains Zn(II) metal ions connected by 2-methylimidazolate (mIm) organic linkers, resulting in periodic frameworks of $Zn(mIm)_2$. ZIF-8 has been extensively studied for its tunable pore size, chemical stability, and thermal robustness [7,8]. The topology of ZIF-8 corresponds to that of the zeolite sodalite [9], which can be described as a space-filling packing of truncated octahedra. In particular, ZIF-8 crystallizes as a cubic lattice (space group I43*m*) containing cavities with diameters of 11.6 Å, connected *via* six-membered ring apertures with 3.5 Å windows and four-ring apertures [10]. The good thermal and chemical stability of ZIF-8 [11], combined with the regular pore architecture and long-range ordering of the structure, has motivated extensive research in the fields of membrane science, gas storage, drug delivery, and catalysis [12–14]. With

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respect to mechanical stability, the crystal structures of ZIFs are more flexible than the analogous aluminosilicate zeolites [15]; hence, they can undergo structural transformations and are susceptible to collapse under the application of either low pressure (0.34 GPa) [16] or temperature (300 °C) [6].

The deposition of MOF thin films and surface coatings is under intense study because of the many possible applications of thin-film MOFs in optical, electronic, and energy harvesting devices [17]. MOF applications would greatly increase if a high-throughput facile processing route were developed to fabricate MOFs as supported homogenous thin films. Despite numerous studies, the majority of reported techniques are not ideal for commercial manufacturing and production scale-up [2,14,4,18]. The most common methods of MOF film deposition are summarized below. Secondary growth is one of these methods, entailing a stepwise deposition in which the first step deposits a seed layer and the second step grows further layers by solvothermal synthesis and dip-coating from solutions [19]. Another method is *in situ* crystallization, where the ZIF layer is grown on a bare substrate by solvothermal synthesis. Crystal orientation can affect the properties of the membranes or films, depending on the applications. Secondary growth is useful to control the crystal orientation of the MOF films [20]. Highly oriented ZIF-8 films were prepared by Bux et al. [19] on alumina discs *via* the secondary growth method. In the first step, they deposited a seed layer by dip-coating using a mixture of ZIF-8 nanocrystals dispersed in water/polyethylenimine (PEI); the seed layer was treated solvothermally to grow the films. They reported the growth of crystalline ZIF-8 films with highly oriented (1 0 0) planes after 2 h of deposition; these membranes showed improved performance in H_2/hydrocarbon separation over typical ZIF-8 films. A set of *b*-oriented (0 1 0) and *c*-oriented (0 0 2) ZIF-L membranes was prepared by Zhong et al. [20] employing the secondary growth method for gas permeation. The *b*-oriented films were grown from an *in situ* seed layer by dip coating on porous alumina. They used seeded alumina for three rounds of secondary growth by the same method to grow *b*-oriented ZIF-L films. For the *c*-oriented films, ZIF-L crystals dispersed in PEI were vacuum-filtered onto porous alumina as a seed layer. Using the secondary growth method, *c*-oriented ZIF-L membranes were prepared by dip coating for 30 min. The gas permeation properties of the *c*-oriented ZIF-L membranes were reported as better than those of the *b*-oriented ZIF-L membranes. Cookney et al. [13] reported the synthesis of ultrathin ZIF-8 nanofilms on silicon by stepwise dip-coating. The films were morphologically dense and homogenous, with crystallinity oriented towards the (1 1 2) plane. Recently, Papporello et al. [21] deposited ZIF-8 films on both metallic and nonmetallic substrates utilizing different solvent media by the solvothermal method. They grew (2 0 0)- and (1 1 0)-oriented ZIF-8 films on copper using a mixed solvent of methanol and acetate, and then prepared structured catalysts based on the films. Hence, the fabrication of oriented ZIF thin films is important for selective gas separation [19,20], structured catalysts [21], and optical applications [3].

While some recent reports describe the application of spray-type processing strategies to fabricate MOF films, the approach we describe in the current study is distinct from those found in the literature. Melgar et al. [22] reported the direct spraying of ZIF-7 membranes by electrospraying on an alumina disk, where the membrane thickness was controlled by changing the electrospray solution flow rate and deposition time. These ZIF-7 membranes showed H_2 permeability and H_2/CO_2 separation capacity. Likewise, Fan et al. [23] used a simultaneous spray self-assembly approach in order to increase the ZIF-8 particle loading while maintaining a uniform dispersion. They synthesized ZIF-8/Polydimethylsiloxane (PDMS) composite membranes on polysulfone for butanol pervaporation. Sanchez and co-workers [24] reported the application of spray-drying to make multicomponent MOF hollow superstructures. Arslan et al. also used a spray process to grow highly oriented crystalline HKUST-1 MOFs on modified Au substrates [25].

We report a new method for the deposition of MOF films by cold-spraying colloidal ZIF-8 sol. The cold-spraying technique is a high-rate coating method in which particles are injected into a supersonic gas stream, created by the expansion of a compressed gas through a convergent-divergent De Laval nozzle. The particles, accelerated to supersonic velocities, possess sufficient kinetic energy to bond to the substrate upon impact. Other technical details of the cold-spraying apparatus have been discussed in earlier reports [26]. The cold-spraying technique utilizes the high kinetic impact energy of the high-velocity particles to promote strong bonding between the substrate and the particles. Herein, we demonstrate that the cold-spray coating method is effective in successfully depositing ZIF-8 films that maintain the original crystal structure of the source nanoparticles. Furthermore, we observed the deposition of ZIF-8 films with (1 1 2)-oriented crystal structures in the presence of 20% dimethylformamide (DMF) in the colloidal sol. To the best of our knowledge, this is the first report on the deposition of oriented ZIF-8 films by supersonic spraying. This work provides new insight on the deposition of ZIF-8 films and the mechanical responses of the films to high-speed impact, and describes the tailoring of the crystallographic orientations and crystallinity of the deposited MOF films.

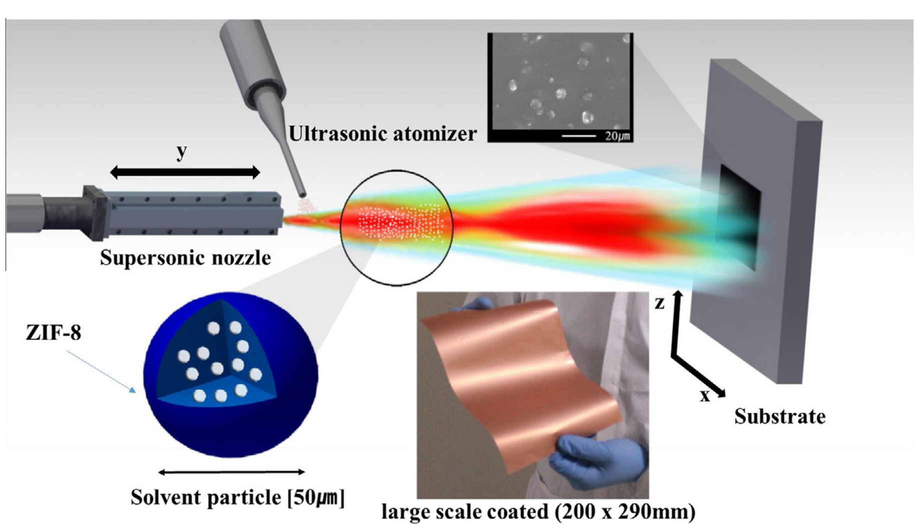

Fig. 1. Schematic of the custom-built supersonic spray-coating system.