



# Tuning crystalline structure of zeolitic metal–organic frameworks by supersonic spraying of precursor nanoparticle suspensions



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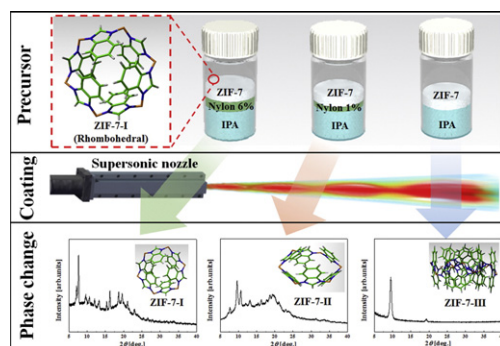
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## HIGHLIGHTS

- Zeolitic Imidazolate Framework-7 (ZIF7) films have been fabricated by a supersonic cold-spraying method.
- Crystalline structures of the supersonically sprayed ZIF7 film can be controlled by adjusting the nylon content.
- Supersonic spraying technique is versatile, it can be used to fabricate ZIF7 phase-I, -II, and -III.
- Inclusion of 6 wt% of nylon improves framework mechanical stability, preventing phase changes upon high-energy impact.

## GRAPHICAL ABSTRACT



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## ABSTRACT

The deposition of sodalite zeolitic imidazolate framework-7 (ZIF7) films by a supersonic cold-spraying technique was successfully accomplished for the first time. The high-speed impact of supersonic cold spraying increased the monodispersity of the ZIF7 crystalline structure. However, the intensity of the structural change decreased with increasing the amount of nylon in the ZIF7 suspension. Mitigating phase changes in ZIF7 occurred by the impact dampening conferred by the polymeric nature of nylon, which preserved the original three-dimensional crystalline structure of ZIF7. The inclusion of *N,N*-dimethylformamide (DMF) in a nylon–ZIF7 suspension improved the dispersion of ZIF7 nanoparticles, which in turn eliminated the dampening effect from the nylon and recovered the distinctive monodispersity arising from the high-speed impact. This characteristic was observed at all impact speeds for ZIF7 suspensions containing DMF. We show that high-rate cold spraying of ZIF7 particles can be combined with nylon and other pressure-transmitting media to control the formation of three distinctive phases. The unique capability to tune the crystalline structure of ZIF7 allows customization of the film functionality for specific applications.

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## 1. Introduction

Zeolitic imidazolate frameworks (ZIFs) are three-dimensional (3D) assemblies of metal ions and imidazole-based organic ligands, whose porous open frameworks mimic those of (inorganic) aluminosilicate zeolites. The crystal structure of ZIFs is analogous to that of zeolites because of the bond-angle resemblance between metal–linker–metal bonds and Si–O–Si linkages, both of which subtend angles of  $145^\circ$  [1]. The combination of metal and organic linkers in ZIFs yields porous materials with high surface areas and tunable functionalities, along with a good combination of thermal and chemical stability [2]. Thus, they can potentially be used in different practical applications such as sensors, catalysts, adsorbents, matrix fillers, membranes, and drug delivery [3–5].

Zinc 2-benzimidazolate (ZIF7) is formed by linking benzimidazolate (blm) anions to divalent  $Zn^{2+}$  cations. First discovered by Huang et al. [6], ZIF7 has a sodalite topology with hexagonal symmetry [7]. It is distinct from Zinc 2-methylimidazole (ZIF8), which also adopts a sodalite topology, because of the presence of a phenyl group in the blm ligand of ZIF7 [8,9]. The pore window size of ZIF7 is 0.30–0.35 nm, thus allowing access of  $CO_2$  molecules over  $N_2$  and showing high selectivity for  $CO_2$  [10]. ZIF7 is capable of  $CO_2$  separation from  $NO_2$  [10] at relatively low pressures and temperatures and from alkanes/alkenes through a gate-opening process [11]. ZIFs display structural flexibility because of their weaker coordination bonds. The mechanical properties of ZIFs (Young's modulus, hardness, and bulk modulus) [12] are approximately one order of magnitude lower than those of inorganic zeolites [13]. Because of the flexibility of the framework, ZIFs can undergo structural transformations or phase changes under high pressures or temperatures, as well as after the adsorption of gas molecules. Aguado et al. [14] and Zhao et al. [15] described the large- to narrow-pore transformation of ZIF7 by gas adsorption induced by temperature and pressure, respectively. Wharmby et al. [16] recently reported the porous-to-dense phase transition of desolvated ZIF4. The phase transition in ZIF4 is due to the rotation of imidazolate linkers, which causes volumetric contraction of pores. The collective lattice dynamics (THz vibrations) and soft modes present in ZIF7 can also cause gate-opening phenomena and trigger mechanical instability, causing shear-induced structural collapse and framework amorphization [17].

The crystal morphology of metal–organic frameworks (MOFs) can be controlled by selecting particular synthesis conditions or processing routes. For example, Low et al. [18] demonstrated that a crystal-to-crystal phase transformation occurred when ZIF-L crystals were transformed to ZIF8 crystals under different solvents and heating processes. This transformation is called a topotactic phase transition, in which a crystalline material undergoes structural changes but the final phase is related to the initial crystal structure by similar crystallography or orientation.

Synthesizing ZIF7 as films or membranes on porous  $Al_2O_3$  or polymer-based membranes [19] makes such films attractive for sensing, adsorption, and gas separation applications [3,20,21]. For the fabrication of ZIF membranes and films, the main approaches used are direct synthesis and secondary growth methods. However, very few methods have been reported for the deposition of ZIF7 films [22]. Melgar et al. [1] deposited ZIF7 films by an electro-spraying technique on an  $Al_2O_3$  substrate and observed the formation of ZnO when the substrate temperature was maintained at  $160^\circ C$ . Peng et al. [23] reported the fabrication of ZIF7 molecular sieve nanosheets that were exfoliated by wet ball milling; the membranes were then deposited on porous  $\alpha-Al_2O_3$  substrates. The prepared membranes were subsequently used for  $H_2$  gas permeance and selectivity. However, these methods are not easily scalable for use in commercial production and industry.

Herein, we report for the first time the use of cold spraying, a fast and highly scalable method, for the deposition of ZIF7 films [24,25]. In the cold-spraying technique, particles are injected into a supersonic gas stream and accelerated to supersonic velocities [26,27]. These high-velocity particles collide with the substrate with substantial kinetic impact energy, resulting in strong adhesion of the particles to the substrate. This is a high-rate coating method with apparatus details discussed in an earlier report [28]. The goal of this investigation was to study the influence of cold-spray impact pressure and the effects of different solvents on the structural properties of ZIF7. We have discovered distinctive changes in the crystalline structure upon supersonic impact of ZIF7 particles, with and without the application of nylon and *N,N*-dimethylformamide (DMF) in the suspension precursor.

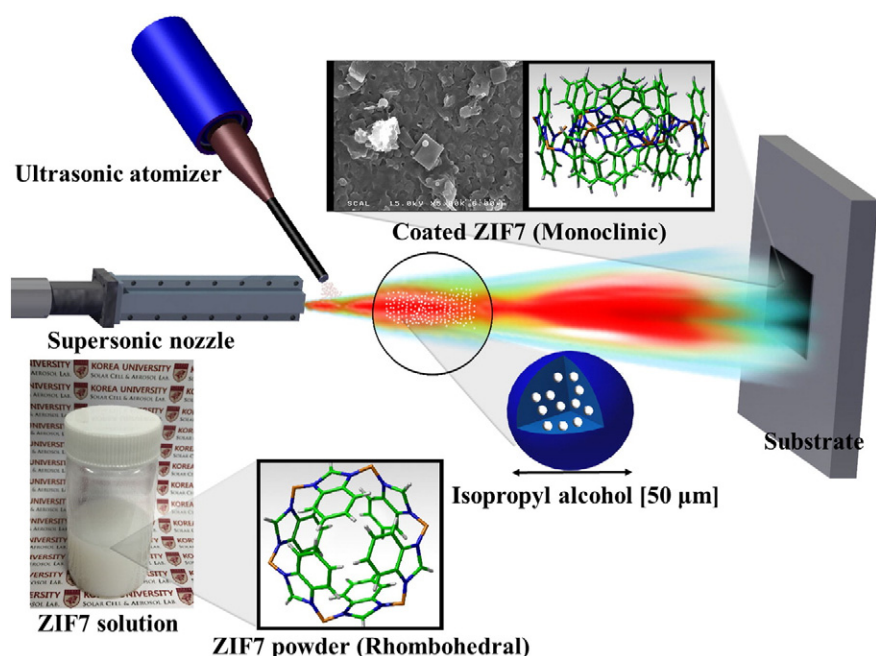


Fig. 1. Graphical illustration of the supersonic cold-spraying ZIF7 process.

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