Large-Area Crystalline Zeolitic Imidazolate Framework Thin Films

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Abstract: We report that continuous MOF films with highly controlled thickness (from 44 to 5100 nm) can be deposited over length scales greater than 80 centimeters by a facile, fast, and cost-effective spray-coating method. Such success relies on our discovery of unprecedented perfectly dispersed colloidal solutions consisting of amorphous MOF nanoparticles, which we adopted as precursors that readily converted to the crystalline films upon low-temperature in situ heating. The colloidal solutions allow for the fabrication of compact and uniform MOF films on a great deal of substrates such as fluorine-doped tin oxide, glass, SiO$_2$, Al$_2$O$_3$, Si, Cu, and even flexible polycarbonate, widening their technological applications where substrates are essential. Despite the present work focuses on the fabrication of uniform cobalt-(2-methylimidazolate) and zinc-(2-methylimidazolate) films, our findings mark a great possibility in producing other high-quality MOF thin films on a large scale.

Introduction

Metal–organic frameworks (MOFs) are an important class of crystalline materials with tunable porosity,$^{[1]}$ topology,$^{[2]}$ and functionality,$^{[3]}$ which have been specifically designed for a wide range of applications such as molecular separation,$^{[4]}$ gas storage,$^{[5]}$ sensors,$^{[6]}$ microelectronics$^{[7]}$ and catalysis.$^{[8]}$ These application areas commonly built on the availability of continuous MOF thin films adopted in related nanotechnological devices. However, the fabrication of MOF films faces significant scientific and technical challenges because processing these crystalline coordination polymers into films often lead to structural inhomogeneities such as wrinkles, cracks and apparent porosity, which would strongly affect the film performances.

Since the seminal work from Fischer and co-workers who prepared MOF-5 film on an Au (111) substrate in 2005,$^{[9]}$ intense research efforts have been made to establish robust synthesis methods for producing high-quality MOF films. Thus far, several strategies that enable the fabrication of well-defined MOF films have been developed, including hybrid mixed-matrix approach,$^{[10]}$ solvothermal synthesis$^{[11]}$ layer-by-layer method$^{[12]}$ and electrodeposition.$^{[13]}$ Other fabrication methods that yield MOF films for specific requirements have also been proposed. Falcaro and co-workers reported the heteroepitaxial growth of polycrystalline MOF film on a copper hydroxide substrate, where the obtained centimeter-scale MOF film is precisely aligned.$^{[14]}$ Ameloot et al. described a chemical vapour deposition (CVD) process for making uniform and conformal ZIF-8 film on high-aspect-ratio features.$^{[14]}$ Bein et al. developed a vapor-assistant conversion (VAC) method to obtain highly oriented zirconium-based MOF thin films.$^{[15]}$ Although remarkable success has been achieved, these methods also impose certain limitations. For example, solvothermal synthesis raises processability and safety concerns, electrodeposition requires (semi)conducting substrates, heteroepitaxial growth requires specific substrate that directs the growth of MOF crystals, and CVD process usually constrains to ultrahigh vacuum. Furthermore, no scalable processing method exists at present that could produce large-area, uniformly high-quality MOF thin-films with thickness smaller than 44 nm.
Herein, we report on the discovery of an unconventional ZIF-67 (i.e., cobalt-(2-methylimidazole),[6] a zeolitic imidazolate framework (ZIF) subclass of MOFs) colloidal dispersion consisting of completely dispersed amorphous nanoparticles in methanol. Using such sticky colloidal solutions as precursors, we show that uniform films can be deposited onto a number of substrates (e.g., fluorine-doped SnO$_2$ (FTO), glass, SiO$_2$, Al$_2$O$_3$, Si, Cu, and even flexible polycarbonate) by a facile, fast, and cost-effective spray-coating approach at low temperatures in air, enabling fabrication of large-area ZIF-67 thin films (up to 4800 cm$^2$) with highly controlled thickness (from 44 to 5100 nm). The same fabrication methodology can be extended to produce other high-quality MOF films, such as ZIF-8 (zinc-(2-methylimidazole)), thin film. We anticipate that the previously unknown colloidal MOF precursor could open up efficient routes of fabricating high-quality MOF thin films through spray coating for various applications.

**Results and Discussion**

ZIFs are an important class of porous materials with zeolite-type tetrahedral topologies, which consist of metal nodes (such as cobalt and zinc) bridged by imidazole.[16] We produced unprecedented amorphous ZIF-67 nanoparticulate precursor by simply mixing cobalt(II) acetate tetrahydrate (Co(CH$_3$COO)$_2$·4H$_2$O) and 2-methylimidazole (Hmim) in methanol at room temperature (Figure 1A). The achieved ZIF-67 colloidal precursor is highly stable without crystallization after aging in lab environment even for even 55 days (Supporting Information, Figures S1 and S2). Replacing Co(CH$_3$COO)$_2$·4H$_2$O with Co(NO$_3$)$_2$·6H$_2$O, however, leads to conventional high-crystalline ZIF-67 crystals that reported previously[17] (Figure 1B; Supporting Information, Figure S3). It is known that ZIF-67 crystals are structurally analogous to zeolites, in which Hmim donates a proton and couples with Co$^{II}$ nodes to form CoN$_4$ tetrahedra.[18] An network of linked CoN$_4$ tetrahedra with Co-Hmim-Co angle of about 145° gives rise to the crystalline ZIF-67 structure[19] (Figure 1B). We hypothesize that, in the presence of CH$_3$COO$^-$, the copolymerization of Co$^{II}$ with Hmim ligands...
would be partially blocked because of the relatively big anion size that brings steric hindrance by binding to Co (Figure 1A). As a result, the nucleation of ordered linked CoN₄ tetrahedra is disrupted, leading to amorphous ZIF-67 precursor.

Representative transmission electron microscopy (TEM) image of the as-prepared ZIF-67 precursor in Figure 1C reveals nanoparticles with an average size of about 40 nm (top inset in Figure 1C). The colloidal dispersion of ZIF-67 precursor is in purple color, showing a Tyndall effect owing to light scattering by the nanoparticles in the colloidal dispersion (down inset in Figure 1C). High-resolution TEM (HRTEM) and its corresponding selected-area electron diffraction (SAED) characterizations displays the absence of a crystalline phase (Figure 1D and inset). Scanning TEM (STEM) elemental mapping reveals a uniform spatial distribution of Co, C, and N of the amorphous ZIF-67 (a-ZIF-67) precursor (Figure 1E). Intriguingly, when methanol was evaporated naturally from the a-ZIF-67 colloidal precursor, a highly viscous gel can be formed (Figure 1F; Supporting Information, Figure S4). Casting such sticky a-ZIF-67 precursor gel between two glass slides can bind them to an extend that withstands the weight of the glass slide (Supporting Information, Figure S5). We reason that the disordered and amorphous structure of a-ZIF-67 precursor gives rich dangling ligands with Hmim hydrogen bonding (N–H=N) chains,[20] which cause the marked adhesion. The a-ZIF-67 colloidal precursor with gel-like state of the concentrated species now enables the easy processing of pure ZIF films onto various substrates, which was thought to be a huge challenge before.

X-ray diffraction (XRD) patterns of our synthesized ZIF-67 precursor are given in the Supporting Information, Figure S6. The spectrum for the sample obtained using Co(NO₃)₂·6H₂O as precursor contains sharp XRD peaks that belong to crystalline ZIF-67 (c-ZIF-67)[17] (Figure 2B), whereas the adoption of Co(CH₃COO)₂·4H₂O gives an amorphous product. Fourier transform infrared (FT-IR) spectroscopy analysis reveals that excess Hmim is retained on the surface of a-ZIF-67 precursor when not thoroughly washed[14,21] (Supporting Information, Figure S7). Moreover, Raman spectroscopy measurements exhibit one prominent peak at 195 cm⁻¹ that corresponds to Co–N bond[22] (Supporting Information, Figure S8), revealing that CoII coordinates with mim links as CoN₄ tetrahedra.

We then systematically optimized the synthetic parameters for achieving high-quality c-ZIF-67 films from the colloidal dispersions. Our control experiments reveal that the addition of some of the stoichiometrically missing Co(NO₃)₂·6H₂O in the recipe causes crystalline ZIF-67 precipitation that precludes the formation of a dense and continuous

\[ \text{ZIF-67} \]
Dielectric material for advanced electronic devices also uncovers that the film consists of small particles.

We thus reason that the robust ZIF-67 thin film does not appear in the simulated structure.

Despite zirconium dioxide and hafnium dioxide have previously been investigated as high-k dielectric materials, the ZIF-67 films deposited by conventional ZIF-67 and our new colloidal a-ZIF-67 precursor exhibits high-quality high-dielectric-constant (high-k) materials for high-electron-mobility transistors and thin-film transistors considering their ready design and functionalization crystaline porous structures. Despite zirconium dioxide and hafnium dioxide have previously been investigated as high-k dielectric materials, they are unfortunately too brittle to be compatible with substrates. We thus reason that the robust ZIF-67 thin film on FTO enabled by spray-coating method opens a way to high-quality high-k dielectric material for advanced electronic devices.

We measured the high-k value of our ZIF-67 thin film, and the dielectric constant of the conventional ZIF-67 powder (press to tablet) was also probed for comparison (Figure 4 A;...
Supporting Information, Figure S21). At room temperature, the ZIF-67 film shows a high-$k$ value of 4.5 at 1 kHz, which is larger than that of 4.25 obtained on the ZIF-67 powder (Figure 4B). Moreover, a very small dissipation factor was observed on the ZIF-67 film. We highlight that the high-$k$ value of the ZIF-67 film compares favorably to previously reported HKUST-1 with a value of 1.7 and $[\text{Zn}_4\text{O} \left( \text{CO}_2 \right)_6]$ with a value of 1.33. These results promise the development of robust MOF thin films with good dielectric properties for microelectronics.

Although the present work focuses on ZIF-67, we note that our approach can be extended to other MOFs, such as ZIF-8-another prototypical MOF material. Amorphous ZIF-8 colloidal dispersion was analogously prepared by the reaction of Zn(CH$_3$COO)$_2$$ \cdot $2H$_2$O and Hmim in methanol at room temperature (Supporting Information, Figures S22, S23A). A slight sediment occurs probably owing to the fast interaction between Zn$^{II}$ and Hmim ligands, which can be readily filtered out. High-quality films of ZIF-8 were then made by spray coating ZIF-8 colloidal solution onto FTO glass substrate, showing exceptional mechanical robustness (Supporting Information, Figure S23B–D).

### Conclusion

Our results demonstrate an inexpensive and convenient spray-coating route to thin, compact and uniform MOF films up to tens of centimeters length scale that were previously unattainable. The spray-coated MOF thin films rely on the unprecedented well-dispersed colloidal dispersions consisting of amorphous MOF nanoparticles, which we used as precursors that readily converted to the crystalline films upon in situ heating. The “sticky” precursor colloidal solution can be deposited onto a number of substrates such as FTO, glass, SiO$_2$, Al$_2$O$_3$, Si, Cu, and even flexible polycarbonate, compatible with future application of MOF thin films in various technological areas where specific substrate is essential. Although we have focused on the fabrication of uniform ZIF-67 and ZIF-8 films, our present results mark a great promise in producing other high-quality MOF thin films on a large scale.

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Figure 4. A) Photograph of the device made by ZIF-67 film sputtered with gold for dielectric measurements. Inset photograph: film testing in the chamber. B) Dielectric constant ε and dissipation factor of ZIF-67 film and ZIF-67 powder.

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Conflict of interest

The authors declare no conflict of interest.

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