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Preparation of metal–organic framework films by electrophoretic deposition method

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ABSTRACT

Thin HKUST-1 and ZIF-8 films were successfully deposited onto porous stainless steel using an electrophoretic deposition (EPD) method. Both anodic and cathodic EPD methods were tested. Cathodic EPD resulted in the degradation of MOF crystals. This problem was avoided by anodic deposition. SEM and XRD were used to characterize the deposited films. Single gas permeation tests of the HKUST-1 films gave an ideal separation factor up to 4.6 for H_2/CO_2, and 3.9 for H_2/N_2.

1. Introduction

Metal–organic frameworks (MOFs) are a class of novel porous materials consisting of metal ions or metal ion clusters bridged by organic ligands. They have well defined pore structures and regular pore sizes, which can be tuned by simply changing metal ion and/or ligand. Many research efforts have revealed potential applications of MOFs in gas separation and storage [1–3], chemical sensing [4,5], etc. Fabrication of MOF films represents one of the important topics nowadays. Different methods have been explored for this purpose, such as dipping substrate into MOF mother solution [6,7], anchoring seed crystal followed by secondary solvothermal growth [8], microwave assisted growth [9], layer-by-layer growth [10] and interfacial or biphasic method [11,12].

EPD is a method based on surface charge of suspended particles. In an electric field, charged particles move towards and deposit onto electrode, as shown in Fig. S1. It is a rapid, low cost, easy control and industry applicable process [13]. Electrochemical properties of Cu-MOF have been studied by Doménech and coworkers [14,15]. In their paper, EPD of Cu from Cu/MOF was studied, where the Cu(II) ions was reduced to Cu(I) first and then to Cu metal. However, to the best of our knowledge, electrophoretic deposition of MOF thin film has not been demonstrated. In this paper, we present a rapid and simple EPD method for preparation of MOF films. HKUST-1 and ZIF-8 thin films were successfully fabricated using this method.

2. Experimental

All chemicals were commercially available and used without further purification. EPS 2A200 power supply was used to prepare the film. Characterization of MOF particles and films were carried out on JEOL JSM 7000 Scanning Electronic Microscopy (SEM) and Brucker D8 Advance X-ray Diffractometer. Single gas permeation tests were performed on a home-made gas permeation setup (See the supporting information).

Copper nitrate hemi(pentahydrate) (98%), trimesic acid (95%), zinc nitrate hexahydrate (98%), 2-methylimidazole (99%), and hyaluronic acid sodium salt were purchased from Sigma-Aldrich. Porous stainless steel sheet with 0.2 μm in pore diameter was supplied by Mott Corporation.

HKUST-1 and ZIF-8 particles were synthesized using the precipitation methods reported by Zhuang [16] and Pan [17]. In brief, 1.22 g copper nitrate hemi(pentahydrate) and 0.58 g trimesic acid were dissolved into 5 g dimethylsulfoxide. Then the precursor solution was added dropwise into 230 mL methanol under stirring. After 10 min, HKUST-1 crystals were collected by centrifugation and washed three times by methanol. 0.15 g zinc nitrate hexahydrate and 2.84 g 2-methylimidazole were dissolved in 1 g and 10 g deionized water respectively. Then the zinc nitrate solution was dropped into 2-methylimidazole solution slowly under stirring. After 10 min, ZIF-8 crystals were collected by ultracentrifugation and washed three times by water.

Different amounts of hyaluronic acid were dissolved in 18 mL deionized water and 42 mL ethanol was added in afterwards. 60 mg MOF particles were suspended into the mixture solution by sonication. EPD of MOF crystals on porous stainless steel was

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carried out under 100 V for 2 min and the resulted substrate was dried under room temperature. It should be noted that the grain size of the HKUST-1 crystals is around 1–2 μm while the substrate has pore diameter of 0.2 μm. The crystals are to be deposited on atop the substrate rather than within the pores of the substrate.

3. Results and discussion

HKUST-1 suspension without additives moved to the cathode under electric field, because the surface charge of HKUST-1 was positive. Unfortunately, the crystals were destroyed after deposition. HKUST-1 particles should be perfect crystals, which have a window size of 0.69 nm and cage size of 1.08 nm. The small pores cannot be seen on SEM and the surface of the crystals should appear smooth. However, as revealed by SEM images shown in Fig. 1, the prepared cathodic materials showed big holes, suggesting the particles were destroyed. It was probably due to copper reduction inside the crystal structure [14,15]:

$$Cu^{2+}L^{2-} + e^{-} = Cu^{+} + L^{2-}$$

and/or

$$Cu^{+} + e^{-} = Cu$$

In order to avoid crystal destruction, an anodic deposition was employed. Hyaluronic acid was then used as additive, which acted as a charge reverse agent, as well as improved interactions between deposited film and the substrate. The dissociation of hyaluronic acid sodium salt resulted the anionic polymer species, which then would reverse the charge of the suspended MOF particles and promote the anodic deposition. Compared to the cathodic deposition, the anodic deposition worked better. SEM images showed the crystal structures intact, while big holes were clearly present in the cathodic deposited crystals. Powder X-ray diffraction (XRD) was used to examine the anodic deposited crystals. As shown in Fig. 2, their XRD patterns were the same, suggesting preservance of the crystal structures in the anodic deposition. The XRD pattern of the film showed enhanced intensities of reflexes (1 1 1) and (2 2 2) and reduced intensities (2 0 0) and (4 0 0), indicating preferred crystallographic orientation of crystals. It is suggested that the interaction of the carboxylic groups of hyaluronic acid with metal atoms of the crystal structure resulted in such crystallographic orientation. The orientation can result from difference in atomic density in different crystallographic planes. The highest atomic density in the (1 1 1) plane of the FCC structure resulted in preferred orientation in the [1 1 1] direction.

Different amounts of the additive were used to find the minimum amount needed for the anodic deposition of HKUST-1 films. At a low concentration, barely any film was deposited on the stainless steel since not enough anionic polymer were there to reverse the charge of the MOF particles. With increase in the additive concentration, the film formation was improved significantly, as shown in Fig. 3. After screening experiments, we chose 0.2 g/L as the optimal additive concentration because it gave uniform films based on the optical observation. All the following films were prepared with 0.2 g/L additive, if not otherwise specified.

Single gas permeation experiments (H_2, CO_2 and N_2) were carried out to study the permeation and separation properties of the anodic deposited films, with the experiment setup shown in Fig. S2. The films gave a higher H_2 permeance than the other gases. Fig. 4 shows gas flux verse pressure. The ideal separation factors, estimated from the slope of the curve, were 4.6 for H_2/CO_2 and 3.9 for H_2/N_2, respectively, similar to the reported results of the pure HKUST-1 crystal films [18–20]. The ideal separation factors are very close to the Knudsen separation factors, which may suggest that the behaviors of these gas molecules permeating through these films follow Knudsen flow.

The same idea was applied to another well-known MOF, i.e., ZIF-8. With help of the same additive (hyaluronic acid), ZIF-8 was successfully deposited onto the anode. Fig. 5 shows the SEM image and XRD pattern of the ZIF-8 thin film, no preferred orientation was observed because of the body centered cubic structure of ZIF-8. Furthermore, we also tried a different type of electrode with carbon felt as substrate, which was very porous that had 95% porosity. HKUST-1 was deposited onto the substrate. Due to the high porosity and large pore of the carbon felt, the substrate was not fully covered or embedded with the crystals, as shown in Fig. S3.

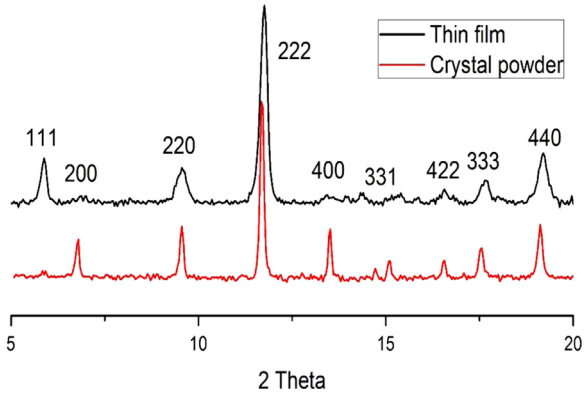

Fig. 2. XRD pattern of the anodic deposited film.

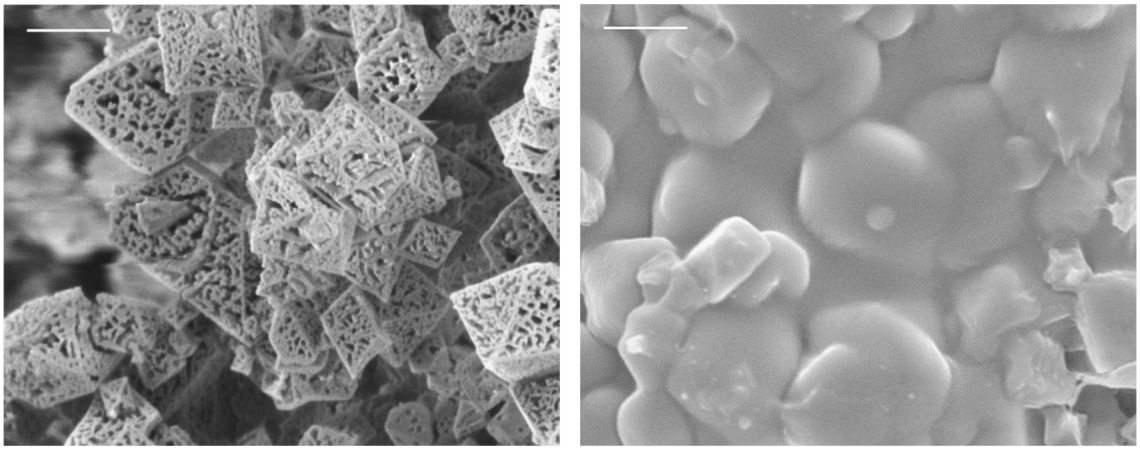

Fig. 1. SEM images of the thin films by electrophoretic deposition. Left: cathodic deposition. Right: Anodic deposition. Bar size is 1 μm.