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Oriented Films of Porous Coordination Polymer Prepared by Repeated in Situ Crystallization

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Zeolite and activated carbon have been known as conventional porous materials used as adsorbents, catalysts, and catalyst supports.[1,2] Attempts to utilize them for advanced applications such as chemical sensing and optoelectronics have been limited because of difficulties in functionalizing frameworks of zeolites and carbon materials as well as the amorphous nature of carbon.[3,4]

As a new class of porous materials, porous coordination polymers (PCPs), also known as metal-organic frameworks (MOFs), constructed from metal ions and organic ligands, have attracted considerable attention because they possess not only large surface area and porosity as observed in conventional porous materials but also original features, that is, synthesis by self-assembly under mild conditions, diverse structures, and flexible frameworks.[5,6] PCPs are synthesized through the assembly of molecular building units leading to desired extended frameworks. Weak intermolecular interactions (e.g., hydrogen bond, $\pi-\pi$ stacking, and van der Waals force) produce flexible parts in the frameworks.[5] PCPs have been expected to be used not only for traditional applications of porous compounds but also for emerging areas of application, such as molecule-recognized devices, gas storage, and magneto-electronics.[5–7] The first step toward this goal is to prepare a highly uniform film of PCPs.

Very recently, PCP thin films were prepared on surface-modified substrates by in situ crystallization[8,9] and layer-by-layer assembly.[10] For in situ crystallization, substrates were immersed in filtrated mother solution. Then, the films were formed only on the surface-modified side of the substrates. Chemical moieties of self-assembled monolayers (SAMs) on the substrates affected formation[8] and orientation[9] of PCP films. These reports suggest that selective interactions of the secondary building units presenting in the filtrated mother solution with the functionalized surfaces induce selective nucleation on the substrates and mimic the chemical moieties of the surfaces. In the case of the layer-by-layer assembly, growth of PCPs was carried out by immersing substrates in a solution of metal precursor and subsequently in a solution of organic ligand repeatedly.[10] The main advantage of the layer-by-layer assembly over the in situ crystallization is homogeneity of the obtained films; namely, the films prepared by the layer-by-layer assembly were homogeneous while the films obtained by the in situ crystallization were very heterogeneous. However, the procedure is quite complicated.

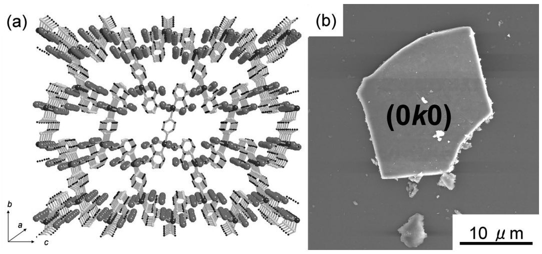

Figure 1. (a) Crystal structure of CPL-1 along the *a* axis; (b) FE-SEM image of CPL-1 crystal.

In this study, we focused on the PCP with pillared layer structure, $[Cu_2(pzdc)_2(pyz)]_n$ (CPL-1; pzdc = pyrazine-2,3-dicarboxylate; pyz = pyrazine).[11] The Cu^{II} center in CPL-1 has a distorted square-pyramidal coordination environment formed by three carboxylate oxygen atoms, one nitrogen atom of pzdc, and one nitrogen atom of pyz. Two-dimensional sheets constructed from Cu^{II} and pzdc units, which have no voids large enough for molecules passing through, are linked by pyz ligands, affording a three-dimensional porous pillared layer structure. One-dimensional channels with dimensions of approximately 4×6 Å^2 run along the *a* axis between the 2D sheets, in which one water molecule is occluded per Cu^{II} ion (Figure 1). Nucleation of CPL-1 is disturbed by the addition of organic polymer, resulting in increased size and preferential orientation of plate crystals.[12] CPL-1 can adsorb small molecules, such as H_2, O_2, N_2, CH_4, and C_2H_2, in which some of them show 1D crystalline array in a nanospace.[11,13] For example, the adsorbed oxygen molecules are arrayed in the channels at 77 K and 1 bar because potential points in the channels are constructed by regular arrangement of Cu^{II} ion and pzdc.[13a] In addition, size and chemical moieties of the 1D channels

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can be tuned by changing pyz to other pillar ligands,[5,11] which opens up the possibility for functionalizing the pore walls. Considering the unique characteristics of CPL-1, CPL-1 films should provide for applications involving molecular recognition.

We have tried to prepare CPL-1 films by in situ crystallization and layer-by-layer assembly. However, no films were obtained by the layer-by-layer assembly due to the structure of CPL-1 constructed from one metal and two kinds of organic ligands. Also, CPL-1 films could not be prepared by in situ crystallization on the SAM surface. We have considered that in situ crystallization needs heterogeneous nucleation on the substrates. In addition, nucleation and crystallization of CPL-1 are very fast, which proceeds for about 30 min after mixing Cu(ClO$_4$)$_2$, Na$_2$pzdc, and pyz. Accordingly, CPL-1 is difficult to nucleate on the substrates. Therefore, the preparation of CPL-1 films needs an alternative method.

As one of the well established methods for preparing films of diamond and zeolite, the crystalline films can be obtained by growth of objective crystals coated on the substrates, the so-called seeded or secondary growth.[14,15] This method has been applied for preparation of PCP films.[16] Due to the fast crystallization of CPL-1, however, the continuous films of CPL-1 cannot be obtained after the secondary growth. Also, efforts to retard nucleation by adding polymer additive were not helpful for film preparation. Combining the in situ crystallization and the secondary growth, we have carried out in situ crystallization repeatedly to obtain continuous CPL-1 films. In this concept, the crystals formed on the substrates act as the seeds for the further growth. First, the gold substrates (60 nm of Au/20 nm of Ti/Si) used as supports were modified by immersing into 1 mM ethanol solution of 4-mercaptopyridine overnight. For comparison, bare gold substrates and Si wafers were also used. These substrates were floated on the CPL-1 synthesis solution freshly prepared by dissolving 0.37 g of Cu(ClO$_4$).6H$_2$O, 0.21 g of Na$_2$pzdc, and 1.00 g of pyz in 40 mL of distilled water at room temperature. After 2 h, the substrates were thoroughly rinsed with distilled water and dried. The procedure (float−wash−dry) was repeated for five cycles. As stated above, due to fast crystallization, freshly prepared solution has to replace the used solution at each cycle to supply enough nutrients for growing continuous films.

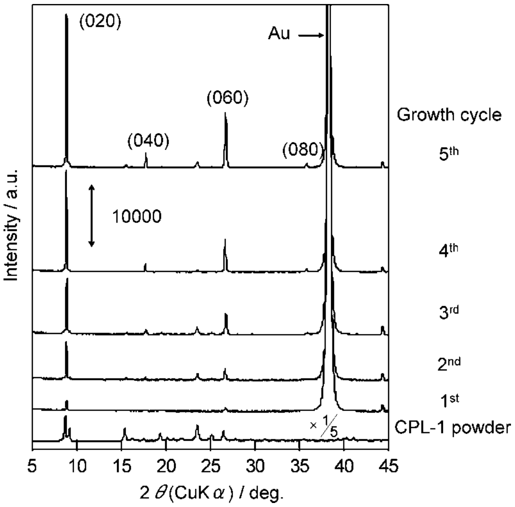

Figure 2. XRD patterns of obtained products on the modified Au substrates after each growth cycle. Peaks are indexed with the crystallographic planes of the CPL-1 structure.

X-ray diffraction (XRD) patterns of the samples prepared by the repeated in situ crystallization on the modified gold substrates are shown in Figure 2. Peaks at $2\theta = 8.8°$, $17.6°$, $26.8°$, and $36.2°$ that are attributed to (020), (040), (060), and (080) planes of CPL-1, respectively, are dominant. The peak around $2\theta = 38°$ is due to the substrate. The peaks attributed to (0*k*0) are observed in all of the grown samples (one to five cycles), and the diffractions corresponding to (0*k*0) become more intense after repeating the procedure, clearly representing preferential *b* orientation.

In order to understand the repeated growth, the evolution of the obtained CPL-1 films was observed by field emission scanning electron microscopy (FE-SEM). After the first cycle, small particles were observed on the surface (Figure 3a). Based on the XRD pattern revealing small peaks arising from (0*k*0), the small particles were identified as CPL-1 crystals. Figure 3b shows an FE-SEM image of the obtained product after the second cycle. CPL-1 crystals become larger and clearly show the plate-like shape. Compared with the XRD patterns, direction of crystal growth was parallel to the *b* plane of CPL-1. After growth for three cycles, as shown in Figure 3c, CPL-1 crystals become larger. The number of crystals also increased after repeated growth because the nuclei newly formed in the synthesis solution were deposited on the substrates. Figure 3d represents that the CPL-1 film is grown and that an almost continuous layer is obtained after the fourth cycle. At this stage, some observed crystals are tilted, which is consistent with the XRD peaks showing other orientations. To obtain the continuous film, the growth procedure was repeated again. After the fifth cycle, no bare surfaces of the substrate were observed (Figure 3e). Figure 3f reveals a cross-sectional FE-SEM image of the CPL-1 film after the fifth cycle. The thickness of the film is uniform and estimated to be 3 μm.

Based on the XRD patterns and the FE-SEM images, we propose the formation scheme of the CPL-1 films as follows. At the first cycle, the nucleation of CPL-1 occurs on the substrates and/or near the substrates in the solution. Hence, the nuclei are deposited on the surface of the substrates and then grown to be small crystals. At the second cycle, the deposited crystals are grown on the substrate by consuming the nutrients in the freshly prepared synthesis solution. The

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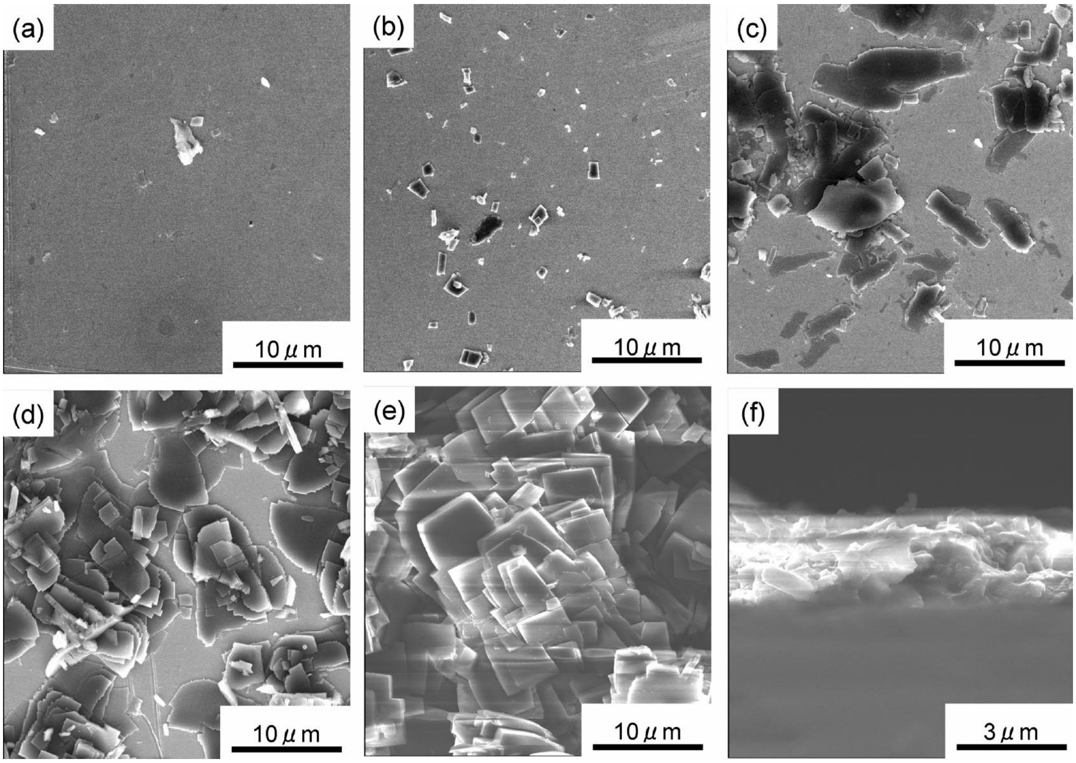

Figure 3. Top-view FE-SEM images of obtained products after the (a) 1st, (b) 2nd, (c) 3rd, (d) 4th, and (e) 5th cycles and (f) a cross-sectional view of (e).

nucleation also occurs, and thus the newly formed nuclei are deposited on the substrates. As a result, the number of crystals is increased. The same phenomena occur at the later cycles. Thus, the repeated in situ crystallization increases seed crystals for the further growth and crystal growth per unit area of the substrates. In the case of CPL-1, the uniform, continuous films are obtained after five cycles with the present condition. As shown in Figures 1b and 3, due to the plate-like shape of CPL-1 crystals in which the *b* plane is much larger than others,[12] the *b* oriented films are easily grown on the substrates.

Figure 4 reveals XRD patterns of the CPL-1 films grown on each substrate. In Figure 4a, the influences of the substrates on the formation of CPL-1 films are clearly marked. The differences at the early stage are probably due to the chemical nature on the surfaces. Pyridine groups presenting on the modified Au substrates could interact with Cu^{II} in the solution and the nuclei of CPL-1 as well. Such interaction should induce the nucleation on the surface of the substrates and increase the number of deposited crystals. In addition, peak intensities of the film prepared on the bare Au substrate are higher than those obtained on the Si wafer. The surface of Si wafers is very flat, while Au substrates prepared by sputtering technique are quite rough. Thus the nucleation might be pronounced in part by surface roughness of the substrates. After growth for five cycles, however, no marked differences in the intensity are observed. These results suggest that repeated in situ crystallization could increase the density of nuclei on the surface regardless of the chemical and physical natures of the substrates.

In conclusion, *b* oriented CPL-1 films are obtained by the repeated in situ crystallization. Compared to the in situ crystallization on the SAMs surface and the layer-by-layer assembly used for preparing PCP films previously,[8–10] the present procedure is simple and the obtained CPL-1 films are continuous and uniform. It is expected that the repeated in situ crystallization would be suitable for other PCPs. We are currently preparing oriented films of CPL-*n* series by changing pyz to other pillar ligands that can provide PCP films with different pore dimensions. Selective guest adsorption is also underway.

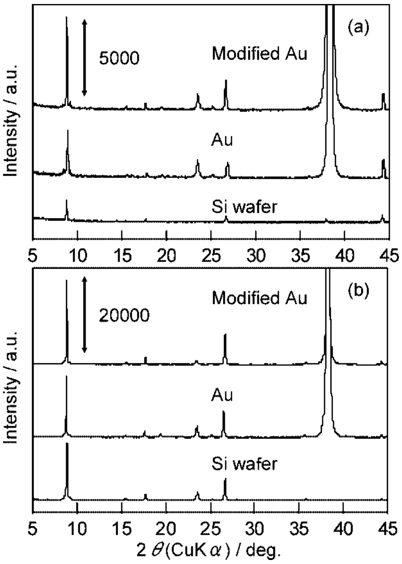

Figure 4. XRD patterns of products prepared on modified Au, bare Au, and Si substrates after the (a) 2nd cycle and (b) 5th cycle.

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