Crystal growth of inorganic-organic hybrid materials on metal hydroxide: epitaxial growth of porous coordination polymer

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Framework compounds such as porous coordination polymers (PCP), also called metal-organic frameworks (MOF), and covalent organic frameworks (COF) are characterized by their micro pores which offer a huge accessible surface for applications in gas storage, catalyst and others. A key aspect of PCP chemistry is that their modular construction, from organic links and metal nodes, allows for control of pore chemistry, structure metrics and network topology. Additional functionalities for electronics, photonics, themal and magnetics applications can be attained vis a host-guest approach by an accommodation of functional guests (molecules, ions, or nano objects) into the pores. Due to these chemical and physical designability, in these days, PCP have attracted more attentions in advanced applications, such as smart membranes, sensors, transistors, and microelectronic devices. An important step towards fully realizing the potential of PCPs in advanced technologies is the development of fabrication methods that allow for controlling orientation of PCP crystals on the cm-scale and depositing the crystals on the desired locations of substrates (patterns). A number of fabrication methods have been developed for the deposition of PCP films and patterns.¹ However, the growth of PCP crystals that are oriented along all crystallographic axes had not been explicitly demonstrated. The development of the fabrication method for controlling orientation and the location of PCPs remained a significant challenge for realizing PCP-based device applications.

Since 2014, we have been developing a new method for controlling orientation and the location of PCP by using ceramics (metal hydroxide) as a metal ion precursor for the PCP synthesis. Metal hydroxides are crystalline nanomaterials and have the following unique features: 1) lower lattice enthalpy than oxides, 2) regularly ordered hydroxyl groups on the surface. Because of their low



Fig. 1. Schematic illustration and corresponding SEM images of the (a and c) oriented $Cu(OH)_2$ nanobelts and (b and d) oriented $Cu_2(BDC)_2$ synthesized via heteroepitaxial growth on $Cu(OH)_2$.

lattice enthalpy, metal hydroxides readily react with the organic ligands, allowing them to be converted to PCP under mild conditions (room temperature and no hazardous solvent). Therefore, pre-deposited Cu(OH)₂ films and their patterns on any substrate (e.g., plastic, metal, or glass) could be converted to uniform Cu-based PCP coatings and its patterns and 3D objects for electrochemical and solid catalysts.²⁻⁵ Furthermore, we found that Cu-based PCP can grow on Cu(OH)₂ surface through a heteroepitaxial approach. The regularly ordered hydroxyl groups on the metal hydroxide contributed to align the organic linkers on the surface, affording heteroepitaxial growth of PCPs. By this heteroepitaxial approach, we succeeded in the fabrication of $Cu_2(BDC)_2$ (BDC: 1,4-benzenedicarboxylate) films with both out-of-plane and in-plane orientations on cm-scale substrates (Fig. 1).⁶ The oriented PCP films could afford an alignment of guest fluorescent molecules over a large area. Multilayered oriented PCP films including metal particles exhibited polarization-dependent plasmon absorption.⁷ It was also found that the direction and the location of regularly ordered 1D nanochannels of Cu-based pillar-layered PCPs (Cu₂(Linker)₂DABCO) could be controlled by optimizing the crystal growth process; 1D nanochannels align either perpendicular or parallel to substrates (Fig. 2).8 Due to the fundamental interest and widespread technological importance of controlling the alignment of functional molecules and polymers in a particular direction, these orientation-controllable PCP films and patterns will open up the possibility of realizing the potential of PCPs in advanced technologies

including electronic, optical, and thermal devices. Furthermore, the regularly ordered hydroxyl groups on the metal hydroxides are expected to provide new potential platform as a scaffold for the orientation of organic molecules and organic crystals such as COF over large areas.

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Fig. 2. (a) 1D nanochannel structures of $Cu_2(Linker)_2DABCO$. SEM images of the PCP films synthesized under (b) the dissolution and precipitation favoured and (c) epitaxial growth condition. (d-f) Optical microscope images of oriented PCP patterns. The white arrows indicate crossed-polarizer orientation in (e) and (f).

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