

Multifunctional porous crystals by hybridizing coordination polymers

Porous coordination polymers (PCPs) or metal-organic frameworks (MOFs) are an intriguing class of porous crystalline materials in which the properties can be modulated by chemical functionalities on organic ligands. The wide variety of organic ligands allows PCPs to exhibit versatile porous properties, such as gas storage, separation and catalysis. A key to accessing advanced PCPs suitable for more specialized and sophisticated applications is to integrate several functionalities into a single crystal. However, an extra chemical modification on organic ligands in PCPs sacrifices the porosities or spoils the original porous properties. One way to overcome this issue is to hybridize different types of PCP crystals, thus creating a core-shell-type PCP crystal [1]. Core-shell PCPs are able to implement multifunctionality even when two contradictory properties are combined; for instance, small and large pore sizes simultaneously provide size selectivity and high storage capacity. Such materials can be designed by attributing the small aperture to the core crystal and large cavity to shell the crystal. Here, we demonstrate a crystal extractor based on PCPs with the core-shell heterostructures, in which the storage container is the core crystal and the size separation filter is the shell crystal (Fig. 1) [2].

A series of three-dimensional PCPs, $[\text{Zn}_2(\text{dicarboxylate})_2(\text{diamine})]_n$, gives a single micrometer-scale crystal with a well-defined cuboid morphology. The key synthetic protocol is the epitaxial growth of the second crystal that surrounds the core crystal because a lattice match results in pore connections at the interface between two crystals. To achieve the significant differences in pore sizes between the core and shell crystals, we selected $[\text{Zn}_2(\text{bdc})_2(\text{dabco})]_n$ (**1**) as the core crystal (bdc = 1,4-benzene dicarboxylate; dabco = 1,4-diazabicyclo[2.2.2]octane; pore sizes: $7.5 \times 7.5 \text{ \AA}^2$ along the *c*-axis and $5.3 \times 3.2 \text{ \AA}^2$ along the *a*- and *b*-axes, and micropore volume: $0.75 \text{ cm}^3/\text{g}$) and $[\text{Zn}_2(\text{adc})_2(\text{dabco})]_n$ (**2**) as the shell framework (adc = 9,10-anthracene dicarboxylate, pore sizes: $1.7 \times 1.7 \text{ \AA}^2$ along the *c*-axis and $4.5 \times 2.7 \text{ \AA}^2$ along the *a*- and *b*-axes, and micropore volume: $0.31 \text{ cm}^3/\text{g}$). Two crystals were successfully hybridized by solvothermal synthesis, in which pieces of single crystals of (**1**) were heated in a solution of $\text{Zn}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$, H_2adc and dabco in *N,N*-dimethylformamide (DMF) for several days. The core/shell crystals (**1/2**) were harvested after cooling to room temperature. The confocal laser scanning

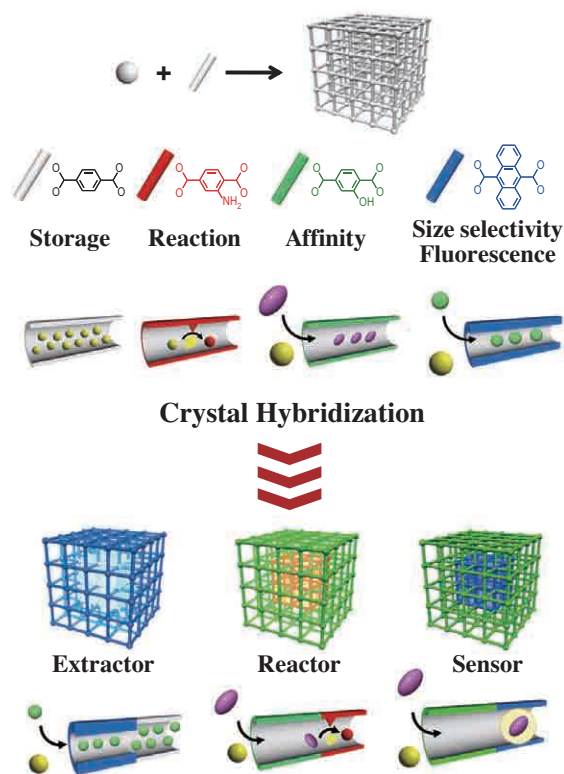


Fig. 1. Schematic illustrations of PCP crystal hybridization for sequential functionalization system.

microscopy and microscopic Raman spectroscopy indicated the formation of the core/shell crystals (**1/2**).

To elucidate the structural relationship between the core framework and the shell framework, we performed synchrotron X-ray diffraction measurements for film structural analysis using a four-circle diffractometer at beamline **BL13XU** for surface and interfacial structures. Both the core (**1**) and the shell crystals (**2**) had the same tetragonal frameworks and similar unit cell parameters ($a = 10.9288(15) \text{ \AA}$ and $c = 9.6084(12) \text{ \AA}$ for **1**, and $a = 10.8444(10) \text{ \AA}$ and $c = 9.541(9) \text{ \AA}$ for **2**). As we observed the sharp and single diffraction peaks at the 110 and $\bar{1}\bar{1}0$ Bragg positions with 180° periodicity and at the 101, 011, $\bar{1}01$, and $0\bar{1}\bar{1}$ Bragg positions with 90° periodicity, we found that the shell crystal grew epitaxially on both the $\{100\}$ and $\{001\}$ surfaces (Fig. 2). These results suggest the hybridization of two frameworks into one crystal with pore connections at the crystal interfaces.

The preference for adsorbing cetane over isocetane was demonstrated by immersing single crystals of (**1**) and (**2**) and the core/shell crystal of

(1/2) into a mixture of cetane/isocetane (1:1). After filtration and drying, these crystals were decomposed by hydrochloric acid and the adsorption ratio was determined by gas chromatography-mass spectrometry (GC-MS). Although the large pores of (1) barely discriminated between these isomers, the small pores of (2) accumulated only the linear cetane molecules. The core/shell crystal also selectively adsorbed cetane owing to the small aperture of the shell crystal. When the cetane/isocetane ratio was decreased to 1:10 and 1:100, the adsorption of isocetane in (1) increased. By contrast, the crystal of (2) and the core/shell crystal maintained their perfect selectivity for cetane.

The storage capacity of cetane in the core/shell crystal of (1/2) was elucidated by thermogravimetric (TG) analysis. For the (1:100) mixture of cetane/isocetane, the amount of cetane adsorbed in the core/shell crystal was estimated as 26.9 wt%, which was twice that in the shell crystal of (2) (10.0 wt%). This significant improvement in the cetane storage capacity arose from the large pore volume of the core framework of (1). By contrast, the single crystal of (1) alone showed no selective adsorption, and both cetane (6.9 wt%) and isocetane (24.5 wt%) accumulated in its pores. Thus, covering the core

crystal with the thin shell crystal is the key to the combination of selectivity and high storage capacity for cetane (Fig. 3).

This successful integration of two contradictory functions into one crystal was achieved by the heterogeneous arrangement of chemical functionalities on one basic framework skeleton. This methodology to create a multifunctional PCP crystal will enable further integration of other porous properties.

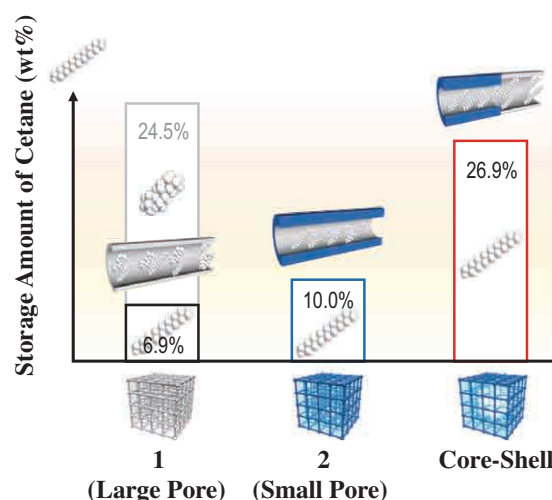


Fig. 3. Amount of cetane stored in (1), (2), and (1/2) when using a (1:100) mixture of cetane/isocetane.

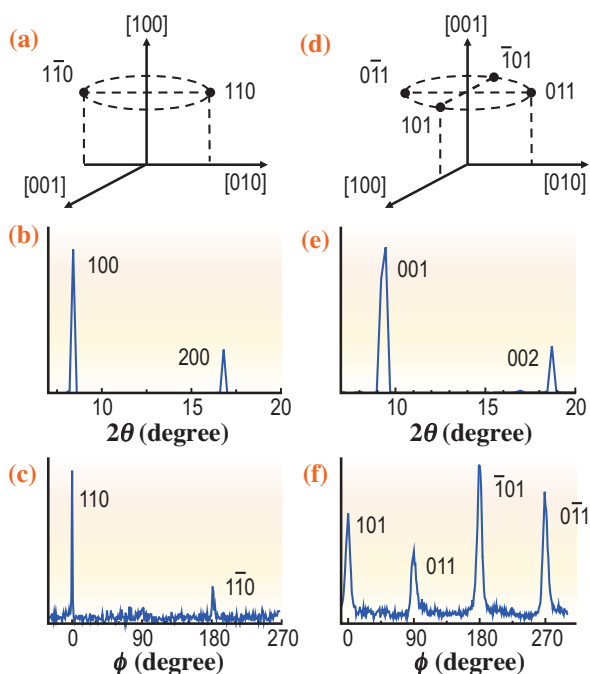


Fig. 2. Reciprocal lattice spaces corresponding to the rotational scan results obtained around the (a) [100] and (b) [001] directions. θ - 2θ scan results of the core/shell crystals (1/2) on the glass substrates at the initial position ($\chi = 90^\circ$) with the (c) a -axis and (d) c -axis orientations. Scan results of the rotation angles around the (e) [100] direction (ϕ scan) and (f) [001] direction.

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