Structural Investigation of Chemiresistive Sensing Mechanism in Redox-Active Porous Coordination Network

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Supporting Information

ABSTRACT: By changing the rate of evaporation, two kinds of crystalline films composed of redox-active porous coordination networks (1 and 2) were selectively prepared on a gold-patterned substrate using a DMF solution of 2,5,8-tri(4-pyridyl)1,3-diazaphenalene and Cd(NO₃)₂. We found the highly sensitive humidity sensing ability of film 1. Single crystal structures and infrared spectroscopic analyses before and after hydration of a single crystal of 1 revealed the sensing mechanism: exchange of nitrate ions with water on Cd atoms occurred in hydrated conditions to generate a conductive cationic network.

While porous coordination networks (PCNs)¹⁻⁸ have widely been developed because of their structural/functional interests, chemical sensor application has been considered as a fascinating target because the large surface area and chemical tunability enable a change in chemical and physical properties which can be influenced by host–guest interaction in the presence of analyte molecules.⁹−¹⁴ However, PCN-based chemiresistive sensors are rare because of their ordinary insulating property and difficulty of integration with substrates. Although several conductive PCNs have been reported using redox-active molecules which provide unpaired electrons or facile charge transfer between nodes,¹⁵−²⁰ to our knowledge, no reported chemiresistive sensors have attained their sensing mechanisms with consideration of structural change.²¹−²³ Herein, we report a redox-active PCN-based chemiresistive humidity sensor and its sensing mechanism investigated by single crystal X-ray analysis and infrared (IR) spectroscopy. The PCN film fabricated from a redox-active ligand, 2,5,8-tri(4-pyridyl)1,3-diazaphenalene (TPDAP)²⁴ (Scheme 1), and Cd(NO₃)₂ by the simple solvent evaporation showed resistivity change depending on a trace amount of water. The mechanism study using X-ray analysis/IR spectroscopy revealed that the dissociation of nitrate ions from Cd²⁺ under hydrated conditions plays a crucial role in achieving electrical conductivity. Understanding of the correlation between conductivity and structure is essential to designing chemiresistive sensors using PCNs.

Two kinds of PCNs composed of TPDAP, nitrate, and Cd²⁺ were selectively prepared by controlling the rate of solvent evaporation. Considering the solubility of TPDAP and proper evaporation conditions, we chose DMF as a solvent. Because DMF is readily decomposed in the presence of water/metal even at temperatures lower than the boiling point, the evaporation of decomposed products resulted in network formation. Network 1, [Cd₂.₅(NO₃)₅(TPDAP)₃(DMF)₃(H₂O)₇.₄] (orthorhombic Cmmm), was synthesized by heating a DMF solution of TPDAP and Cd(NO₃)₂·4H₂O under sealed conditions at 90 °C. The reddish block crystals of 1 were densely crystallized on the bottom of a container. The single crystal X-ray analysis revealed that network 1 has a π−π stacking columnar structure and 8-Å-sized diagonal channels along the [1 1 0] direction (Figures 1a,b, S1). The structure is very similar to that which we previously reported except for the arrangement of monodentate TPDAP ligands. The previously reported monoclinic network (Cd₁mono)²⁵ has ordered monodentate TPDAP layers. On the other hand, network 1 has both ordered and disordered monodentate TPDAP layers, resulting in more defects in a crystal than that of Cd₁mono. It comes from higher reaction temperatures, a shorter reaction time, and, more importantly, higher hydrated reaction conditions, compared with the reaction condition for Cd₁mono. In contrast to the sealed conditions, the fast evaporation under open conditions at 90 °C produced reddish thin plate crystals of a totally different structure, [Cd₄.₅(NO₃)₂.₇(TPDAP)₀.₇₅(TPDAP⁻)(DMF)₂(H₂O)] (2;
monoclinic C2/c). The single crystal X-ray analysis revealed that network 2 has a 2D slipped π−π stacking structure possessing 3D tangled pores with a window size of 7 Å (Figures 1c,d, S1). However, the 2D layer structure of network 2 drastically changed after exposure to air. It was observed that severe cracks and color change gradually appeared in a single crystal of 2 by exposure to air from the mother solution. The powder X-ray diffraction of single crystals of network 2 measured under air was significantly different from the pattern simulated from single crystal X-ray analysis measured at 100 K (Figure S2). This result can be understood such that faster reaction generated a kinetic network in the multi-interactive system.

The simple solvent evaporation method was applied for the device fabrication based on the redox-active networks of 1 and 2 on an Au-patterned SiO2/Si wafer. By changing the rate of solvent evaporation, we selectively prepared dense and uniform crystalline films of networks 1 and 2 on the substrate by replacing a glass plate with a wafer under the same conditions as their single crystal growth conditions (Figure 2a). The solvent evaporation method is not conventional for film fabrication of ordinary PCNs because PCNs are apt to crystallize as a free-standing crystal, which means the specific substrates are mostly needed to control its growth.26-33 However, a large π-planar ligand, TPDAP, and crystallization mechanism of networks enable deposition of crystalline films on the nonfunctionalized substrate uniformly and densely. The powder diffraction patterns of both films well matched with those of both single crystals (Figure 2b). In addition, film 1 showed preferred orientation along the a direction, which was consistent with the π−π stacking direction. Therefore, the pore was efficiently open for guest encapsulation.

Film 1 composed of a 3D network showed better electrical stability than film 2. First, in order to investigate the intrinsic electrical properties of redox-active PCNs, the current−voltage curves of both single crystals were measured with silver paste as an electrode. As expected from the redox-activity of TPDAP, single crystals of 1 and 2 showed electron conductivity of 1.80 × 10−8 S cm−1 (23 ± 1 °C, 72% RH, in air) and 1.05 × 10−7 S cm−1 (23 ± 1 °C, 72% RH, in air), respectively, along the π−π stacking direction (Figure S3). We reported that radical TPDAP species in Cd-1 mono generated by air oxidation considerably increased the conductivity along the π−π stacking direction.25 The difference of the conductivity value between 1 and 2 can be rationalized by the π−π distance: the π−π distance (3.32 Å) in the 2D structure of 2 is shorter than that of 1 (3.43 Å). The simple architecture of the deposited films on Au-patterned wafers enabled measurement of current−voltage characteristics by applying voltage via the gold electrode. Although films 1 and 2 showed conductivity (Figure S4), an accurate conductivity value could not be obtained because the determination of channel area was difficult. However, the stability of films could be confirmed by monitoring the change of conductance in one channel under air. While the current of film 1 slightly decreased during the measurement, that of film 2 significantly decreased (Figure S5). This result was expectedly in line with the structural stability.

Film 1 composed of a very dense crystalline layer with open channels showed a significant change in its resistivity with high sensitivity and selectivity (vide infra). First, we investigated air/vacuum-dependent conductivity of film 1. Conductive film 1 in air (on-state) was changed to an electrically quenched state (off-state) under a vacuum (10−6 Torr). The conductivity recovered when film 1 was exposed to air again, even though the value slightly decreased due to the decay in crystallinity (Figure S6). To study the electric switching mechanism, we measured the current change under humid/dry N2 conditions. When the humid N2 gas was introduced to the devices by passing the N2 stream through a water bath, the current significantly increased by 2 orders of magnitude. In contrast, when dry N2 gas was introduced to the device, the current decreased by 2 orders of magnitude compared with the initial state (Figure 3a). Notably, similarly to the results upon exposure to dry N2, other vapors, such as ethanol and acetone,

Figure 1. Crystal structures of the Cd-PCN networks (a,b) 1 and (c,d) 2. Hydrogen atoms and solvents in a pore are omitted for clarity. Blue, N; yellow, Cd; red, O.

Figure 2. (a) Optical microscopic images of films. (b) Powder X-ray diffractions of single crystals and films measured under air. It should be noted that powder X-ray diffractions of film 2 and single crystals of 2 measured under air do not indicate the structure of initial network 2 (Figure S2).

Figure 3. (a) Current change of film 1 under humid N2 (red)/dry N2 (green) when the applied voltage was 10 V. Yellow area indicates the duration of gas flowing. (initial condition: 12 ± 1 °C, 50%RH). (b) Current−voltage characteristics of film 1 depending on the vacuum level (initial condition: 15 ± 1 °C, 68% RH). The graph in linear scale is shown in the Supporting Information (Figure S10).
also reduced the conductivity, leading to the electrical off-state (Figure S7). It is considered that they decreased the relative humidity compared to air conditions, indicating that only water can promote a high conductive state among vapors that we investigated. On the other hand, it is noteworthy that, as a control experiment, we confirmed that a nonporous film composed of only TPDAP showed no humidity sensing ability (Figure S8). Even though it is extremely difficult to measure the exact concentration of water in a N₂ gas, it is expected that the device could sensitively detect water. Instead of the quantitative measurement, the conductance of film 1 was measured depending on the vacuum level to investigate the sensitivity (Figure 3b). Considering that the change in humidity as a function of the vacuum level is relatively small, the remarkable difference in the conductance clearly indicates that film 1 is highly sensitive to water. In addition, the structural stability of film 1 as a sensing material was confirmed by powder X-ray diffraction, which showed that crystallinity was retained after 30 cycles of humid N₂ sensing (Figure S9).

Single crystal X-ray analysis before and after hydration of a single crystal of 1 revealed that the key mechanism of humidity sensing is the dissociation of NO₃⁻ from Cd ions under hydration. The unit cell volume of a hydrated crystal of 1 (1-hyd) under fully hydrated conditions in a capillary was a quarter of that of 1 before hydration. One of two monodentate ligands being part of the columnar layer in an asymmetric unit cell was disordered in 1, while every monodentate ligand in 1-hyd was severely disordered (Figure S11). It should be noted that the previously reported Cd-I mono synthesized under dry conditions has only ordered monodentate TPDAP layers, indicating that hydration makes monodentate TPDAPs disordered. In this sense, 1 is a kind of intermediate state between Cd-I mono (ordered monodentate TPDAP layer) and 1-hyd (disordered one). It is reasonable that the fully hydrated network (1-hyd) showed that every monodentate layers were disordered. In addition, importantly NO₃⁻ on Cd2, Cd3, Cd5, and Cd6 facing a pore was partially replaced by water (Figure 4). Both disordering of the monodentate ligand and dissociation of NO₃⁻ were also confirmed by powder X-ray diffraction, clearly indicating that the diffraction intensities corresponding to each plane for the columnar layer and coordinated NO₃⁻ drastically changed after hydration (Figure S12). The partial hydration in sensing measurement induced this event in a local part. The locally dissociated NO₃⁻ made the framework positively charged, leading to an electronically deficient state in the network framework, resulting in increasing the electronic interaction between TPDAPs in the pillar. In other words, the water acted as a dopant to decrease the resistivity in 1. IR spectroscopic measurements of 1 depending on the vacuum level revealed that all bands related to NO₃⁻ vibration modes (ν(NO₃⁻) at 1420 cm⁻¹, ν(NO) at 1030 cm⁻¹, and out of plane mode at 820 cm⁻¹) were shifted, indicating the coordination of dissociated NO₃⁻ to Cd ions under low humid conditions (Figure S13). Both X-ray and IR analysis results indicate that higher humidity conditions induced the dissociation of NO₃⁻ from Cd ions by coordination of water. The coordination/dissociation of water/NO₃⁻ plays a crucial role in conductivity change.

In conclusion, stable and dense crystalline film 1 prepared by the simple solvent evaporation method showed highly sensitive and selective humidity sensing ability as a chemiresistive sensor. Single crystal X-ray analysis and IR spectroscopy revealed that the key mechanism of sensing is the dissociation of NO₃⁻ on Cd ions under humid conditions. The dissociation of anions from the metals makes the network positively charged like a doping state. This knowledge will help to realize the electrical conduction in the redox-active PCNs and open the way for the practical use of redox-active PCNs as a chemiresistive sensor.

■ ASSOCIATED CONTENT

Supporting Information

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Details on the experimental procedures; syntheses of 1, 2, film 1, and film 2; and supplemental figures (PDF)

Accession Codes

CCDC 1541112 and 1541115–1541116 contain the supplementary crystallographic data for this paper. These data can be obtained free of charge via www.ccdc.cam.ac.uk/data_request/cif, or by emailing data_request@ccdc.cam.ac.uk, or by contacting The Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: +44 1223 336033.

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Notes

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■ REFERENCES


