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International Conference and Exhibition on
Mesoscopic and Condensed Matter Physics

Peculiar physical properties and material synthesis by self-organization:

New Hydrogen Storage Material

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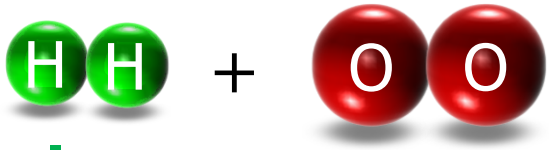
Outline

1. Introduction & Motivation; self-organization
2. New material with a one-dimensional space structure
3. Hydrogen uptake and release
4. Mechanism of hydrogen storage

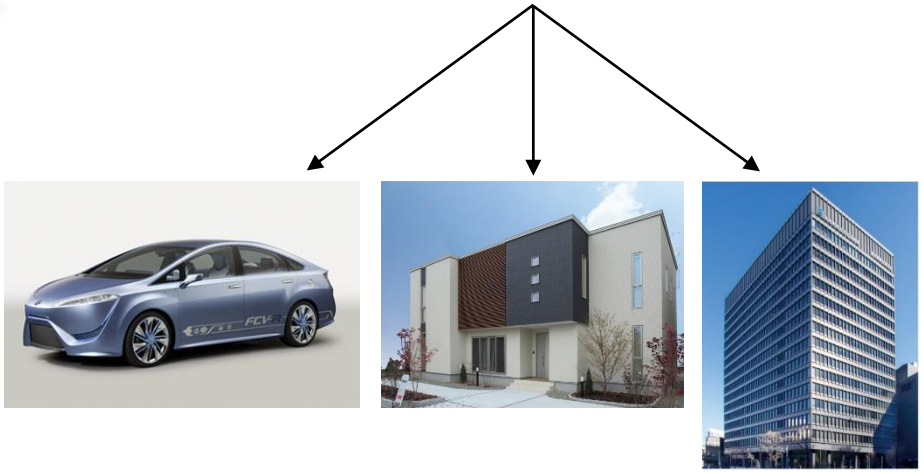
Introduction



⇨ **Electricity**

Ideal energy source

- inexhaustible
- No emission of CO_2



Conventional Hydrogen Storage Materials

- Hydrogen Adsorbing Alloys ($LaNi_5$, TiFe, ···)
- Porous Materials (Carbon, MOFs, ···)

Motivation

【Problem】

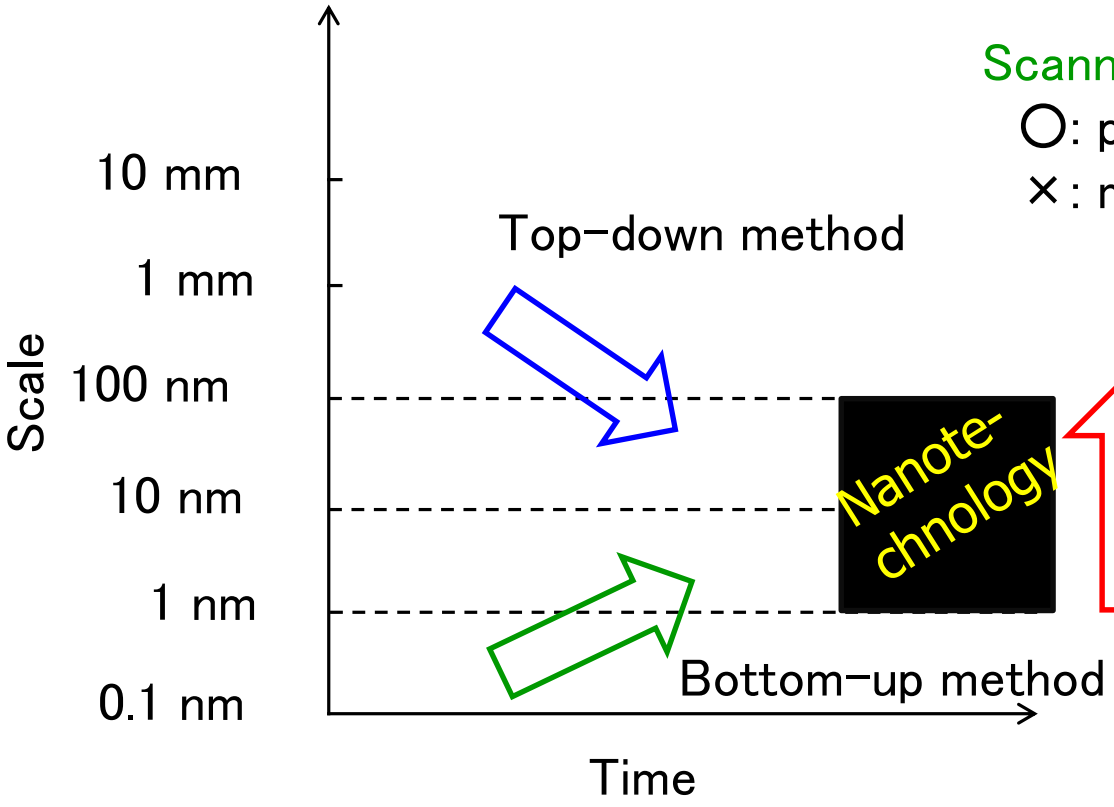
- ♦Heavy weight, rare metal
- ♦Small adsorption amount at room temperature
- ♦Irreversibility of adsorption/desorption
- ♦Exothermic upon adsorption

Motivation

We develop new hydrogen adsorbing material to overcome above problems.

Introduction

《Materials Science》



Fine processing technology

○: mass production

×: cost, limit of the size

Scanning probe microscopy

○: processing at the atomic size

×: mass production

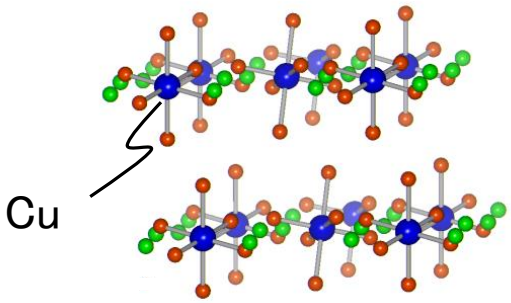
Self-organization

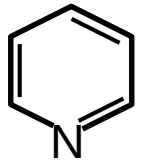
○: cost, mass production

×: not well established

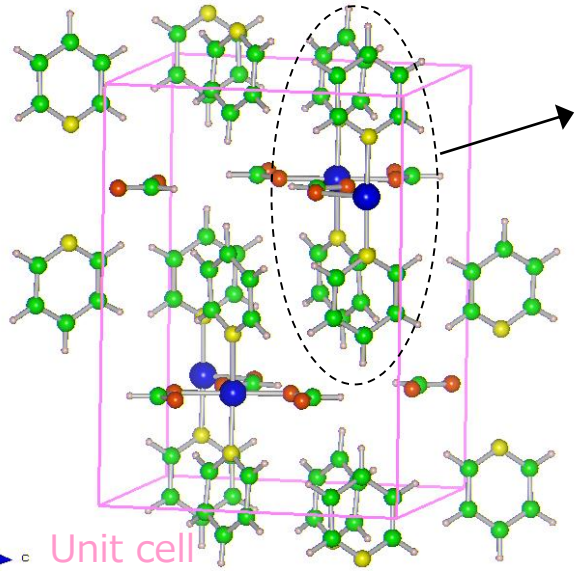
New material

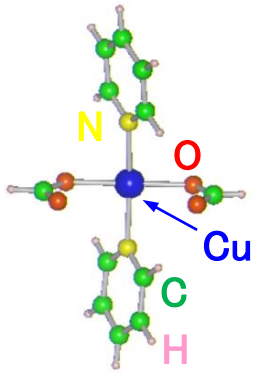
1. $Cu(HCO_2)_2 \cdot 4H_2O + C_5H_5N \rightarrow C_{12}H_{12}CuN_2O_4$





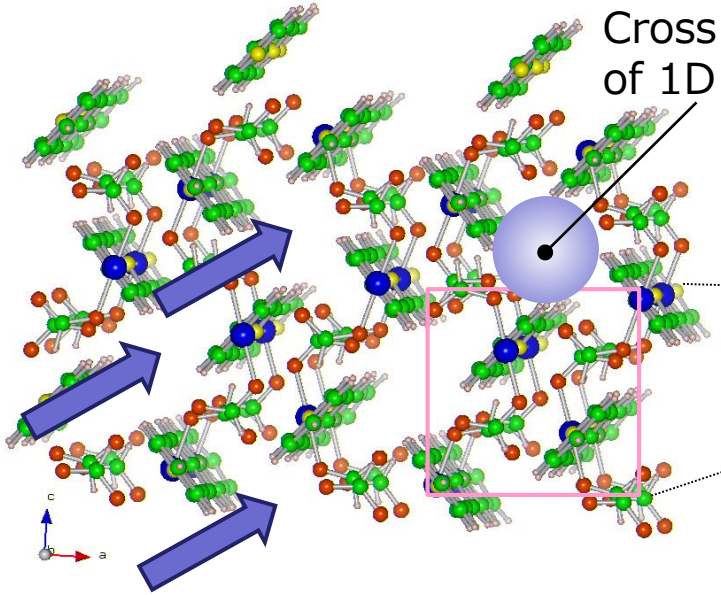
Self-organization



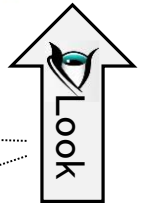


Unit cell

Cross section of 1D space



Direction of 1D space

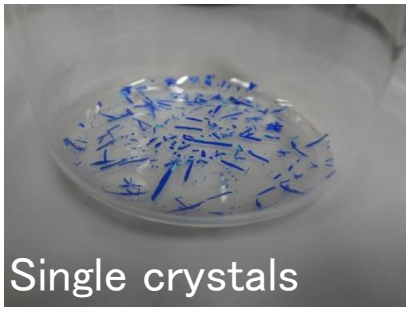


$C_{12}H_{12}CuN_2O_4$

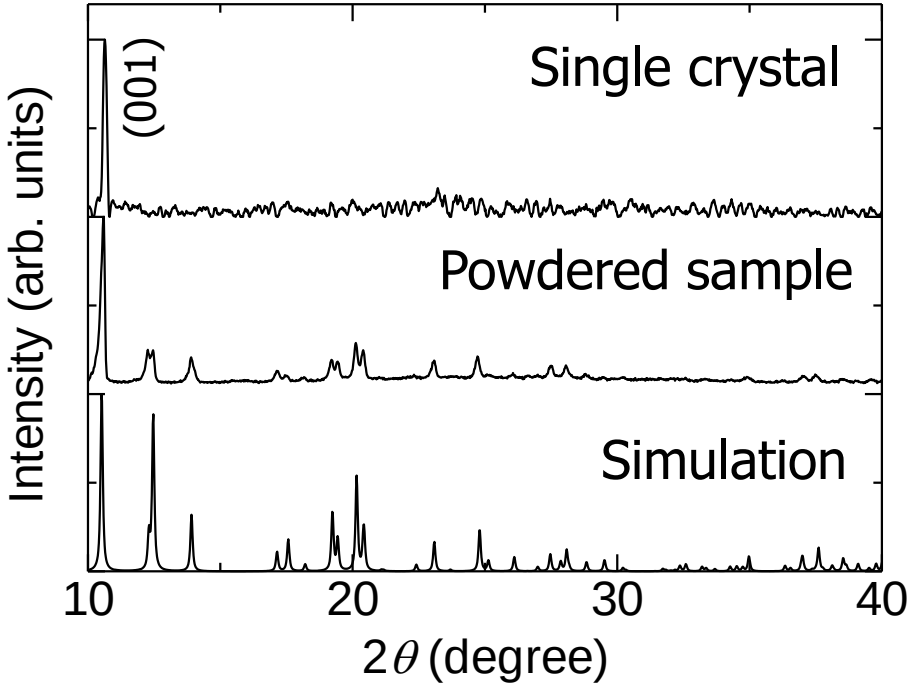
Characterization

Single-crystal X-ray analysis

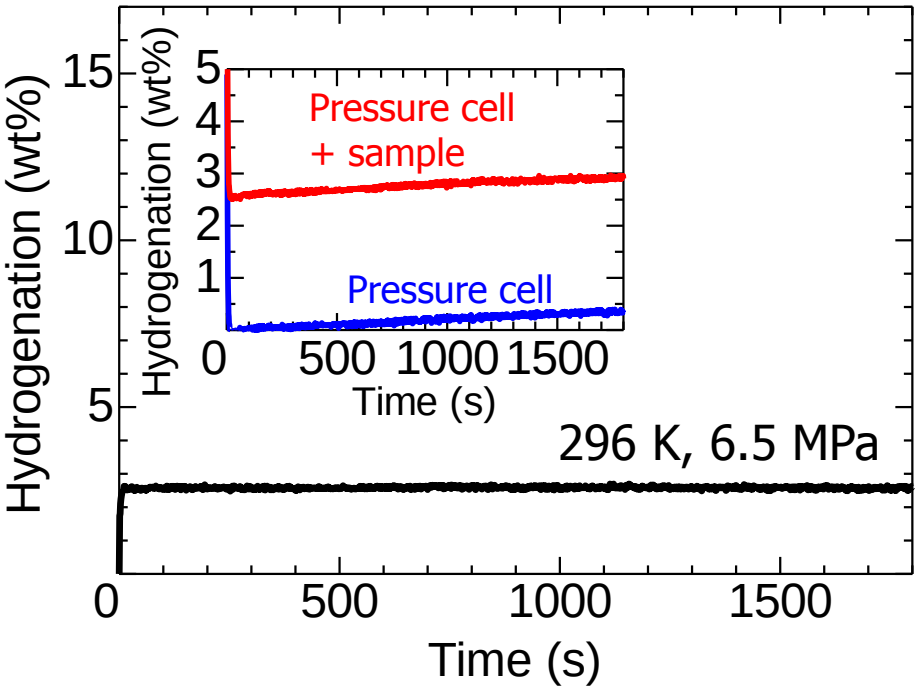
Empirical formula	$C_{12}H_{12}CuN_2O_4$
Formula weight	311.78
Temperature (K)	200
Wave length (Å)	0.71075
Crystal system	orthorhombic (Pnma, No.62)
a (Å)	9.7182
b (Å)	14.3322
c (Å)	10.3144
Crystal size (mm^3)	0.19 × 0.16 × 0.14
Crystal color	blue
Reflections measured	13357
Refinement method	Full-matrix least-squares on F^2
Goodness of fit on F^2	1.17
R1 (Final R index)	0.0401
R index (All data)	0.0430
wR	0.1015



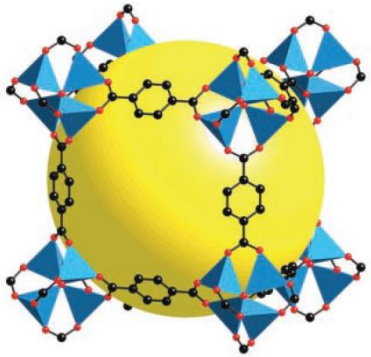
X-ray diffraction



Hydrogen storage



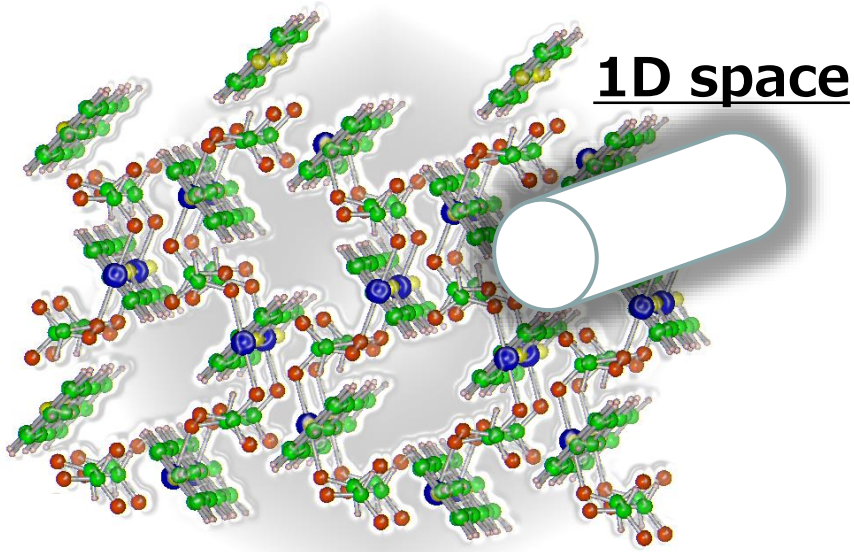
2.6 wt% hydrogen is **rapidly** adsorbed in the single-crystal material at room temperature.



3D space

▲ Metal–Organic Frameworks

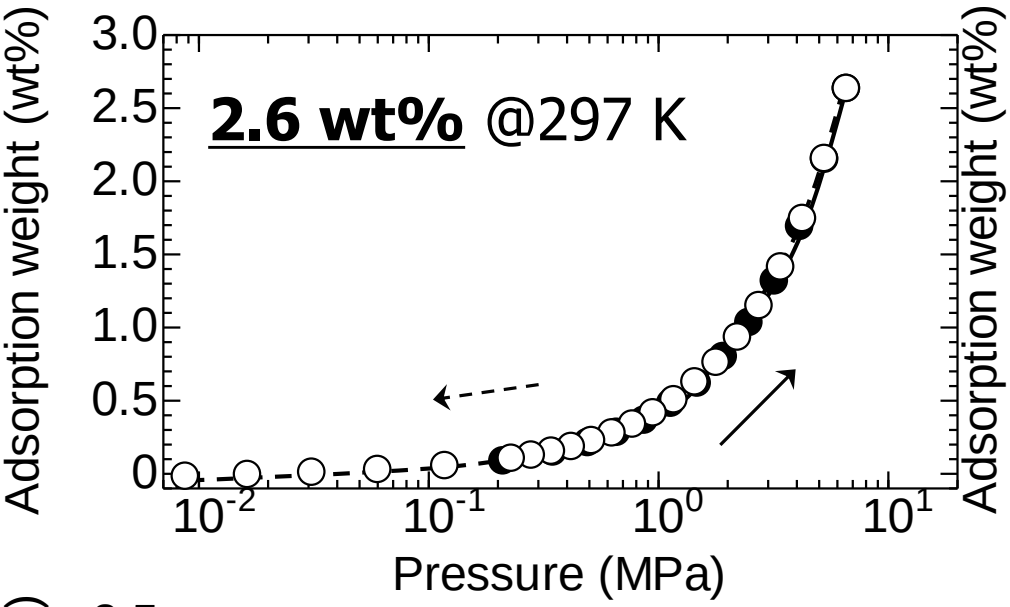
N. L. Rosi *et al.*, Science **300**, 1127 (2003).

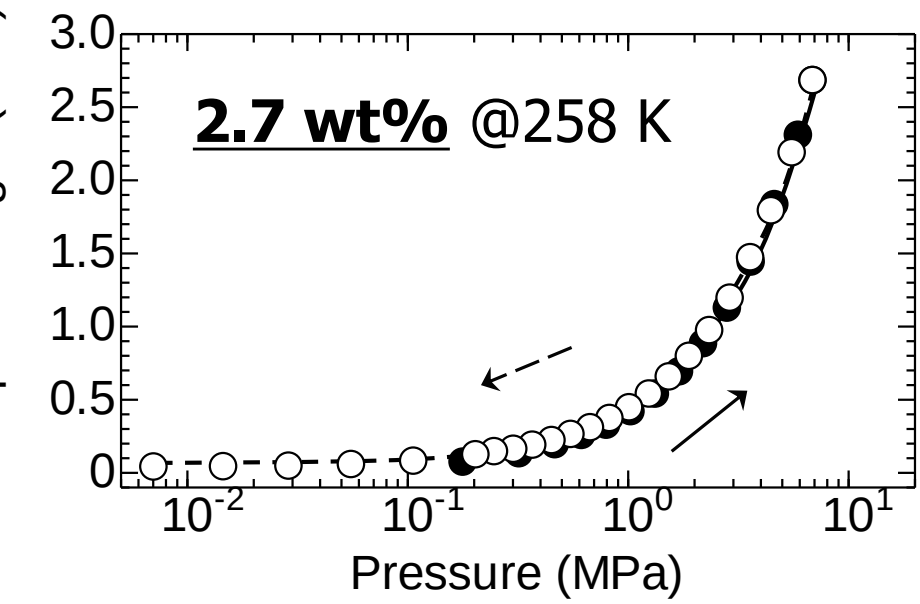


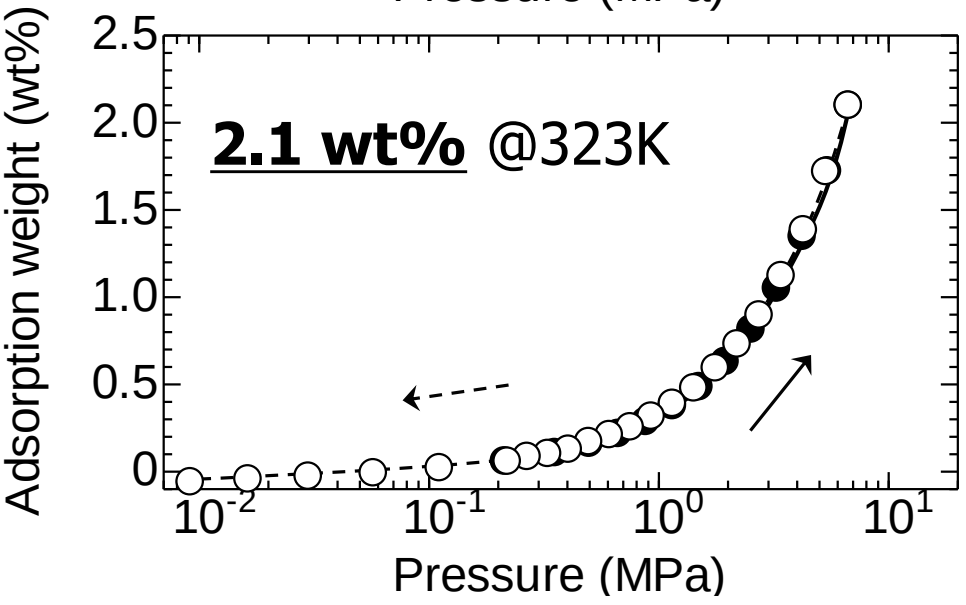
1D space

▲ Our material

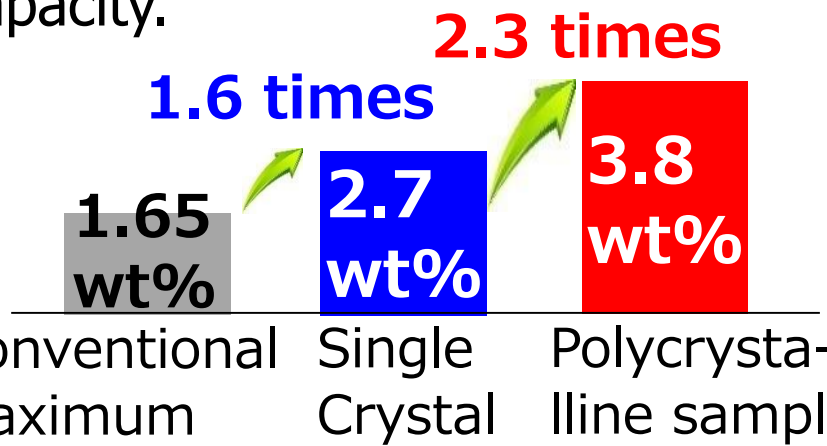
Hydrogen uptake and release



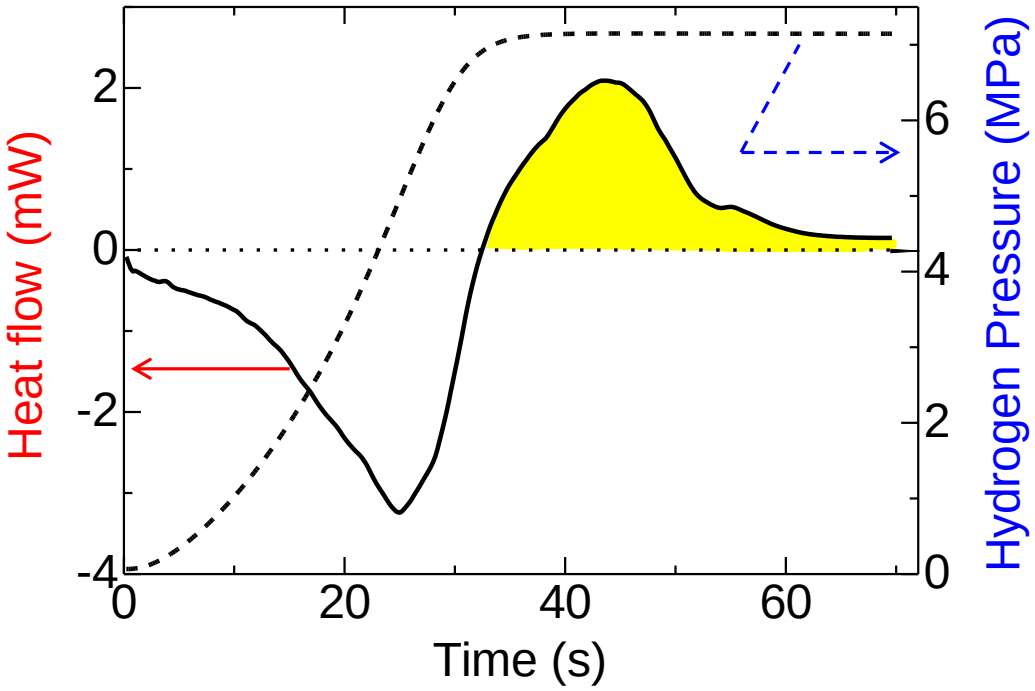




Our crystal can reversibly adsorb and desorb hydrogen with a good capacity.

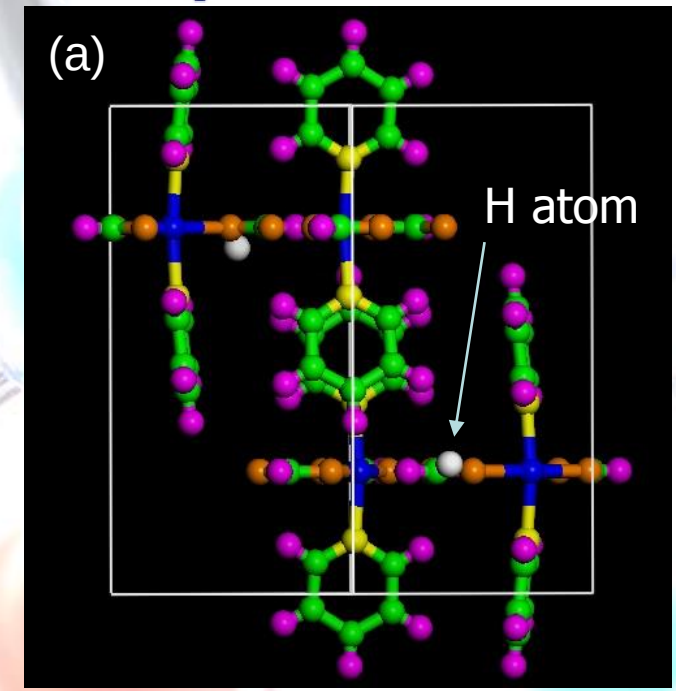


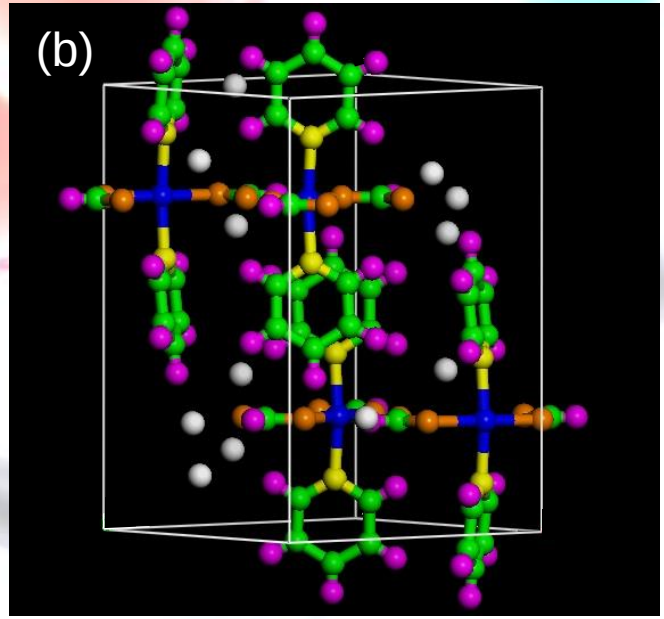
DSC under high pressure



As hydrogen pressure was increased, an exothermic peak was observed; this trend is characteristic of hydrogen adsorption.

Mechanism





Grand Canonical Monte Carlo method

Q: Is hydrogen adsorbed as H atoms or H_2 molecules?

A: H atoms.

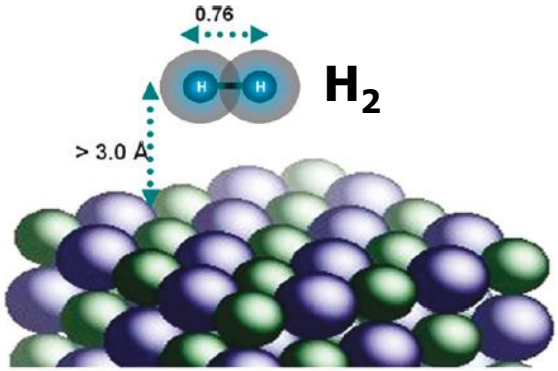
Q: Which structure of adsorbed hydrogen is energetically stable?

A: Organic linkers are preferential adsorption sites and the organic unit is a key to achieving good adsorption capacity.

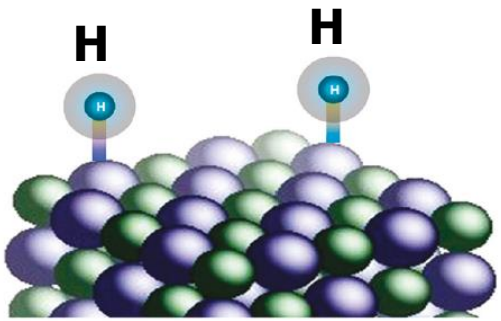
Discussion

Materials	Carbon system	MOFs	Metal Hydrides	Complex Metal Hydrides
Advantage	reversible	reversible	reversible	High H density
Disadvantage	Too cold	Too cold	Too heavy and expensive	irreversible

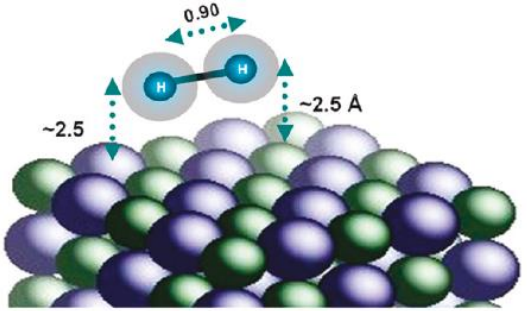
Physisorption



Chemisorption



Quasi-molecular bonding



P. Jena, J. Phys. Chem. Lett. **2**, 206 (2011).

Conclusions

We reported the synthesis and characterization of the $C_{12}H_{12}CuN_2O_4$ single crystal whose structure, operating capacity, and physical mechanism contrast with existing MOFs.

- Structure･･･1D void space
- Operating capacity･･･2.6 wt%, 3.8 wt%
- Mechanism･･･Hydrogen is adsorbed as atoms.

- T. Takami and K. Kawamura, APL Mater. **2**, 096104 (2014).
- PCT/JP2015/63176

Conclusions

Problems

× Heavy weight, rare metal
× Small adsorption amount at room temperature
× Irreversibility of adsorption/desorption
× Exothermic upon adsorption/desorption

Conclusions

× Heavy weight, rare metal

⇒ ○ **light** element, element with the large Clarke number

× Small adsorption amount at room temperature

⇒ ○ **2.3 times larger** adsorption amount
(**World record among MOFs**)

× Irreversibility of adsorption/desorption

⇒ ○ reversibility due to a specific mechanism

× Exothermic upon adsorption/desorption

⇒ ○ small exothermic («10 kJ/mol)

Applications

Present Tank

▲FCV

70 MPa
122 L
100 kg

91% Down

28% Down

3.8 wt%

6.5 MPa

88 L

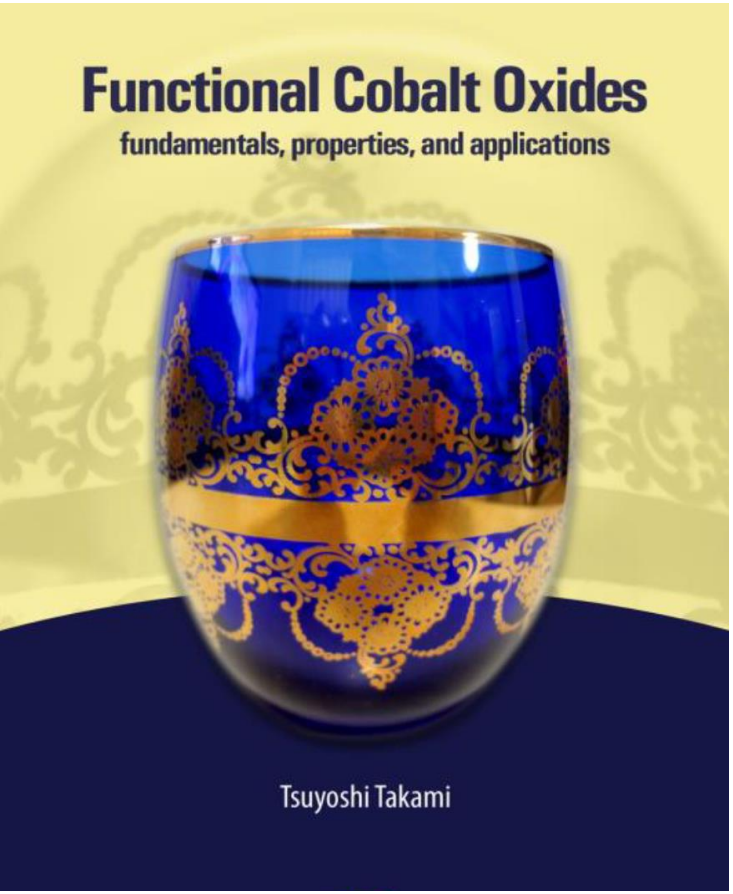
127 kg

Future(5.0 wt%)

6.5 MPa

66 L

95 kg



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Key Features

- Covers widely functional cobalt oxides from basics to application, including recent progress focusing on their functionality and physics behind their peculiar physical properties
- Offers numerous cobalt oxide materials, functionalities, and applications, uniquely observed for cobalt oxides among many transition metal oxides
- Includes three major topics—fundamentals, properties, and applications—with their essence and mechanism by applying suitable theories

Chapter	Title	Author(s)
1	Introduction	Tsuyoshi Takami
2	Spin-State Crossover	Tsuyoshi Takami
3	Li Ion Battery	Tsuyoshi Takami
4	Huge Thermoelectric Power	Tsuyoshi Takami
5	Room-Temperature Ferromagnetism	Tsuyoshi Takami
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FIN.