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Experiment Report for Prefectural Beamline

Proposal no. : 2209082T

Beamline no. : BL-11

Report date : 07/11/2023

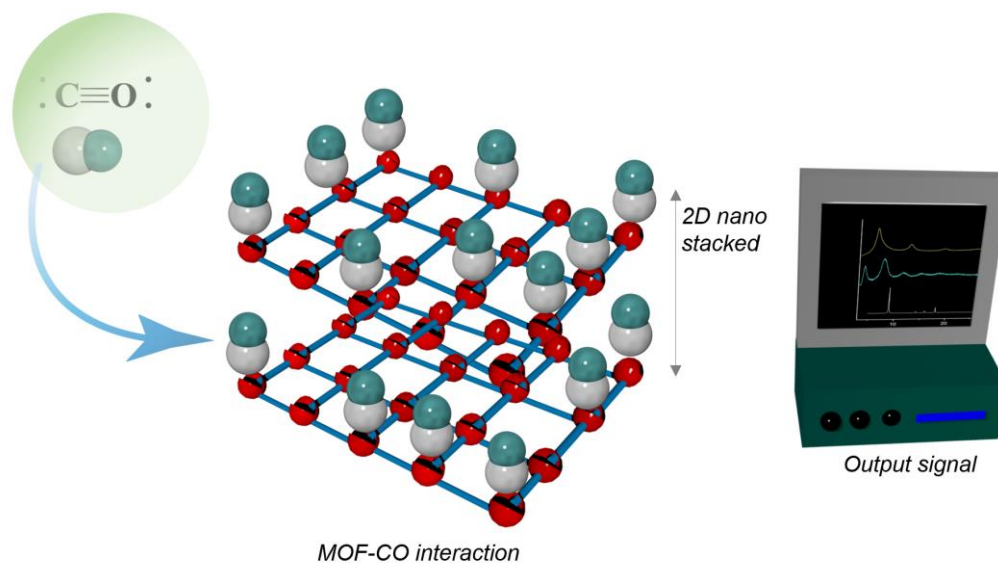
CO recognition using 2D nano CP**Biplab Manna****IINA, Kumamoto University****1 . Summary**

In this preliminary report, we introduce a new kind of phase namely 2D nano stacked coordination polymers (here after referred as **1_{OP}-2D-heated**). The material is observed to show nano level thickness and contain open metal-sites which recognize toxic gas like carbon monoxide (CO) than that of other coordinating guests.

2 . Purpose of experiment and background

CO is well known as major emission from large number of industrial process and later on it mixed with other gases like N₂.¹ Such mixture of gases on burning produces large amount of CO₂, which gives an alarm to the whole world an unprecedented rise in temperature throughout the planet. Hence recognition of CO remains a major topic of research interests. Till now, chemisorption on low valent metal center has been extensively utilized but requirement of very high temperature for CO desorption makes it much difficult. Apart from that metal-oxide based approach also required high temperature for detection.^{2,3} Porous coordination polymers (PCPs) / metal-organic frameworks (MOFs) is being well recognized for its adaptable porosity. ⁴ Apart from other gases, literature reports on CO sorption were very rare owing its toxic nature. ^{5,6} Very recently, Mirica et al. showed chemo resistive detection of CO using a conductive two-dimensional MOF.⁷ But, designing a 2D conductive PCP/ MOF using a conjugated ligand is quite difficult and is not cost effective. Hence, present situation demands a cost effective and feasible method for CO recognition. **Here, we hypothesises** 2D stacked

nano CPs/ MOFs with unsaturated metal centers which can be built from easily available precursors (**Scheme 1**). These stacked 2D nano MOFs can be tailored into tunable thickness which eventually can adjust their performance.



Scheme 1: CO recognition by using unsaturation of metal node in 2D nano stacked CP/ MOF

3. Experimental

Here, we use a DUT-8(Ni) (denoted as 1_{op} hereafter) as a starting MOF, that has been synthesized in our laboratory using a previously reported method.⁸ 1_{op} contains 2,6-naphthalenedicarboxylate (NDC) and a pillar linker (DABCO) represented as $[\{Ni_2(NDC)_2(DABCO)\}.xG]n$. The porosity of original phase was confirmed from its N_2 -adsorption isotherm. 1_{op} -2D was synthesized from the water sonication of the 1_{op} . 1H -NMR of 1_{op} -2D was analyzed with $DCI/DMSO$ (1:9) following a protocol.⁹ Evacuated phase of 1_{op} -2D generates 1_{op} -2D-heated (Figure 1). The surface morphological analysis were performed with 1_{op} -2D and 1_{op} -2D-heated. EXAFS and XANES have been analysed using BL-11 for 1_{op} -2D-heated phase to know the coordination environment around metal centre. The XRPD patterns were analyzed with the 1_{op} , 1_{op} -2D, 1_{op} -2D-heated. The 1_{op} -2D-heated was checked with AFM analysis. Temperature programmed desorption (TPD) analysis of the above vapors on 1_{op} -2D-heated phase will be performed to elucidate the affinity and binding strength. Other vapors (Aromatic (benzene, Toluene) and non-aromatic solvent (cyclohexane, hexane, heptane) adsorption are under consideration. HR-TEM and electron diffraction analysis of the 1_{op} -2D and 1_{op} -2D-heated phases will be examined to investigate the lattice patterns.

In-situ-solid state UV and DRIFT under vapor exposure phases will be performed to understand the detailed mechanisms of interactions. Theoretical insights using DFT analysis will be checked.

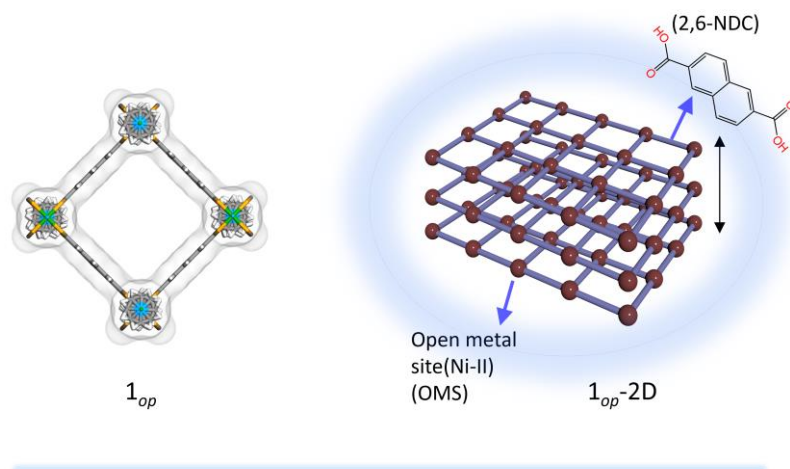


Figure 1: Original MOF in the left (1_{op}); 2D nano stacked CP (model structure) in the right showing the ligand chemical structure.

4. Results and Discussions

The water sonication of the 1_{op} gives rise a 2D stacked sheet as observed in FE-SEM (Figure 2). $^1\text{H-NMR}$ of 2D stacked sheet (1_{op-2D}) evidenced the complete removal of the DABCO.

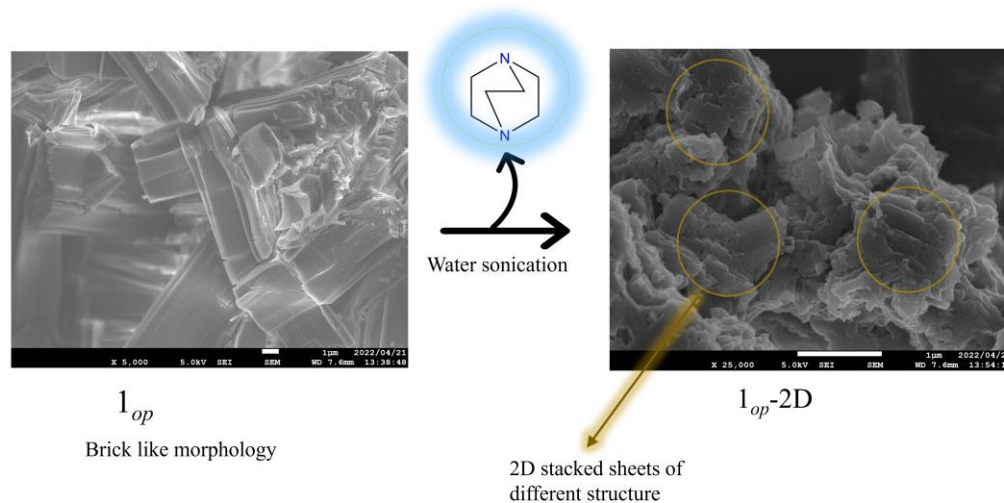


Figure 2: Morphology changes upon pillar linker removal from 1_{op} to 1_{op-2D} . Here, 1_{op-2D} showed stacked 2D sheets like morphology (right) whereas 1_{op} exhibited brick like morphology (left).

The XRPD patterns showed a significant change in lattice structure with maintaining the surface morphology

(Figure 3a) but with a significant change in color. The AFM analysis of **1_{op}-2D-heated** exhibited a stacked sheet nature with a height around 20nm (Figure 3b).

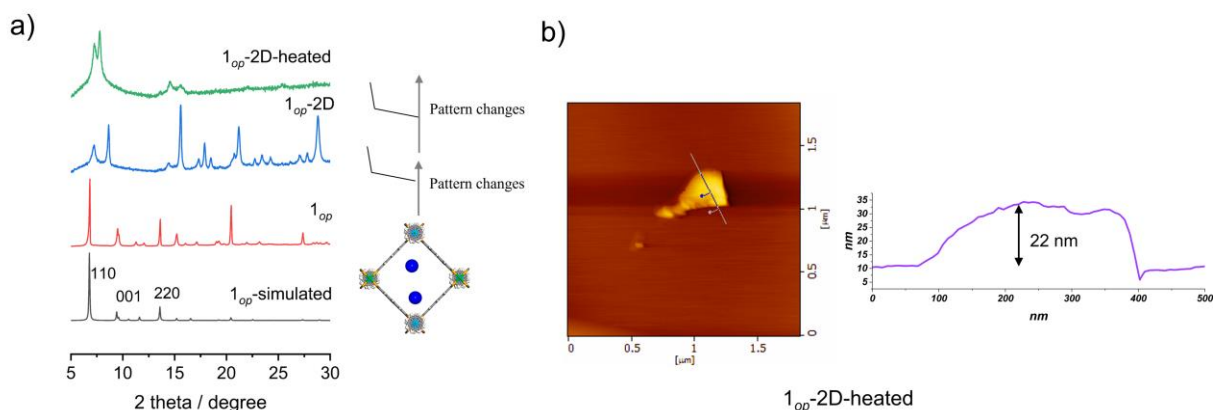


Figure 3: a) XRPD patterns **1_{op}**, **1_{op}-2D** and **1_{op}-2D-heated** indicating dynamic nature of 2D nano CP/ MOF; b) AFM images of **1_{op}-2D-heated** indicating stacked nature of 2D nano MOF. Height profile is shown to be around 20nm.

Temperature programmed desorption (TPD) analysis of CO adsorptive was analyzed with the **1_{op}-2D-heated** phase to elucidate the affinity and binding strength. The adsorption temperature of CO to the sample is -60°C . We observed the sharp desorption peak at low temperature (-22°C) but no desorption peak was not detected at ambient temperature. This indicated the strong affinity of CO to the OMS at low temperature of the adsorbent **1_{op}-2D-heated** (Figure 4).

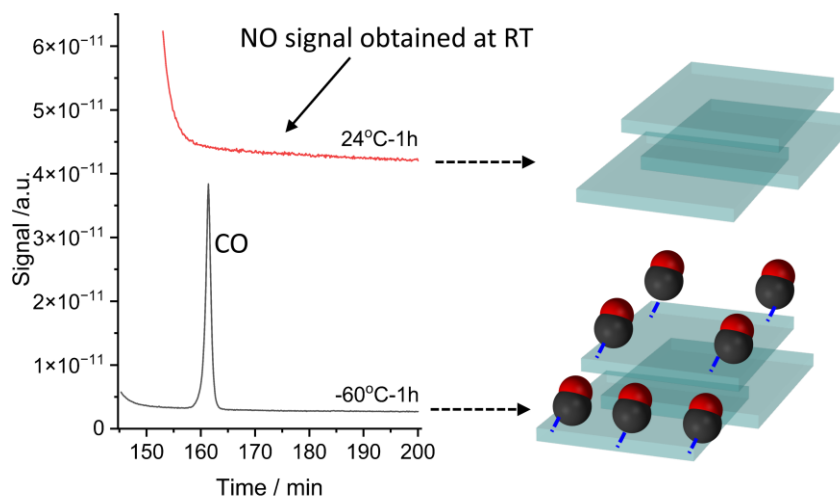


Figure 4: TPD analysis of **1_{op}-2D-heated**. Low temperature adsorption was seen to occurred and desorption peak came at -22°C . No TPD signal was detected at room temperature indicating no adsorption at RT on **1_{op}-2D-heated**.

5 . Future issues

In future, we are looking forward to making devices that can sense CO selectively using MOF as template. But, for this, stability issues of 2D MOF, nano MOF could be addressed.

6 . References

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7 . Publications

Related articles:

- i) B. Manna, M. Asami, N. Hosono, T. Uemura, *Chem.* **2023**, 10.1016/j.chempr.2023.05.041
- ii) B. Manna,* M. Yamaguchi, H. Setoyama, M. Fadil, M. Iwai, T. Kida* *Manuscript under preparation*, **2023**

8 . Keywords

Metal-organic framework, 2D materials, stacking, Molecular Recognition