Zinc-Imidazole-Based Metal-Organic Framework Nanosheet Membrane for Gas Separation

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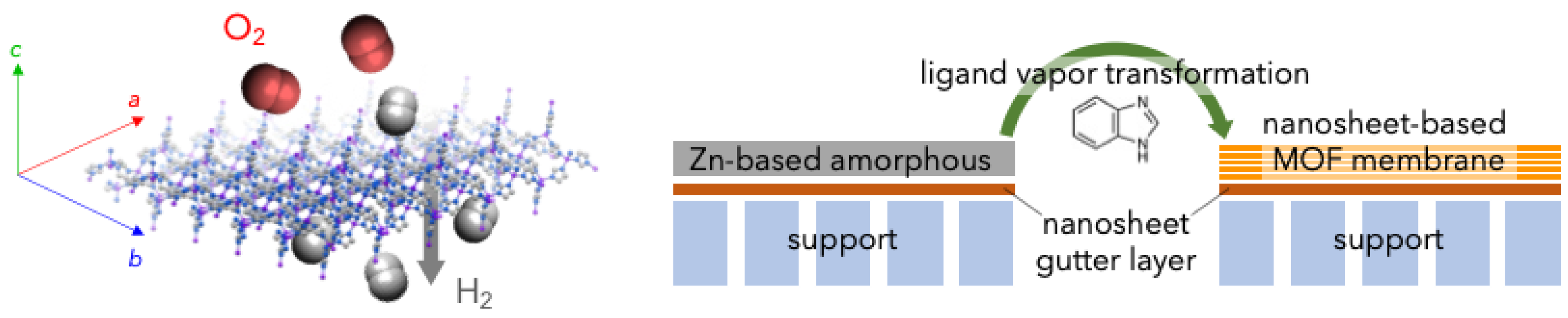
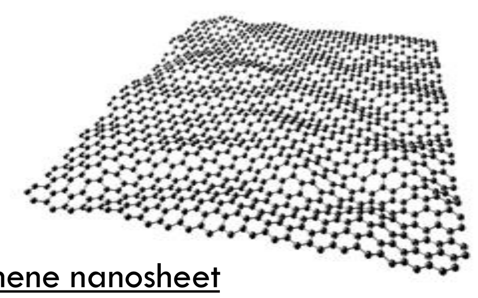
Metal-organic framework (MOF) nanosheets are promising candidates for molecular sieve because of their structural diversity and minimized mass transfer barrier. However, design of appropriate MOF nanosheets and preparation of high-performance MOF nanosheet-based membranes, especially for gas separation, remains great challenges. Structural degradation may simultaneously occur with conventional exfoliation method, which has hindered its widespread application in high-performance membrane preparation. Even if nanosheets could be stacked, *grain boundaries would form between the nanosheets, which could be applied to liquid separation but not to gas separation*.

In this study, we developed a bottom-up method of nanosheet membrane formation in which zinc-based amorphous layer is applied on top of an intermediate gutter layer of $Zn_2(benzimidazole)_4$ nanosheets fabricated by conventional interface synthesis, followed by crystallization of zinc-based layer by supplying benzimidazole vapor. ***The concept of our method is to anisotropically control the crystallization of $Zn_2(benzimidazole)_4$ during crystallization of the zinc-based amorphous layer by using surfactant.***



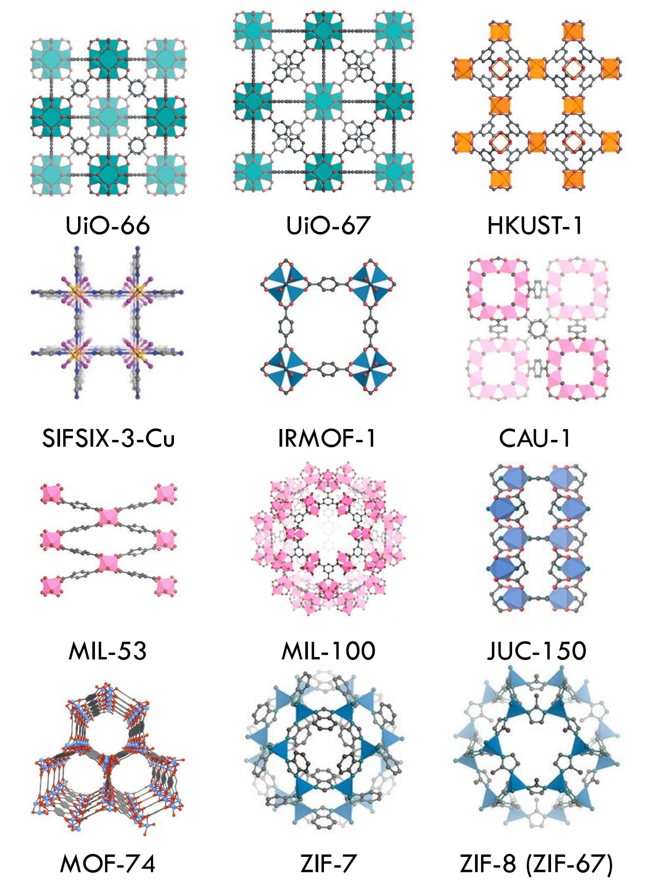
Metal Organic Frameworks (MOF)

- No template necessary
- Easy activation
- Chemical variability (metal × linkers)
- Structural variability
- High surface area
- Framework flexibility



like graphene nanosheet

➔ **MOF nanosheet membrane**



Experimental

Synthesis of $Zn_2(benzimidazole)_4$ nanosheet

↓ benzimidazole in dichloromethane / zinc nitrate in aqueous solution

$Zn_2(benzimidazole)_4$ nanosheet gutter layer on AAO

↓

Zinc-based amorphous layer on gutter layer/AAO

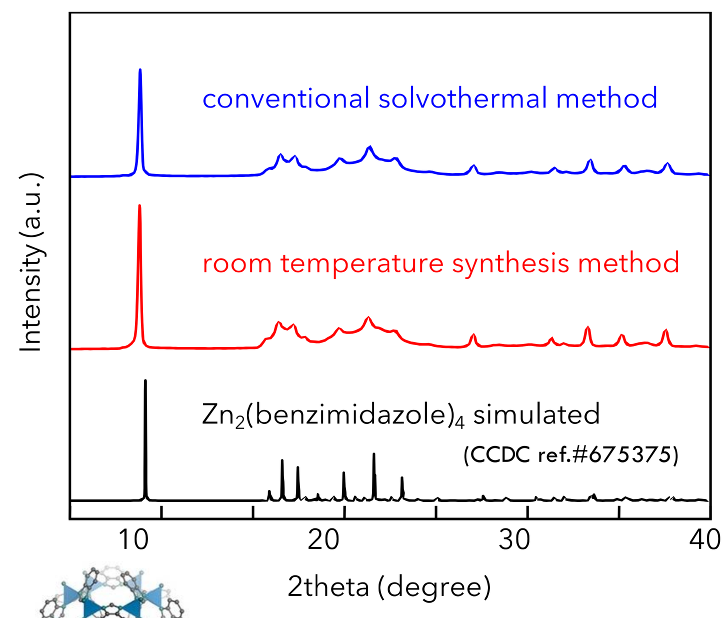
↓ zinc nitrate, benzyltrimethylammonium chloride, 2-methoxymethanol

Conversion of zinc-based layer to $Zn_2(benzimidazole)_4$ nanosheet

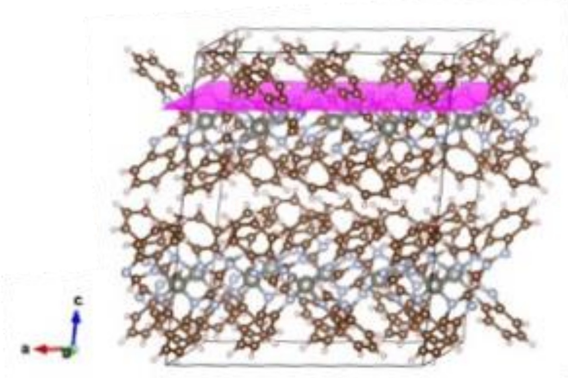
↓ benzimidazole vapor deposition at 180 degC for 2 h

$Zn_2(benzimidazole)_4$ nanosheet on gutter layer/AAO

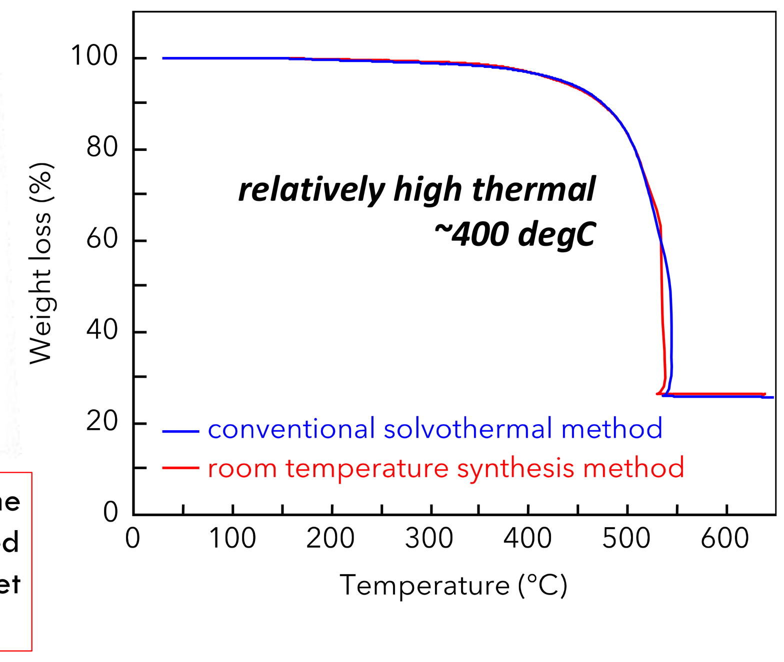
Structure and thermal stability of bulk $Zn_2(benzimidazole)_4$

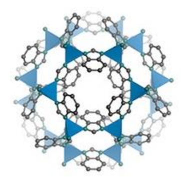


layered structure



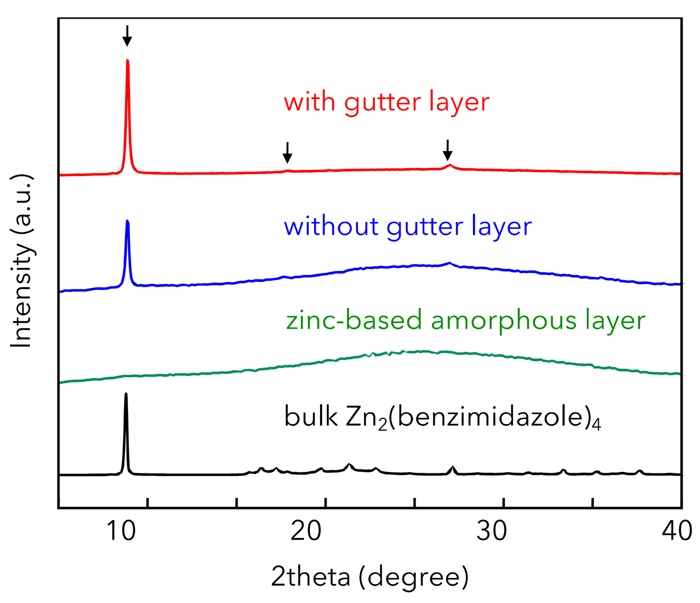
$Zn_2(benzimidazole)_4$, with the same composition as ZIF-7 and layered structure, is a promising nanosheet precursor for hydrogen sieving





ZIF-7
sodalite topology, which comprises of interconnected six-membered rings with an inner cage size of 5.6 Å and pore aperture of 2.9 Å

Conversion of zinc-based amorphous layer to $Zn_2(benzimidazole)_4$



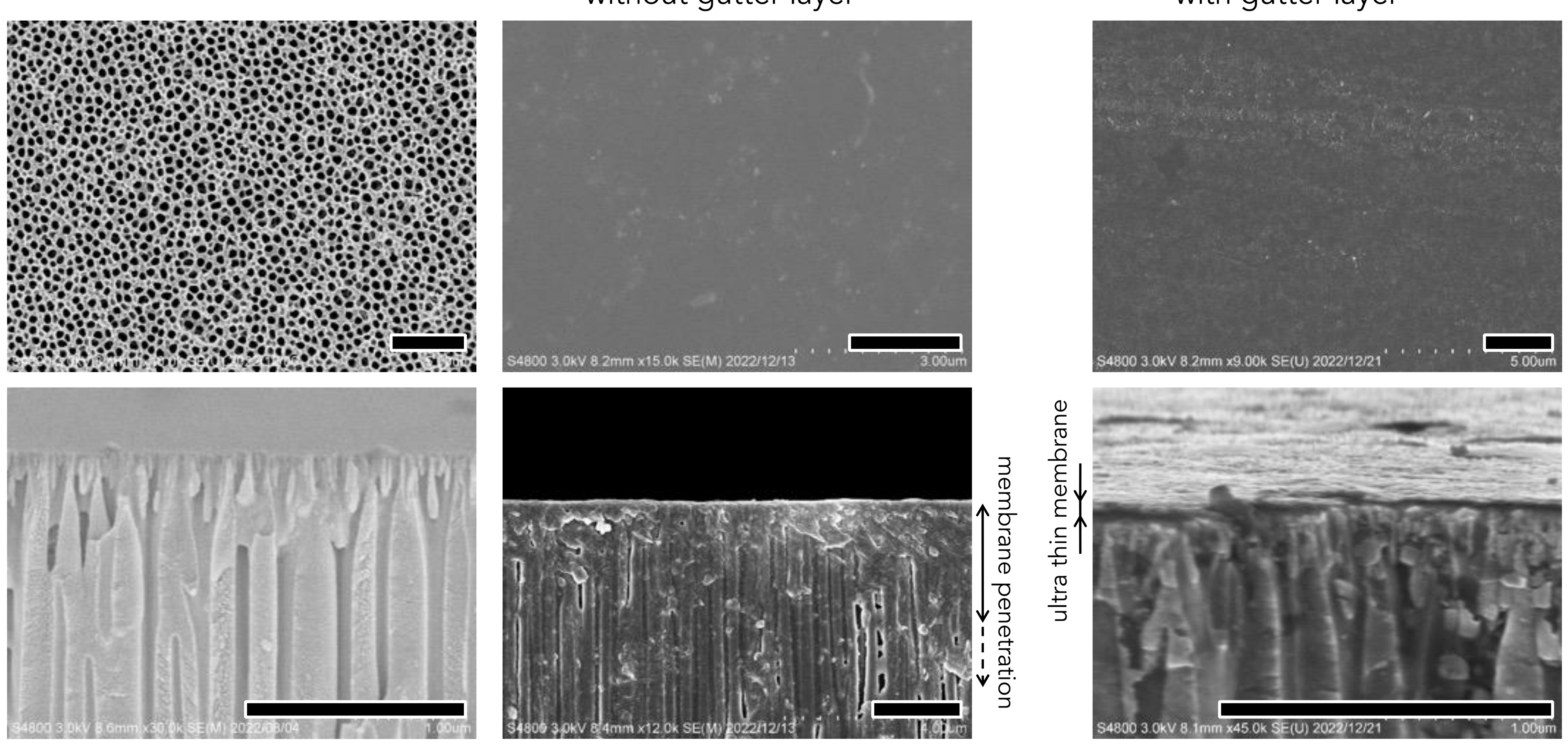
After Zn-based layer was exposed to benzimidazole vapor at 180 degC, sharp diffraction peaks appeared.

Zn-based layer shows broad diffraction.

The PXRD shows 1st, 2nd and 3rd order diffraction peaks, indicating that the structure of the layer is strongly oriented along the c axis.

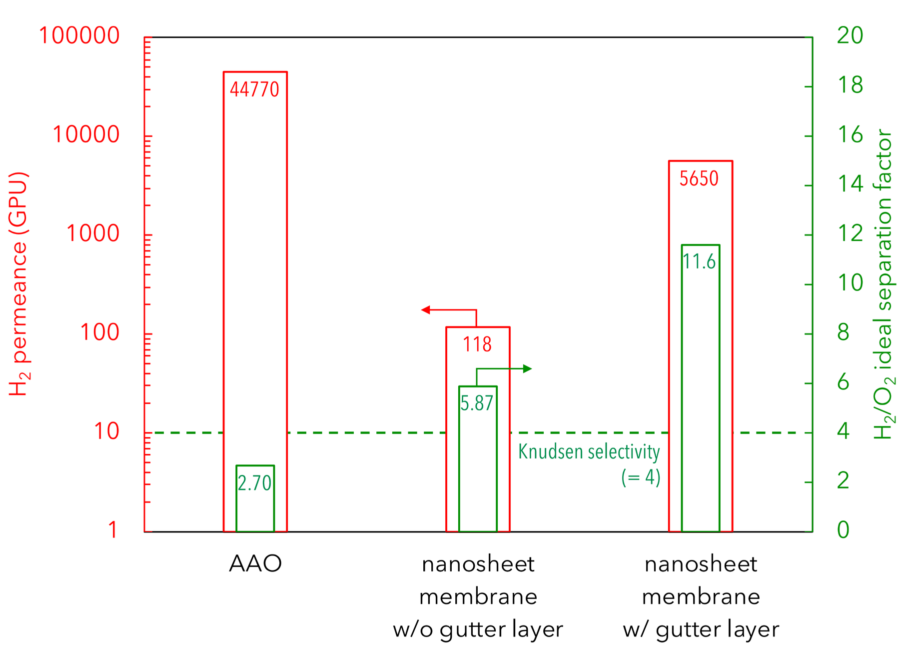
Crystallinity:
w/gutter layer ≫ w/o gutter layer

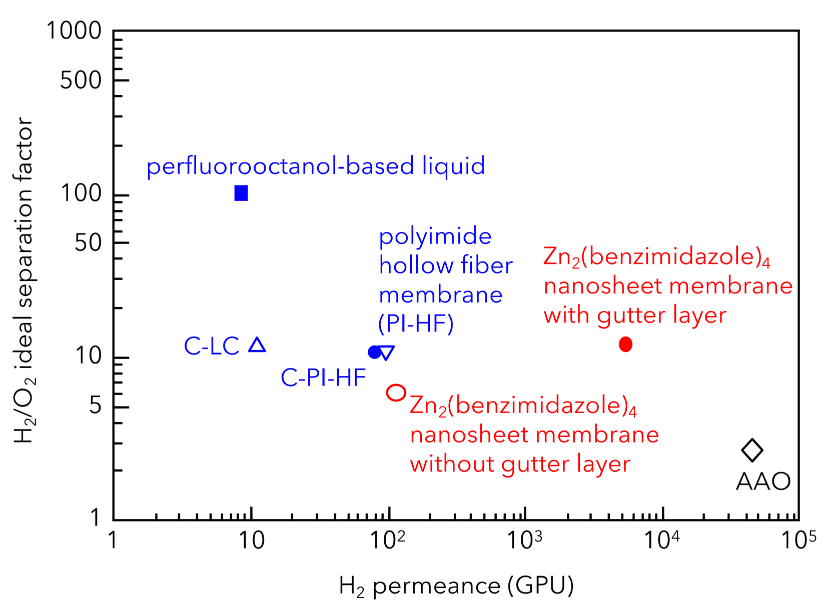
When the $Zn_2(benzimidazole)_4$ gutter layer was not coated on AAO, the broad diffraction around 25° still remained after benzimidazole vapor deposition, indicating that the membrane contains crystalline structure and amorphous region.



scale bar: 2µm

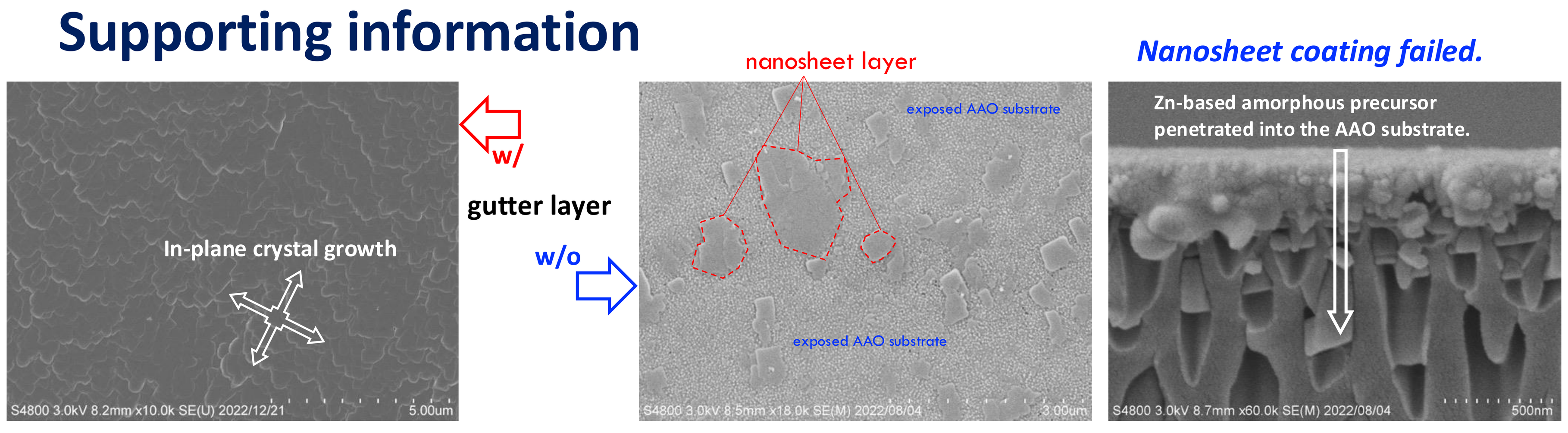
Gas permeation properties





The prepared $Zn_2(benzimidazole)_4$ nanosheet-based membranes show separation performance in hydrogen purification with H_2/O_2 ideal separation factor of 11.6 and H_2 permeance of 5650 GPU.

Supporting information



Successful nanosheet coating
on AAO substrate with gutter layer

Zinc-based amorphous layer penetrated into the pores of AAO substrate without gutter layer, resulting in failure to fabricate thin nanosheet membranes on the AAO surface.

Acknowledgements

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