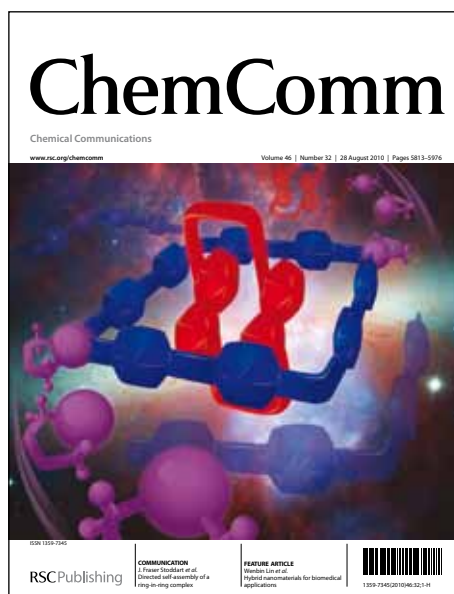


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## COMMUNICATION

Fabrication of a COF-5 membrane on functionalized  $\alpha$ -Al<sub>2</sub>O<sub>3</sub> ceramic support using microwave irradiation methodDandan Hao,<sup>ab‡</sup> Jinna Zhang,<sup>bc‡</sup> Hui Lu,<sup>\*b</sup> Wenguang Leng,<sup>b</sup> Rile Ge,<sup>\*b</sup> Xiaonan Dai<sup>a</sup> and Yanan Gao<sup>b</sup>

Received (in XXX, XXX) Xth XXXXXXXXX 20XX, Accepted Xth XXXXXXXXX 20XX

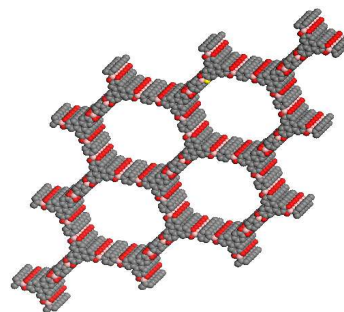
DOI: 10.1039/b000000x

A novel surface modification strategy was developed by using 3-aminopropytriethoxysilane and 4-formylphenylboronic acid successively as covalent linkers between COF-5 and the porous  $\alpha$ -Al<sub>2</sub>O<sub>3</sub> ceramic support, and then COF-5 membrane was further grown successfully on the modified  $\alpha$ -Al<sub>2</sub>O<sub>3</sub> support by using microwave irradiation method.

Porous covalent organic frameworks (COFs) linked by strong covalent bonds with well-defined pore sizes, was emerged recently<sup>1-3</sup>. The COF materials possess many desirable properties such as highly thermal stability, permanent porosity, high specific surface area, and the low mass densities<sup>1-6</sup>. As promising gas storage and separation materials, the synthesis, design and applications of the two kinds of porous framework materials, namely the COFs and metal organic frameworks (MOFs), have gained tremendous attentions recently<sup>2-14</sup>. However, to improve the adsorption/membrane separation and energy efficiency of the COF and MOF materials, the development of the gas storage/separation technology was also highly crucial. A number of excellent advancements for the molecular sieve membranes based on MOFs have been presented<sup>7-12</sup>. These studies have shown that the MOFs-based membrane technique exhibited high separation efficiency and convenience for gas separation and pervaporation applications<sup>7-11</sup>. Thus, it is significantly attractive and potential to develop the novel COF membranes for the promising applications in gas storage and separation.

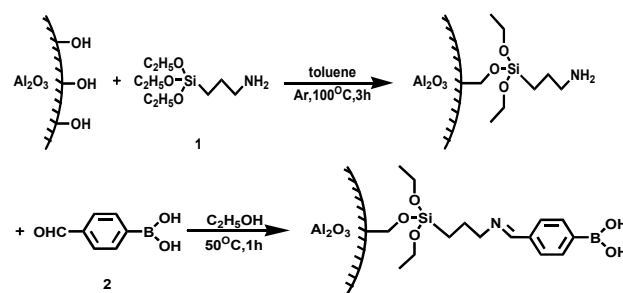
The COF-5 is one of the two COFs materials which were firstly reported by Yaghi *et al.* in 2005<sup>1</sup>. The COF-5 possesses a hexagonal array of 2D mesopores whose pore diameter is 2.7 nm, and with an interlayer spacing of 0.35 nm (Scheme 1). Herein we design a novel approach for the COF-5 membrane fabrication, which involved the surface functionalization and modification of the porous  $\alpha$ -Al<sub>2</sub>O<sub>3</sub> support, and the COFs membrane growth on the modified porous ceramic support under microwave irradiation conditions. This attractive strategy may significantly extend the choices of support materials, which is usually subject to the crystal facets such as Au(111), graphite (001), Cu(111) and Ag(111)<sup>15-19</sup>. In addition, the porous ceramic supports are of importance for the practical utilizations in the separation, purification, and catalysis fields, which may provide the strong strength, the high porosity, and the low costs. The need to explore inexpensive supports, which meet the desired characteristics in terms of porosity, pore size distribution, thermal and chemical stability, is also important<sup>20</sup>. To the best of our

knowledge, this is the first report of the COFs membrane grown on a commonly used porous  $\alpha$ -Al<sub>2</sub>O<sub>3</sub> ceramic substrate.



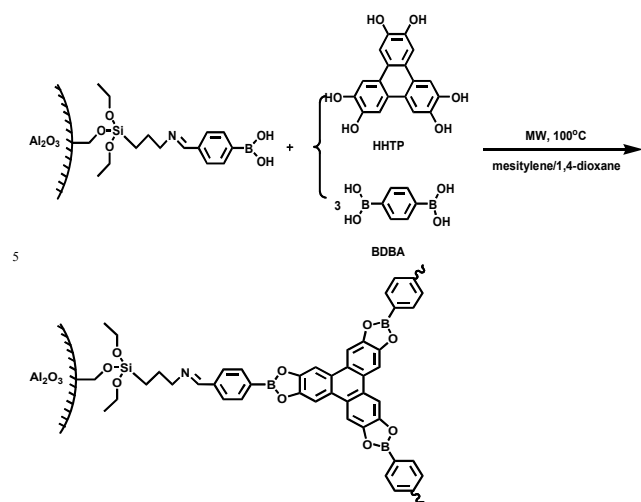
**Scheme 1.** Structural representation of the COF-5. Carbon, boron, and oxygen are represented as gray, pink, and red spheres, respectively, and H atoms are omitted here.

The surface functionalized  $\alpha$ -Al<sub>2</sub>O<sub>3</sub> porous supports by using 3-aminopropytriethoxysilane (APTES, 1) and 4-formylphenylboronic acid (FPBA, 2) linkers were obtained, as shown in Scheme 2. In the first step, the ethoxy groups of the APTES reacted with the surface hydroxyl groups of the porous  $\alpha$ -Al<sub>2</sub>O<sub>3</sub> ceramic support<sup>8</sup>. Next, the amino groups of APTES reacted with the aldehyde groups of FPBA *via* imines condensation, and then the modified surface of the APTES functionalized  $\alpha$ -Al<sub>2</sub>O<sub>3</sub> with boronic acid groups were formed. The COF-5 powder and membrane were prepared according to a slightly modified microwave method<sup>21</sup>. The dehydration reaction between boronic acid from the surface of the functionalized  $\alpha$ -Al<sub>2</sub>O<sub>3</sub>, 1,4-benzenediboronic acid (BDBA, 3) and 2,3,6,7,10,11-hexahydroxytriphenylene (HHTP) (Fig. S1 and Fig. S2, ESI<sup>†</sup>) generates the supported COF-5 membrane under microwave irradiation (Scheme 3).



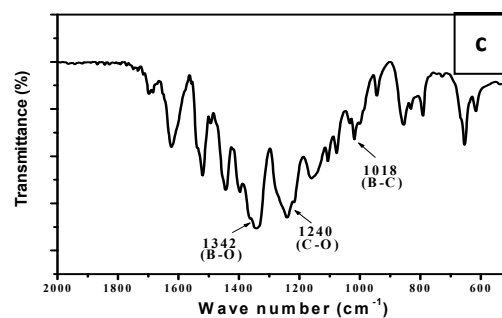
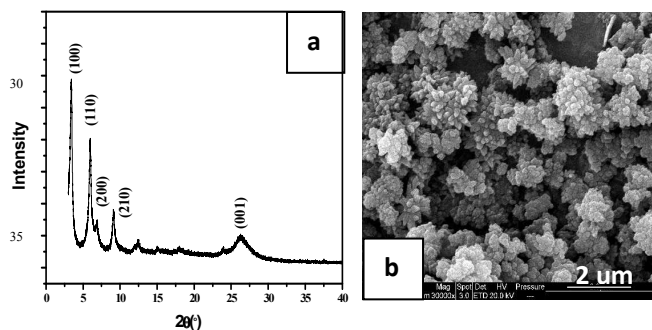
**Scheme 2.** Surface functionalization and modification of the porous  $\alpha$ -Al<sub>2</sub>O<sub>3</sub>

ceramic support using 3-aminopropyltriethoxysilane (APTES, 1) and 4-formylphenylboronic acid (FPBA, 2).

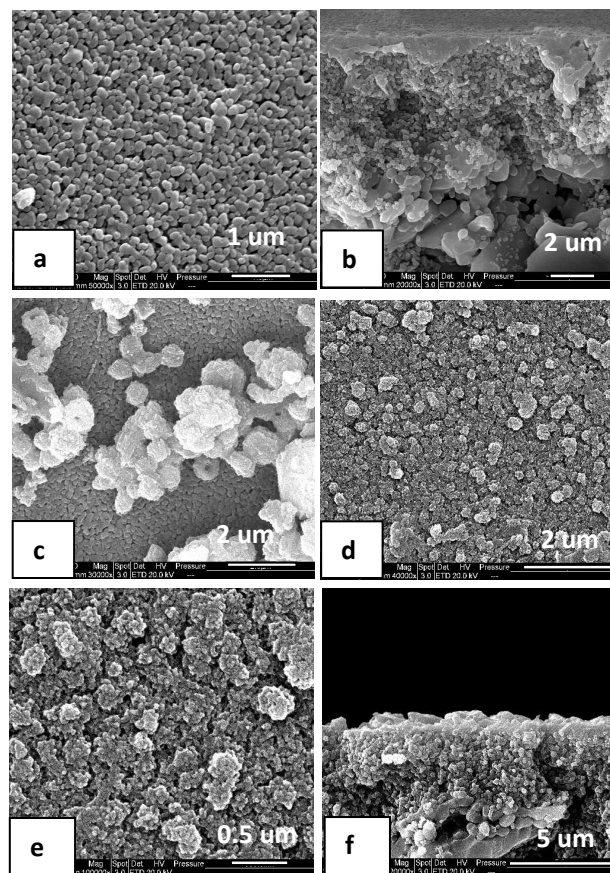


**Scheme 3.** Condensation reaction for the COF-5 membrane formation of HHTP and BDBA along with the APTES and FPBA modified  $\alpha$ - $\text{Al}_2\text{O}_3$  ceramic support.

The crystallinity and particle morphology of the bulk COF-5 powders, collected from the same reaction tube where the supported COF-5 membrane was simultaneously formed, had been studied. A powder X-ray diffraction (PXRD) pattern of the COF-5 powder showed a high degree of crystallinity (Fig. 1a), and all of the peaks at  $2\theta = 3.5, 6.0, 9.0,$  and  $26.0^\circ$ , corresponding to the (100), (110), (210), and (001) reflections respectively, which match well with ones of the COF-5 as reported previously<sup>1,21,22</sup>. The results reveal no diffraction peaks that can be assigned to the starting materials or their known solvates. In addition, the COF-5 powders have a wide particle size range of  $0.5 \sim 2.0 \mu\text{m}$ , showing the significant particle aggregation of the COF-5 powders in the bulk (Fig. 1b). Furthermore, the FTIR spectra of the COF-5 powders confirmed the formation of the expected boron-based ring, displaying the bands corresponding to the respective boronate ester ring (Fig. 1c), and the hydroxyl bands of the starting materials were strongly attenuated in the COF-5 material.



**Fig. 1.** PXRD pattern (a), SEM image (b), and FTIR spectrum (c) of the as-synthesized COF-5 powder collected in the reaction tube bottom by using the microwave irradiation growth method during fabricating the supported COF-5 membrane.



**Fig. 2.** Surface and cross-sectional SEM images of the  $\alpha$ - $\text{Al}_2\text{O}_3$  porous support (a, b), the COF-5 membrane grown on the unmodified  $\alpha$ - $\text{Al}_2\text{O}_3$  surface (c), the COF-5 membrane grown on the modified  $\alpha$ - $\text{Al}_2\text{O}_3$  surface with various scales (d, e), and the cross-sectional view (f) of the COF-5 membrane grown on the 65 modified  $\alpha$ - $\text{Al}_2\text{O}_3$  support.

Fig. 2 (a) and (b) show the SEM images of the surface and cross-section of the ceramic porous support. The asymmetrical support has a smooth and uniform surface with a pore size of  $\sim 40 \text{ nm}$ , and a thickness of the  $\alpha$ - $\text{Al}_2\text{O}_3$  layer of  $3 \sim 4 \mu\text{m}$ . The SEM image shows the discrete COF-5 layer was formed if the support surface was not treated with the covalent linkers of the APTES and FPBA, as shown in Fig.2c. On the contrary, the

SEM images indicate that the functionalized  $\alpha$ -Al<sub>2</sub>O<sub>3</sub> support was completely covered with the well intergrown COF-5 layers, with a thickness of the COF-5 membrane  $\sim 1 \mu\text{m}$  (Fig. 2d-f). No obvious cracks or defects are visible on the surface of the as-fabricated COF-5 membrane. The results indicate that the covalent linkages between the COF-5 and the porous  $\alpha$ -Al<sub>2</sub>O<sub>3</sub> ceramic support indeed facilitate the formation of the continuous and compact COF-5 layers on the functionalized porous  $\alpha$ -Al<sub>2</sub>O<sub>3</sub> ceramic support. Furthermore, Fig.3 shows the XRD pattern of the COF-5 membrane grown on the porous  $\alpha$ -Al<sub>2</sub>O<sub>3</sub> support. The XRD result confirmed the formation of the COF-5 membrane on the  $\alpha$ -Al<sub>2</sub>O<sub>3</sub> support; the poor diffraction peaks can be assigned to the as-fabricated COF-5 membrane, in addition to the strong peaks of the  $\alpha$ -Al<sub>2</sub>O<sub>3</sub> support. The COF membranes fabricated on the porous ceramic support may be promising and attractive in the gas storage, separation and enrichment fields.

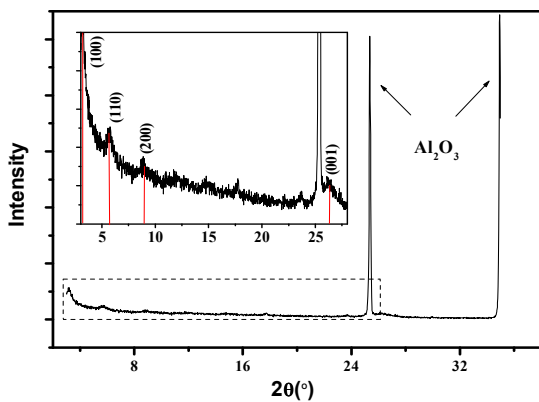


Fig. 3. XRD pattern of the supported COF-5 membrane grown on the modified ceramic  $\alpha$ -Al<sub>2</sub>O<sub>3</sub> support.

In summary, *via* the formation of the covalent linkage between the COF-5 and the  $\alpha$ -Al<sub>2</sub>O<sub>3</sub> ceramic support, we have developed a novel approach to promote the nucleation and growth of the COF-5 layered film on the porous support. This is the first COF membrane successfully fabricated and grown on a usually used porous  $\alpha$ -Al<sub>2</sub>O<sub>3</sub> support.

Financial support was provided by the Liaoning Scientific Research Starting foundation for Ph. D., Research Foundation for Ph. D. Program, and the “Hundred-Talent Program” of Dalian Institute of Chemical Physics, Chinese Academy of Sciences, China. Dr. Yong Wang was gratefully acknowledged for the structural drawing of COF-5.

## Notes and references

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<sup>†</sup> Electronic Supplementary Information (ESI) available: Materials, characterization and experimental details. See DOI: 10.1039/b000000x/

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