## Electronic supplementary information (ESI)

## Theoretically Designed Two–Dimensional γ-C<sub>4</sub>O as Effective Gas

## Separation Membrane for Hydrogen Purification

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Fig. S1 Schematic illustration of the first Brillouin zone of  $\gamma$ -C<sub>4</sub>X



**Fig. S2** (a) Top view and (b) side view of  $\gamma$ -C<sub>4</sub>O after 10 ps FPMD simulation at 300K, and (c) temperature and (d) total energy changes during the simulation. Grey and red balls stand for C and O atoms.



Fig. S3 (a) Top view and (b) side view of  $\gamma$ -C<sub>4</sub>O after 10 ps FPMD simulation at 600K, and (c) temperature and (d) energy changes during the simulation. Grey and red balls stand for C and O atoms.



**Fig. S4** (a) Top view and (b) side view of  $\gamma$ -C<sub>4</sub>S after 10 ps FPMD simulation at 300K, and (c) temperature and (d) energy changes during the simulation. Grey and yellow balls stand for C and S atoms.



Fig. S5 (a) Top view and (b) side view of  $\gamma$ -C<sub>4</sub>S after 10 ps FPMD simulation at 600K, and (c) temperature and (d) energy changes during the simulation. Grey and yellow balls stand for C and S atoms.



**Fig. S6** (a) Top view and (b) side view of  $\gamma$ -C<sub>4</sub>Se after 10 ps FPMD simulation at 300K, and (c) temperature and (d) energy changes during the simulation. Grey and brown balls stand for C and Se atoms.



**Fig. S7** (a) Top view and (b) side view of  $\gamma$ -C<sub>4</sub>Se after 10 ps FPMD simulation at 600K, and (c) temperature and (d) energy changes during the simulation. Grey and brown balls stand for C and Se atoms.



Fig. S8 Electron densities of the TS structures for  $H_2$ ,  $O_2$ ,  $CO_2$ ,  $CO_2$ ,  $CO_3$ ,  $N_2$  and  $CH_4$  penetrating  $\gamma$ -C<sub>4</sub>S. The isovalue is 0.021 e Å<sup>-3</sup>.



**Fig. S9** Selectivity *versus* temperature for  $H_2/O_2$ ,  $H_2/CO_2$ ,  $H_2/CO_2$ ,  $H_2/N_2$ ,  $H_2/CH_4$  and  $CO_2/CH_4$  separation by  $\gamma$ -C<sub>4</sub>O. The solid and dash lines stand for selectivity derived from the permeance and from the diffusion rate, respectively.



Fig. S10 The geometric structure of (a)  $\gamma$ -graphyne and (b) graphdiyne, with the size of intrinsic pore being marked.

**Table S1.** Top view and side view of the structures of Initial State (IS), Transition State (TS) and Final State (FS) for H<sub>2</sub>, O<sub>2</sub>, CO<sub>2</sub>, CO, N<sub>2</sub> and CH<sub>4</sub> passing through the intrinsic pore of  $\gamma$ -C<sub>4</sub>O.

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		IS	TS	FS
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**Table S2.** Top view and side view of the structures of IS, TS and FS for  $H_2$ ,  $O_2$ ,  $CO_2$ ,  $CO_3$ ,  $N_2$  and  $CH_4$  passing through the intrinsic pore of  $\gamma$ -C<sub>4</sub>S.

		IS	TS	FS
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	Side View	••••••	~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~	••••••
CO <sub>2</sub>	Top View			
	Side View	*******	*******	••••••
СО	Top View			
	Side View	•••••••	******	• • • • • • • • • • • • • • • • • • •
N <sub>2</sub>	Top View			
	Side View	•••••	*****	• • • • • • • •
CH <sub>4</sub>	Top View			
	Side View	یقی • • • • • • • • • •	00000000000000000000000000000000000000	محمد محمد م پلان

**Table S3.** Top view and side view of the structures of IS, TS and FS for  $H_2$ ,  $O_2$ ,  $CO_2$ ,  $CO_3$ ,  $N_2$  and  $CH_4$  passing through the intrinsic pore of  $\gamma$ -C<sub>4</sub>N.