SUPPLEMENTARY INFORMATION

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1 CREATION OF THE FUNCTIONALIZED NANOPORES

In our work, three different functionalized nanopores on monolayer graphene are designed and the theoretical creation processes of them are displayed in Fig. S1. First of all, the carbon atoms which are marked with red color in a sheet of pristine graphene nameed OS are removed. As a result, there will be nine unsaturated carbon atoms (marked with yellow) at the rim. Then, some (all) of these unsaturated carbon atoms either be passivated with hydrogen atoms or be substituted with nitrogen atoms. By reasonably arranging the positions of hydrogen and nitrogen atoms in the rim, different kinds of functionalized nanopores will be created. The three different nanopores involved in our work are shown in the second row of Fig. S1. The first nanopore (named I_S) is terminated by positively charged hydrogens. For the second nanopore (named II_S), six of the unsaturated carbon atoms are passivated with hydrogen atoms while the rest of the unsaturated carbon atoms are substituted with nitrogen atoms. The third nanopore (named III_S) is terminated by negatively charged nitrogens. As we all know, the size and shape of the nanopore are the essential parameters for the graphene membrane-based separation process. In our research, the electron density isosurfaces are empoyed to characterize these two parameters. The third row of Fig. S1 displays the electron density isosurfaces of the three nanopores. As is well-known, nitrogen substitution was found to be a suitable way to fine-tune the size and shape of nanopores in graphene.[1, 2, 3] In our case, the nanopore's size increases with increasing of the nitrogen atom number. Meanwhile, the nitrogen atom also exertes considerable influence on the nanopore's shape. In practice, as reported before, nitrogen doping of carbon nanotubes and graphene can be readily accomplished in the laboratory.[4, 5, 6, 7] These positive results indicate that our graphene with functionalized nanopores will probably be prepared experimentally rather than theoretically.

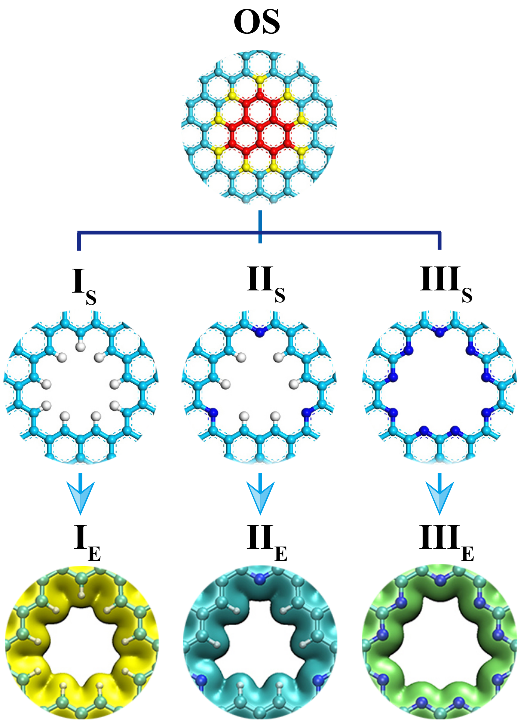

Fig. S 1: Creation the functionalized nanopores. A sheet of pristine graphene named OS is shown in the first row. The carbon atoms marked with red will be removed. Meanwhile, the carbon atoms marked with yellow will be passivated or substituted with hydrogen or nitrogen atoms, respectively. The three nanopores created in our work are shown in the second row. The corresponding electron density plots (isovalue is 0.01 a.u.) are shown in third row. Carbon is printed in cyan, hydrogen in white, and nitrogen in blue.

2 INFLUENCE OF NANOPORE SIZE ON THE SEPARATION PERFORMENCE

As shown in Fig. S1, we have designed three kinds of nanoporous graphene membrane in our research. By analysing the MD simulations results, we can figure out the most suitable membrane for the C_2H_2/C_2H_4 separation. The MD simulations (nanopre density is 12 n.u., total simulation time is 30 ns) results are shown in Fig. S2. As we can see, the first nanopore I_S (Fig. S2a) can separate C_2H_2 and C_2H_4 more efficiently (SF ~ 16) than nanopore II_S (Fig. S2b) and III_S (Fig. S2c), but its permeability is too small (N ~ 16 for C_2H_2). For the third nanopore III_S, the permeability is the largest (~82 for C_2H_2 and ~53 for C_2H_4), but its SF value (~ 1.5) is the samllest. Overall, by comparing the permeability and SF values of each nanopore, we find that the second nanopore II_S is the most suitable nano-structure for the separation task due to its relatively large permeability (N ~ 57 for C_2H_2) and SF value (~ 9.7). Such a result is mainly caused by the difference of nanopore size. Hence we will focus on II_S in the following research.

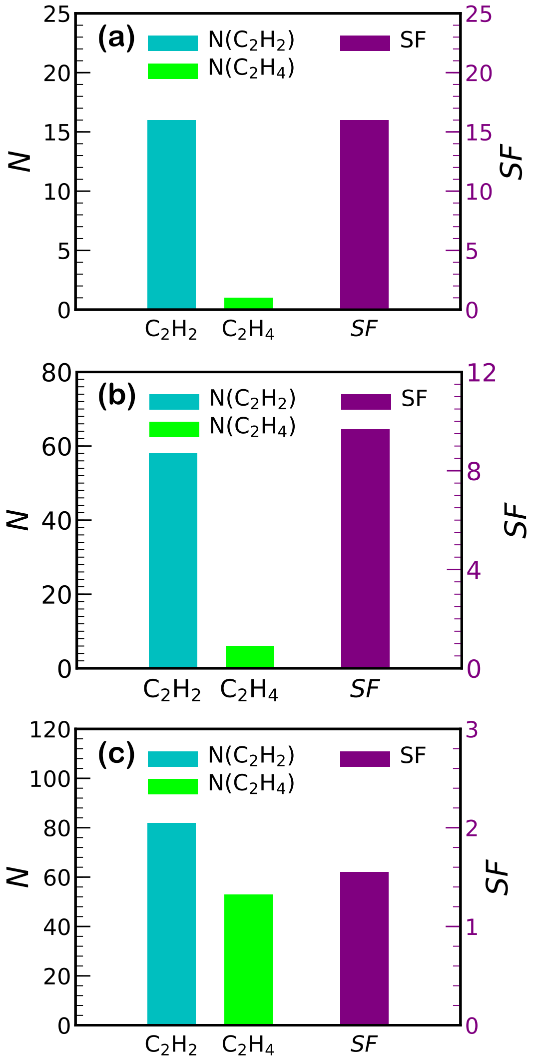

Fig. S 2: The number of passing C_2H_2 and C_2H_4 gas molecules (permeability) through the three nanopores and the corresponding separation factor (SF) of C_2H_2 over C_2H_4. Nanopre density: 12 n.u.; total simulation time: 30 ns. (a) for I_S, (b) for II_S, and (c) for III_S.

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