Supporting Information

Creation of hierarchical structures within membranes by incorporating mesoporous microcapsules for enhanced separation performance and stability

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1. Molecular structures of dopamine and Ti-BALDH

Figure S1 Molecular structures of (a) dopamine and (b) Ti-BALDH.
2. **Schematic of the mineralization process upon removing the template**

**Figure S2** Schematic of the mineralization process upon removing the CaCO3 template
3. SEM image of the microcapsules

**Figure S3.** SEM image of the DATi microcapsules with different synthesizing conditions.
4. **FTIR spectra analysis of the membranes**

The FTIR spectra of the PDMS control and PDMS-DATi membranes were recorded in Figure 5(a). The characteristic peak at about 788 cm$^{-1}$ was corresponded to the stretching vibrations of Si-C in the membranes. The characteristic peaks appeared at around 1009 and 1084 cm$^{-1}$ represented the stretching vibrations of Si-O-Si. The characteristic peak at about 1257 cm$^{-1}$ assigned to the deformation vibrations of the two -CH$_3$ linked with Si. The weak absorption peaks around 1410 and 2960 cm$^{-1}$ were the dissymmetry deformation vibrations of -CH$_3$ joined with Si and stretching vibrations of C-H, respectively. The FTIR spectra of the PDMS-DATi membranes did not generate new absorption peaks compared with the PDMS control membrane, revealing that the DATi microcapsules were physically blended within the PDMS matrix.
5. **TGA measurements of the microcapsules**

The TGA of DATi microcapsules was shown in Figure 9. The thermal decomposition of DATi microcapsules could be divided into three stages. The first stage indicated a loss of 3.2 wt%, between 40 and 150 °C, attributed to the elimination of adsorbed water on the surface of microcapsules. The second stage indicated a loss of 12.4 wt%, between 150 and 670 °C, probably due to the decomposition of polymerized dopamine in the microcapsules. And the third stage from 670 to 800 °C was the decomposition of dopamine chelated on the Ti-O-Ti frameworks. The superior thermal stability of DATi microcapsules was arisen from the steady Ti-O-Ti frameworks and strong metal-organic coordination between Ti(IV) and dopamine.
6. FTIR spectra of the DATi(2.1.2.2), DATi(2.2.2.2) and DATi(2.3.2.2) microcapsules

![FTIR spectra](image)

**Figure S4.** FTIR spectra of the DATi(2.1.2.2), DATi(2.2.2.2) and DATi(2.3.2.2) microcapsules.
7. Arrhenius relationship for permeation of n-octane and thiophene through the membranes

Figure S5. Arrhenius plots of permeation flux for separation of thiophene/n-octane mixture by (a) PDMS control and (b) PDMS-DATi membranes for a feed of 1,500 ppmw thiophene in n-octane with a flow rate of 40 L h⁻¹.