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

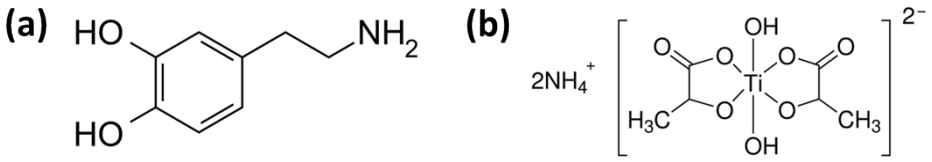

Figure S1 Molecular structures of **(a)** dopamine and **(b)** Ti-BALDH.

2. *Schematic of the mineralization process upon removing the template*

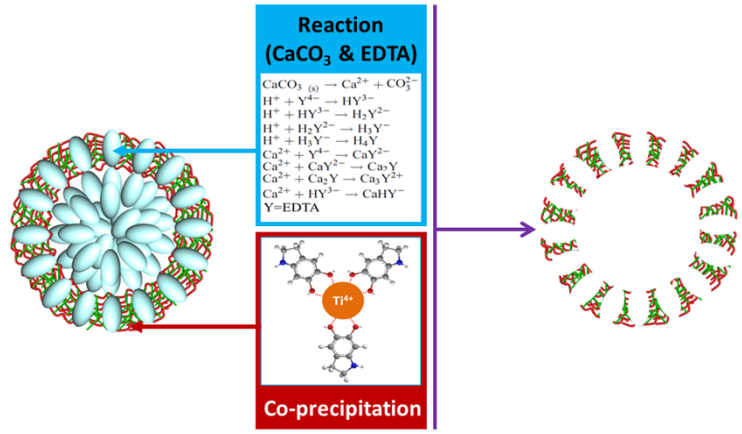

Figure S2 Schematic of the mineralization process upon removing the CaCO3 template

3. SEM image of the microcapsules

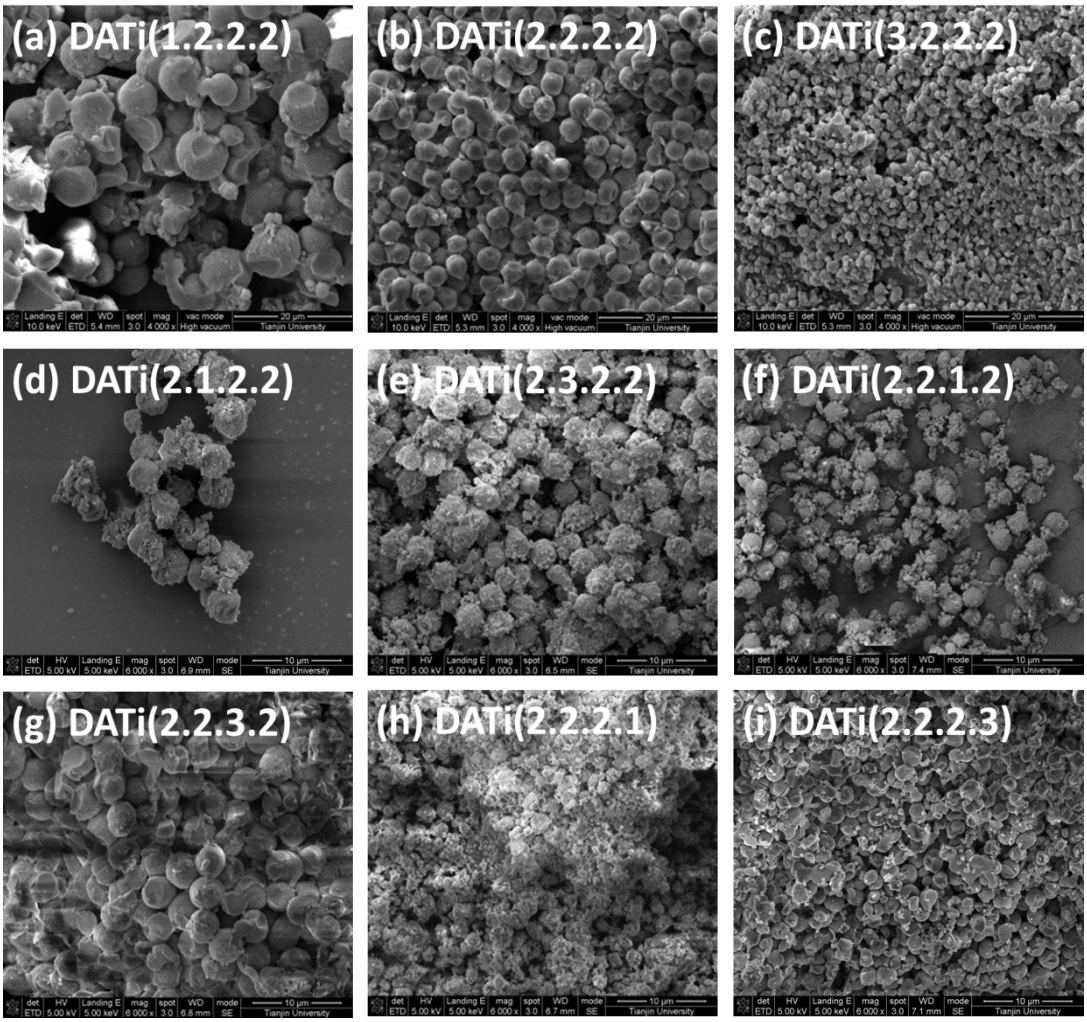

Figure S3. SEM image of the DATi microcapsules with different synthesizing conditions.

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 ^{o}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 ^{o}C, probably due to the decomposition of polymerized dopamine in the microcapsules. And the third stage from 670 to 800 ^{o}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

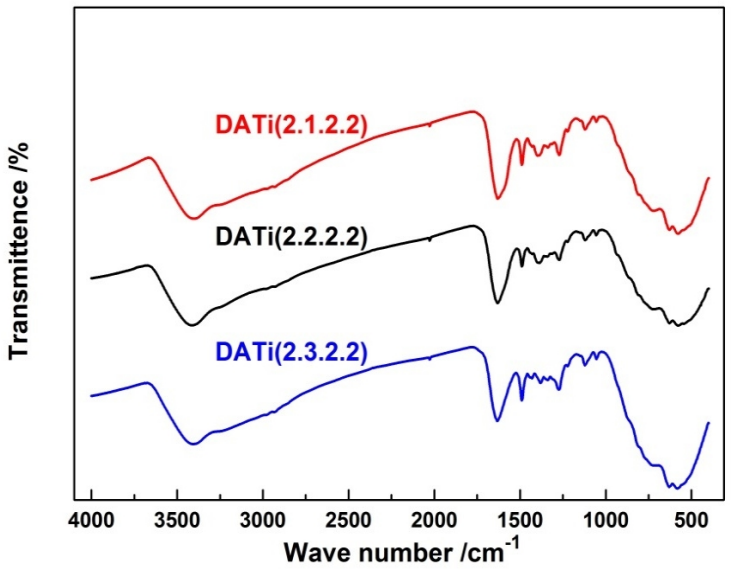

Figure S4. FTIR spectra of the DATi(2.1.2.2), DATi(2.2.2.2) and DATi(2.3.2.2) microcapsules.

7. Arrhenius relationship for permeation of n-octane and thiophene through the membranes

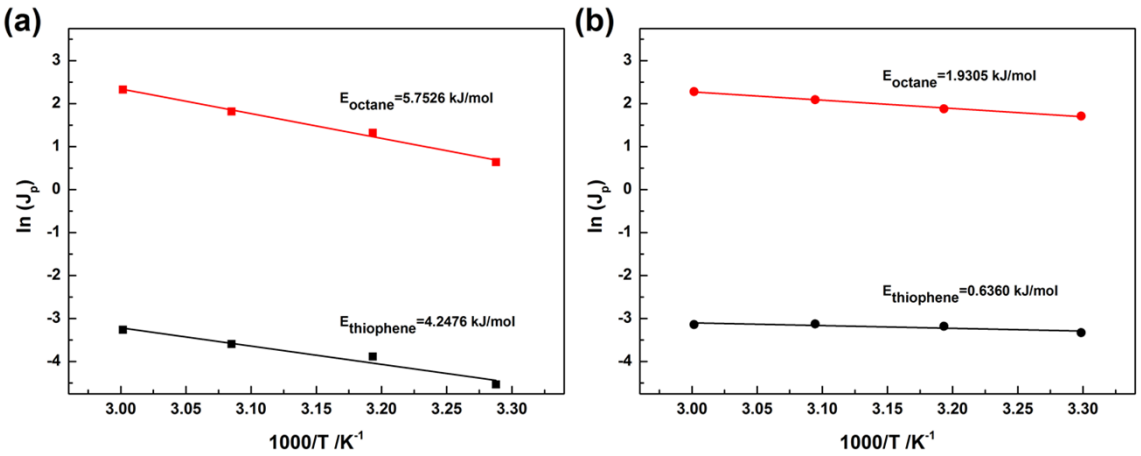

Figure S5. Arrhenius plots of permeation flux for separation of thiophene/*n*-octane mixture by (a) PDMS control and (b) PDMS-DATi membranes for a feed of 1,500 ppmw thiophene in *n*-octane with a flow rate of 40 L h^{-1}.