

Supplementary Information

Liquid-like CNT/SiO₂ nanoparticle organic hybrid materials as fillers in mixed matrix composite membranes for enhanced CO₂ selective separation

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1. Preparation of nanoparticle organic hybrid materials (NOHMs) based on CNT/SiO₂ composite core

The preparation of nanoparticle organic hybrid materials (NOHMs) can be found elsewhere [1,2]. In a typical run, the acidified CNT were firstly obtained using mixed acids (H₂SO₄/HNO₃, volume ratio= 3:1) under ultrasonic stirring conditions at 50 °C for 4 h. Then the resulting products were washed with deionized water until pH was 7 and then dried at 100 °C for 8 h to remove any residual water. Subsequently, the as-prepared acidified CNT was placed into desiccators for following experiments.

Specifically, a molar equivalence of KH560 was diluted with methanol to obtain 5.0 wt% solution and was added dropwise into diluted polyetheramine M2070 (10.0 wt% methanol solution). The resulting mixed solution was stirred for 12 h at 50 °C.

Then the composite core (the weights of two components of each NOHMs are shown in Table 1) was mixed with methanol under ultrasound dispersion for 30 min. Then the composite core CNT/SiO₂ was continuously stirred at 25 °C for 1 h to deposit SiO₂ particles on the surface of acidified CNT, and then added to the above mixed solution.

Subsequently, the mixture was reacted at 25 °C for 6 h under stirring conditions. Next, the resulting solution was dialyzed with dialysis bag (3500 MWCO) for 48 h to remove any excessive unbounded polyetheramine-silane. The solvent was removed under vacuum at 70 °C for 72 h. Finally, the black liquid-like NOHMs based on CNT/SiO₂ composite core were obtained as depicted in Fig. 2. For comparison, NOHMs based pure SiO₂ as core was also prepared, which was abbreviated as NOHMs-SiO₂. The preparation process was the same as the NOHMs based on CNT/SiO₂ composite core.

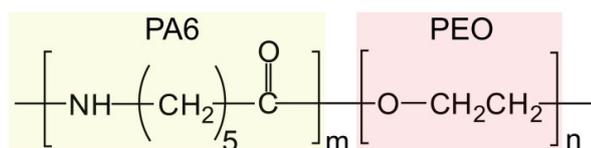


Fig. S1 The chemical structure of Pebax-1657 (the weight ratio of PA6 to PEO (x:y) is 40:60).

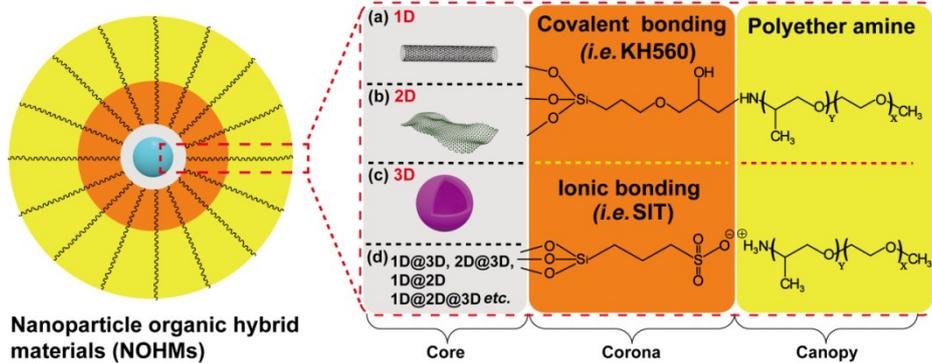


Fig. S2 The structure illustration of typical structure of NOHMs.

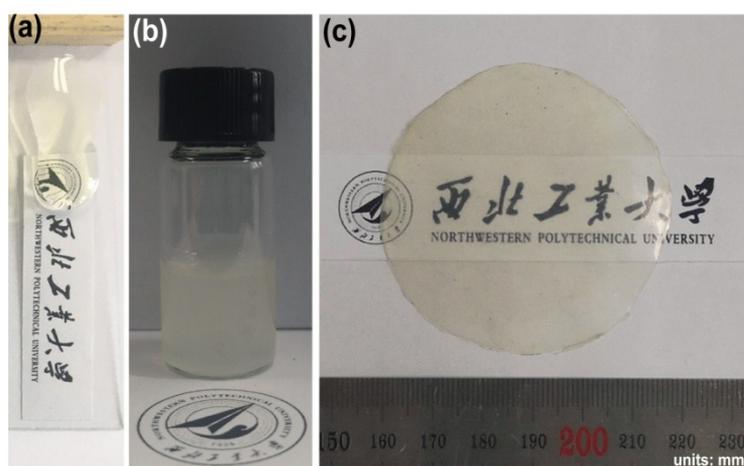


Fig. S3 (a) The optical images of NOHMs-SiO₂, (b) Solubility of NOHMs-SiO₂ in Pebax solution, and (c) Digital photos of NOHMs-SiO₂-(10) membrane.

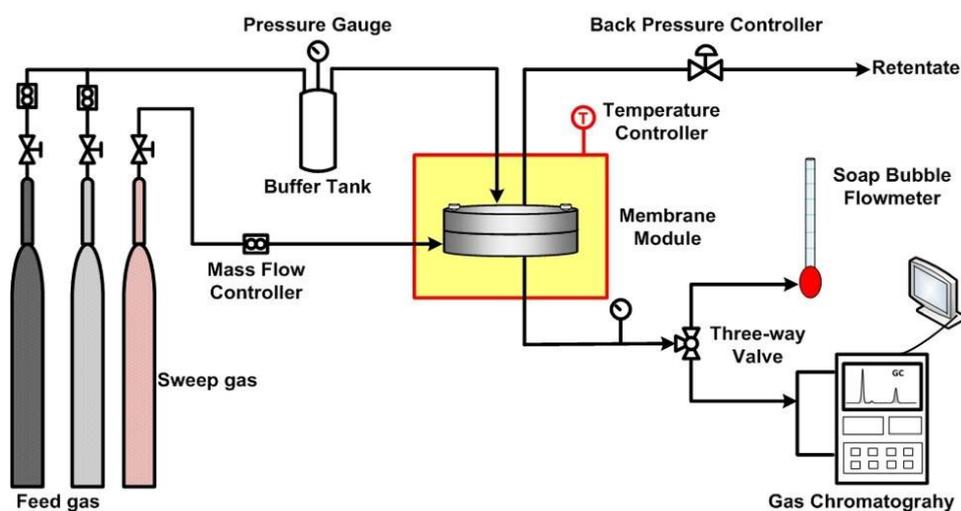


Fig. S4 Schematic diagram of gas permeation apparatus.

2. Characterizations of CNT/SiO₂ NOHMs

TGA

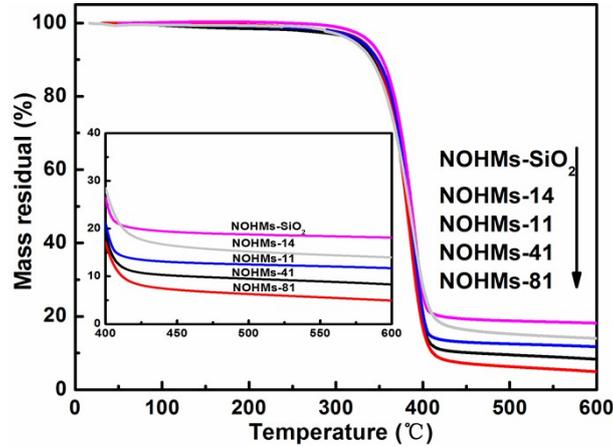


Fig. S5. The TGA curves of NOHMs.

The TGA curves of NOHMs were shown in Fig. S5. Obviously, NOHMs are in a solvent-free, liquid-like state at room temperature which can be confirmed by the fact that there is almost no weights loss below 300 °C [3]. This is due to the long, flexible chains of the polyetheramine canopy M2070. Meanwhile, a great mass loss is observed above 350 °C because of complete decomposition of KH560-M2070 (the corona and canopy of NOHMs) [4].

Therefore, it can be calculated that contents of core of NOHMs-81, NOHMs-41, NOHMs-11, NOHMs-14, and NOHMs-SiO₂ were 5.4%, 4.9%, 11.6%, 13.7%, and 18.1%, respectively. The filler loading was determined according to these values of core content as described in Eq. (1). For example, the filler content of P- NOHMs-81-(20) is calculated as follows:

$$\text{The NOHMs-81 filler content of P-NOHMs-81-(20) (g)} = \frac{m_{\text{Pebax}} \times 20\%}{5.4\%} \quad (1)$$

FT-IR

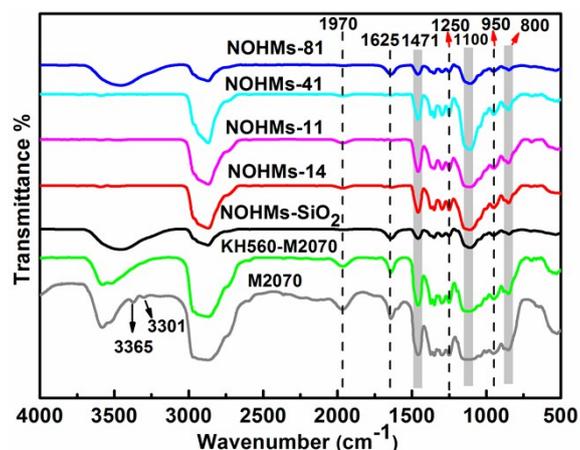


Fig. S6. FT-IR spectra of samples in the preparation process of NOHMs.

FT-IR spectra (Fig. S6) of NOHMs were illustrated to verify that organic chains were grafted onto the surface of cores successfully. Compared with KH560-M2070, the disappearance of absorption peaks in pristine M2070 (3301 cm⁻¹ and 3365 cm⁻¹) confirms the successful reaction between KH560 and M2070. Meanwhile the significant absorption band at 1290 cm⁻¹ is attributed to the secondary amine group (-NH-) vibrations, which is consistent with the literature [5]. This is due to the successful reaction between epoxy groups of KH560 and the -NH₂ of M2070. Moreover, the absorption bands at 1000-1200 cm⁻¹ and 800 cm⁻¹ are ascribed to Si-O-Si(C) vibrations and O-Si-O vibrations, respectively. All of these results confirm the successful preparation of CNT/SiO₂ NOHMs [1,2].

DSC

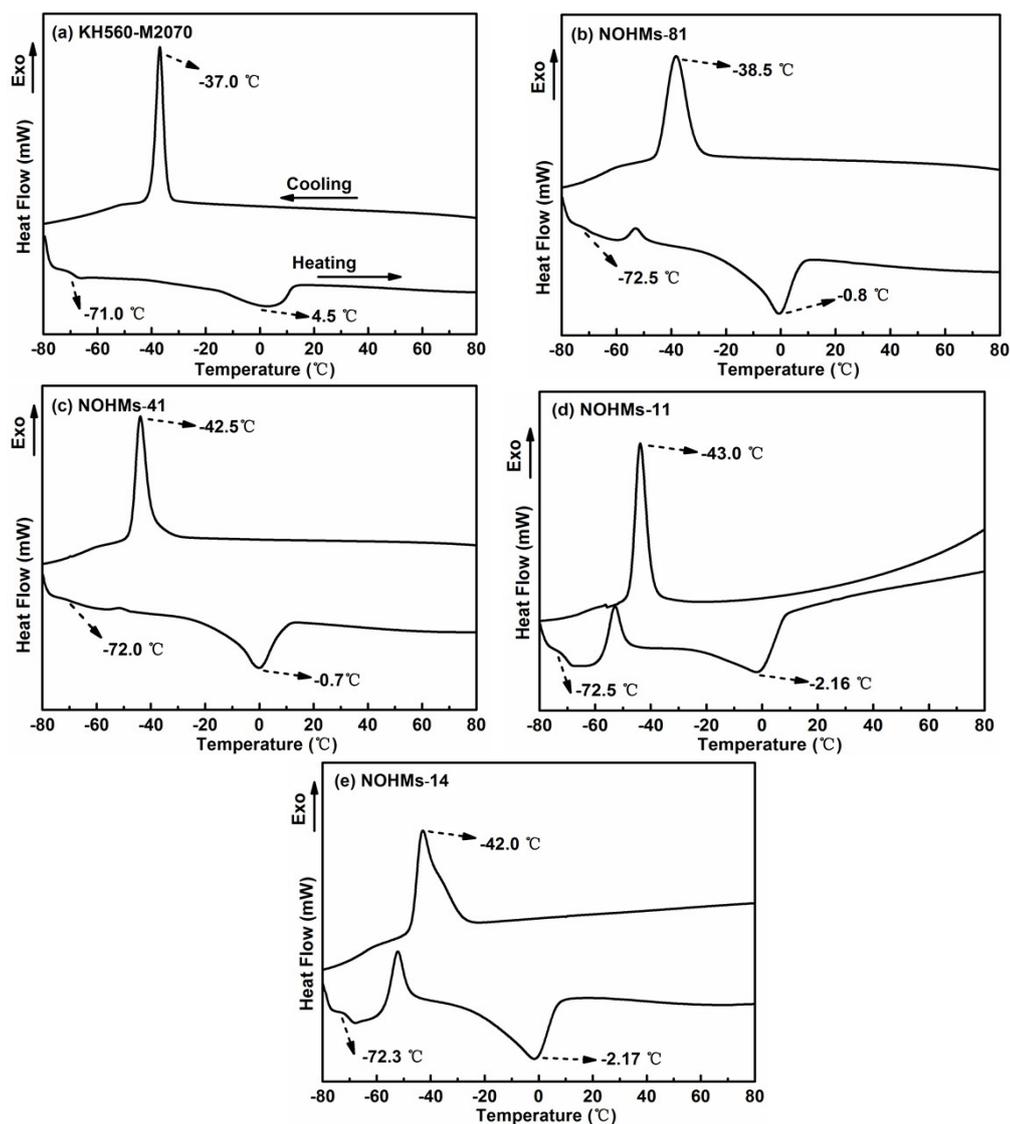


Fig. S7. DSC curves of KH560-M2070 and NOHMs, (a) KH560-M2070, (b) NOHMs-81, (c) NOHMs-41, (d) NOHMs-11, and (e) NOHMs-14.

DSC was employed to investigate thermal property of NF as shown in Fig. S7. The crystallizing point (T_c) of NOHMs-81, NOHMs-41, NOHMs-11, NOHMs-14 and KH560-M2070 are -37.0 °C, -38.5 °C, -44 °C, -43.0 °C and -44 °C, respectively. The decreasing or increasing T_c was related to addition of the core CNT/SiO₂. T_c is influenced by both flexibility of molecule chains and the addition of core [3]. In this study, the canopy is the same, while the composition of the core CNT/SiO₂ in NOHMs is different. From Fig. S7, the T_c decreased with increase in the weigh ratio of SiO₂ to CNT. It is because there will be more chains of canopy, which consists with the TGA analysis.

Viscosity curves

In order to further confirm the liquid-like behavior of NOHMs, the viscosity curves were performed as shown in Fig. S8. It is obviously found that viscosity is stable at 25 °C which also reveals the fluid property. Besides, the viscosity is increased with increasing weight ratio of SiO₂ to CNT. The reason is that the SiO₂ with small spherical structure acts as lubricant in NOHMs. Besides, more long organic chains (corona and canopy) are coated onto the surface of cores at higher weight ratio of SiO₂ to CNT, which is also consistent with the TGA analysis.

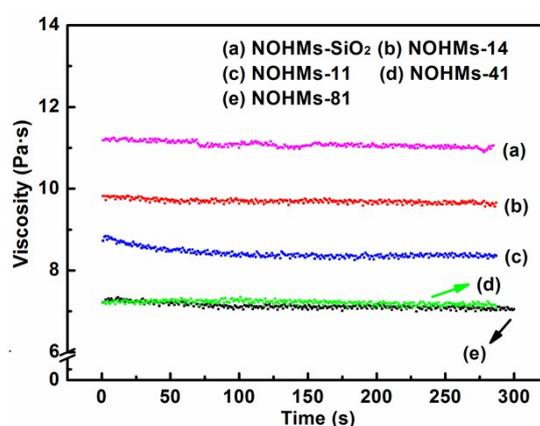


Fig. S8 Viscosity curves of NOHMs at 25 °C

References

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