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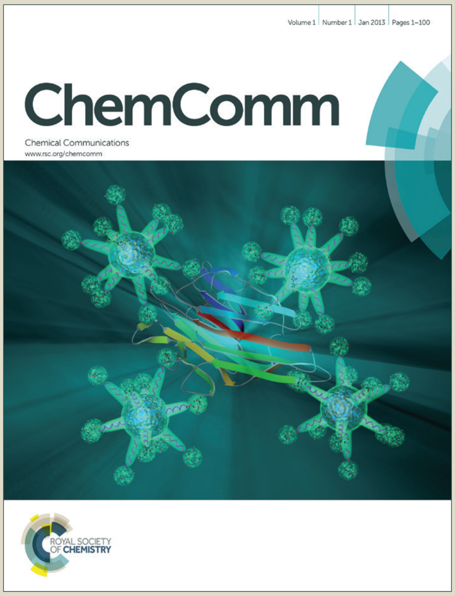

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Dual-Functionalized Mesoporous TiO_2 Hollow Nanospheres for Improved CO_2 Separation Membranes

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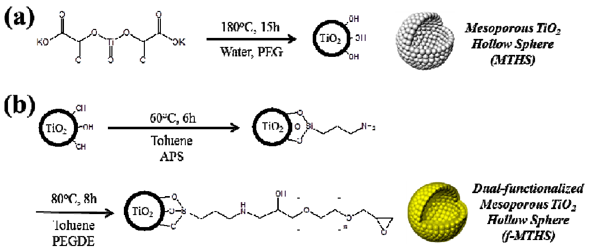
Simultaneous improvement in CO_2 permeability and CO_2/N_2 selectivity was obtained from mixed matrix membranes (MMMs) containing dual-functionalized mesoporous TiO_2 hollow nanospheres (f-MTHS). Dual functionality resulted in the increased CO_2 affinity and improved interfacial properties between inorganic nanofillers and polymer matrix.

Gas separation through membranes is a promising solution for the stabilization of greenhouse gas levels in the atmosphere due to CO_2.[1,2] Membrane processing has advantages including low energy requirements, low cost, and ease of operation.[3,4] However, most polymer membranes show a trade-off behavior between permeability and selectivity. Mixed matrix membranes (MMMs), consisting of a polymer and inorganic filler as an organic matrix and dispersed phase, are considered to be a promising solution to overcome the trade-offs in polymeric membranes, and have been studied by many researchers.[5,6] It was reported that some MMMs containing inorganic fillers such as ZIF,[7] MOF[8] and POF[9] were effective in improving gas permeation properties due to a size exclusive sieving mechanism. However, many MMMs are prepared using nonporous or microporous filler with small pore sizes (0.7-2.0 nm), and thus the diffusion transport is often hindered while the solution transport is not fully utilized. Thus, it is still challenging to simultaneously improve the permeability and selectivity even in MMMs.[10-13] Here, we report an effective way to obtain simultaneous improvement in the CO_2 permeability and the CO_2/N_2 selectivity based on MMMs consisting of amphiphilic graft copolymer and dual-functionalized mesoporous TiO_2 hollow nanospheres (f-MTHS).



Scheme 1. Synthesis of (a) mesoporous TiO_2 hollow sphere (MTHS) and (b) dual-functionalized mesoporous TiO_2 hollow sphere (f-MTHS).

Titanium dioxide (TiO_2), an inexpensive and non-toxic metal oxide, has recently received a great deal of attention due to its excellent properties in photocatalytic applications.[14,15] However, most TiO_2 is typically less porous, leading to reduced diffusivity, and thus was not effective in membranes to remove CO_2. Thus, first we synthesized mesoporous TiO_2 hollow nanosphere (MTHS) with higher porosity through a hydrothermal reaction at 180 °C for 15 h using potassium titanium oxide oxalate dehydrate (PTO), water, and poly(ethylene glycol) (PEG), as shown in **Scheme 1a**. The formation of hollow MTHSs was confirmed by scanning electron microscopy (SEM) and transmission electron microscopy (TEM), as shown **Figure 1a-c**. MTHSs showed an outer diameter of 280 ± 30 nm, an inner diameter of 250 ± 30 nm, and a wall thickness of 28± 2 nm. Also, the MTHSs consisted of numerous nano-sized TiO_2 crystals approximately 16 nm in size, indicating that multitudinous mesopores can be formed between the nano-sized crystals in the shell of the MTHSs.

The formation mechanism of the hollow structure is based on the Ostwald ripening process, by which small particles inside the solid sphere are dissolved and grow on the outside of the sphere. In the hydrothermal reaction, PEG works as a capping agent and slows down the hydrolysis of PTO to provide control over crystal growth and organization, eventually generating a hollow structure. By slowing down the reaction rate and choosing a suitable precursor such as PTO, a variety of nanostructures with different sizes and shapes are obtainable. Without PEG such nanostructures were not formed, rather, only irregular small nanoparticles were generated. The mesoporous hollow structure in MMMs plays an important role in promoting the gas permeability due to the following dual functionalities. First, the pores on the surface allow for easier diffusion transport of small gas molecules. Second, the hollow structure makes it possible for the gases to pass rapidly through the vacant space inside the sphere, in which there is no steric hindrance to obstruct the movement of gases, resulting in increased permeability of gas.

However, TiO_2 is one material that does not have a specific interaction with CO_2, resulting in lower solubility. Also, the other critical issue in MMMs is to remove void formation at the interface between the inorganic and organic phases, which results in reduced selectivity. Thus, the surface of MTHS was covalently modified to provide dual-functionality using (3-aminopropyl)-trimethoxysilane (APS) and poly(ethylene glycol) diglycidyl ether (PEGDE), which help increase CO_2 affinity as well as improve interfacial contact with the polymer matrix, as shown in **Scheme 1b and Figure 1d**. Basic polar groups such as ethylene oxide units and amines are known to have a great affinity for acidic CO_2 molecules through acid-base interaction, resulting in a high solubility of CO_2 molecules.[16,17] As a result, the f-MTHS has

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† Electronic Supplementary Information (ESI) available: Experiment, BET and BJH plots, cross-sectional SEM image of MMM, photos of MMMs. See DOI: 10.1039/b000000x/

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a possibility of enhancing both CO$_2$ permeability and CO$_2$/N$_2$ selectivity. Furthermore, these functional groups on the f-MTHS surface may strongly interact with the polymer matrix containing ethylene oxide units, possibly improving adhesion between the inorganic f-MTHS phase and the organic polymer matrix phase. This may result in better dispersion of nanofiller in the polymer matrix and elimination of defects between both organic/inorganic phases. Poor miscibility and defects between the two phases should be avoided due to the detrimental impact on the mechanical and separation properties of membranes.

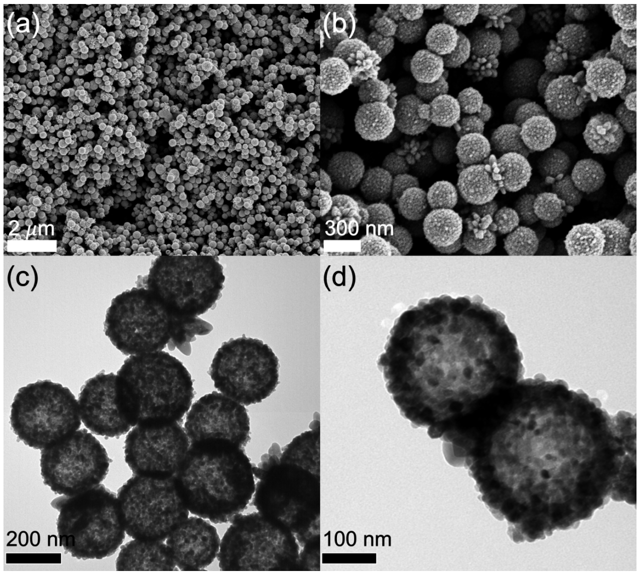

Figure 1. (a, b) SEM images of MTHS, (c) TEM image of MTHS, (d) and TEM image of f-MTHS.

The surface modification of MTHS with APS and PEGDE was confirmed by FT-IR spectroscopy, as shown in **Figure 2a**. The -OH groups on the TiO$_2$ surface can easily react with the silane of APS; thereafter, epoxide-functionalized PEG molecules such as PEGDE were covalently grafted onto the aminosilane modified TiO$_2$ surface. The FT-IR spectrum of f-MTHS showed characteristic peaks at 2926, 1635, 1549 and 1035 cm^{-1}, which are assigned to the C–H stretching, N-H deformation, N–H bending and Si–O bond of APS, respectively. The new characteristic peaks at 2870 and 1100 cm^{-1} were also observed from f-MTHS due to C–H asymmetric stretching and C–O–C stretching vibrations of PEGDE, respectively, indicating successful modification of MTHS with APS and PEGDE. The amount of grafted PEGDE and APS was verified by TGA analysis, as seen in **Figure S1**. The TGA curve of f-MTHS exhibited a two-step degradation mode at 230–370 and 370–540 °C, respectively. It was found that approximately 15 % of the organic materials were grafted on the f-MTHS surface, which is an appropriate value for MMM performance. This is because a higher grafting degree could be advantageous in selectivity enhancement, but the permeability was reduced due to the blockage of pores with organic chains.

The surface area of f-MTHS (29.3 m^2/g) was reduced compared to neat MTHS (45.9 m^2/g) due to some surface blockage by PEGDE, supporting surface modification of MTHS. Thus, pore size distribution curves were significantly different between MTHS and f-MTHS. As shown in **Figures 2b, S2**, a Gaussian-like distribution curve was observed for neat MTHS with a maximum pore diameter of 18 nm. The peak maximum intensity was significantly reduced and shifted to a smaller pore diameter of 6 nm, after which the pore volume continuously increased with pore diameter. This probably results from surface modification of MTHS with APS and PEGDE because of the additional pores of the organic molecules, which contribute to additional free-volume formation. The pore sizes of MTHS and f-MTHS are much larger than the pore size of the microporous nanoparticles commonly used in MMMs,[5-9] suggesting they would be effective in facilitating gas transport via Knudsen diffusion through mesopores.

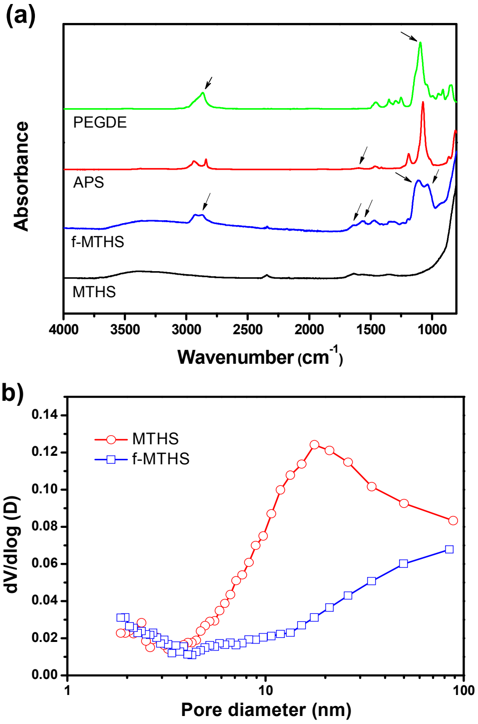

Figure 2. (a) FT-IR spectra of MTHS, f-MTHS, APS and PEGDE, and (b) Pore size distribution of MTHS and f-MTHS.

An amphiphilic graft copolymer consisting of poly(vinyl chloride) (PVC) main chains and poly(oxyethylene methacrylate) (POEM) side chains, i.e., PVC-g-POEM, was synthesized via atom transfer radical polymerization (ATRP) and was used as a matrix in MMMs. The PVC-g-POEM graft copolymer is microphase-separated into hydrophobic glassy PVC domains and the hydrophilic rubbery POEM domains, providing good dimensional stability of MMMs. Also, the chemical similarity of PVC-g-POEM and f-MTHS through ethylene oxide-based functionality provides good interfacial contact of the organic/inorganic phases, resulting in good mechanical properties; thus, all MMMs were mechanically strong with thicknesses of 70 μm. Furthermore, the coil size (~ 40 nm) of the PVC-g-POEM graft copolymer was larger than the pore size of f-MTHS surface (~ 6 nm), as determined from the relation: $R_g = 0.063 \times M_w^{0.5}$, where R_g is the radius of gyration. Thus, the Knudsen diffusion through f-MTHS mesopores might not be hindered by pore-filling of the graft copolymer.

As shown in the cross-sectional SEM image of **Figure S3,** the f-MTHSs were uniformly and well dispersed in the polymer matrix to have a good interfacial contact between the inorganic f-MTHS and organic PVC-*g*-POEM phases without any voids or cracks. The PVC-g-POEM graft copolymer membrane becomes translucent with increasing f-MTHS content, as shown in **Figure**

S4. Due to the high porosity, the density of f-MTHS (2.3 g/cm^3) is much lower than that of nonporous TiO_2 (4.23 g/cm^3) and is not significantly higher than that of PVC-g-POEM (1.3 g/cm^3). Also, the chain-chain entanglement and secondary bonding interactions between f-MTHS and PVC-g-POEM assist in providing a uniform distribution of f-MTHS.

Table 1. Pure gas permeability (P) and selectivity of CO_2/N_2 of the MMMs with different amounts (wt %) of f-MTHS and 20wt% of MTHS measured at 800 mmHg and 35 °C.

	$P(CO_2)$ (Barrer)	$P(N_2)$ (Barrer)	Selectivity (CO_2/N_2)
Neat polymer	44.81	1.17	38.3
f-MTHS10	71.18	1.84	38.7
f-MTHS20	79.33	1.93	41.1
f-MTHS30	85.41	1.97	43.4
MTHS20	127.35	7.18	17.7

To verify the feasibility of membranes for CO_2 separation, the pure gas permeation properties and CO_2/N_2 ideal selectivity through the MMMs were measured via time-lag method and are summarized in **Table 1**. The CO_2 permeability and selectivity of the neat PVC-*g*-POEM membrane were 44.81 Barrer and 38.3, respectively. Addition of unmodified MTHS at 20 wt.% significantly increased the CO_2 permeability to 127.35 Barrer, but the selectivity was diminished to 17.7, which is a typical trade-off behavior in gas separation membranes. In unmodified MTHS systems, the major factor influencing the gas permeation properties is Knudsen diffusion through the hollow spaces inside the MTHS, in which diffusion is inversely proportional to the square of gas molecular weight. Because the molecular weight of CO_2 (44 g/mol) is larger than that of N_2 (28 g/mol), N_2 gas can quickly transport through the MTHS inside, resulting in a decrease in the selectivity of CO_2/N_2. Furthermore, unmodified MTHS lacks an interfacial interaction with the polymer matrix, which provides interfacial defects between two phases resulting in a decrease in selectivity.

It is a great challenge to improve both permeability and selectivity because conventional polymer membranes and even many MMMs suffer from a trade-off between permeability and selectivity. Nevertheless, we obtained excellent results by introducing f-MTHS into the membrane. Compared to the neat PVC-*g*-POEM membrane, both permeability and selectivity of MMMs containing f-MTHS were simultaneously and continuously increased with f-MTHS loading. The CO_2 permeability was increased up to 85.41 Barrer, which is a 90.7% enhancement from the neat polymer, while the CO_2/N_2 selectivity was also increased up to 43.4, which is a 13.3 % enhancement. The first reason for such enhancement in permeability is due to the hollow structure of f-MTHS, through which both CO_2 and N_2 gas molecules could be rapidly transported. A second reason is the dual-functionalized surface modification with APS and PEGDE, which allows for more facile and selective passage of CO_2 gas through the pores (through acid-base interactions) than N_2 gas, leading to an increase in CO_2/N_2 selectivity. Furthermore, a high degree of dispersion and the strong miscibility of f-MTHS with the polymer matrix prevented void formation and resulted in uniform MMMs, which could minimize the selectivity loss of MMMs. We were able to prepare free-standing MMMs with f-MTHS above 30 wt% loading, but, unfortunately, their mechanical properties were not sufficient to endure gas permeability measurement conditions using the time-lag method, which requires a high vacuum of less than 20 mmHg. However, the material with high f-MTHS loading is applicable as a coating layer deposited on the porous substrate to make a composite membrane, which might show much enhanced permselective properties. This work will be reported in the near future.

In conclusion, an approach to enhance the permeability and selectivity simultaneously was demonstrated using dual-functionalized f-MTHS in MMMs. The MTHSs were synthesized through hydrothermal reaction using PTO, water and PEG. The MTHS surface was covalently modified with APS and PEGDE to provide dual functionality, which could improve CO_2 affinity via acid-base interactions and increase the interfacial properties at the organic/inorganic interface, leading to void-free MMMs and uniform distribution. The MMM with 30wt% f-MTHS improved not only the CO_2 permeability by 90.7 %, but also the selectivity by 13.3 %. Thus, we proved that the mesoporous hollow spheres are a very effective way to improve the gas permeability, while the surface modification with APS and PEGDE plays an important role in improving the selectivity. This strategy could be applied to various other inorganic materials such as SiO_2, Fe_2O_3, Al_2O_3 and MgO, and is very versatile and can be applied to various polymer matrixes. Thus, we believe our work may provide an excellent framework for the design of a new class of MMMs for CO_2 gas separation.

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