An organic/inorganic hybrid mesoporous silica membrane: preparation and characterization

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Published online: 6 April 2010

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Abstract An organic/inorganic hybrid mesoporous silica membrane composed of mesoporous silica materials inside the channels of polycarbonate filtration membrane (PC) was synthesized by using aspiration-induced infiltration method, and the surfactant in as-prepared membrane was removed by employing template-extraction method. The obtained materials were characterized by scanning electron microscopy (SEM), energy dispersive spectroscopy (EDS), X-ray diffraction (XRD), transmission electron microscopy (TEM) and N₂ adsorption–desorption measurement. The SEM images and EDS elemental analyses show that as-synthesized materials in PC are one-dimensional silica rods estimated as 200 nm in diameter and 9 μm in length. Moreover, the results of XRD, TEM and N₂ adsorption–desorption analysis clearly demonstrate that such silica rods are mesoporous materials with two-dimensional hexagonal mesostructure and the average mesopore diameter is about 3.0 nm. In addition, the porosity of organic/inorganic hybrid mesoporous silica membrane was further examined by molecule permeation. It is found that small molecule, such as rhodamine B, can transport across the membrane, but relatively large molecule, such as horse radish peroxidase, can not transport across the membrane, indicating that it is size-selectivity of such a membrane for molecule permeation, which has the potential application in the molecule filters to separate bio-macromolecule from small molecule.

Keywords Hybrid membrane · Membrane synthesis · Mesoporous · Molecule permeation · Size-selectivity

1 Introduction

Since the first report of MCM-41 by Kresge et al. in 1992 [1], the synthesis, characterization, and application of ordered mesoporous materials (OMMs) has attracted extensive attention, because these materials with uniform pores in the 2~50 nm size range have wide application in catalysis, separations, drug delivery, etc. [2–4]. While most investigations on the OMMs have focused on powder materials, the possibility to make OMMs as thin films is particularly attractive due to that these OMMs membranes have important applications in a wide variety of fields including optics [5], sensors [6], adsorption and separation processes, etc. [7, 8]. Recently, the conventional mesoporous films formed on the surface of a solid substrate have been extended to the hybrid mesoporous membranes composed of arrays of OMMs with unique and tunable mesophase structures within the confined channels of porous membrane by numerous academic labs [9–16]. However, all of those investigations have almost focused on the inorganic hybrid mesoporous silica membranes formed by using inorganic porous membrane, that is anodic alumina membranes (AAMs), as the hard template [9–16].

It is well-known that, in addition to AAMs, organic porous membranes (OPMs), such as polycarbonate filtration membrane (PC), have often been used as the hard template in the template-synthesis of one-dimensional nanomaterials [17, 18]. Therefore, if OPMs are employed as the hard templates in the synthesis of hybrid mesoporous silica membranes, the organic/inorganic hybrid mesoporous silica membranes composed of inorganic mesoporous silica materials in

Electronic supplementary material The online version of this article (doi:10.1007/s10934-010-9377-1) contains supplementary material, which is available to authorized users.

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organic porous membranes could be obtained. In view of some advantages of OPMs over AAMs, such as mechanical flexibility and chemical stability under the acid or basic condition, it is expected that those organic/inorganic hybrid mesoporous silica membranes can expand the application area of such hybrid membranes.

To our knowledge, only one example of organic/inorganic hybrid mesoporous silica membranes has been reported by Liang *et al.* until now [19]. However, it should be noticed that, in their work, the synthesis process took four days by employing conventional hydrothermal method. Moreover, the prepared membrane was destroyed during the procedure of calcination up to 550 °C for removing the surfactants from membrane, which undoubtedly restrict the application of as-synthesized materials in the membrane science and technology. Therefore, it is indeed necessary to further explore more efficient methods to shorten the preparation time and especially to ensure the structural integrity of as-prepared membrane, such as the simple and rapid aspiration-induced infiltration method proposed by Yamaguchi *et al.* [10], as well as the template-extraction method under low temperature to remove surfactant from mesoporous silica materials [20].

Herein, we present the synthesis of an organic/inorganic hybrid membrane composed of CTAB-templated rodlike mesoporous silica materials in PC by employing the aspiration-induced infiltration method. In addition, the template-extraction method was employed to remove the surfactant from the as-synthesized membrane. Moreover, the molecule permeation across such an organic/inorganic hybrid mesoporous silica membrane was examined to investigate its porosity and explore its potential application in the size-selective separation of bio-macromolecule from small molecule.

2 Experimental

2.1 Synthesis

The preparation of precursor solution and procedure for the synthesis of a hybrid mesoporous silica membrane, in short HMSM in this work, by using PC as the hard template is similar with the previous reports on the CTAB-templated mesoporous silica films or AAMs-templated hybrid mesoporous silica membrane [3, 10]. Firstly, the precursor solution containing cetyltrimethylammonium bromide (CTAB), tetraethylorthosilicate (TEOS) was prepared as follows: a mixed solution containing ethanol (7.7 g), TEOS (11.6 g) and 1 mL of HCl (2.8 mM) was refluxed at 60 °C for 90 min. After that, ethanol (15 g), 4 mL of HCl solution (55 mM) and CTAB (1.5 g) were added to the refluxed solution, which was stirred for 30 min to give the precursor solution. Then the precursor solution were dropped onto a

porous polycarbonate filtration membrane with pore diameter of 0.2 µm (Anodisk 47, Whataman), which was set in an ordinary membrane filtration apparatus. Under moderate aspiration, two millilitres of the precursor solution filtrates across the membrane twice, and the membrane was dried for 5 min under vacuum at room temperature every time. Finally, the surfactant CTAB was removed from the membrane not by calcination, but by the template-extraction method with EtOH/HOAc as described in the *ref.* [20] due to the low temperature of heat-resistance of PC (<140 °C). After that, an organic/inorganic HMSM was successfully synthesized.

2.2 Characterization

SEM images were measured on a HITACHI-3400 equipped with Quantax-400 EDS (Bruker, Ins. Germany), and TEM measurements were conducted using a JEM-2100 (JEOL, Japan). To obtain the SEM images and TEM side-view of silica rods, the prepared membranes are completely or partly etched by the organic solvent dichloromethane. After completely etching hard template PC, the free silica rods were collected by the porous filtration membrane of polyvinylidene fluoride (PVDF, Φ50 mm, 0.22 µm, Mosutech, Inc, China). The TEM side-views of as-synthesized membrane were obtained after the membrane was embedded in an epoxy resin and cut by mechanical polishing. N₂ adsorption–desorption measurements were conducted on a micromeritics ASAP2020 instrument (Micromeritics, USA), and the as-prepared membranes were cut into small pieces of about 5–6 mm square and placed into the measurement cell. In addition, the product was identified by XRD with Cu Kα radiation by using PW3040/60 X'Pert PRO X-ray (Panalytical, Ins. Netherlands).

2.3 Molecule permeation measurements

For the experiments on the molecular permeation across the membrane in this work, the membranes were glued with a glassy tube by silicon sealant to form the cell, which has successfully been applied in the studies on the ion-transfer across OPMs-templated liquid/liquid interface [21]. As illustrated in Scheme. 1, a randomly cut polycarbonate filtration membrane or organic/inorganic HMSM (13 mm²) was glued with a glassy tube (outer diameter = 13 mm and inner diameter = 10 mm) by the silicon sealant, which is used as the feed cell. Then, the feed cell was immersed an outer cell acting as the receiver cell to form the whole permeation cell. The feed solutions (10 mL) respectively contained 0.20 mmol L⁻¹ rhodamine B, 8.0 × 10⁻³ mmol L⁻¹ horse radish peroxidase (HRP), or double molecules (0.20 mmol L⁻¹ rhodamine B and

Scheme 1 The configuration of permeation cell

8.0×10^{-3} mmol L⁻¹ HRP) in a 100 mM phosphate buffer solution (pH 7.0), and the receiver solution (20 mL) only contained the same buffer solution. The amount of transported molecule was analyzed by measuring UV–Vis absorption spectra of each molecule in the receiver solutions. The absorption measurements were carried out using a Cary100 UV–Vis Spectrophotometer (Varian, USA).

3 Results and discussion

3.1 SEM and EDS measurements for organic/inorganic HMSM and silica rods

Figure 1a, b show the SEM image on the top-view of an as-synthesized organic/inorganic HMSM without etching hard template PC, and it is obvious that some rods can be observed inside the pores on the surface of PC with comparison to the top-view of bare PC (Fig. S1a). After partially etching the PC, as shown as Fig. 1c, d, the SEM images on the side-view of organic/inorganic HMSM obviously showed that those rods penetrated through the channels of PC. Moreover, Fig. 1e, f show that a number of one-dimensional rods could be obtained after completely etching PC, and it is evident that those rods are 200 nm in diameter and 9 μ m in length, which completely accords with the diameter and the length of channels of PC employer in this work (see Fig. S1).

However, with comparison to the inorganic HMSM obtained by using the same method [10], it is found that the structure of organic/inorganic HMSM is obviously different from that of inorganic HMSM. As for the inorganic HMSM, the rodlike materials can not be observed on the surface of membranes and those rods are only formed in the middle of channels of AAMs. Moreover, the length of those rods formed inside the AAMs is 40 μ m for the inorganic HMSM, which is shorter than the length of channels of AAMs ($\sim$ 60 μ m). Those structural differences between inorganic HMSM and organic/inorganic HMSM should be related to the different membrane thickness between PC and AAMs. It can be expected that, under the

Fig. 1 SEM images of the surface of organic/inorganic HMSM without etching PC (a, b); on the side view of organic/inorganic HMSM after partially etching PC (c, d); silica rods collected on the PVDF membrane after completely etching PC (e, f)

similar experiment condition, the rate of precursor solution filtration and EISA process [2] inside the PC should be faster than that inside AAMs because the thickness of PC (9 μ m) is much less than that of AAMs (60 μ m), which results in not only the appearance of silica rods on the surface of PC but also the formation of silica rods inside the whole channels of PC for the organic/inorganic HMSM. In addition, it should be noticed that there is not strong chemical bonds between mesoporous silica and polycarbonate wall during the growth of silica rods inside the channels of PC, thus the formation of silica rods in the whole channels of PC observed above indicates that the physical adsorption of as-synthesized silica rods to the channel wall of PC maybe play important role in the mechanical stability of the organic/inorganic HMSM.

In order to investigate the composition of materials observed above, EDS was used to analyze the surface of membranes (Fig. 1b) and those rods (Fig. 1e, f) observed above. As shown as Fig. 2a, it is found that, in addition to the component elements of PC (Fig. S2), namely carbon and oxygen, the silicon can be found from the surface of organic/inorganic HMSM, which not only accords with the structure of organic/inorganic HMSM as shown in Fig. 1a, namely the rodlike materials can be observed on the surface of membrane, but also indicates those rods are composed of silicon. Moreover, the EDS data and mapping (Fig. 2b–d) further demonstrate that those rods collected on the PVDF are composed of silicon and oxygen, which indicated that the rodlike product formed inside channels of

Fig. 2 EDS data of **a** the surface of organic/inorganic HMSM, **b** the silica rods collected on the PVDF after completely etching PC; and EDS mapping of silica rods; **c**, **d** on the SEM images as shown as the Fig. 1e (**c**: silicon element mapping and **d**: oxygen element mapping)

PC is silica rods. On the contrary, as for the inorganic HMSM, the silicon can not be found on the surface of inorganic HMSM [10], which completely accords with the structural difference between inorganic HMSM and organic/inorganic HMSM as discussed above.

3.2 XRD and N_2 adsorption–desorption measurements for organic/inorganic HMSM

The mesostructure of organic/inorganic HMSM was investigated by X-ray diffraction (XRD). The low angle XRD patterns of an organic/inorganic HMSM and a bare PC membrane are shown in Fig. 3. Although the silica rods are embedded inside the PC as shown in Fig. 1a, one diffraction peak can be observed from the organic/inorganic HMSM at 2θ low angles between 2.0° and 4.0° , which should be assigned to the (100) reflection of a hexagonal

Fig. 3 The low angle XRD patterns of a bare PC membrane and an as-synthesized organic/inorganic HMSM

Fig. 4 N_2 adsorption-desorption isotherms for the organic/inorganic HMSM

symmetry mesostructure [3]. Furthermore, the mesoporosity of HMSM was evaluated by N_2 adsorption–desorption measurement. As shown as Fig. 4, the isotherm is similar to the type-IV mesopore adsorption–desorption behavior [22], and the inflection position in p/p^0 is close to the previous reports on the CTAB-templated mesoporous silica materials [1, 3]. Therefore, as-synthesized membrane can be regarded as the organic/inorganic hybrid mesoporous silica membrane due to the inorganic mesoporous silica rods formed inside the channels of PC. The average pore diameter of silica mesopores was estimated as 3.0 nm based on Barret–Joyner–Halenda (BJH) analysis, which almost agrees with the values of CTAB-templated mesoporous silica materials reported previously [1, 3]. However, it should be noticed that a significant increase of adsorbed volume can be observed at the highest value of relative pressure in Fig. 4, which indicates the presence of macropores in the product. Indeed, the edge of bare PC membrane does not contact the precursor solution during the process of aspiration-induced infiltration, which leads to the presence of macroporous channels at the edge of as-synthesized organic/inorganic HMSM.

3.3 TEM measurement for organic/inorganic HMSM

The mesostructure of organic/inorganic HMSM was further investigated by TEM measurements. As shown as Fig. 5a, b on the TEM side-views of as-synthesized membrane, the silica rods can be observed inside the channels of PC (Fig. 5a). From the higher resolution TEM image of such silica rod (Fig. 5b), the two-dimensional (2D) hexagonal structure with each pore surrounded by six neighbors is observed and the pore diameter is estimated as about 3.0 nm, which accords to the value estimated from the N_2 adsorption–desorption isotherm (Fig. 4). Moreover, after completely etching PC, as shown as Fig. 5c–e, some silica rods with 200 nm in diameter are collected, and the ordered stripes perpendicular to the longitudinal axis of rod

Fig. 5 TEM images of side-view of organic/inorganic HMSM (a, b) and silica rods obtained after completely etching PC (c, d, e)

are found on the silica rods (Fig. 5d), where the 2-D hexagonal pore arrays also can be observed (Fig. 5e).

The hexagonal mesostructure is a typical mesophase structure for the CTAB-templated MCM-41 powder materials [1]. As for the conventional mesoporous silica thin film, it has also been reported that the CTAB-templated mesoporous silica film formed on a solid substrate could present from cubic to hexagonal mesostructure under different experimental condition [3]. However, the mesostructure of silica rods observed above is different from that of CTAB-templated inorganic HMSM [10]. For the

inorganic HMSM, the mesostructure of silica rods formed in AAMs is partially ordered one-dimensional nanochannel arrays. The possible reason for the difference of mesostructure between inorganic HMSM and organic/inorganic HMSM may be due to the different channel hydrophobicity between organic template PC and inorganic template AAMs, because the hydrophobicity of channels can affect the structure of mesoporous materials formed inside the porous membranes [9]. Indeed, according to all above discussion on the difference of membrane structure between inorganic HMSM and organic/inorganic HMSM based on SEM and TEM characterizations, it is found that, as for the organic/inorganic HMSM, silica rods can form inside the whole channel of PC and the ordered mesopores present continuity, which indicates the better affinity of channel of PC than AAMs with the precursor solution. As a result, the channels of PC is more homogeneously filled by the precursor solution than that of AAMs due to the better wettability of channel of PC with the precursor solution than AAMs.

3.4 Molecule permeation through organic/inorganic HMSM

According to all above results of XRD, TEM and N₂ adsorption–desorption measurements, as-synthesized organic/inorganic HMSM is found to be a porous membrane, and its porosity is further investigated by the followed molecule permeation measurements including small molecule rhodamine B (molecular size ~1.0 nm) and relatively large molecule HRP (molecular size ~5.0 nm).

As shown as Fig. 6, as for the single-molecule permeation across organic/inorganic HMSM, small molecule rhodamine B can transport across the membrane, but relatively large molecules HRP can not transport across the membrane, which is confirmed by that rhodamine B, not HRP, can be detected in their corresponding receiver solution according to the UV–vis spectra of receiver solution (rhodamine B λ_{max} :552 nm; HRP λ_{max} :402 nm).

Fig. 6 The time-course of UV–Vis absorption spectra of receive solution for the single-molecule permeation of rhodamine B (a) and HRP (b) across organic/inorganic HMSM

In contrast, as for single-molecule permeation experiments of rhodamine B and HRP across bare PC, it is found that two molecules can transport through the membrane, which can be verified by that these two molecules were detected in the receiver solution during all the permeation period according to their corresponding UV–vis spectra of receiver solution (Fig. S3).

According to molecule permeation experiments as discussed above, it can be further confirmed that such an organic/inorganic HMSM is porous membrane with size-selectivity for the molecule permeation, which should be due to the size-rejection effect caused by the mesoporosity of silica rods formed in PC. In other words, the organic/inorganic HMSM is compactness with capability of rejection to the molecules whose size is larger than the mesopore diameter (3.0 nm) of mesoporous silica rods in PC, which was further testified by the followed double-molecule permeation experiments, namely the feed solution containing two molecules rhodamine B and HRP. Although the absorption bands of rhodamine B and HRP are in the same wavelength range, their characteristic absorption peak is obviously different and the difference of absorption peak wavelength is about 150 nm according to the corresponding UV–vis spectra of rhodamine B and HRP (Fig. S4), which should be enough for the qualitative analysis. Therefore, for the double-molecule permeation experiments, the qualitative analysis of transported molecule into the receiver solution can be identified according to the absorption peak of the UV–vis spectra of receiver solution. However, the quantitative analysis of transported molecule should consider the interference between Rhodamine B and horse radish peroxidase if rhodamine B and HRP transport across membrane into the receive solution at the same time, because it is necessary to deduct the adsorption of one molecule from the absorption peak of the other. In this work, the quantitative analyses of transported molecule mainly focus on the transport flux of molecule across organic/inorganic HMSM.

As shown as Fig. 7a, for the double-molecule permeation across bare PC, not only rhodamine B but also HRP can be

detected in the receiver solution because the absorption peaks of rhodamine B and HRP can be observed, which indicates that both of rhodamine B and HRP can transport across bare PC. However, Fig. 7b shows that, as for the organic/inorganic HMSM, only the characteristic absorption peak of rhodamine B can be observed in the receiver solution, which indicates that only rhodamine B in the double-molecule solution can transport across organic/inorganic HMSM. This result not only further supports the mesoporosity and the size-selective molecule permeation property of organic/inorganic HMSM, but also directly demonstrates such a membrane have the potential application in the membrane-based molecule filters to separate bio-macromolecule from small molecule.

It has been reported that inorganic HMSM has also presented size-selective molecule permeation property [10], but molecule transport flux is regarded as one of crucial problems needed to be overcome for the practical application of such membrane with pores in pores as molecule filters [23]. Therefore, the molecule transport behaviors across organic/inorganic HMSM were investigated more in detail according to the permeation time lag and the transport rate obtained from all the above molecule permeation experiment. On the one hand, it can be found from Fig. 6 that, there is time lags (0.25 h) for the transport of rhodamine B across organic/inorganic HMSM, but there is not obvious significant time lags for the transport of rhodamine B across bare PC (Fig. S3a). The appearance of time lag in the permeation of rhodamine B across organic/inorganic HMSM could be due to the diffusivity of rhodamine B from feed solution into the mesopores of membrane, which might reduce the transport rate of rhodamine B and delay the permeation time. Additionally, the permeation time lag of rhodamine B in the double-molecule permeation across organic/inorganic HMSM (0.5 h) is relatively larger than that observed in single-molecule permeation, which should be due to the transport hindrance caused by HRP co-existed in the feed solution.

Fig. 7 The time-course of UV–Vis absorption spectra of receive solution for the double-molecule permeation of rhodamine B and HRP across bare PC (a) and organic/inorganic HMSM (b)

Fig. 8 Transport flux plots of rhodamine B (filled square), HRP (filled circle) in the single-molecule permeation and rhodamine B (filled star) in the double-molecule permeation across organic/inorganic HMSM

On the other hand, the molecules transport fluxed across organic/inorganic HMSM are shown in the Fig. 8. According to Fig. 8, the transport flux of rhodamine B in single-molecule permeation across organic/inorganic HMSM is evaluated to be 95 nmol h^{-1} , which is much less than the value obtained from the single-molecule permeation of rhodamine B across bare PC (391 nmol h^{-1}), but larger than that for the double-molecule permeation (91 nmol h^{-1}). The obvious difference of transport flux of rhodamine B in the single-molecule permeation across between organic/inorganic HMSM and bare PC should be due to the much too difference of channel size between bare PC (200 nm) and organic/inorganic HMSM (3.0 nm). The little difference of transport flux of rhodamine B between single-molecule and double-molecule permeation across organic/inorganic HMSM also should be due to the transport hindrance caused by HRP as discussed above on the transport time lag.

Moreover, it is found that there is obvious difference between the transport of rhodamine B across organic/inorganic HMSM and inorganic HMSM [10, 23]. Firstly, the permeation time lag of rhodamine B across organic/inorganic HMSM (0.25 h) is much smaller than that previously reported on the inorganic HMSM (4 h), which indicates that the transport rate of small molecules across organic/inorganic HMSM might be faster than that across the inorganic HMSM. Indeed, the transport flux of rhodamine B across organic/inorganic HMSM is almost as ten times as that evaluated from the previous reports on inorganic HMSM (9.8 nmol h^{-1}) [23], which also accords to the above discussion on the permeation time lag, namely much smaller permeation time lag of rhodamine B across organic/inorganic HMSM than across inorganic HMSM. Those differences of molecule transport time lag and rate of small molecule across between organic/inorganic HMSM and inorganic HMSM should mainly be ascribed to the different thickness and mesostructure between organic/

inorganic HMSM and inorganic HMSM as discussed above, indicating the thinner organic/inorganic HMSM with 2-dimensional hexagonal mesostructure shows better molecule transport property than inorganic HMSM for their potential application in the membrane-based molecule filters.

4 Conclusions

In summary, an organic/inorganic hybrid mesoporous silica membrane composed of one-dimensional mesoporous silica rods inside the channels of polycarbonate filtration membrane was successfully synthesized by the combination of aspiration-induced infiltration with template-extraction method. The characterization results demonstrate that as-synthesized materials in PC are one-dimensional silica rods estimated as 200 nm in diameter and 9 μm in length. Moreover, such silica rods are mesoporous materials with two-dimensional hexagonal mesostructure and the average diameter of mesopores is about 3.0 nm. In addition, the molecule permeation across organic/inorganic hybrid mesoporous silica membrane is investigated, and it is found that such a membrane is size-selectivity for the molecule permeation with rapider transport rate and smaller transport lag time than inorganic hybrid mesoporous silica membrane, which has the potential application in the molecule filters such as the separation of bio-macromolecule from small molecule. Moreover, in addition to the cationic surfactant CTAB, surfactant can be extent to others, such as nonionic block copolymers P123 or F127, to form other organic/inorganic hybrid mesoporous silica membranes with different mesostructure, which is in progress in our group.

Acknowledgments This work was supported by the Scientific Research Foundation for the Returned Overseas Chinese Scholars, Ministry of Education of China (No. ZX2008-04), the Science Innovation Foundation of Shanghai Educational Committee (No. 09YZ386), and the Science Foundation for The Excellent Youth Scholars of Shanghai Educational Committee (No. k08204), China.

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