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Preparation of hybrid ion channel membrane for recognizing and transporting sodium ion

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ABSTRACT

A kind of self-organized hybrid material, 3-(ureidobenzene) propyltriethoxysilane, was obtained from 3-isocyanatopropyltriethoxysilane and aminobenzene with chloroform as solvent. The structure and the morphology of the materials were characterized by FTIR, ^{1}H-NMR, and XRD methods. The ion channel membrane was obtained by coating the hybrid material onto the commercial polyacrylonitrile (PAN) supports via sol-gel process. The chemical structure and surface morphology of the membrane was characterized by ATR-FTIR and SEM separately. The ion transport property of the membrane was tested by our self-made device with the conductivity. SEM showed that the surface of ion channel membrane was dense and thickness of the dense layer was about 8.5 µm. The transport experiment suggested that the membrane had the properties of recognizing and transporting Na^+.

Keywords: Hybrid material; Self-organization; Ion channel membrane; Ion-recognition; PAN membrane; 3-(ureidobenzene) propyltriethoxysilane

1. Introduction

Ion transport across membranes is one of the most important processes in living cells. The fundamental processes appear to depend on the unique properties of ion channel protein. Ion channels have several unusual features, which make them the subject of much biochemical, biophysical, and physiological research. For one, they are highly selective. They discriminate not only between anions and cations, but even between different monovalent and divalent ions, for example, Na^+, K^+, and Ca^+. Other important feature is their efficiency, the energetic barriers in the channel have to be very low, nearly not consume the ATP [1,2]. Hence artificial ion channel which has the similar function of the biological pathway is developed for two decades. It increases the transport efficiency of the membrane and provides some of new ideas for studying science problems in the membrane separation field.

Many artificial membrane transports systems using carriers, channel-forming or self-organized polymeric superstructures have been developed in the last decades [3,4]. These systems can select and pump the ionic transport across membranes. New polytopic receptors which can recognize cations, anions or molecular species have been designed to mimic natural ion channel [5]. In the last few years, crown-ethers, cyclodextrin, calixarene and porphyrin have been used for preparing artificial ion channel membranes. Seminal work by Perce et al. [6,7] has demonstrated the self-assembly of dendronized crown ethers into ion channels. Davis et al. [8–10] showed the formation of the G-quadruplex transporting device in the presence of cation templating, the columnar architecture formed by the vertical stacking of four G-quartets. Functional organic or inorganic materials and other

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self-organized devices designed to mimic natural ion channel proteins, which moved the field of the bio-inspired supramolecular systems to a nanometric scale.

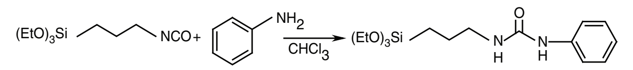
Hybrid organic-inorganic materials offer the opportunity to obtain nanostructured functional materials. Many groups found new methods to prepare hybrid self-organized materials. Barboiu M et al. [11] has demonstrated the self-assembly of guaninesiloxane, G-quadruplex supramolecular hybrid materials. The same group [12–13] showed new hybrid organic- inorganic membrane materials in which alkali cations were envisioned to diffuse along cation-π aromatic conduction pathways.

Recently, we found that the urea and a silica matrix can be used to create ion-conduction pathways by self-assembly and orient the directional transporting super-structures in hybrid membrane materials. In this context, herein, we used 3-isocyanatopropyltriethoxysilane and aminobenzene to obtain a hybrid compound which can form ion channel membrane with dense surface by self-organization. And this ion channel membrane can recognize and transport Na^+.

2. Experimental

2.1. Materials and methods

The 3-(ureidobenzene)propyltriethoxysilane compound was obtained from 3-isocyanato- propyltriethoxysilane and aminobenzene ($CHCl_3$, 80°C, 5 h) to afford, after crystallization, as a white powder. Fourier Transform Infrared Spectroscopy (FT-IR, BRUKER EQUINOX 55, potassium bromide pellet) demonstrated the structure of the membrane material. The structure of the compound was confirmed by NMR spectroscopy (BRUKER AVANCE 400, $CDCl_3$-D6 as solvent).



Scheme1. Synthesis of 3-(ureidobenzene) propyltriethoxy-silane.

2.2. Preparation and characterization of membrane

The membrane was obtained by coating a chloroformic solution of 3-(ureidobenzene) propyltriethoxysilane with the addition of HCl used as acidic catalysis to form the cross-linking of the siloxane network onto commercial planar polyvinylidenefluoride (PVDF) microporous support by using a Spin Coater. The membrane was then dried at room temperature. Attenuated Total Reflection Fourier Transform Infrared (ATR-FTIR, BRUKER TENSOR–27) spectroscopic analysis demonstrated the formation of self-organized hybrid material. Scanning electron microscopy (SEM, HITACHI S-3400) allowed the thickness and the quality of the active deposited layer to be determined.

2.3. Dialysis transport procedure

Membrane transport experiment was performed with a bi-compartment device. It consists of two cells device separated by the solid membrane (S=0.5024 cm^2) with the active dense film face to the feed phase. The feed phase was an aqueous solution of a 0.10M NaCl (V=500 ml) solution, while the receiving phase consisted of the same volume of deionized water. The Na^+ electrical conductivity was monitored at different time intervals. This experiment was carried out under the static state.

3. Results and discussions

3.1. Hybrid material and membrane structure characterization

3.1.1. FT-IR and ^{1}H-NMR

The FT-IR spectrum of hybrid material compound is shown in Fig. 1. FT-IR spectrum of the hybrid material shows the appearance of vibrations of $\nu_{Si\text{-}O\text{-}Et}$=956, 1080 and 1103 cm^{-1}, $\nu_{N\text{-}H}$=3315 cm^{-1}, $\nu_{C=O}$=1641 cm^{-1}, $\nu_{C\text{-}N}$=1569 cm^{-1}. In general, all hydrogen peaks in the ^{1}H-NMR (Fig. 2) were in good agreement with the proposed hybrid material structure. As expected, the aromatic protons were detected around 6.99–7.35 ppm, depending on the opposition in the aromatic ring. The δ observed at 3.70–3.84 ppm due to the –NH(C=O)NH– in the ureido. The δ observed at 1.61–3.28 ppm due to the three $–CH_2–$. The δ at 0.62–1.27 ppm is due to the $–OCH_2CH_3$. The result of ATR-FTIR spectra of the membrane (Fig. 3) shows the surface structure of the membrane. Compared to free urea, the self-association behaviour of the urea units through hydrogen bonding in ion channel membrane was revealed by the downfield shift of the $\nu_{N\text{-}H}$(from 3315 cm^{-1} to 3305 cm^{-1}) and the upfield shift of the $\delta_{N\text{-}H}/\nu_{C=N}$ coupling bond vibration (from 1569 cm^{-1} to 1595 cm^{-1}+1550 cm^{-1}). From the Fig. 3, we can see the appearance of broad vibration of the $\nu_{Si\text{-}O\text{-}Si}$=1000–1200 cm^{-1} instead of the vibrations of the $\nu_{Si\text{-}O\text{-}Et}$=956, 1080 and 1103 cm^{-1}, which reveals that the

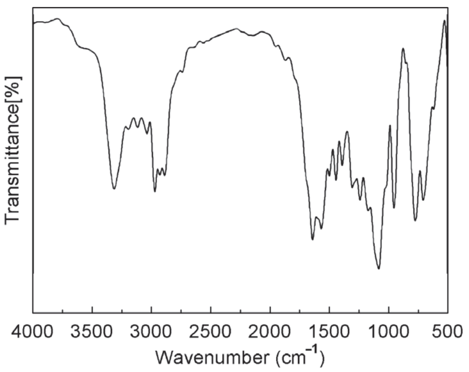


Fig. 1. FT-IR spectra of the hybrid material.

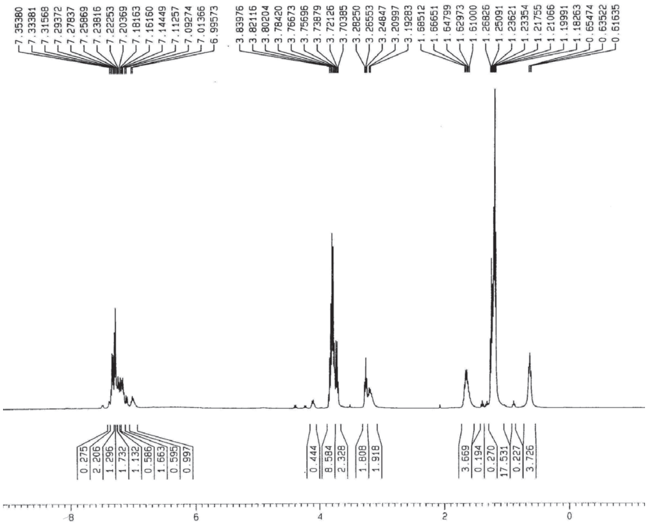


Fig. 2. ¹H-NMR spectrum of hybrid material.

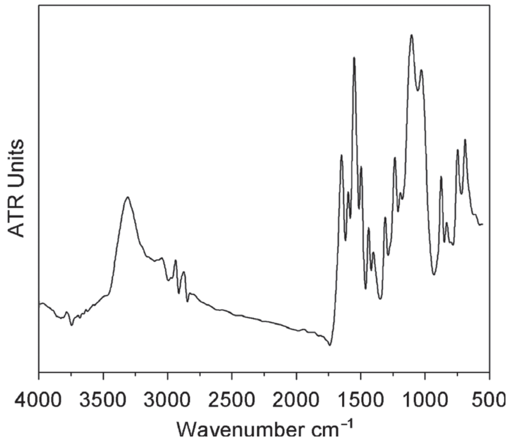


Fig. 3. ATR-FTIR spectra of membrane.

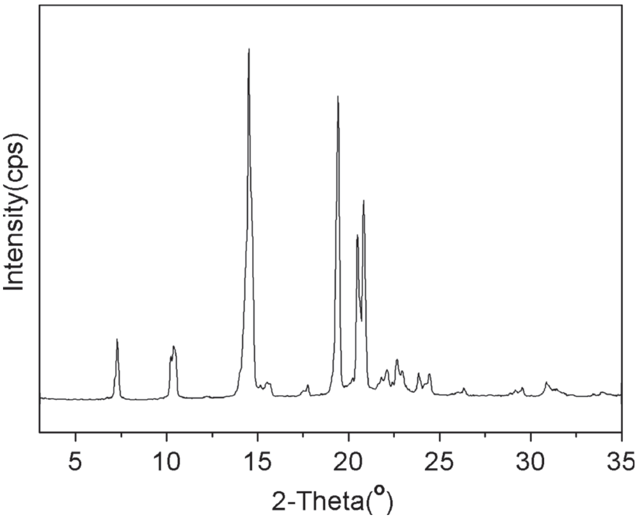


Fig. 4. X-ray powder diffraction pattern of the hybrid material.

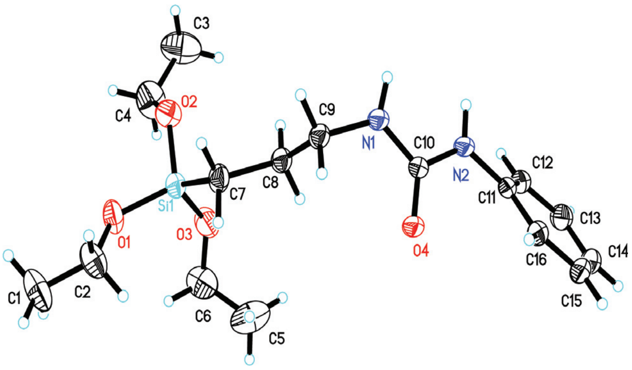


Fig. 5. Crystal structure of the hybrid material.

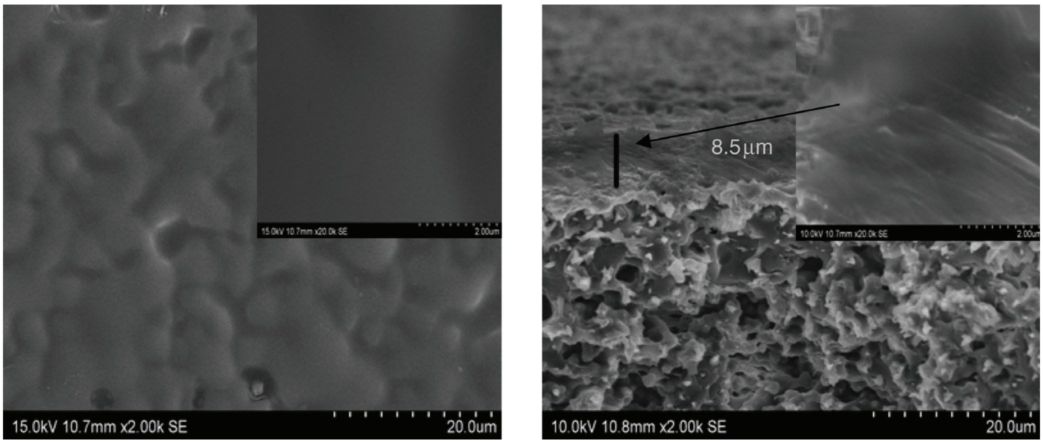
siloxane network was successfully formed by the sol-gel process. The ion channel membrane was formed by the method of self-organized from the hybrid material. Compared to free urea, the self-organized behavior of the urea units through hydrogen bonding in ion channel membrane was revealed by the downfield shift of the $\nu_{N\text{-}H}$ (from 3315 cm^{-1} to 3305 cm^{-1}) and the upfield shift of the $\nu_{C\text{-}N}$ (from 1569 cm^{-1} to 1595 cm^{-1}+1550 cm^{-1}).

3.1.2. XRD

Structural insights on the hybrid material were obtained by X-ray powder diffraction (Fig. 4). From the Fig. 4, we can see the hybrid material is the crystal structure. For the compound, it was possible to obtain full atomic structure determination and to generate the corresponding diffractogram using the data of the single-crystal measurement. The molecular structure and packing are presented in Fig. 5. The hydrogen bonds have an average N···H···O distance involving H-bonds of 2.83 Å, and the average H-O distance of 2.09 Å is consistent with urea system. The crystal structure of the hybrid material indicates that the arrangement is mainly defined by periodic parallel sheets, resulting from the alignment of hydrophobic organic and inorganic silica layers. On the other hand, a very good compatibility between the bulk powers X-ray fingerprint and the single-crystal structure has been found.

3.1.3. SEM

Fig. 6 shows the morphology of the surface and the cross-section of the membrane. They reveal that the surface of the active thin-layer of the membrane was dense without cracks or bubbles. The thickness of the dense layer was about 8.5 μm.



(a) (b)

Fig. 6. SEM images of the ion channel membrane: (a) the surface of membrane (b) the cross-section of membrane.

3.2. .Membrane transport experiment

The sol-gel conditions preserving the urea head-to-tail self-assembly were taken up again for the preparation of urea hybrid membranes. The sols were cast to thin film on PAN support. Drying at room temperature and heating at 60°C complete the formation of the inorganic network. For the transport of NaCl, the only effective driving force is caused by the difference of the concentration on both sides. Under this weak driving force, Na^+ can't transfer from the NaCl solution to the deionized water through the dense membrane, and then the electrical conductivity on the deionized water should remain unchanged (Fig. 7 dot line). But the experimental result of ion channel membrane shows that the electrical conductivity on the deionized water changed with time. It increased fast before 48 h and slowed down gradually. This indicated that the membrane can transport Na^+ and the transport occurs mainly through siloxane network (—Si—O—Si(OH)—Si—) containing residual hydrophilic Si-OH groups. In addition, the 3-(ureidobenzene) propyltriethoxysilane can form ion-conducting pathway by the intermolecular hydrogen bonding with the ureido (Fig. 8), which can transport Cl^-. The mechanism of the membrane transport was showed in Fig. 9. The ion channel membrane prepared in our work can be considered as reference membranes in which the ionic transport occurs mainly via siloxane network (—Si—O—Si(OH)—Si—) containing residual hydrophilic Si-OH groups.

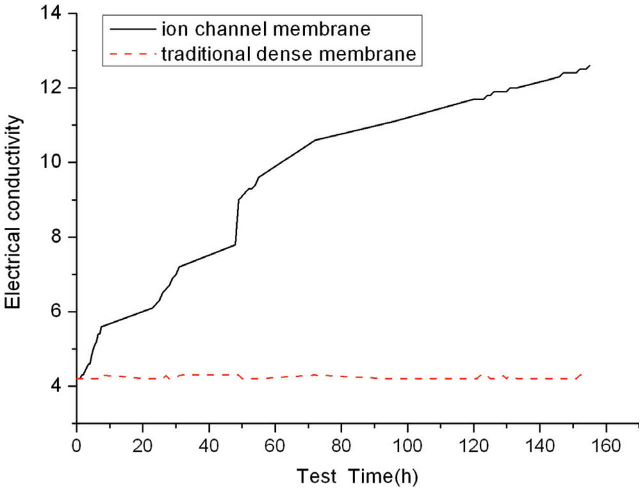


Fig. 7. Na^+ concentration profiles in the strip phase as a function of time.

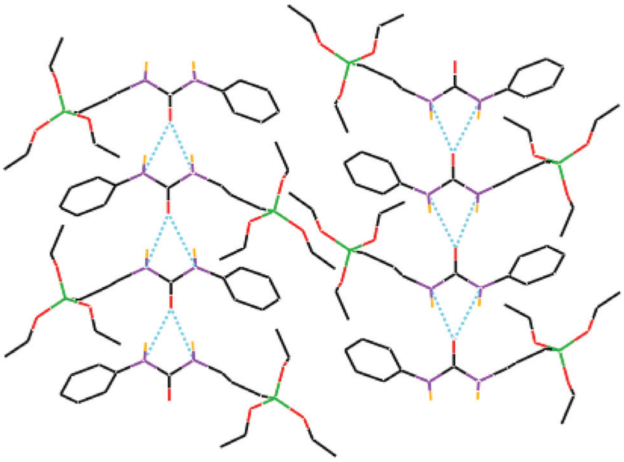


Fig. 8. Structure of 3-(ureidobenzene) propyltriethoxysilane interconnected by H-bonded.

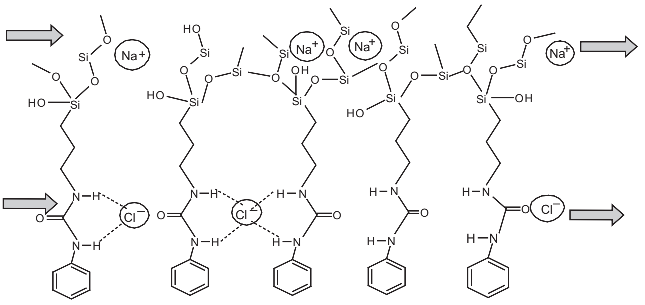


Fig. 9. Schematic drawing of transportation of the membrane.

4. Conclusion

3-(ureidobenzene) propyltriethoxysilane can generate organogel in chloroform, leading in a second sol-gel transcription step to hybrid membrane material. The thickness of the active thin-layer of the membrane was about 8.5 µm. The result of membrane transport experiment shows that the membrane can transport Na^+. The mechanism of the formation of ion channel can be explained by siloxane network and intermolecular H-bonds.

Acknowledgements

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