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Title: Modulated enhancement in ion transport through carbon nanotubes by lipid decoration

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Abstract: Biomimetic channels based on carbon nanotubes (CNTs) with fast and selective transport have attractive applications in many fields. In this work, a remarkable and modulated enhancement in the ion transport rate through CNTs is facilitated by means of lipid decoration, by a factor of up to 20 times. A type of CNT membrane is firstly prepared, composed of well aligned multi-wall carbon nanotubes with an inner size of ~10 nm. An inter-diffusion method is used to efficiently incorporate lipids within the CNTs. It is found that the lipid phase state as well as the surface property of the tubes' inner walls corporately determine the assembly behavior, such as location and stability of lipids, which further influence the ion transport rate through the tubes. For example, the incorporation and self-assembly of liquid-phase DOPC and polymerized Diyne-PC within the tubes induces an enhancement in steady ion transport rate through CNTs by a factor of 5 and 20 times, respectively. In contrast, the gel-phase DPPC prefers to stay at tube tips, which increases the ion transport rate during the initial stage only. This work provides a practical guide to regulate the ion transport behaviors through CNTs for versatile applications.

We are quite thankful for the referees' careful reviewing and thoughtful comments, which do help us think over the underlying mechanism deeply and improve the paper. The responses are detailed as follows.

Response to referee 1's comments.

Comments: The paper by Liu et al. reported a remarkable and modulated enhancement in the ion transport rate through lipid decorated CNTs. They found that the lipid phase state as well as the surface property of the tubes' inner walls corporately determine the assembly behavior, such as location and stability of lipids, which further influence the ion transport rate through the tubes. This is an interesting experimental work that could provide some guidance for separation and sensing applications. I would recommend this manuscript for publication in Carbon if the authors could satisfactorily address the following issues.

Comment 1. For the TOC, please add the unit of the rate and what the colors represent.

Response 1: (1) Color legend has been complemented in the TOC image now. (2) The histogram refers to the NORMALIZED ion transport rate through CNT-membranes before or after lipid decoration (Line 235 in the main text). Therefore, the value in y-axis represents the enhancement factor without units.

Comment 2. For the detection of lipids location, it would be better to adopt Elemental Mapping Images to reflect P atom distribution to highlight the decoration results.

Response 2: Thanks for the suggestion. Actually, we have tried Elemental Mapping repeatedly in our experiment. However, no signal of P or Br can be distinguished, probably due to the relatively low content of them (**Fig. R1**).

Fig. R1 Elemental mapping image of MWNTs after lipid decoration. No signal of P or Br (at 2.0~3.0 keV) was obtained. For sample preparation, the organics in the membrane was dissolved with acid etchant solution following tip sealing of the MWNTs. After that, the MWNTs were collected and supported on a copper grid for observation.

Comment 3. In the introduction, it would be better to mention that molecular simulation studies on ionic hydration confined in carbon nanotube would complement experimental studies and provide atomistic level explanations, such as, Fluid Phase Equilib, 2010, 297(2):215-220; J Phys. Chem. C, 2013, 117(21):11412-11420; ACS Nano., 2013, 7(11): 10148-10157; Nanoscale, 2014, 6(7):3686-3694; Mol. Simul., 2016, 42(10):784-798.

Response 3: Thanks for reminding. The reports mentioned by the referee were complemented as Ref. 8, 9, 14, 20 and 21, respectively, in the main text.

Comment 4. The underlying mechanism should be detailed discussed. Please add more description in explaining experimental phenomenon. What is the motivation for lipid decorated inside the MWNT to facilitate ion transport? The authors mentioned that "the strong affinity between the alkyl tails of lipid molecules and the hydrophobic aromatic plane of tubes facilitates the localization of lipids within the interior of the tubes". It would be better to discuss the connection of configuration of lipid molecules to the inner diameter of MWNT.

Response 4: More calculations and explanations are complemented in the supporting information now. These include: (1) LJ interaction energy profiles between lipids (including lipid head and lipid tail), MWNT surface, and water, to help understand the assembly structure and stability of lipids within MWNTs (Line 294 in the main text; complemented as **Section S3** in ESI). (2) Energetic analysis on DOPC and DPPC lipids in the interior of MWNTs, to explain the influence from substrate curvature on lipid assembly, and the different assembly state of the liquid-phase DOPC and gel-phase DPPC (Line 300; complemented as **Section S4** in ESI).

For detailed explanations, please refer to Response 1 and 2 to the third referee.

Comment 5. The authors adopted a KCl solution to study the ion transport. It would be more interesting to compare the results derived from different types of ionic aqueous solution, say NaCl? Does the enhancement phenomenon in the ion transport rate will be also occurred for other types of electrolyte solution?

Response 5: (1) KCl ions are usually used as probes to measure the ion-flux behavior of a nano-channel because the diffusion coefficients of K^+ and Cl^- are quite close which will eliminate the liquid junction potential. Also the ion flux is easy to monitor by conductivity measurements (*Hinds, B. J., Nature, 2005, 438, 44; Pan, Y. Y., J. Mater. Chem. A, 2015, 3, 11111*).

(2) The transport test of NaCl through the DOPC-decorated MWNTs was performed and shown in **Fig. R2**. An enhancement is also obtained, with a factor of ~ 2 during both the initial and steady state.

(3) In previous reports, similarity or difference between a variety of ions was investigated. For example, diffusive transport of ions of different charge and size (e.g. KCl, MV^{2+} , $Ru(bipy)_3^{2+}$, NDS^{2-} , and Rhod) through CNTs, which have been functionalized with carboxylic acid groups at the CNT entrance, was found to be close to bulk diffusion expectations (*Hinds, B. J., ACS Nano, 2011, 5, 3867-3877*). Meanwhile, ion selectivity for Na^+ and K^+ was achieved through graphene nanopores with tunable voltage (*He, Z., ACS Nano, 2013, 7, 10148-10157*).

Fig. R2 Ion transport test through MWNT membranes, before and after DOPC lipid decoration, with NaCl. (a) Electrical conductivity changes with time for the diffusion solution during NaCl transfer process. (b) Corresponding normalized ion transport rate. Error bars were based on the SD of 3 parallel samples. The black and red curve/histogram refer to the MWNT membrane without and with lipid decoration, respectively.

Response to the second referee's comments.

Comments: In this study, the authors have prepared two types of vertically-aligned CNT membranes composed of MWNTs or AAO-based amorphous CNTs, and investigated the influence of lipid decoration on the ion transport properties through the inner core of the nanotubes. Ion transport tests demonstrated an enhancement in the steady ion transport rate through MWNTs due to lipid incorporation, by approximately 5 times for DOPC or DPPC, and up to 20 times for Diyne-PC after polymerization. The results are very impressive and can be used to regulate the ion transport behaviors through CNTs. I have some questions and suggestions on this manuscript:

Comment 1. The authors attribute the enhanced ion transport rate of lipid decorated MWNTs to the complicate ion-lipid interactions, which could create a preferred distribution of ions near the zwitterionic lipid headgroups. I suggest the authors could decorate MWNTs by amphiphilic and electroneutral polymers, and compare the results with lipid decorated MWNTs. The additional experiments could prove if zwitterionic lipid headgroups play a key role in enhancing ion transport.

Response 1: Thanks for suggestion. Two types of molecules, i.e. PS-PAA and calcein, were used

instead of lipid for MWNT decoration in complement experiments, to check their influence on ionic transport through tubes.

Note: PS-PAA (PS:PAA, 4.2k:5k) is a representative type of amphiphilic copolymer. It was pre-conjugated with Si quantum dots (3.4 ± 0.6 nm) based on the carboxylic acid groups for fluorescence labeling before use. Calcein is a type of water soluble fluorescence molecule with aromatic scaffold to attach to the MWNT surface. Molecular structure of PS-PAA and calcein is shown as insets in **Fig. R3**.

With the same concentration-driven inter-diffusion method as lipids, PS-PAA and calcein was incorporated and localized within MWNTs, which was confirmed under confocal fluorescence observation. Ionic transport test was performed for the MWNT membranes both before and after molecular decoration. As shown in **Fig. R3**, the decoration of MWNT membranes with PS-PAA or calcein reduces the ion transport rate through tubes, to ~60% of the initial value (during the steady state).

This result further confirms that the zwitterionic lipid headgroups play a key role in enhancing ion transport through tubes. For possible reasons, please refer to the discussion in Response 4 to the third referee.

These results were complemented as **Fig. S4** in the main text and ESI. The following words were added in the main text (Line 311-313):

“Electroneutral or negatively charged molecules were also used instead of the zwitterionic lipids for MWNT decoration, which, however, reduced the ion transport rate (Fig. S4).”

Fig. R3 Ion transport through MWNT membranes before and after molecular decoration with PS-PAA (a, b) or calcein (c, d). (a, c) Electrical conductivity changes with time for the diffusion solution during ion transfer process. (b, d) Corresponding normalized ion transport rate. Error bars were based on the SD of 3 parallel samples. The black and red curve/histogram refer to the MWNT membrane without and with molecular decoration, respectively. Molecular structure of PS-PAA and calcein was shown as insets in (a) and (c), respectively.

Comment 2. The authors compared ion transport rate of each MWNT-membrane before and after lipid decoration. How about oxidized and functionalized MWNT-membrane? Comparing different MWNT-membrane is helpful to uncover the mechanism of enhanced ion transport rate of lipid decorated MWNTs.

Response 2: The condition of oxidized or functionalized MWNT-membrane is not included in this work. There are some related publications working on it. For example: (1) It is reported that treatment of CNT interior with HCl would increase the ionic flux through tubes by a factor of over 10. (2) Diffusive transport of ions of different charge and size (e.g. KCl, MV^{2+} , $Ru(bipy)_3^{2+}$, NDS^{2-} , and Rhod) through CNTs, which have been functionalized with carboxylic acid groups at the CNT entrance, was investigated. The diffusion of oppositely charged ions was found to be

close to bulk diffusion expectations of the ions, while that of similarly charged ions was reduced due to electrostatic interactions. (*Hinds, B. J., Science, 2004, 303, 62-65; Hinds, B. J., ACS Nano, 2011, 5, 3867-3877*)

Comment 3. The inner core of MWNT-membrane is about 10 nm, and the inner diameter of AAO-CT-membrane is about 70 nm. The reviewer is confused on the size difference in this comparison.

Response 3: The AAO-CT-membrane was used as a control to study the influence from the “surface property of the tubes’ inner walls” on assembly behavior of lipids within tubes.

Here, MWNTs have a hydrophobic inner surface and a size of ~10 nm; In contrast, AAO-CTs have a hydrophilic inner wall and a size of ~70 nm. It is noted that, compared with a highly-curved surface (e.g. tubes with a smaller size), it would be much easier for lipids to assemble and localize stably on a flatter surface (e.g. tubes with a larger size).^{*} However, in the experiments, it is found that DOPC lipids prefer to stay in the interior of MWNTs, while they stay at tube tips of AAO-CTs. Based on the above, it can be concluded that the difference in assembly state of lipids in the MWNT- and AAO-CT-membranes is probably due to the different surface property of MWNTs and AAO-CTs.

The following words were complemented in the main text (Line 295-298):

“However, for AAO-CTs, the hydrophilic surface of the amorphous carbon layer makes it difficult for lipids to stay inside the tubes, although it is much easier for an assembled lipid layer to attach to a less curved surface (i.e. AAO-CTs with a larger size) in comparison with a highly curved one (i.e. MWNT with a smaller size; Supporting Information, Section S4).”

(*For further details, please refer to Response 1 to the third referee.)

Comment 4. Fig. 3f and Fig. 3g show the TEM images of MWNT/Diyne-PC and MWNT/Br-PC. Why are the structures not symmetric around the axis of MWNTs?

Response 4: The asymmetric distribution of lipids within CNTs is repeatedly observed under TEM. (It is speculated that such an asymmetry is as a result of the heterogeneity in the inner-wall structure of the MWNTs, or the instability of lipid assemblies on the MWNT surface.^{**}) Although

this, a continuous distribution of lipids along the tubes is supposed to occur, which works as a highway for the ion transport throughout the whole tube.

For accuracy, the description “homogeneous distribution of lipids within the tube” has been deleted (Line 66). Moreover, the sentence (Line 190) was changed to:

“the dark region located continuously within the cavity, indicating an uninterrupted distribution of lipids along the tube.”

The sentence (Line 316-318) was changed to:

“the incorporation and continuous localization of lipids along the tubes might provide successional binding sites for ions with lipid headgroups,”

(**For more detailed explanation, please refer to Response 2 to the third referee.)

Response to the third referee’s comments.

Comments: The authors prepared carbon nanotube (CNT) membranes, in which multi-wall carbon nanotubes (MWCNTs) with an inner diameter of ~10 nm were well aligned along the membrane thickness direction. They further used a diffusion method to incorporate lipid molecules within the MWCNTs. They found that the incorporation of liquid phase DOPC and polymerized Diyne-PC lipid molecules within the tubes induced an enhancement in steady-state ion transport rate by a factor of 5~20 times. In contrast, the gel-phase DPPC preferred to stay at tube tips, and thus was only able to increase the ion transport rate during the initial stage.

I believe the experimental results are interesting. However, I have several concerns over the explanation, interpretation and discussion of their experimental results, considering, in particular, the fact that molecular modeling on the interaction between carbon nanotubes and lipid molecules has been done extensively.

Comment 1. Some simple energetic analyses should be given to explain why some lipid molecules would like to stay inside MWCNTs while others would like to stay at the ends of MWCNTs.

Response 1: For simplicity, the lipids are supposed to attach to the inner wall of MWNTs with their hydrophobic tails in the form of monolayers. According to the theoretical and simulation

models (*J. Phys. Chem. B*, 2004, 108, 750–760; *J. Phys. Chem. B*, 2013, 117, 12113–12123), the tails of DOPC and DPPC lipids have similar affinity to the MWNT surface. However, in the interior of MWNTs, the energy cost for bending DOPC and DPPC monolayers is largely different. The explanation is as follows:

Based on Helfrich model (*Huh, C., J. Soc. Pet. Eng.*, 1983, 23, 829; *Paunov, V. N., Langmuir*, 2000, 16, 8917-8925), the free energy per unit area of a cylindrical monolayer, f , can be taken as: $f = f_0 - 2\kappa \frac{1}{R} + \frac{\kappa}{2} \frac{1}{R^2}$. Here, κ refers to the bending modulus, R is the radius of the tube, f_0 refers to the corresponding free energy of a flat monolayer, and the spontaneous curvature of the monolayer is assumed to be zero. In our case, R is quite small, of approximately 10 nm. Therefore, the value of $\Delta f = f - f_0$, which is mainly dominant by the term $\frac{\kappa}{2} \frac{1}{R^2}$, linearly increases with κ . For lipids in different phase conditions, κ is significantly different (it is noted that the bending modulus of a monolayer approaches half of that of a corresponding bilayer, *J. Chem. Theory Comput.*, 2013, 9, 3866–3871). The κ value of a gel-phase DPPC monolayer is roughly 10 times larger than that of a liquid-phase DOPC monolayer (*Dimova, R., Advances in Colloid & Interface Science*, 2014, 208(24), 225-234; *Uline, M. J., Faraday Discuss.*, 2013, 161, 177–303). This means that the energy cost for bending DPPC monolayer could be 10 times larger than that of a DOPC one.

Therefore, it would be much easier for the DOPC molecules to attach to the inner wall of MWNTs in comparison with the DPPC ones.

These explanations were complemented as **Section S4** in the Supporting Information. The corresponding introduction was also added in the main text:

Line 298-301, “Furthermore, in comparison with gel-phase DPPC, the flexible tails of liquid-phase DOPC promotes the the assembly and localization of lipids on the highly-curved inner surface of CNTs as a result of a much lowered energy cost for layer bending (Supporting Information, Section S4)”.

Comment 2. The membrane thickness is about 10 micrometers (from Fig.1c) and the inner diameter of MWCNTs is about 10 nm. In general, DOPC lipid molecules are much smaller (a few nanometers long and sub-nanometer in diameter). In aqueous solution, lipid molecules can form

different structures, for example, micelle or lipid bilayer. How do these lipid molecules self-assemble within the nanotubes in a homogeneous distribution? Between lipid-lipid and lipid-nanotube wall, which interaction is stronger? Answers to these questions may be important to answer how lipid molecules are distributed within the tubes.

Response 2: (1) For clarity, the statement of “homogeneous distribution” has been deleted in the main text. It is speculated that, the lipids attach to the inner wall of MWNTs with their hydrophobic tails in the form of *monolayers*. A continuous distribution of lipids along the tubes is supposed to occur, which works as a highway for the ion transport throughout the whole tube. However, the lipids might not homogeneously spread over the whole inner wall of MWNTs, which is confirmed by TEM images in which the structure of lipids is not symmetric around the axis of MWNTs. (Please refer to Response 4 to the second referee.)

(2) The interaction energy between lipids (including lipid head and lipid tail), CNT surface, and water, is analyzed and shown in **Fig. R4** (*J. Phys. Chem. B*, 2004, 108, 750–760; *J. Phys. Chem. B*, 2013, 117, 12113–12123). Here, the minimum energy value of each profile (marked with orange arrow) is used to describe the interaction state under each condition.

It is clearly shown that, the hydrophilic lipid head prefers to stay with water ($E_{\min(\text{water-lipid head})} = -5.6k_B T$) while the hydrophobic lipid tail prefers to stay away from it ($E_{\min(\text{water-lipid tail})} = -2.0k_B T$). However, for the other conditions, e.g. the interaction between lipid tail-lipid tail ($E_{\min(\text{lipid tail-lipid tail})} = -3.6k_B T$), lipid tail-CNT ($E_{\min(\text{lipid tail-CNT})} = -3.2k_B T$), or lipid head-CNT, water-CNT ($E_{\min(\text{lipid head-CNT})} = E_{\min(\text{water-CNT})} = -2.7k_B T$), there is not much difference between them. For example, the minimum energy value between lipid head (or water) and CNT, is only $0.5k_B T$ larger than that between lipid tail and CNT, and $0.9k_B T$ larger than that between lipid tail and lipid tail. On the other hand, it is noted that the bending energy of a lipid monolayer on the highly-curved inner surface of CNTs is greatly large especially for the gel-phase DPPC monolayer (as mentioned in Response 1). Therefore, under external disturbance (e.g. drying and rehydration of the membrane during repeated tests, Line 257 in the main text), the structure of lipid monolayer within interior of CNTs might be disrupted. This might be the reason why the lipid molecules escape from the interior to outside of the tubes during repeated tests (Line 266 in the main text).

These explanations were complemented as **Section S3** in the Supporting Information (Line

294 in the main text).

Fig. R4 LJ interaction energy distribution between different components in the system. The minimum values, marked with orange arrow, are used for comparison between different conditions.

Comment 3. The authors state that lipid molecules are stable within MWCNTs. In what form? Why? Is there any evidence to back up this statement?

Response 3: Experiments (confocal and ionic transport test) show that the localization of DOPC or DPPC lipids in interior of MWNTs is not stable during repeated tests (Line 263-266). For possible reasons, please refer to Response 2. In contrast, Diyne-PC, after polymerization, shows a good stability even after more than five cycles' test (Line 285-286).

For clarity, the statement of “stable localization” of DOPC or DPPC has been deleted in the main text (Line 294).

Comment 4. When lipid molecules are inserted into MWCNTs, polarized heads might attract ions, which in turn might exert forces to counter further ion diffusion. In addition, the presence of lipid molecules with MWCNTs might effectively reduce the cross-sectional area, which might reduce the flux of ion transport. Thus, the authors need to consider these issues to discuss what is

going on in the initial and steady-state stages.

Response 4: Thanks for the suggestion, which makes us further think over the underlying mechanism. Ionic transport through MWNTs is determined by various factors:

(1) Steric interactions. The decrease in pore size due to molecular incorporation would probably hinder the ion transport through MWNTs. The amphiphilic and electroneutral or negatively charged (copolymer) molecules, e.g. PS-PAA and calcein which reduce the ion transport rate in our complemented experiments, are good examples to prove this (refer to Response 1 to the second referee).

(2) Electrostatic interactions. Hinds et al. reported that, functionalization of tube entrance with carboxylic groups through water-plasma oxidation, would influence the ion transport through tubes in the following manners: diffusivity of the positively charged species is close to bulk diffusion predictions, while the negatively charged species is slower than bulk diffusion predictions (*Hinds, B. J., ACS Nano, 2011, 5, 3867-3877*).

It is also noted that: 1' Treatment of CNT interior with HCl would increase the ionic flux through tubes by a factor of over 10 (*Hinds, B. J., Science, 2004, 303, 62-65*). 2' For the charge screening effect. It is influenced by the tube size as well as the ion concentration. For example, Fornaseior et al. once demonstrated salt rejection by electrostatic means in sub-2 nm CNT channels at millimolar salt concentrations (*Proc. Natl. Acad. Sci., 2008, 105, 17250–17255*).

(3) In our work, the diffusion situation of KCl through tubes with lipid decoration is quite complicated, which involves two types of ions (K^+ , Cl^-), polarized lipid headgroups, and solvent. Interaction between ions and the zwitterionic headgroups of lipids is supposed as a key factor for the enhancement of ion transport through tubes. To understand this, a simple consideration of the coulomb interaction between an electric dipole and an ion (in one-dimension case) would be helpful. As shown in **Fig. R5**, the interaction strength between ion and dipole (both attraction and repulsion) is significantly lower in comparison with that between ion pairs ($\oplus \leftrightarrow \oplus$, or $\ominus \leftrightarrow \ominus$). This means that it is much easier for an ion (K^+ or Cl^-) to approach to or escape from a dipole, compared with a positively or negatively charged group. In this condition, the continuously distributed lipid headgroups work as a highway for the ion transport throughout the tube, which finally enhances the diffusion rate of ions.

Fig. R5 Coulomb interaction energy profiles between ions and dipoles. $\oplus$, $\ominus$, and $\oplus\text{-}\ominus$, refer to a positively charged ion, a negatively charged ion, and a dipole, respectively.

Comment 5. For comparison, the electrical conductivity vs. time for MWCNT membrane and AAO-CT membrane without decoration of lipid molecules should be given.

Response 5: The data mentioned by the referee is provided and shown in black in Fig. 4. (Line 232-238)

Also, for the corresponding ion transport rate shown in Fig. 4-insets, the values for lipid-decorated NT-membranes are normalized by that of the naked carbon membrane.

Modulated enhancement in ion transport through carbon nanotubes by lipid decoration

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ABSTRACT. Biomimetic channels based on carbon nanotubes (CNTs) with fast and selective transport have attractive applications in many fields. In this work, a remarkable and modulated enhancement in the ion transport rate through CNTs is facilitated by means of lipid decoration,

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by a factor of up to 20 times. A type of CNT membrane is firstly prepared, composed of well aligned multi-wall carbon nanotubes with an inner size of ~10 nm. An inter-diffusion method is used to efficiently incorporate lipids within the CNTs. It is found that the lipid phase state as well as the surface property of the tubes' inner walls corporately determine the assembly behavior, such as location and stability of lipids, which further influence the ion transport rate through the tubes. For example, the incorporation and self-assembly of liquid-phase DOPC and polymerized Diyne-PC within the tubes induces an enhancement in steady ion transport rate through CNTs by a factor of 5 and 20 times, respectively. In contrast, the gel-phase DPPC prefers to stay at tube tips, which increases the ion transport rate during the initial stage only. This work provides a practical guide to regulate the ion transport behaviors through CNTs for versatile applications.

1. Introduction

Owing to their unique and outstanding properties, extensive research has been carried out on carbon nanotubes (CNTs) for practical applications in such as novel nanomaterial science and biomedical fields [1–4]. In particular, CNTs offer the potential as a candidate of mimicking biological channels due to their inner-core diameter in the size range of many proteins and other important biological macromolecules [5,6]. However, compared with biological protein channels, which can realize extraordinarily complicated cellular functions such as selective transport and high-efficient transmission of various chemicals across cell walls, the fabrication of such CNT-based biomimetic channels still poses a significant challenge [\[7–9\]](#).

In fact, transport phenomena through the hollow conduits of CNTs have been attracting intense interest in terms of both theoretical and experimental researches [\[10–15\]](#). Namely, the successful preparation of a polymer membrane composed of large quantities of CNTs arranged

in parallel makes it possible for macroscopic measurement of the trans-nanotube transportation [5,6,16]. By this method, it is proven that CNTs have a distinct advantage in fluid transport with four to five orders of magnitude faster than that predicted by conventional fluid-flow theory [11–13]. It is assumed that such a high flow velocity is attributable to the near-frictionless movement of liquid molecules along the walls of CNTs. Hydrophilic treatment can further enhance mass transfer rate of CNTs. For example, by functionalizing CNTs with carboxylic acid groups through plasma treatment, liquid flow through the cores of CNTs could be further accelerated by ~1,000-10,000 times faster than that predicted by the conventional no-slip hydrodynamic theory [11,17]. This finding indicates that surface modification of CNTs is a powerful method to improve their mass transport capability. However, for ion transportation through CNTs, the transport situation becomes much more complicated, although water is still the main transport medium [18–21]. It was found that, even after plasma treatments, ion diffusion through CNT was close to the bulk diffusion expectations and no obvious acceleration was detected [7]. Moreover, if there are charged groups near the CNT entrance, the transport of ions would be further hindered and even rejected due to the Donnan-type ion rejection mechanism [16].

Functionalization of CNTs with phospholipids is of significance for biomedical applications [22,23]. Modification of the CNT surface with PEGylated phospholipid molecules has been widely used to improve the aqueous stability and biocompatibility of CNTs [24–26]. It is assumed by some models that phospholipids would attach to the exterior walls of CNTs and even assemble into a helical structure [27–29]. However, to the best of our knowledge, few experimental studies have been reported on the assembly of phospholipids within the inner cores of CNTs, and particularly its impact on the ion transportation through CNTs, which is mostly

caused by difficulties in controllable filling of lipids into the CNT cavity and limitations in characterization methods [30–34].

In this work, based on the millimeter-sized CNT membrane comprising well aligned multi-wall carbon nanotubes (i.e., MWNT-membrane, with an inner size of ~10 nm), an inter-diffusion method was employed to incorporate phospholipid molecules into the CNTs under mild conditions. Another type of CNT membrane composed of Anodic Aluminium Oxide-based carbon tubes (i.e., AAO-CT-membrane, with an inner diameter of ~70 nm) was used as a reference. We found that lipids could stay inside the tubes or stack at their tips, depending on lipid types and surface properties of the inner walls of the tubes. Ionic transport tests showed the manner of lipid decoration on CNTs significantly influenced the behavior of ion transport through the tubes. Incorporation of lipids in the tube interior enhances ion transport rate by a factor of more than five, whereas CNT tip-exclusive lipid decoration would lead to an improvement during the initial ion transport stage only. These results provide a practical guide for designing advanced biomimetic nanoscale channels with controllable and high efficiency ion transportation.

2. Experimental Section

2.1 Materials

1,2-Dioleoyl-sn-glycero-3-phosphocholine (DOPC), 1,2-dipalmitoyl-sn-glycero-3-phosphocholine (DPPC), 1-palmitoyl-2-(9,10-dibromo)stearoyl-sn-glycero-3-phosphocholine (Br-PC), 1,2-di-(10Z,12Z-tricosadiynoyl)-sn-glycero-3-phosphocholine (Diyne-PC), and 1,2-dipalmitoyl-sn-glycero-3-phosphoethanolamine-N-(lissaminerhodamine B sulfonyl) (Rh-PE), were purchased from Avanti Polar Lipids and used as received (**Fig. 1a**). All other chemicals

(AR) were purchased from Sinopharm Chemical Reagent Co., Ltd. and used without further purification.

2.2 Preparation of MWNT- and AAO-CT-membrane

The MWNT-membrane was fabricated based on the preparation of a vertically-aligned MWNT-array as detailed in our previous reports [35,36]. Briefly, a 1–10 mm thick MWNT-array was first grown via the classical chemical vapor deposition (CVD) method on a Si wafer substrate. After sealing the tubes' tips with polypropylene, ethoxyline was employed to fill the spaces within the nanotube array, and this was followed by solidification. The bulk material was then sliced (parallel to the substrate) using a microtome (RMC, Boeckeler Instruments, Inc.) into freestanding membranes with a thickness of 10 ± 1 μm . Oxygen plasma etching was then applied with a PDC-32G plasma cleaner (Harrick Plasma Inc.) to remove the organic residues around the tips of the CNTs (18 W for 20 min, O_2 , 500 mtorr). The AAO-CT-membrane was fabricated by depositing a layer of amorphous carbon onto the porous AAO structure by the template method. After eliminating the carbon on both surfaces of the film, an aligned carbon tube membrane with penetrating pores was obtained [37].

2.3 Diffusion and ion transport test

Diffusion-unit set-up. The home-made diffusion unit was setup as demonstrated in Fig. 1b. The unit was comprised of two cells, A and B (both in resin, each with a pore 4 mm in diameter), and two spacers, E and F (in silicone, also had a 4 mm size pore in the middle). The solution in the two cells could communicate through the pores and the membrane sandwiched between the spacers. Each time for solution (or membrane) replacement, solutions in the two cells were

103 poured out simultaneously, and the unit was disassembled, washed completely and dried under
104 N₂ flow for its next use.

105 Ion transport test. The tests were performed based on the diffusion procedure. The membrane
106 was first installed within the diffusion unit. After that, 7 mL KCl solution (0.1 M and 0.5 mM)
107 were filled into the feed and the permeate cells A and B, respectively. Thus, the total mass of
108 KCl in the feed solution was more than two orders of magnitude greater than that in the
109 permeate, effectively eliminating depletion effects. Such a concentration gradient led to the ionic
110 transport across the membrane from A to B. The changes in electrical conductivity of the
111 permeate (cell B) were monitored simultaneously during incubation by a water analyzer
112 (Ultrameter II, Myron L Company).

113 Lipid decoration. Lipid decoration for the membrane was realized by a similar inter-diffusion
114 method. A homogeneous lipid solution (0.2 mg mL⁻¹) was used as a mother solution. Briefly, a
115 700 µL lipid solution (2.0 mg mL⁻¹, containing 0.5 mol% Rh-PE for fluorescent labeling) was
116 transferred into an ampoule (wrapped with tin foil paper), dried under an N₂ flow and kept in a
117 vacuum overnight. The membrane was then rehydrated with 7 mL distilled water and sonicated
118 for a complete dispersion of lipids. During lipid decoration, a naked carbon membrane was first
119 installed within the diffusion unit. 7 mL lipid mother solution and distilled water were added into
120 cells A and B, respectively. After incubation at room temperature for 48 h, a fluorescent signal of
121 lipids can be detected from cell B, which indicates that the lipids have successfully permeated
122 through the membrane. The membrane was then gently removed, washed with water and dried
123 under N₂ flow for further experiments.

Experiment steps. For each carbon membrane, the experiment was carried out as follows. First, the naked membrane was set up for a KCl diffusion test in order to obtain baseline ion diffusion data. Second, the membrane was decorated with lipids, followed by other characterizations including TEM and confocal imaging. Third, the carbon membrane was reassembled and step 1 was repeated so that the ionic diffusion rate of the membrane with incorporated lipids could be measured. Fourth, the KCl solution was renewed, and the membrane was washed and dried, then the ionic diffusion test was repeated, as described in the main text. Specifically, for lipid Diyne-PC, after step 3, the carbon membrane was removed, dried and placed on a glass slide under UV exposure for 30 min (285 nm wavelength) for lipid polymerization. Finally, the membrane was reassembled for the following ionic diffusion test.

Fig. 1 Chemical structures of lipids and images demonstrating the diffusion unit and process. (a) Molecular structure of lipids DOPC, DPPC, Br-PC and Diyne-PC. (b) Digital photo of the diffusion unit, including cells (A, B) with pores on one side (C, D), spacers (E, F) with pores, and the sandwiched membrane (G; cannot be seen here). Another spacer (and membrane) was

placed aside for reference. (c) Schematic showing the transport of ions through CNTs within a membrane from the feed side to the permeate side.

2.4 Characterizations

The morphology of the carbon membranes was characterized with SEM (Hitachi S-4700, Hitachi). The structure of the lipids within the membrane was further characterized with TEM (FEI Tecnai G-20) at 200 kV and small angle X-ray scattering (SAXS) at Shanghai Synchrotron Radiation Facility (SSRF).

Optical observation was performed on an inverted confocal laser scanning microscope (LSM 710, Zeiss) equipped with a 100 $\times$ oil objective. Rhodamine-conjugated phospholipids were excited by a He–Ne laser (EX 543 nm), and the fluorescence was observed through filter set 20 (EM BP 575–640 nm). In the meantime, the transmission channel illuminated with a halogen lamp was acquired. All experiments were carried out at room temperature.

3. Result and discussion

3.1 Characterization

Fig. 2 shows schematic and SEM images of the as-fabricated MWNT- and AAO-CT-membranes. For a MWNT-membrane with a thickness of 10 ± 1 μm , the nanotubes, which are normal-oriented and parallel-aligned in the membrane, are clearly distinguishable from the cross-sectional image under SEM (Fig. 2b, c). On the other hand, for the AAO-CT-membrane, the carbon tubes with similar orientation and alignment have a much larger pore diameter of ~ 70 nm and a length of 43 ± 4 μm . It is worth noting that the nanopores of CNTs are the only paths for mass transportation due to the impermeable polymer matrix (or AAO template). Thus, the

macroscopic transport measurements of ions through membrane were performed to determine the transport through the inner cores of both types of CNTs [35].

Fig. 2 Schematic and SEM images of the MWNT- (a-c) and AAO-CT- (d-f) membranes. (a) Schematic, (a-inset) digital and (c) cross-sectional SEM images of a MWNT-membrane. (b) presents the aligned MWNT array grown vertically on a substrate. (d) Schematic, (e) cross-sectional and (f) top-view SEM images of an AAO-based amorphous CT-membrane.

The membrane was then sandwiched within the diffusion unit for lipid decoration and the subsequent ion diffusion test. **Fig. 3** shows confocal fluorescence images of the MWNT- and AAO-CT-membranes right after DOPC decoration. The membrane surfaces and location of the fluorescent lipids can be distinguished from the transmission and red fluorescence channels, respectively. Moreover, based on the three dimensional (3D) scanning, it was observed that for the MWNT-membrane, the lipids were located within the interior of the CNTs (Fig. 3b, i). However, for the AAO-CT-membrane, the lipids were uniformly distributed on the two ends of the CNTs, with an inter-layer distance similar to the thickness of the initial AAO-CT-membrane (Fig. 3d). Z-stack images of both membranes are shown for reference in Fig. S1 in the supporting information. Here, DOPC is replaced with various other types of lipids, including DPPC (in gel

phase at room temperature), Diyne-PC (a kind of diacetylene phospholipid) and Br-PC (labeled with two Br atoms in each molecule). All the above-mentioned lipids share similar assembly states of CNTs with DOPC.

To obtain more details of the assembly method of lipids within CNTs, the scaffold (polymeric or AAO) membranes were digested and the CNTs (with loaded lipids) were redispersed and loaded on a lacey support membrane for TEM imaging. To have a good contrast under TEM, Br-PC and Diyne-PC were used here instead of DOPC or DPPC. **Fig. 3e-g** show TEM images of the MWNTs (with an inner core diameter of ~10 nm) without and with lipid decoration, from which the multilayer structure of the tube walls can be obviously distinguished (Arrow 1). It should be noted that for the native MWNTs, the cavity region is much dimmer in comparison with the wall region. However, for the lipid-decorated tubes, the cavity region is even darker in contrast with the walls (Arrow 3). This is reasonable considering that, compared with C, the P (and/or Br) atoms from the lipids contribute a much stronger influence on the electron beam during TEM imaging. This result further confirms the existence of lipids within the MWNTs (although a gap might appear somewhere between the wall and the encapsulated lipid molecules as indicated with Arrow 2) [37]. Furthermore, the dark region located continuously within the cavity, indicating an uninterrupted distribution of lipids along the tube. In contrast, similar morphologies were obtained for the AAO-CT membranes without and with lipid decoration. The inner core region is much dimmer than the wall region, indicating that hardly any lipid remains inside the amorphous carbon tubes (Fig. 2h). Synchrotron X-ray scattering was also carried out to characterize the lipid structure within both membranes. However, only signal of an ordered structure with a period of ~155 nm (Fig. S2), probably referring to the parallel-distributed amorphous carbon tubes (i.e. porous aluminum template), was acquired from the AAO-CT-

membrane. No signal of ordered lipid structures (such as lamellar or hexagonal assembly) was acquired from either membrane (Supporting Information).

Fig. 3 Confocal fluorescence microscopy, TEM and schematic images of the MWNT/lipid and AAO-CT/lipid membranes. (a) Confocal 2D (in red fluorescence, transmission and overlaid channels) and (b-d) 3D images of the MWNT/DOPC (a, b) or AAO-CT/DOPC (d) composite membrane. (c) Redistribution of lipids within the MWNT/DOPC composite membrane after approximately five cycles of the ionic diffusion test. Red fluorescence comes from the Rh-labeled lipid. (e-h) TEM images of MWNT, MWNT/Diyn-PC, MWNT/Br-PC and AAO-

CT/Br-PC samples. Arrows 1-3 refer to the graphite layer, the gap and the encapsulated lipid molecules, respectively. (i, j) Schematics representing the relative locations of fluorescent lipids and CNTs within a MWNT/DOPC membrane, corresponding to (b) and (c), respectively.

3.2 Influence from lipid decoration on ion transport rate through tubes

Ion transport rates through tubes both with and without lipid decoration were measured based on the concentration-driven diffusion of KCl across the membranes. The membranes were fixed between a feed cell and a permeate cell within the diffusion unit, and the concentration gradient between the two cells led to ion diffusion through tubes (Fig. 1b, c). Based on the time-dependent increase in conductivity of the solution in the permeate cell, the ion transport rate across the tubes was obtained. Furthermore, for the native MWNT-membrane, the conductivity values were used to calculate the permeable pore area (cm^2) and density ($\#/\text{cm}^2$) which can satisfactorily characterize the permeability of the membrane (Supporting Information, Section S2). On the other hand, for the tubes with lipid decoration, the influence from lipid functionalization was described by comparing the ion transport rate of each membrane before and after lipid decoration, and consequently an average from more than three independent samples was calculated. This is suspected to be more direct and accurate concerning the deviation among various membrane samples.

Fig. 4 shows the time-lapse distribution of conductivity of the solution in the permeate cell, corresponding to the ion transport rate through a membrane. For the native MWNT-membrane (Fig. 4a, in black), the changes in conductivity are characterized with two typical stages: in Stage I, the value increases quickly, referring to a fast transport of ions through tubes; then, in Stage II, the value increases gradually with a linear dependence on time, indicating a dynamically-

balanced transfer of ions in the tubes. Moreover, based on the steady state flux in Stage II, the permeable pore density of our MWNT-membranes was calculated to be $2.2 \pm 0.2 \times 10^8 \text{ cm}^{-2}$, which indicates a good permeability of the membrane (i.e., tubes in the membrane).

Fig. 4 Electrical conductivity changes with time for the diffusion solution during KCl transfer process through typical MWNT/lipid (a, c, e) or AAO-CT/lipid (b, d, f) membranes. Insets, corresponding ion transport rate calculated from the electrical conductivity distribution (normalized by the value of the naked carbon membrane and averaged from 3 independent samples). The black curve/histogram refers to the naked carbon membrane while the red (or blue) one refers to that in the first (or repeated) ionic diffusion test; in (e, f), the red and blue curves refer to the membrane before and after UV polymerization of Diyne-PC, respectively. Right-inset in (e), schematic diagram demonstrating the polymerization of Diyne-PC lipids under UV exposure.

245

246 After DOPC decoration, obvious changes appear (Fig. 4a, in red). The evolution of
247 conductivity still shows a typical two-stage process, but the corresponding values experience a
248 significant increase. By fitting the conductivity profile, ion transport rates through tubes were
249 obtained. Before lipid decoration, the ion transport rates in stages I (concerning the almost linear
250 period before 60 min) and II are 3.13×10^{-10} and 4.68×10^{-11} moles s^{-1} , respectively. After DOPC
251 decoration (in red), factors of ~ 2 (for Stage I, analyzed from more than three independent
252 samples) and ~ 5 (for Stage II) times increases occur (Fig. 4a, inset). Such improvements clearly
253 suggest that the assembly of lipids in the tube's interior is able to enhance ion transport through
254 CNTs.

255 Moreover, ion transport through tubes is significantly affected by the location and/or assembly
256 of lipids within tubes. Compared with the MWNT-membrane, the ion transport rate in the AAO-
257 CT-membrane only increases slightly during Stage I (from $\sim 2.75 \times 10^{-8}$ to $\sim 9.78 \times 10^{-8}$ moles s^{-1} ,
258 referring to the typical membrane shown in Fig. 4b), while in Stage II, the value recovers to its
259 pre-lipid modification state (of around 2.2×10^{-9} moles s^{-1}). Note that in this case lipids mainly
260 accumulate at the tips of the tubes while small molecules remain inside of the tubes.

261 The type of lipid used in lipid decoration also has an impact on the enhancement effect on ion
262 transport through tubes. For the MWNT/DOPC composite membrane, it was found that in
263 repeated ion-transport tests (after drying and rehydration of the membrane as stated in the
264 experimental section), the conductivity profile (Fig. 4a, in blue) almost overlaid with the initial
265 one (in red). This indicates that the enhancement effect on ion transport (i.e. the stability of lipid
266 decoration within tubes) is relatively stable. However, when we replaced DOPC with DPPC
267 which exists in gel phase at room temperature (Fig. 4c, black and red), it was found that the

lipid-induced enhancement on ion transport occurred only in the first measurement (with an enhancement rate being similar to that of DOPC); whereas in the following repeated cycles, the ion transport rate recovers to the level of a case without lipid decoration (except for an enhancement in Stage I). In fact, even for DOPC decoration, after a repetition of 3-5 cycles, the escape of DOPC molecules from the interior to the tips of the tubes (Fig. 3c), and the corresponding recovery in ion transport rate, were observed. On the other hand, for the AAO-CT-membrane, no obvious difference was observed when DOPC was replaced with DPPC, indicating the stable accumulation of lipids at the tips of this type of tubes (Fig. 4d).

The stability of lipid decoration, especially inside the tubes, is crucial for practical applications. To conquer this, another type of diacetylene lipid, Diyne-PC, was employed. It is known that under UV radiation, the adjacent tails of Diyne-PC lipids tend to polymerize with covalent bonds, leading to the formation of a continuous π bond within the layer [38]. This significantly improves the stability of the assembled lipid structure (Fig. 4e right-inset). By the same concentration-driven method, Diyne-PC was incorporated into the MWNT-membrane, which showed a similar distribution as that of DOPC inside the CNTs (Fig. S3a,b). UV irradiation was then performed to polymerize the lipids. Fluorescence spectra of model membranes before and after lipid polymerization are shown in Fig. S3c-e to confirm the successful polymerization of lipids within membrane.

Fig. 4e shows the conductivity profiles for the condition of model MWNT-membrane, with and without Diyne-PC incorporation, both before and after UV-polymerization. Before UV irradiation, the influence of Diyne-PC decoration on steady ion transport rate was similar to (although lower than) that of DOPC, with a 3-4 times enhancement (Fig. 4e in red); however, in a sharp striking contrast, after polymerization, the steady ion transport rate was increased up to

20 times larger than that of the native membrane (Fig. 4e in blue). Furthermore, repeated tests showed a good stability of such a promoted transport rate even after more than five cycles' test. However, for the AAO-CT/Diyne-PC composite membrane (Fig. S3b), UV-polymerization had little effect on the steady ionic transport (Fig. 4f).

3.3 Discussion

By an inter-diffusion method, lipids were successfully incorporated into CNTs. According to our results, lipids can self-assemble inside or outside the tubes, probably depending on the surface properties of the inner-walls of the tubes and the phase state of lipids. For MWNTs, the strong affinity between the alkyl tails of lipid molecules and the hydrophobic aromatic plane of tubes facilitates the localization of lipids within the interior of the tubes (Supporting Information, Section S3). However, for AAO-CTs, the hydrophilic surface of the amorphous carbon layer makes it difficult for lipids to stay inside the tubes, although it is much easier for an assembled lipid layer to attach to a less curved surface (i.e. AAO-CTs with a larger size) in comparison with a highly curved one (i.e. MWNT with a smaller size; Supporting Information, Section S4). Furthermore, in comparison with gel-phase DPPC, the flexible tails of liquid-phase DOPC promotes the assembly and localization of lipids on the highly-curved inner surface of CNTs as a result of a much lowered energy cost for layer bending (Supporting Information, Section S4).

It is clearly demonstrated that the assembly of lipids inside the MWNTs significantly facilitates the ion transport through the tubes, on the basis of confocal, TEM and ion transport tests. Moreover, polymerization of Diyne-PC inside the tubes further enhances the steady ion transport compared with that of DOPC/DPPC; this is probably due to the more uniform and stable distribution of lipid molecules caused by inter-molecule binding between adjacent Diyne-PCs. In addition, accumulation of lipids at the tips of the CNTs could also boost the ion transport

rate at the initial stage, although without much influence on the steady ion transport process. These results all promise the regulation of ion transportation behaviors through CNTs for practical applications.

The influence of lipid decoration on ion transport is suspected to be associated with the complicate ion-lipid interactions, which could create a preferred distribution of ions near the zwitterionic lipid headgroups [39–41]. Electroneutral or negatively charged molecules were also used instead of the zwitterionic lipids for MWNT decoration, which, however, reduced the ion transport rate (Fig. S4). In this regard, the accumulated lipids at tube-tips would increase the local ionic concentration at the tube entrance, and consequently enhance the ion transport under the effect of flow during the initial period (i.e. Stage I). In contrast, the incorporation and continuous localization of lipids along the tubes might provide successional binding sites for ions with lipid headgroups, which could work as a highway for the ion transport throughout the whole tube, and thus significantly increase the steady ion transport rate (although the pore size might decrease due to lipid incorporation). The remarkable increase in ion transport due to the polymerized Diyne-PC decoration further confirms this speculation.

4. Conclusion

In this study, we prepared two types of vertically-aligned CNT membranes composed of MWNTs or AAO-based amorphous CNTs, and investigated the influence of lipid decoration on the ion transport properties through the inner core of the nanotubes via macroscopic transport measurements. Concentration-driven diffusion was employed for the incorporation of lipids within the tubes. Confocal imaging and TEM observation indicated the continuous distribution of lipids inside the MWNTs, probably due to the hydrophobic interaction between the alkyl tails

of lipids and the aromatic wall plane of MWNT. In contrast, for the AAO-CT-membrane, lipids tended to accumulate at the two sides of the membrane, likely at the tips of the carbon tubes. Ion transport tests demonstrated an enhancement in the steady ion transport rate through MWNTs due to lipid incorporation, by approximately 5 times for DOPC or DPPC, 3-4 times for Diyne-PC, and up to 20 times for Diyne-PC after polymerization. Furthermore, the accumulation of lipids at the tips of the carbon tubes (both MWNTs and AAO-CTs) accelerated the ion transport during the initial stage, but hardly influenced the steady transport rate of ions. The increase in local ionic concentration due to the binding of ions to zwitterionic headgroups of the decorated lipids is supposed to be one of the key factors for the enhanced ion transport rate. Our results provide promising possibilities for selective and high-efficiency transport of CNTs for separation and sensing applications [16], after further functionalization of lipids.

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Appendix A. Supplementary data

Confocal z-stack images of the MWNT/DOPC and AAO-CT/DOPC composite membranes; synchrotron SAXS pattern of the AAO-CT/DOPC membrane; confocal 3D images and PL profiles of the MWNT/Diyne-PC and AAO-CT/Diyne-PC membranes; ion transport through

MWNT membranes after PS-PAA or calcein decoration; estimation of the permeable pore area and density from KCl diffusion measurements; interaction energy analysis between components of a lipid-decorated MWNT system; energetic analysis of DOPC and DPPC assemblies in MWNTs. These materials can be found, in the online version, at ...

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