

## Ionic Rectification through the Formation of Complexes or Precipitation in Carbon Nanotube Membranes

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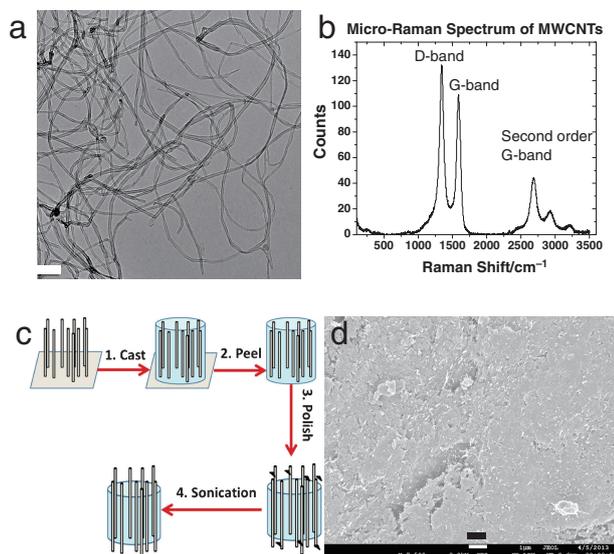
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Carbon nanotube membranes were fabricated using arrays of millimeter-long multiwalled carbon nanotubes (MWCNTs) with an inner diameter of about 8 nm through a low-cost cast–polishing method. The fabricated carbon nanotube membranes demonstrated a unique ionic rectification phenomenon through two fundamentally different mechanisms: a) the formation of metal ion complexes and b) the precipitation of insoluble lead molybdate inside the carbon nanotubes. These discoveries could be applied to detecting the presence of toxic metal ions in contaminated water resources through a relatively simple approach.

Recently, solid-state nanoporous membranes have attracted significant attention owing to their potential applications in the fields of fast DNA sequencing,<sup>1–3</sup> gas separation,<sup>4</sup> biosensors,<sup>5</sup> water desalination,<sup>6</sup> ionic rectification,<sup>7,8</sup> drug delivery and mimicking of biological membranes,<sup>9–12</sup> nanomaterial synthesis,<sup>13</sup> etc. These membranes can be made from inorganic, organic, or composite materials.<sup>2,3,8,14–16</sup> Compared with inorganic membranes, inorganic/polymer composite membranes have shown much stronger mechanical strengths.<sup>17,18</sup> Several strategies are currently available to obtain an ionic rectification effect from these solid-state nanoporous membranes. First, if the two ends of the nanopores are functionalized with molecules of different charges, an ionic depletion zone can be created inside the nanopore. When a bias of a certain polarity is applied, it can result in a significant ionic rectification effect.<sup>8,19,20</sup> Because this type of ionic rectification is based on charge repulsion, all metal ions of the same charge are similarly rectified. The second strategy is based on the electrostatic actuation of the active “gate-keeping molecules” anchored on these nanopores.<sup>9,21,22</sup> Electrostatic actuation of these charged gating macromolecules or small molecules can change either the electrostatic repulsion force or the steric hindrance in the tube core dramatically, leading to asymmetry in the curve of ionic current versus voltage. However, this strategy requires a complicated surface modification, and Li<sup>+</sup>, Na<sup>+</sup>, and K<sup>+</sup> metal ions showed a similar ionic rectification response. Third, if one side of the nanoporous membrane is filled with an aqueous solution of bulky cations and small anions and another side is filled with an aqueous solution containing bulky anions and small cations, a significant ionic current reduction can be observed, provided that the total size of bulky cation and bulky anion is bigger than the pore size.<sup>11</sup> Fourth, the transmembrane ionic current can be fluctuated through the formation of insoluble precipitates at one side of the track-etched conical polymeric nanopore.<sup>23</sup> However, these types of ionic rectifications suffer from low selectivity and nonspecificity, i.e., all kinds of ionic species are rejected simultaneously when a bias of a certain polarity is applied.

Carbon nanotube (CNT) membranes possess many unique properties. CNTs have an atomically smooth hydrophobic graphite core, allowing fluid flow a thousand times faster than in conventional polymeric membranes.<sup>14,24,25</sup> Their excellent electrical conductivity can greatly facilitate efficient electrochemical functionalization and electrostatic actuation of charged tethers.<sup>9,21</sup> The electro-osmosis flow in 1-nm CNTs is nearly four orders of magnitude higher than that in microporous channels owing to the nanoscale confined geometry and the atomically smooth core surface.<sup>11,12</sup> The primary goal of this report is to show that the realization of more specific ionic rectification is possible. When a metal ion complex or precipitation is induced inside carbon nanotubes using specific ligands or anions, the transmembrane current can be shut down, resulting in significant ionic rectification. These findings can be utilized to develop a highly sensitive and selective sensor for toxic metal ions in contaminated water resources through a facile detection technique.

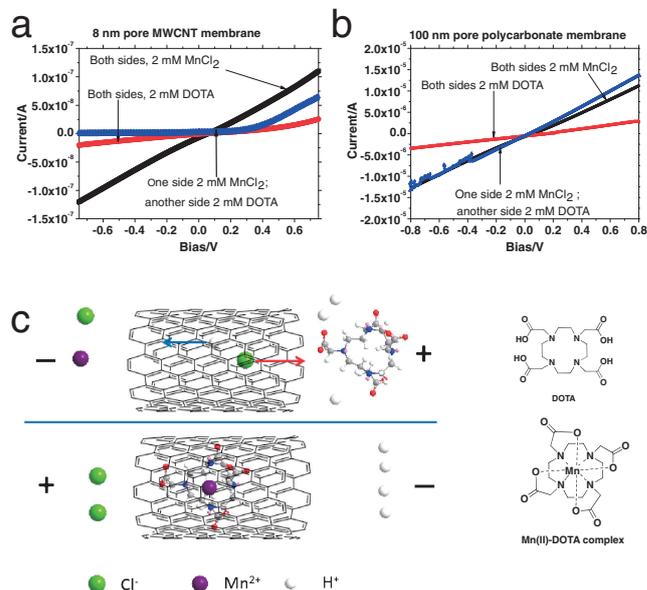
In general, there are four fabrication methods currently available for CNT membranes, which either rely on the usage of expensive semiconductor-industry techniques or do not utilize uniformly aligned CNTs, thus leading to a low porosity.<sup>10,15,24,26,27</sup> Herein, a low-cost polishing method is proposed for the fabrication of CNT membranes utilizing millimeter-long CNT arrays, with advantages including its low cost, high yield, and high scale-up potential. First, the millimeter-long CNT array was synthesized through a well-known water-catalyzed CVD method.<sup>28</sup> The detailed synthetic procedure for the CNT arrays is shown in S1.<sup>29</sup> The synthesized multiwalled (MW) CNTs have an average core diameter of approximately 8 nm with a standard deviation of 1.9 nm (Figures 1a and S1<sup>29</sup>), and the length of the CNTs can be up to around 5 mm after a reaction time of 3 h (S1).<sup>29</sup> The typical length of the CNT arrays used for membrane fabrication is ca. 2 mm, obtained using a reaction time of 1.5 h. The G/D ratio of these millimeter-long MWCNTs as shown in the micro-Raman spectrum (Figure 1b) is close to 1, which is in accordance with that reported in the literature.<sup>30</sup> In the next step, the synthesized CNT arrays were utilized to fabricate membranes by using a unique cast–polishing method as shown in Figure 1c. Initially, the CNT array grown on a Si(100) substrate was embedded in an epoxy matrix, which was then peeled off from the silicon substrate after being cured at 85 °C in air for 3 h. Next, the CNT array and epoxy composite was polished with a Phoenix Beta Polisher (BUEHLER Co.) until the top surface of the membrane became conductive, indicating that the extra epoxy polymers had been removed completely and, thus, that the membrane had become permeable (Figures 1d and S2<sup>29</sup>). The final thickness of the CNT membrane was about 1 mm. As shown in Figures 1d and S2,<sup>29</sup> the CNTs protrude out of the membrane with a typical area density of 20 pieces of CNTs per square micrometer.



**Figure 1.** (a) Transmission electron microscope (TEM) image of the multiwalled carbon nanotube with an average inner diameter of ca. 8 nm (scale bar: 100 nm); (b) micro-Raman spectrum of the multiwalled carbon nanotubes; (c) schematic of the carbon nanotube membrane fabrication via a facile polishing method; (d) SEM image of the top view of the carbon nanotube membrane (scale bar: 1000 nm).

The millimeter-long CNT membranes were then employed as the key component to build ionic rectifiers through two strategies, the experimental setups of which are shown in S3.<sup>29</sup> The performance of the CNT membrane was compared with that of commercially available polycarbonate membranes with a larger pore size (Whatman, 100 nm).

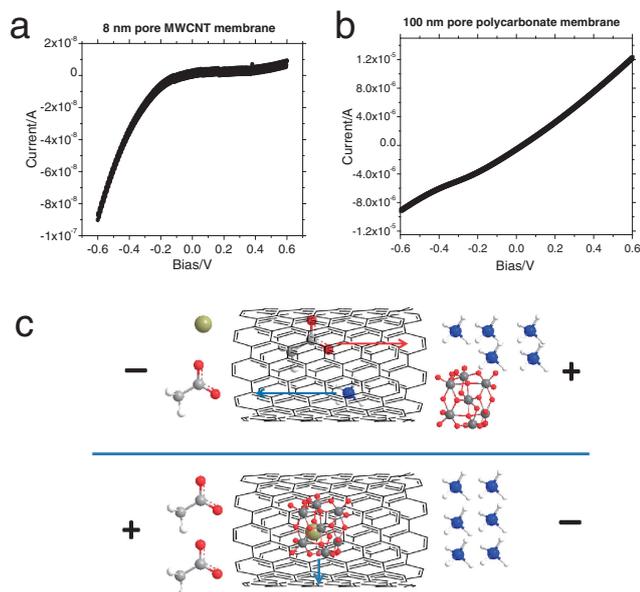
In strategy 1, the working electrode side of the U-tube was filled with a 2-mM aqueous solution of 1,4,7,10-tetraazacyclododecane-1,4,7,10-tetraacetic acid (DOTA, STREM), while the reference electrode side was filled with 2 mM aqueous solution of  $\text{MnCl}_2$  (Fisher Scientific) (S3).<sup>29</sup> The measured pH value of the aqueous DOTA solution was 6.0.  $\text{Mn}^{2+}$  ions were chosen because they can form a very stable complex with DOTA (stability constant,  $\log K = 20$ ; soluble in aqueous solution).<sup>31</sup> As shown in Figure 2a, the ionic current while applying a negative bias on the working electrode was significantly lower than that when a positive bias was applied. In contrast, no such rectification phenomenon was observed when using a track-etched polycarbonate membrane with a typical pore size of 100 nm (Figure 2b). The top view of the 100-nm polymeric membrane is shown in S4.<sup>29</sup> As control experiments, when both sides of the U-tube were filled with either DOTA solution or  $\text{MnCl}_2$  solution, no such rectification was obtained for either type of membrane. It is believed that the formation of metal ion complexes between  $\text{Mn}^{2+}$  cations and DOTA macrocyclic molecules in the highly space-confined channels can shut down the cationic transport when a negative bias is applied, and thus, the trans-membrane ionic current is reduced significantly (Figure 2c). When a positive bias is applied,  $\text{H}^+$  cations and  $\text{Cl}^-$  anions can be forced through the membrane channels under an external electric field, leading to an enhancement of ionic current (Figure 2c). It should be pointed out that the membrane pore size is critically important for obtaining such an ionic



**Figure 2.** (a)  $I$ - $V$  curve of multiwalled carbon nanotube membrane with a pore size of ca. 8 nm; (b)  $I$ - $V$  curve of track-etch polycarbonate membrane with a pore size of 100 nm (Whatman.com); (c) diagram shows the mechanism underlying the ionic rectification using strategy 1 (formation of complex to shut down the cationic transportation).

rectification effect. If the pore size is too large, as in the case of 100-nm polycarbonate membranes, there is a probability that  $\text{Mn}^{2+}$  cations and deprotonated DOTA anions can pass by each other without forming complexes in the pores. Therefore, there are only periodic current reductions as shown in Figure 2b. In the case of the CNT membrane with ca. 8-nm pores, most  $\text{Mn}^{2+}$  cations can react with DOTA ligands to form bulky complexes in the millimeter-long CNT channels (nanoreactors). It is notable that bulky complexes move much more slowly than small cations such as  $\text{Mn}^{2+}$ . It is also highly possible that there is stronger friction between the walls of the CNTs and DOTA than with the much smaller sized  $\text{H}^+$  and  $\text{Cl}^-$  ions.

In the case of strategy 2, the working electrode side of the U-tube was filled with a 2 mM aqueous solution of  $\text{Pb}(\text{OAc})_2$  (Sigma Aldrich), while the reference electrode side was filled with 0.67 mM aqueous solution of  $(\text{NH}_4)_6\text{Mo}_7\text{O}_{24}$  (J.T. Baker) (S3).<sup>29</sup> It is well known that lead [ $\text{Pb}^{2+}$ ] ions are one of the most toxic water contaminants,<sup>32</sup> and  $\text{Mo}_7\text{O}_{24}^{6-}$  and  $\text{Pb}^{2+}$  can form insoluble precipitates.<sup>33</sup> The Environmental Protection Agency (EPA) has set strict concentration limits on this ion in drinking water. Even very low levels of lead exposure can cause serious health problems such as neurological, reproductive, cardiovascular, and developmental disorders.<sup>34</sup> Considering its side effects, any method that can help detect this metal cation using a simple technique is highly desirable. As shown in Figure 3a, the ionic current while applying a positive bias on the working electrode was significantly lower than that when a negative bias was applied. No such rectification phenomenon was observed when using a track-etched polycarbonate membrane with a typical pore size of 100 nm (Figure 3b). Because of the precipitation of the insoluble  $\text{Pb}_3\text{Mo}_7\text{O}_{24}$  compounds in the tubes while the positive bias was applied, the ionic transport of



**Figure 3.** (a)  $I$ - $V$  curve of multiwalled carbon nanotube membrane with a pore size of ca. 8 nm; (b)  $I$ - $V$  curve of track-tech polycarbonate membrane with a pore size of 100 nm (Whatman.com); (c) diagram shows the mechanism underlying the ionic rectification using strategy 2 (formation of precipitate between  $\text{Pb}^{2+}$  and  $\text{Mo}_7\text{O}_{24}^{6-}$  in tubes to shut down the ionic transportation). N: Blue; H: white; O: red; Mo: gray; Pb: pale golden.

both cations and anions was blocked significantly, whereas acetate anions and  $\text{NH}_4^+$  cations could be forced through the CNT membrane channels when the bias was switched to negative, owing to their much smaller dimensions and high solubility (Figure 3c). It cannot be concluded exclusively that the precipitate will not occur near the tip entrance of the CNTs. The detection of heavy metal ions like  $\text{Pb}^{2+}$  through such a unique and simple ionic rectification method would have broad applications in environmental sciences, and this research direction is being explored extensively by our research groups. It should be pointed out that although a single polymeric nanopore could also be employed to realize such an ionic rectification effect, the detection of an extremely low ionic current (pA) with satisfactory accuracy and repeatability would be very challenging and costly. In contrast, the dramatically enhanced electro-osmotic flow through a large number of crystalline carbon nanotubes in the membrane geometry can help to magnify the ionic current signal output, thus making the measurement of the ionic current much easier.<sup>11,35</sup>

In conclusion, MWCNT membranes were fabricated successfully from arrays of millimeter-long carbon nanotubes by utilizing a low-cost cast-polishing method. The ionic rectification effects were demonstrated through two distinct mechanisms. One originates from the formation of metal ion complexes inside the CNT cores. The second mechanism is based on the formation of an insoluble precipitate. In contrast with other types of ionic rectifications, our system is unique in its selective detection of certain toxic heavy metal ions such as  $[\text{Pb}^{2+}]$  or  $[\text{Mn}^{2+}]$  via ionic rectifications. In the future, we intend to enhance the selectivity of this system further by utilizing size-selective ligands such as crown ether, calixarene, etc.

These two types of ionic rectification effects could be applied to the detection of toxic heavy metal ions in contaminated water resources for environmental protection purposes, provided that the formation of metal ion complexes and precipitates is highly selective.

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