Nanofluidic Diodes

Deutsche Ausgabe: DOI: 10.1002/ange.201505269
Internationale Ausgabe: DOI: 10.1002/anie.201505269

A Bioinspired Switchable and Tunable Carbonate-Activated Nanofluidic Diode Based on a Single Nanochannel

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Abstract: *A smart nanofluidic diode that exhibits both ion gating and ion current rectification has been developed using a 1-(4-amino-phenyl)-2,2,2-trifluoro-ethanone-functionalized, conical nanochannel in a polyimide (PI) membrane. The switch-like property can be tuned by controlling the wettability and charge distribution with carbonate ions. Such a nanodevice is advantageous for precisely controlling conductive states with an ultrahigh gating ratio of up to 5000, and a high rectification ratio of 27. By virtue of the high selectivity and sensitivity for carbonate ions, this nanofluidic diode may find applications in carbonate or carbon dioxide detection.*

Bioinspired solid-state nanochannels for functional nanofluidic devices have gained widespread attention.[1] Nanofluidic diodes possess interesting ion transport characteristics and are similar to biological ion channels with respect to their gating and rectification properties.[2] Two of the critical factors in constructing this type of diode-like nanodevice are symmetry-breaking in the charge distribution and wettability (other factors include channel geometry and bath concentrations), and these can precisely control the pore surface properties.[1a,3] In nature, biological ion channels are capable of fine-tuning their pore surfaces to regulate mass transport in response to various stimuli, such as ligands.[4] There is evidence that a hydrophobic ion channel is beneficial to regulating ion transport.[4a,5] The *Gloeobacter violaceus* ligand-gated ion channel (GLIC), for example, is a bacterial member of the large family of pentameric ligand-gated ion channels that open or close in response to ligand binding by switching the pore surface polarity between nonpolarity and dipolarity to dewet and wet the pore surface.[4a,c] Although these ion channels possess excellent tunable gating and rectification properties, the fragility of the lipid bilayer in vitro limits their practical applications. Therefore, scientists have developed artificial nanochannels with switchability that can be tuned by external stimuli, such as temperature,[6] pH,[2a,7] specific molecules,[8] voltage[9] and light.[10] For example, Siwy and co-workers reported single hydrophobic nanopores that undergo reversible wetting and dewetting in response to an electric field.[9e] Soler-Illia and co-workers demonstrated the gradual tuning of transport properties by controlling the charge density inside mesoporous amino-silica.[11] These nanodevices displayed excellent gating or rectification properties by undergoing surface wettability or charge changes, which ultimately results in changes in the transmembrane ion current. However, there are still several challenges in precisely controlling ion transport through nanochannels. First, reducing ion current leakage remains a challenge for nanofluidic devices because of the limitation of volume blockage and wettability control.[12] Second, it has rarely been reported that the gating and rectification of the nanochannels can be activated and tuned by only one stimulus, as in some biological ion channels.

Here, inspired by the wettability-induced gating and cation-selective transporting properties of biological ion channels, we demonstrate a nanofluidic diode that exhibits both ion gating and ionic current rectification tuned by carbonate ions. In this system, carbonate functions as a trigger and regulator for this smart nanodevice by specifically reacting with the modified hydrophobic molecule 1-(4-amino-phenyl)-2,2,2-trifluoro-ethanone (APTE). Such a nanodevice has the advantages of precisely controlling conductive states and tuning the rectification effect with an ultrahigh gating ratio of up to 5000 and a high rectification ratio of 27 that can be used to precisely control mass transport. Moreover, such a tunable nanofluidic diode may help to better understand the ion transport of biological ion channels involving wetting and dewetting changes, and can be applied in the fields of drug delivery and carbonate or carbon dioxide detection.[13]

Scheme 1 describes the operational principle of the tunable nanofluidic diode. This smart nanodevice, which was prepared using a functionalized polymer nanochannel, displayed carbonate-tuned ion gating and ionic current rectification, similar to a tunable switch. A single conical nanochannel was fabricated in a polyimide (PI) membrane using a well-developed track-etched technique. The diameter at the base side of the conical nanochannel was about 500 nm

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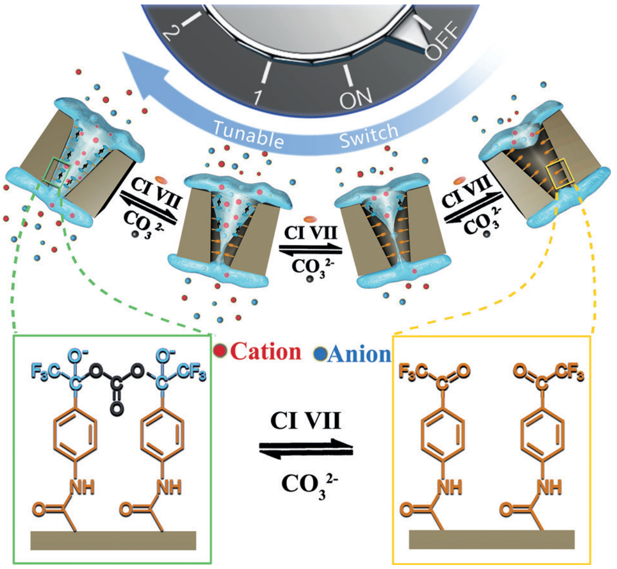
Supporting information for this article is available on the WWW under http://dx.doi.org/10.1002/anie.201505269.



Scheme 1. The operational principle of bioinspired carbonate-activated and tuned nanofluidic diodes. After modification with the hydrophobic molecule APTE, the pore surface can absorb carbonate ions and be recycled by the removal of these absorbed ions with carbonate ionophore VII (CI VII) (bottom). Consequently, ion currents through the functional nanochannel can be precisely controlled. Such control can also be achieved by using different concentrations of carbonate solution, which can function like a tunable switch (top).

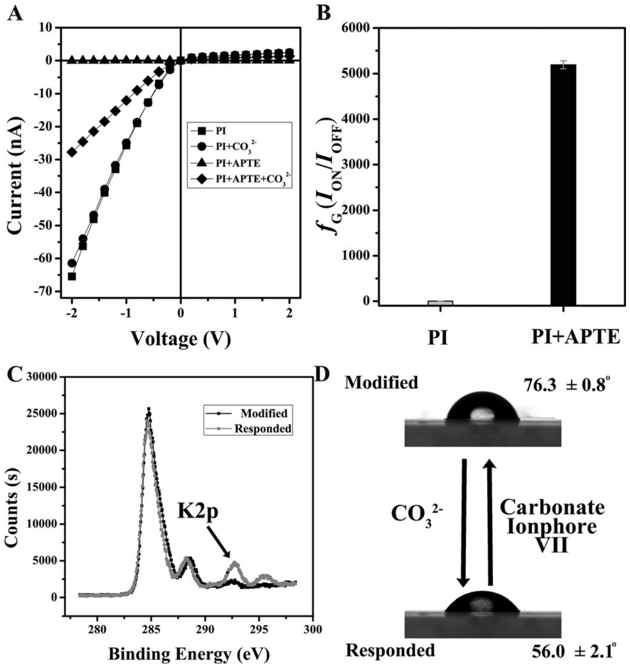


Figure 1. Changes in the properties of the functionalized nanochannel: (A) *I-V* responses of the conical single nanopore prior to (squares and circles) and after (triangles and diamonds) modification with APTE in the absence (squares and triangles) and presence (circles and diamonds) of carbonate ions. B) The current ratio (f_G) of the unmodified (gray column) and modified (black column) nanochannel. C) XPS of the modified PI membrane before and after responding to 1 M K_2CO_3. The new peak of K2p indicated that the modified APTE on the PI surface reacted with carbonate ions. D) Photographs of the water droplet shape on the APTE-modified and K_2CO_3-treated PI films with water contact angles of 76.3 ± 0.8° and 56.0 ± 2.1°, respectively.

(Supporting Information, Figure S2) and the corresponding diameter at the tip side (d_{tip}) was about 20 nm, as determined by an electrochemical method (see the Supporting Information).[14] Then, the inner surface of the pore was modified with APTE molecules by reacting with the residual carboxyl groups by a two-step coupling method.[15] After immersing this system in a carbonate solution, the grafted APTE molecules bound the carbonate ions[16] and thereby influenced the ion transport through the channel in terms of ion gating and ionic current rectification.[17] When carbonate ionophore VII (CI VII) was added, the bound carbonates were removed,[18] and the nanodevice switched from the conducting-state (on) to the nonconducting-state (off). The switching was tuned by using different concentrations of carbonate solution. Unless otherwise stated, the properties of this system were studied by measuring the current-voltage (*I-V*) characteristics with the following parameters: $d_{tip} \approx 24$ nm, 1 M KCl, and 25 °C.

The current-voltage (*I-V*) characteristics of the PI single nanochannel, before and after modification with APTE molecules, and in the absence and presence of carbonate ions, were measured as transmembrane ion currents. As shown in Figure 1 A, the etched conical nanochannel can rectify ionic currents because of the asymmetric distribution of negatively charged carboxyl groups.[1a] After modification with APTE, the nanochannel changed to a closed state because the APTE molecules covered the charged zone, thus increasing the hydrophobicity of the pore surface and producing the nonconducting state (Supporting Information, Figure S4). After responding to carbonate, the surface recovered its negative charge and hydrophilicity; the current increased substantially but was still lower than that of the etched nanochannel, and the rectification effect reappeared. These pore surface changes can also be reflected by the gating ratio (f_G, defined as I_{ON}/I_{OFF}, where I_{ON} and I_{OFF} are the currents measured at −2 V before and after treatment with carbonate ion solution, respectively; Figure 1 B). A significant difference in f_G between the unmodified (ca. 1) and modified (ca. 5000) nanochannels was observed, and the excellent switchability of this nanodevice could serve to minimize the current leakage. These changes were also confirmed by measuring the X-ray photoelectron spectroscopy (XPS) and contact angles of a planar etched PI surface that was subjected to the same chemical modification as the single nanopores (Figure 1 C, D; Supporting Information, Figures S3, S4). After treatment with 1 M K_2CO_3, a new peak of K2p appeared in the XPS spectrum, which indicated that the APTE-modified PI surface had reacted with carbonate ions. Furthermore, the contact angle changes between the APTE-modified membrane (76.3 ± 0.8°) and carbonate-responded membrane (56.0 ± 2.1°) also reflected the wettability changes of the pore surface. IR spectroscopy was also used to obtain evidence of carbonate binding (Supporting Information, Figure S5).

To confirm the tunability of the system in gating and rectification, carbonate solutions with concentrations of 0–1 M

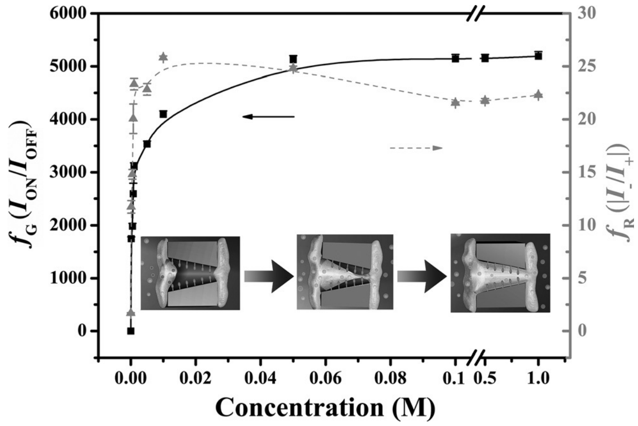


Figure 2. Concentration dependence of the ion gating ratio (f_G) (black squares and line relative to the left axis) and ion rectification ratio (f_R) (gray triangles, dashed line relative to the right axis) on the APTE-modified single-nanochannel device with the following parameters: $d_{tip} = 24$ nm, 1 M KCl, and 25 °C. The f_G and f_R values were tuned with different potassium carbonate solutions ranging from 0–1 M. As the concentration of the carbonate increased, the current and f_R of the device also increased.

were used to test this system with a 1 M KCl electrolyte solution. As shown in Figure 2, the gating and rectification properties of this nanofluidic diode were fine-tuned with a series of carbonate solutions. As the carbonate concentration of the solution increased from 0 to 0.05 M, the f_G exhibited a dramatic increase from 1 to around 5000, which indicated that the switch was gradually turned on by the carbonate ions. As the carbonate ion concentration continued to increase, the f_G-concentration curve plateaued at the ultrahigh f_G value of 5000; in other words, the system was completely switched on. We believe that this tunability in the gating resulted from the interaction between the modified APTE and carbonate, which made the pore surface increasingly hydrophilic to transport ions; the maximum value was achieved at 0.05 M. However, the increase in the rectification ratio (f_R, defined as $|I_-/I_+|$, where I_- and I_+ are the currents at -2 V and $+2$ V, respectively) was not monotonic, and its maximum value was obtained at 0.02 M, not 0.05 M. The value of f_R grew rapidly from 1 to the high value of 27 as the concentration of carbonate ion increased from 0 to 0.02 M. As the concentration continued to increase, f_R exhibited a slight decrease. In this case, asymmetric geometry, surface charge distribution, and wettability were involved. For this conical system, when carbonate ions reacted with the APTE on the pore surface, the absorbed carbonate imbued the pore surface with negative charges and thereby made the surface hydrophilic, resulting in an asymmetric charge distribution. Therefore, the negatively charged, conical nanochannel possessed rectification properties that preferentially transported anions from the small opening (tip) towards the large opening (base) of the channel. Different carbonate ion concentrations led to different charge distributions and, therefore, different rectification ratios.[19] Thus, we could tune the nanofluidic diode. Because rectification was the result of wettability, charge, and geometry, the concentration of the ceiling value of f_R was different from that of gating, whose main impact factor was wettability in this system.[1a] The results implied that we could tune the nanodevice in both gating and rectification with different concentrations of carbonate ions.

Because APTE exhibits a high binding affinity to carbonate ions, we examined the selectivity of this APTE-modified nanochannel for carbonate ions in comparison with that for other anions. The excellent selectivity of the pore gating for carbonate ions is shown in Figure 3. When the APTE-modified nanochannel was immersed in 1 M KCl, KNO_3, K_2SO_4, K_2SO_3, $KHSO_3$, KOAc, or KBr for 1 h, the corresponding f_G and f_R were all approximately 1. The switch turned on with rectification of the *I-V* curve after treatment with a 1 M carbonate ion solution. Therefore, this nanodevice was selective for carbonate ions. First, the carbonate-treated nanochannel exhibited significant currents at both forward and backward voltages, and its f_G was as high as 5000, demonstrating the triggering of the switch and the potential application of this device for precise mass delivery. Second, the current at the backward voltage was much larger than that at the forward voltage, and the value of f_R was high (ca. 27); these are typical diode-like characteristics and suggested that carbonate ions endowed the pore surface with negative charges. Additionally, the control experiments with unmodified nanochannels also indicated the key-like significance of carbonate ions to this system (Supporting Information, Figure S6). Such results were in agreement with our above-mentioned model, and indicated that the carbonate ion was critical to the APTE-modified nanofluidic diode.

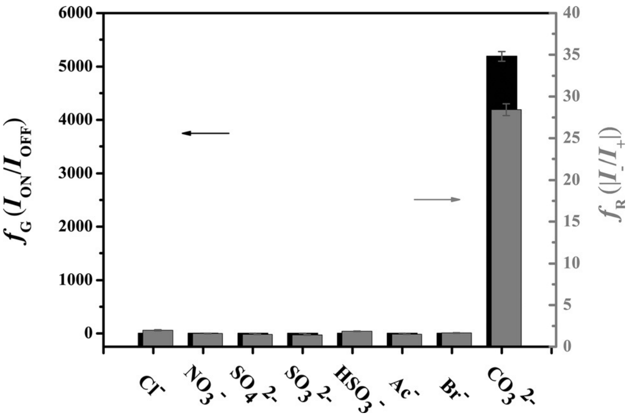


Figure 3. Selectivity of the carbonate-activated nanofluidic diode with the following parameters: $d_{tip} = 24$ nm, 1 M KCl, and 25 °C. f_G (black column and the left axis) and f_R (gray column and the right axis) of APTE-modified single nanochannel by treating with 1 M KCl, KNO_3, K_2SO_4, K_2SO_3, $KHSO_3$, KOAc, KBr, and K_2CO_3 for 1 h, respectively. The f_G and f_R values of the functional nanodevice show much higher values after treatment with K_2CO_3 than with other salts.

Because ionic conductance is a function of pore size, we also studied the relationship between ion current and pore size using a series of APTE-modified, single nanochannels with tip diameters ranging from 6 nm to 100 nm (calculated by Equation S1 in the Supporting Information). The relationship between f_G and tip diameter is shown in Figure 4 A. A drastic increase in f_G was observed with the tip diameter in the range of 6–24 nm. At 24 ± 1.2 nm, f_G peaked (ca. 5000) (black

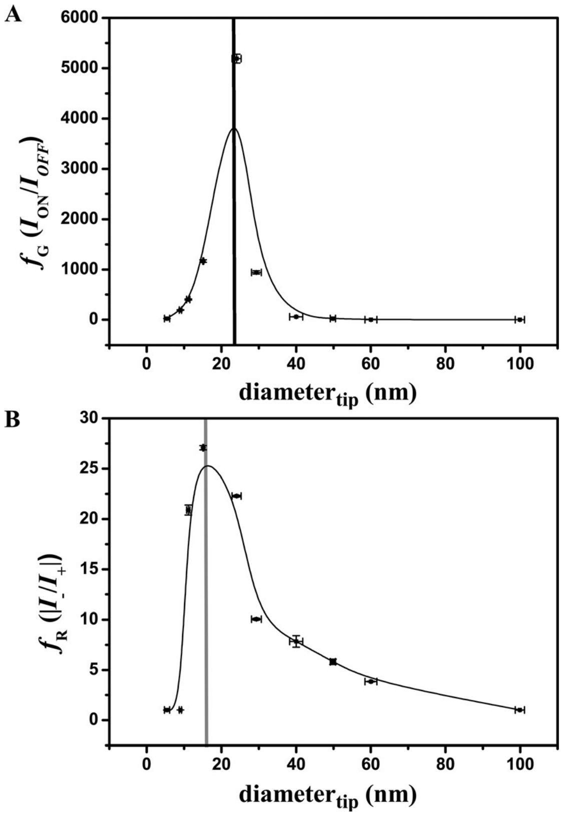


Figure 4. Pore size dependence of the carbonate-activated nanofluidic diodes at 1 M KCl and 25 °C. A) Gating ratio (f_G) of APTE-modified nanochannels with pore sizes ranging from 6 nm to 100 nm measured at −2 V. When the pore diameter was 24 nm (black line), the current ratio peaked (ca. 5000). B) The rectification ratio (f_R) of this functional nanodevice with pore sizes of 6-100 nm. The maximum of f_R was 27 at 15 nm (gray line).

line). When the tip diameter exceeded 24 nm, the ratio decreased gradually and stabilized at around 1 after 45 nm. When the tip diameter of the nanochannel was too small, the APTE molecules blocked the gating, resulting in minimal change in the ionic current after treatment with carbonate ions. When the tip diameter was too large (>45 nm), the APTE did not influence the ion transport and solution movement through the channel, resulting in a ratio of 1. Only at a tip diameter of approximately 24 nm, for which the wettability combined with the charge distribution could affect the transport of ions and water through the nanochannel, could the nanodevice function as expected.

The influence of pore size on the rectification ratio (f_R) was similar to that of the current ratios. However, there were differences in the location and amplitude of the peaks. The f_R-diameter$_{tip}$ curve initially increased and then decreased, and the peak value was 27 at 15 nm (gray line, Figure 4B). Similar to the concentration-dependence, varying the influential factors affecting gating and rectification led to different results. The rectification was the result of the asymmetric geometry, wettability, and charge density, whereas the main influential factor for gating ratio (f_G) was wettability.

We also studied the reversibility of the switching of this carbonate-activated nanofluidic diode by the addition and

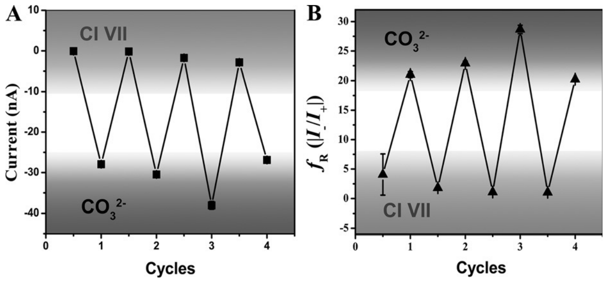


Figure 5. Reversibility in gating and rectification switching of this APTE-modified nanochannel with the following parameters: d_{tip} = 24 nm, 1 M KCl, and 25 °C. A) Switching between conducting and non-conducting states. B) Changes between the two states of rectification.

removal of carbonate ions. Excellent reproducibility of pore gating and rectification switching was demonstrated in Figure 5. When the APTE-functionalized nanochannel was treated with carbonate ions, the switch changed from a non-conducting state to a conducting state, and the transmembrane current increased from 0 to 30 nA. After being soaked in CI VII solution, the nanochannel recovered to the closed state because the carbonate ions were absorbed by CI VII molecules, which resulted in a dewetting surface and thus blocked the nanochannel. The repeatability of this process was tested by measuring the ionic current. After several cycles, no damping of the ion current was observed (Figure 5A). Similar results for the rectification switching are presented in Figure 5B. Therefore, this carbonate ion-activated nanodevice has acceptable stability and cycling performance.

In summary, we have developed a nanofluidic diode that exhibits tunable gating and rectifying properties. Tunability was achieved by treating with different concentrations of carbonate ions and was recovered by removing carbonate ions with CI VII. The switchable property was attributed to the reversible reactions between the hydrophobic APTE molecules and carbonate ions, which controlled the states of the nanofluidic diode by dewetting and wetting the pore surface. This device with ultrahigh f_G and high f_R could represent an ideal system for controlling mass delivery, which could effectively decrease unwanted leakage without any stimulus. Additionally, this wettability- and charge-controlled nanofluidic diode may facilitate a better understanding of the hydrophobic reactions in the nanoconfinement and mass transport of biological ion channels. Furthermore, because of its sensitivity and selectivity for carbonate ions, this system may be applied in detecting carbonate ions and carbon dioxide.[13]

Acknowledgements

This work was supported by the National Research Fund for Fundamental Key Projects (2011CB935703), National Natural Science Foundation (21171171, 21434003, 91427303, 21201170, 91127025, 21421061), and the Key Research Program of the Chinese Academy of Sciences (KJZD-EW-M01, KJZD-EW-M03).

Keywords: carbonate ions · nanofluidic diodes · tunability · wettabilty

How to cite: *Angew. Chem. Int. Ed.* **2015**, *54*, 13664–13668
Angew. Chem. **2015**, *127*, 13868–13872

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Received: June 9, 2015
Revised: July 26, 2015