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Light and pH Cooperative Nanofluidic Diode Using a Spiropyran-Functionalized Single Nanochannel

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Ion channels open and close in response to external stimuli, which lays the foundation for life sciences. Among them, light-gated ion channels are a newly discovered type of light-sensitive membrane channels, in contrast to the previously reported light-driven proton channels.[1] Under light irradiation, the channels become selectively permeable for specific cations. Inspired by nature, some groups have synthesized porous materials to mimic light-gated ion channels.[2] For example, Brinker and coworkers[3] attached azobenzene ligands to mesoporous silica, the effective pore size of which changed as a result of photoisomerization of the azobenzene ligands. White and coworkers[4] modified the interior of a single glass nanopore with spiropyran moieties, which allowed light-gated transport of redox molecules based on electrostatic repulsion. Smirnov and coworkers[5] ascribed this light-gated phenomenon to the hydrophobic/hydrophilic force in the nanoporous alumina membranes.

Another important aspect of ion channels is current rectification behavior.[6] Namely, the ion channels allow the ionic current to flow in one direction preferentially, which is one of the characteristics of a nanofluidic diode. A nanofluidic diode is constructed by breaking the symmetry of the nanochannel and introducing excess surface charge.[7] With smart modification, the nanofluidic diode can respond to a single stimulus, such as pH,[8] specific ions,[9] temperature,[10] biomolecules,[11] or pressure[12] or to dual stimuli such as pH and temperature.[13] However, to remotely control the states of the diodes using light is still a challenge.

Here we report an artificial functional nanochannel system as a novel nanofluidic diode that displays both light-gated and pH-tunable transport properties, as well as exhibiting current rectification. In this light and pH cooperative nanofluidic system, UV light manipulation provides a way to remotely switch the channel from the off-state to the on-state, and variation of pH leads to the reversal of the current rectification direction. When UV light was off, the channel was non-selective and the transport caused by pH was trivial and negligible. However, under UV light, the pH had a tremendous impact on the ionic transport behavior of the nanochannel, that is, the channel could be either cation selective or anion selective according to the pH of the solution. The asymmetric shape of the nanochannel allowed the system to exhibit current rectification as well because the channel possesses higher resistance when the ions are driven from the base to the tip than from the tip to the base although the electrolyte in contact with the two pore openings is the same.[6]

This function can be realized by modifying the inner surface of the conical nanochannel with the spiropyran 1′-(3-carboxypropyl)-3′,3′-dimethyl-6-nitro-spiro[2*H*-1]benzopyran-2,2′-indoline (SP-COOH).[14] As shown in **Scheme 1**, the spiropyran has three metastable states. The neutral spirocyclic form is hydrophobic and the channel is in the closed state. Irradiation with UV light opens the C–O pyran bond and results in a hydrophilic state. At pH 7, it takes the negatively charged form. The channel becomes cation selective and the current prefers to flow from the tip (small opening) to the base (large opening). At pH 3, the phenolate anion may be protonated, leading to a positively charged form. The channel becomes anion selective and the current direction is reversed. Irradiation with visible light converts the molecule back to its closed form (or it can be converted thermally in nonpolar solvents after being stored in darkness). Unlike previously reported systems that rely on conformational changes,[6] here the nanochannel is determined by the surface charge discrimination and has higher rectification efficiency. Besides, the configuration of spiropyran changes in response to light and the pH of the solution and, as a result, the surface charge changes from neutral to either negatively or positively charged according to ambient stimuli. Namely, the rectification direction and efficiency can be controlled by the cooperative effect of light and pH of the solution. Therefore, this

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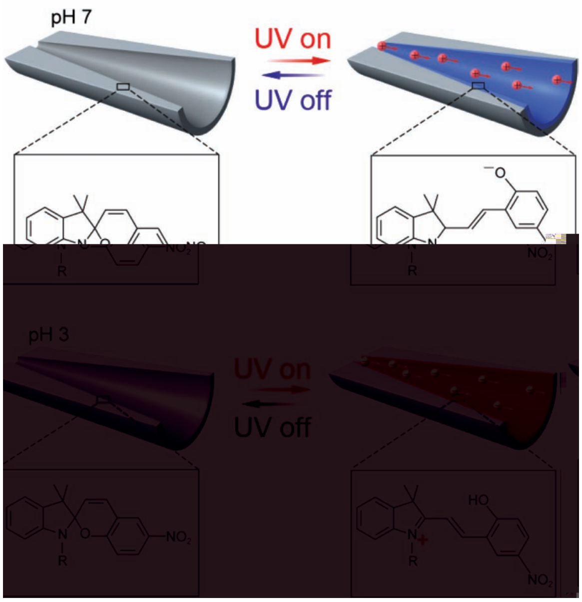

Scheme 1. Scheme of the light-gated nanofluidic diode system at different pH values. The nanochannel is initially in the closed state owing to the neutral and hydrophobic spiropyran, indicated by the gray color (left). At pH 7, under UV light irradiation, the nanochannel turns into the open state because the spiropyran is hydrophilic and negatively charged, indicated by the blue color. Therefore, cations are the majority carriers and prefer to flow from the tip to the base (top right). At pH 3, under UV light irradiation, the nanochannel is positively charged, indicated by the red color. Therefore, anions are the majority carriers and prefer to flow from the base to the tip (bottom right).

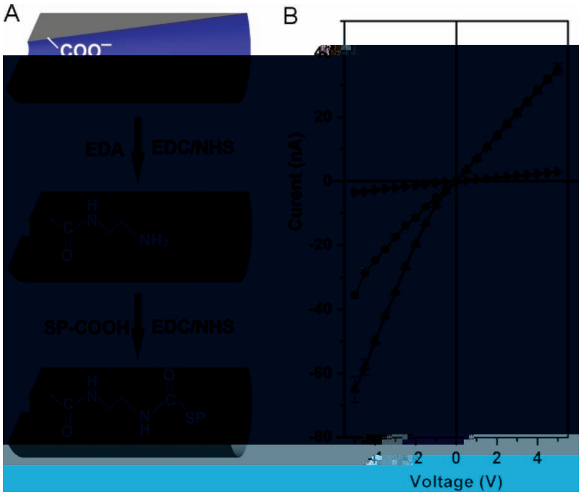

Figure 1. The modification processes (A) and the corresponding *I–V* curves (B). The blue color indicates that the interior of the nanochannel is negatively charged. The gray color indicates that the interior of the nanochannel is neutral. The pristine nanochannel rectifies the current as a result of the negatively charged carboxyl groups (triangles, blue). After modification with step 1, the curve becomes nearly linear because the amino groups are neutral at pH 7 (circles, green). After modification with step 2, the nanochannel turns into the closed state (triangles, orange). The PET membrane was placed between two half-cells of electrolyte using 1 M KCl electrolyte solution at pH 7.

(SEM; see Supporting Information I), and the tip was calculated to be ~12 nm by an electrochemical measurement.[16] We modified the interior surface of the nanochannel with SP-COOH by a two-step coupling reaction. First, ethylenediamine was covalently coupled to the surface after activation with 1-ethyl-3-(3-dimethylaminopropyl) carbodiimide hydrochloride (EDC·HCl) and *N*-hydroxysuccinimide (NHS),[13a] and then reacted with SP-COOH (**Figure** 1A). The success of the surface modification was evidenced by the corresponding current–voltage (*I–V*) curves measured using 1 M KCl electrolyte solution at pH 7 in both half-cells. As shown in Figure 1B, before modification, the negatively charged carboxyl groups on the inner surface initially attracted the cations in order to neutralize the immobilized surface charge.[17] Besides, the cations preferred to flow from the tip to the base to maintain lower resistance, resulting in current rectification behavior. When the carboxyl groups were replaced by amino groups, the current rectification property vanished because the channel became non-selective in neutral solutions. After SP-COOH was attached to the surface, the current dramatically decreased because the channel was hydrophobic (see Supporting Information II) and non-permeable to ions.

Having achieved closure of the nanochannel, we set out to open the gate by UV light (365 nm) irradiation from the tip of the nanochannel. As shown in **Figure 2**, when UV light is off, the nanochannel is in the closed state regardless of the polarity of the voltage. After irradiation of the nanochannel with UV light for 30 min, the ionic transport properties are influenced by the polarity of the voltage.[7] At pH 7 the channel is negatively charged, hence, the high conductance state is obtained when the cations are driven from the tip to the base by electrophoresis (Figure 2A). Conversely, at pH 3 the channel is positively charged, hence, the high conductance state is obtained when anions are driven from the tip to the base by electrophoresis. As expected, the current direction is opposite to the direction of flow of anions (Figure 2B). In other words, the preferential current direction can be either from tip to base or vice versa, induced by the sign of the surface charge, which depends on the pH of the solution. We intended to use visible light to switch back to the off-state. However, because we carried out our experiment in aqueous solution, it is difficult to switch the nanochannel from the on-state back to the off-state by visible light in situ because dewetting of the membrane does not occur spontaneously with a high activation barrier despite the photoisomerization of the spiropyran back to the hydrophobic form.[5] As a result, it is relatively easy to make the nanochannel hydrophilic and conductive by UV light irradiation, but the nanochannel has to be dried in order to make the nanochannel hydrophobic and resistive when UV light is off.

It has been demonstrated that pH alone can exert a big influence on the dual-responsive nanochannel,[13] but in our case, pH influenced the states of the channel cooperatively with the light, rather than independently. **Figure 3** illustrates that when UV light was off, the effect caused by pH was trivial and negligible. However, under UV light irradiation, pH had a tremendous impact on the ionic transport properties of the nanochannel. Under UV light irradiation, the current increased at both pH values, but the magnitude was different according to

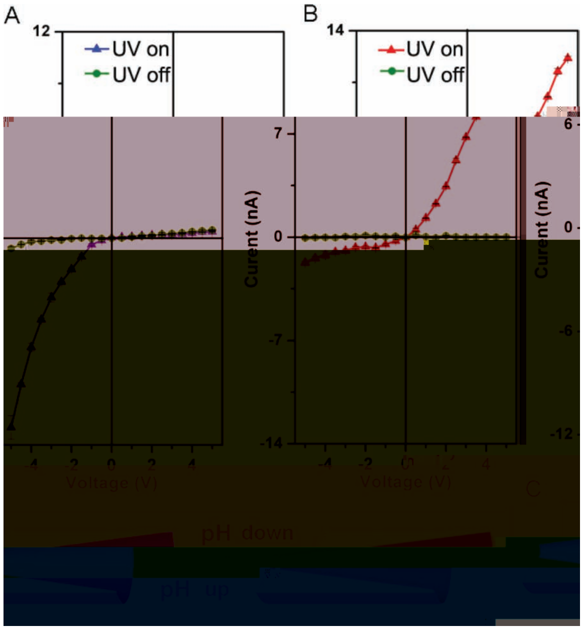

Figure 2. Current–voltage (*I*–*V*) curves of the spiropyran-modified nanochannels when UV light is off and under UV light irradiation. A) At pH 7, the nanochannel is in the closed state when UV light is off (circles, green). Under UV light, the nanochannel is negatively charged and cations are the majority carriers. The cations prefer to flow from the tip to the base to maintain the lower resistance, leading to current flowing in the same direction (triangles, blue). B) At pH 3, the nanochannel is in the closed state when UV light is off (circles, green). Under UV light, the nanochannel is positively charged and anions are the majority carriers. The anions prefer to flow from the tip to the base to maintain the lower resistance, leading to current flowing in the opposite direction (triangles, red). C) Explanation of the pH-tunable nanofluidic diode induced by the different polarities of the excess surface charge. Under UV light, the blue color indicates that the interior of the nanochannel is negatively charged when pH is high (left); the red color indicates that the interior of the nanochannel is positively charged when pH is low (right). The electrolyte solution was 0.1 M KCl in both half-cells separated by the membrane.

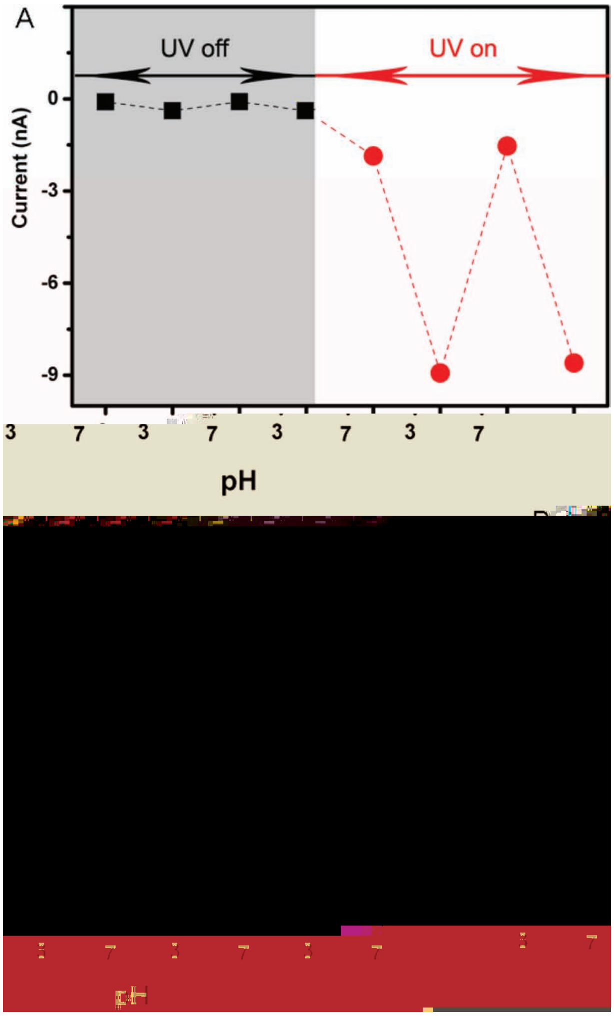

Figure 3. Reversible variation of the ionic current when UV light is off (squares, black) and under UV light (circles, red) by changing pH of the solution between 3 and 7. A) At –5 V, the current remains nearly unchanged when UV light is off. Under UV light, the current increases dramatically at pH 7. B) At 5 V, the current remains nearly unchanged when UV light is off. Under UV light, the current increases dramatically at pH 3.

the polarity of the voltage: At –5 V (anode facing the tip), the current flowed from the tip to the base and was large in neutral solutions (Figure 3A); at +5 V (anode facing the base), the current flowed from the base to the tip and was large in acid solutions (Figure 3B). This nanofluidic diode system stresses the importance of the UV light that other pH-responsive nanofluidic diodes[8] do not have.

The diode-like behavior is quantified by the current rectification ratios of on-state versus off-state at a given voltage (±5 V). As shown in **Figure 4**, the ratio was approximately 1 when UV light was off. Under UV light irradiation and at pH 7, the ratio of absolute values of ionic currents recorded at –5 V (anode facing the tip) and +5 V (anode facing the base) was 30. Under UV light irradiation and at pH 3, the ratio of absolute values of ionic currents recorded at +5 V (anode facing the base) and –5 V (anode facing the tip) was 7. The rectification ratio is the same order of magnitude as for a unipolar diode,[18] besides, it could be further enhanced by designing a bipolar diode with a p-n junction.

To obtain a comprehensive understanding of the light and pH cooperative nanofluidic diode, we adopted a theoretical Poisson/Nernst–Planck (PNP) model[19] to calculate the relationship between ionic currents and the bias voltage. For the model of the nanopore we took the length (L) as 12 μm, the diameter of the tip (α_L) as 12 nm, and that of the base (α_R) as 350 nm. We set the surface charge density as –1 e nm^{-2} for pH 7 and +1 e nm^{-2} for pH 3 under UV light irradiation. We calculated I–V curves using 0.1 M KCl electrolyte solution according to the PNP model (see Supporting Information IV, Figure S4). In addition, we calculated the net surface charge of the nanochannel along the pore axis (see Supporting Information IV, Figure S5). The conical shape of the channel contributes to the asymmetric distribution of ions near the surface, which is the quantitative explanation of the current rectification property. The preferential current direction is from the tip to the base

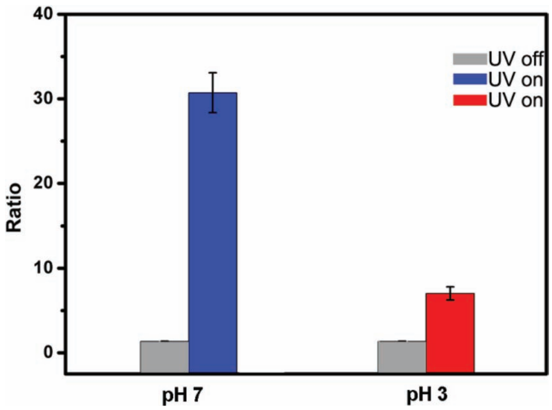

Figure 4. The current rectification ratios of on-state versus off-state. At pH 7 and under UV light irradiation, the ratio of absolute values of ionic currents recorded at –5 V and +5 V was 30 (blue). At pH 3 and under UV light irradiation, the ratio of absolute values of ionic currents recorded at +5 V and –5 V could was 7 (red). When UV light was off, the ratio was approximately 1 (gray).

when the surface is negatively charged. On the other hand, the preferential current direction is from the base to the tip when the surface is positively charged. These models quantitatively explain the cooperative effect of UV light and pH on the conducting states of the nanofluidic diode.

In conclusion, we have demonstrated a dual-responsive nanofluidic diode that is actuated by the cooperation of light and pH. The function of this nanofluidic diode is dependent on the asymmetric shape of the nanochannel and the excess surface charge induced by spiropyran under UV light irradiation. Compared with fragile transmembrane protein systems,[20] this abiotic system is robust and has the advantage that it does not have to work in the lipid environment. Furthermore, this nanofluidic diode moves one step further towards mimicking complex biological ion channels with ionic gate and ionic rectifier properties at the same time. It could find applications in areas such as light-responsive mass delivery, sensing devices, and energy conversion[21] systems.

Experimental Section

Nanochannel fabrication: The fabrication of single nanochannels in 12 μm thick PET films was performed by the track-etching technique. Briefly, the PET membrane was embedded between the two chambers of a conductivity cell at 35 °C. One chamber was filled with etching solution (9 M NaOH) and the other with stopping solution (1 M KCl + 1 M HCOOH). A voltage of 1 V was applied across the membrane.

SP-COOH immobilization: Step 1: The PET film was first exposed to an aqueous solution of EDC·HCl (15 mg mL^{-1}) and NHS (3 mg mL^{-1}) for 1 h. Then 0.1 mL ethylenediamine anhydrous (EDA) was added to the solution and reacted for 4 h at room temperature. Step 2: The film reacted with an ethanol solution containing SP-COOH (3 mg mL^{-1}), EDC (3 mg mL^{-1}) and NHS (3 mg mL^{-1}) for a day. The film was washed with thoroughly deoxygenated MilliQ water (18.2 MΩ) before *I–V* measurement.

Ionic current measurement: The ionic transport properties of the nanochannel were studied by measuring ionic current through the nanochannel. Ionic current was measured by a Keithley 6487 picoammeter (Keithley Instruments, Cleveland, OH). A single conical shaped PET membrane was mounted between two chambers of the etching cell. Ag/AgCl electrodes were used to apply a transmembrane potential across the film. A scanning voltage varied from –5 V to +5 V at a scanning rate of 40 s during the modification process. During UV light irradiation of the spiropyran-modified sample, a scanning voltage varied from –5 V to +5 V at a scanning rate of 40 s.

Contact angle measurements: Contact angles were measured using an OCA20 (DataPhysics, Germany) contact-angle system at ambient temperature. Before the CA test, the sample was blown dry by N_2. In each measurement, a 2 μL droplet of water was dispensed onto the substrates under investigation.

The Supporting Information includes more experimental details: SEM image of the base of the nanochannel; contact angle measurements when UV light is off and under UV light irradiation; the current–time curves of the nanochannel under UV light irradiation; the calculated *I–V* curves based on the PNP model, the calculated net surface charge of the nanochannel along the pore axis, and the detailed formula derivation of the model.

Supporting Information

Supporting Information is available from the Wiley Online Library or from the author.

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