

# Nanofluidic Diodes with Dynamic Rectification Properties Stemming from Reversible Electrochemical Conversions in Conducting Polymers

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## S Supporting Information

**ABSTRACT:** The use of solid state nanochannels as nanofluidic diodes is currently a topic of large interest in nanotechnology. Particularly, there is a focus in the development of nanochannels with surface functionalities that make them responsive to multiple environmental variables. Here, we present for the first time the construction of electrochemical potential- and pH-responsive nanofluidic diodes using a novel approach based on a controlled electrochemical polymerization of aniline on gold-coated polycarbonate asymmetric nanochannels. The polyaniline-modified nanochannels showed three different levels of reversible ionic rectification corresponding to the degrees of oxidation of the conducting polymer. Our results demonstrate that this strategy enables an accurate and reversible control of the rectification properties due to the well-defined and predictable electrochemical conversion of charged species generated on the pore walls. We envision that these results will create novel avenues to fabricate electrochemically modulated nanofluidic diodes using conducting polymers integrated into single conical nanopores.

During the past decades synthetic nanofluidic devices have attracted the attention of different scientific areas due to their high significance in better understanding transport phenomena of biological membranes.<sup>1–3</sup> Concurrently, the quest for technological applications of nanochannels have been propelled. It has been shown that the modification of both the geometry and the surface charge of nanochannels are responsible for their ability to regulate ionic current. Broken symmetry in either the geometry or in the surface charge density generates also an asymmetry in the ionic conductivity leading to current rectification. There is a special interest in obtaining nanofluidic diodes equipped with surface functionalities capable of rendering them responsive to different physical or chemical inputs.<sup>4</sup> Within this framework, a broad variety of nanochannels with asymmetrical ionic conductivities responsive to different stimuli such as pH,<sup>5</sup> temperature,<sup>6</sup> molecules and ions,<sup>7,8</sup> and light<sup>9</sup> have been developed.<sup>10,11</sup> Moreover, several nanochannels with characteristics responsive to dual-stimuli have been developed.<sup>12–15</sup>

Controlling the permeation through membranes with redox-tunable groups has attracted considerable attention during recent years. Seminal work of Martin and co-workers described the electromodulated selective transport of cations through ferrocene-modified gold-coated nanotubules demonstrating the versatility of electrochemistry as a key enabling tool to manipulate the nanopore surface charge.<sup>16</sup> In spite of its relevance, little is known about the behavior of rectifying conical nanopores equipped with built-in electrochemically addressable surface charges and how electrochemistry can contribute to gain more control over their rectification properties. In this regard, the use of conducting polymers (CPs) for coating nanopore surfaces offers a suitable option. CPs have largely attracted the attention of the scientific community for the last decades due to their interesting electric and electrochemical properties.<sup>17,18</sup> CPs also represent a low-cost option for applications in organic electronic devices like light emitting diodes, photovoltaic devices and field effect transistors.<sup>19–21</sup> Particularly, polyaniline (PANI) has been one of the most studied CPs, mainly due to its ease of preparation and stability. Currently, PANI is considered as one of the archetypical CPs as it has been extensively studied and characterized. However, there are no previous reports on the synthesis of PANI to construct functional nanofluidic devices. PANI can be found in three different oxidation states called leucoemeraldine (LE), emeraldine (E), and pernigraniline (PG).<sup>17,22</sup> Each state is characterized by different relative compositions of imine (or quinoid units) and secondary amine-like (aromatic units) repetitive units; consequently, each state has a different  $pK_a$ . Being a polyelectrolyte with protonable groups, PANI shows a coupling of the proton binding and the redox potential.<sup>23,24</sup> This implies that changes in the applied electrochemical potential promote changes in the proton binding state, hence in its net charge. Conversely, pH variations modify the proton binding degree, which also alters the redox state.<sup>24</sup>

Here, we present the development of a dual responsive nanofluidic diode based on the electrochemical polymerization of aniline in asymmetric gold-coated polycarbonate nanochannels. Furthermore, it is shown that the site-selective electrosynthesis of PANI at the small opening of the nano-

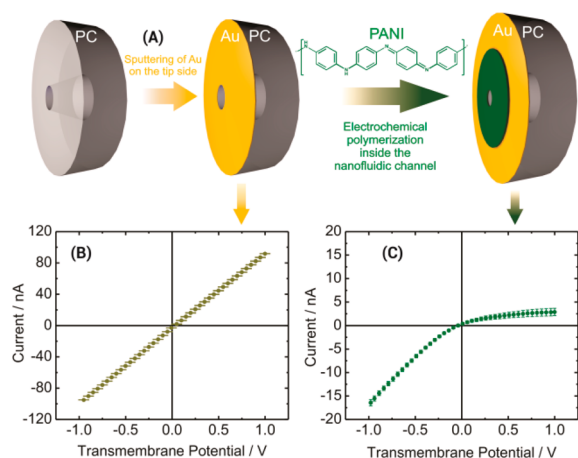
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channel, i.e., the tip, can confer properties of pronounced ionic rectification to the nanofluidic devices.

Polycarbonate foils (30  $\mu\text{m}$ -thick) were irradiated with one individual swift heavy ion (e.g., 2 GeV Au). By chemical etching, the single ion tracks were converted into conical-shaped nanopores (see Supporting Information for further details).<sup>25</sup> The resulting conical nanochannels exhibited a base diameter ( $D$ ) of  $\sim 4 \mu\text{m}$  and a tip diameter ( $d$ ) of  $\sim 100 \text{ nm}$ . These nanochannels behave as ohmic resistors and do not present rectification of the ionic current, probably due to the large diameter of the tip.<sup>26</sup> Even after the deposition of a gold layer on the tip side by sputter-coating, the nanochannels showed no or very low rectification ( $f_{\text{rec}} < 2$ , see Scheme 1A,B). The thickness

Scheme 1<sup>a</sup>



**Figure 1.** Change in the ionic conductance of the nanochannel as a function of the voltammetric charge of the polymer film. The electro-synthesis was carried out by cyclic voltammetry in 0.1 M aniline + 0.5 M  $\text{H}_2\text{SO}_4$  solution using a nanochannel with a tip diameter of  $\sim 100 \text{ nm}$ . Conductance measurements were performed in 0.1 M KCl.

conditions (see SI for details).<sup>27</sup> Nevertheless, greater integrated charges refer to thicker films. Results in Figure 1 indicate that the nanochannel tip is getting narrower and narrower as the conducting polymer layer grows. Particularly, the conductivity, which can be related to the diameter of the tip of the nanochannel, decreases up to a limiting value of 10 nS, 1 order of magnitude lower than the initial one.

Further indication of the closure of the tip of the nanochannel is given by the nonohmic behavior of the transmembrane conductivity after polymerization (Scheme 1C). Further information on the change of rectification factors during the polymerization is included in the SI file. The electro-synthesis of PANI on the tip side of the nanochannel allows creating a rectifying nanofluidic diode from a nonrectifying nanochannel and represents a novel top-down approach to obtain nonohmic nanofluidic devices. The closure of the pore was corroborated by SEM imaging (see Figure S3 in the SI).

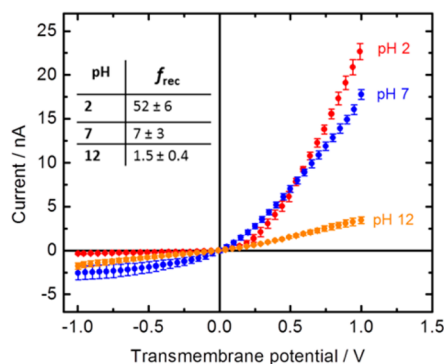
The finding of a nonzero limiting value for the nanochannel conductivity could be explained by a change in the synthesis thermodynamics due to the increasing confinement of the reacting species that limits the polymerization in the inner part of the tip. Alternatively, the polymer could actually fill the nanochannel in a hydrated state that would allow some ionic conductivity. A similar effect has recently been observed for the functionalization of nanochannels by oxidative polymerization of dopamine.<sup>28</sup>

The pH response of the modified nanochannel was studied by measuring  $I$ - $V$  curves in 0.1 M KCl solutions of different pH values while releasing the PANI-modified nanopore from electrochemical control, i.e., without applying an electrochemical potential. The results for three pH values are presented in Figure 2. As no external potential is applied to the PANI-modified membrane, the redox state of the polymer is emeraldine, E. In ambient conditions, this is the more stable state and is also the conducting form. It has been described as a combination of aromatic and quinoid-type units (Scheme 1A). Due to its particular chemical and electronic structure, the protonation equilibrium of the backbone nitrogen groups has been difficult to describe, and no widely accepted models are available. Nevertheless, some efforts have been performed to rationalize the complex acid base behavior in terms of apparent  $\text{p}K_a$  values, which result to be dependent on the synthesis<sup>29</sup> and experimental conditions.<sup>29,30</sup> Moreover, being a polyelectrolyte,

<sup>a</sup>(A) Schematic representation of the metallization of the polycarbonate (PC) membrane and electrochemical polymerization of aniline.  $I$ - $V$  measurements for the nanochannel before (B) and after (C) the polymerization.  $I$ - $V$  measurements were performed in 0.1 M KCl using a nanochannel with an initial tip diameter of  $\sim 100 \text{ nm}$ .

of the Au layer in the direction normal to the surface was  $\sim 80 \text{ nm}$  and SEM imaging revealed that the tip size reduction is 10–15 nm (see SI file for further details).

The metallized foils were further modified by *in situ* electropolymerization of aniline. To perform the functionalization, the 0.1 M KCl solution employed for the  $I$ - $V$  curve measurements was replaced by 0.1 M aniline in 0.5 M  $\text{H}_2\text{SO}_4$  and the electro-synthesis was carried out by cyclic voltammetry (see SI for further details). With the metal layer acting as working electrode, the membrane was subjected to subsequent potential scans in the aniline solution. The whole functionalization is depicted in Scheme 1. During the course of the voltammetric electro-synthesis, after a number of scans, the aniline solution was replaced by 0.1 M KCl, and  $I$ - $V$  curves were recorded by cycling the potential between  $-0.1$  and  $0.1 \text{ V}$  due to the linear behavior exhibited by the system within this range. After the recording of the  $I$ - $V$  curves, the electro-synthesis was continued using a fresh monomer solution. Figure 1 shows the variation of the nanochannel ionic conductance as a function of the voltammetric anodic charge of PANI after successive polymerization steps. The integrated charge corresponds to the oxidation process and accounts for all the redox units, thus being proportional to the amount of polymer. Although some correlations between this charge and the polymer film thickness have been reported, particular care must be taken when employing them for thickness estimations as they strongly depend on the experimental



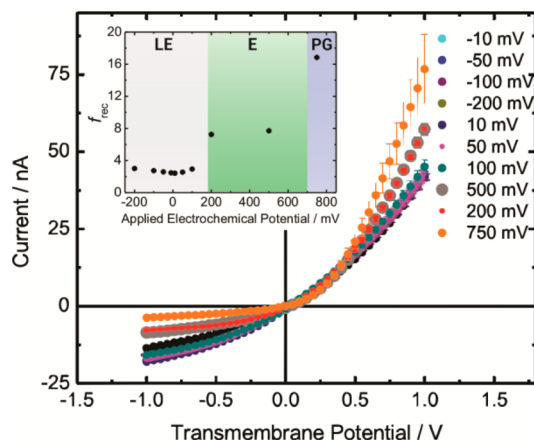
**Figure 2.**  $I$ – $V$  curves of PANI-modified nanochannel at different pH. The inset table shows the corresponding rectification factors.  $I$ – $V$  measurements were performed in 0.1 M KCl.

the titration curves of PANI are wider than those expected for simple substances.<sup>23</sup> As a consequence of this, a broad dispersion of  $pK_a$  values from 3 to 8 were reported for the E state.<sup>31</sup> Figure 2 shows  $I$ – $V$  curves for different pH values. The rectification factor ( $f_{rec}$ ) is defined as the ratio between currents measured at voltages of the same amplitude but different polarities (see SI file for further details). At pH 12 the nanochannel showed no ionic rectification, which corresponds to a low net surface charge density. Decreasing the pH to 7 produces a 5-fold increase in the rectification, from a rectification factor of  $\sim 1.5$  to  $\sim 7$ , evidencing an increase in the surface charge in agreement with a higher degree of protonation. Further lowering of the pH to 2 yields a rectification factor of  $\sim 52$ .

The pronounced pH dependence of the ionic conductance of the nanochannel can be explained by an increasing protonation degree from nearly zero as the pH decreases. At pH 12, neither the imine nor the amine groups are charged; therefore, an absence of net surface charges is expected. The increase of the rectification factor at pH 7 and then again at pH 2 is a clear indicative of a higher state of charge of PANI that may correspond to the successive protonation of imine and amine moieties.

Next, we evaluated the transport properties of the nanochannel at different potentials (at different oxidation states of PANI). A PANI-modified nanochannel was subjected to different applied electrochemical potentials for 2 min at pH 1 due to the higher stability of PANI to the electrochemical switching in acidic conditions. The 2 min time was selected in order to ensure a full conversion of PANI.<sup>32</sup> After the application of each potential,  $I$ – $V$  curves were measured (Figure 3). As shown in Figure 3, the modulation of the electrochemical potential of the PANI-modified membrane alters the features of the  $I$ – $V$  curves as a consequence of the change in the oxidation degree of the conducting polymer. The working electrochemical potential window allowed us to observe the three oxidation states of PANI (Figure 3, inset). The pH throughout all  $I$ – $V$  measurements was adjusted to 7 because at this pH the difference in the protonation binding between each oxidation state was more noticeable.

The changes in the ionic current rectification behavior with the applied potential can be explained by taking into account the coupling between the redox state and the proton binding equilibrium in this family of CPs. At  $-200$  mV, PANI can be completely reduced.<sup>24</sup> In its completely reduced form (LE), PANI is composed by single benzenic units. The repetitive acid base moiety of LE resembles that of the *N,N*-diphenylamine<sup>29</sup>

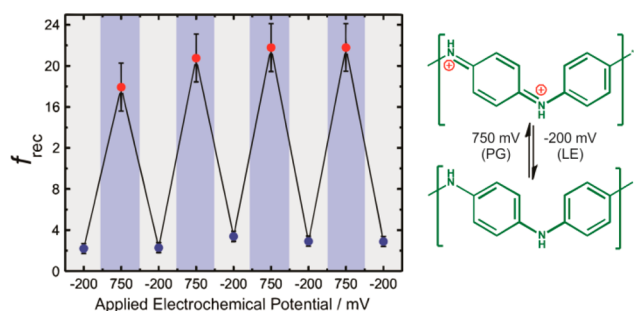


**Figure 3.**  $I$ – $V$  curves for PANI-modified nanochannel after different applied potentials at pH 7. Inset: rectification factors as a function of the applied electrochemical potential. The three redox states of PANI are indicated: leucoemeraldine (LE), emeraldine (E), and pernigraniline (PG). Electrochemical potential values preapplied for 2 min are referred to the Ag/AgCl/3 M NaCl electrode.  $I$ – $V$  measurements were performed in 0.1 M KCl.

and its experimental  $pK_a$  has been recently reported to be about 1.<sup>24,31</sup> Therefore, it is expected to have a low proton binding degree at pH 7 equivalent to a small surface charge. As the applied potential is increased, the ionic transport features remain practically constant until a value of about 200 mV is attained. At this potential the transition from LE to E takes place.<sup>24</sup> As mentioned above, the apparent  $pK_a$  of the conducting form is higher, yielding a higher proton binding degree. The experimental consequence in this case is an increase in the rectification factor up to a value of  $\sim 8$  that is about twice the factor at potentials below 200 mV.

If the potential is further increased, the current rectification of the nanochannel increases to  $\sim 17$  when the applied potential reaches the values needed for the transition from E to PG state.<sup>17,22,33</sup> As this state has a larger relative composition of imine to amine groups, an even higher proton binding degree is expected. The  $pK_a$  of this state has not been accurately measured, but it is supposed to be higher than 8. Hence, PANI is supposed to be almost fully protonated at pH 7.

In order to test the reversibility of the system, two extreme potentials were successively applied to the PANI-modified foil at pH 1. Again, after the application of each potential, the solution was replaced by 0.1 M KCl adjusted to pH 7, and  $I$ – $V$  measurements were made. At the lower potential ( $-200$  mV) the polymer is in the LE state, which is practically deprotonated, whereas at the highest potential (750 mV) the polymer is converted into the PG form, which is highly protonated at pH 7. By switching the applied potential between  $-200$  and 750 mV, PANI alternates between two extreme protonation degrees promoted by the applied electrochemical potential (Figure 4). This alternation of the net surface charge induces a pronounced change in the nanochannel transport properties, turning the behavior of the nanochannel from a practically nonrectifying to a highly rectifying type as shown by the changes in the rectification factors depicted in Figure 4. It is important to notice that the applied electrochemical potential has a stronger effect on the behavior of the lower conductivity state at negative potentials, thus producing a completely reversible gating effect. These experiments clearly demonstrate that the modification with PANI turns the nanochannel into a tunable nanofluidic device in



**Figure 4.** Reversibility test for changing in the ionic current rectification as a function of the applied electrochemical potential, measured at pH 7. Electrochemical potential values preappplied for 2 min are referred to the Ag/AgCl/3 M NaCl electrode. Measurements were performed in 0.1 M KCl.

which the applied electrochemical potential switches the ionic rectification according to the redox conversions occurring in the PANI film.

In summary, we showed for the first time the integration of conducting polymers into asymmetric single nanochannels to obtain electrochemically addressable, dual-responsive, and switchable nanofluidic diodes exhibiting reversible rectifying properties. Our experimental evidence describing the use of electropolymerized polyaniline, and exploiting the electrochemical switching of their monomer units, demonstrates that fine-tuning of the ionic transport by presetting the applied electrochemical potential is achievable and enables a higher degree of control over the ion transport properties of the system. The magnitude of the electrochemically generated surface charges arising from the coupling of the proton binding and the redox potential is responsible for controlling the transmembrane ionic transport and the rectification properties of the nanodevice. We expect that the combination of conducting polymers and asymmetric nanopores can lead to a myriad of new designs of switchable nanofluidic diodes with prospective applications in different technological areas such as biosensing, tailored drug delivery and energy conversion.

## ■ ASSOCIATED CONTENT

### Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/jacs.5b10692.

Characterization of polymer-modified nanopores (PDF)

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### Notes

The authors declare no competing financial interest.

## ■ ACKNOWLEDGMENTS

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