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Supporting information for

pH- and Light-Regulated Ion Transport of Hourglass Shaped Al₂O₃ Nanochannels Patterned with N719 and APTES

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Figure S1. Schematic illustration of the processes for fabricating hourglass shaped Al_2O_3 nanochannels.

The processes for fabricating symmetric shaped Al_2O_3 nanochannels: (1) the two sides of electropolished Al foil were separately anodized for 1 h. (2) the resulting porous oxide layer on Al foil was removed in a solution containing 6 wt% phosphoric acid and 3.5 wt% chromic acid. (3) the etched Al foil with highly ordered hemispherical concaves on each side was further anodized until the anodized current decreased to zero, and two layers of Al_2O_3 nanotube arrays with a barrier oxide layer at each bottom of the nanotubes were prepared. (4) An in-situ pore opening was carried out to form the conducting symmetric hourglass shaped alumina nanochannels.

Upon completion of the first anodization and removing the oxide layer (procedure (1) and (2)), the asymmetric hourglass shaped Al_2O_3 nanochannels were prepared as follow: (5) The etched Al foil was mounted in a tailor-made groove, and only one side of Al surface got in touch to the electrolyte. The etched Al foil was anodized for 4 h and the Al_2O_3 nanotube arrays grew on one side of the Al foil. (6) The resulting Al foil was taken out from the groove, and was further

anodized until the anodized current decreased to zero. (7) After an in-situ pore opening process for 30 min, asymmetric hourglass shaped Al₂O₃ nanochannels were built.



Figure S2. Schematic illustration of the process of APTES and N719 patterned onto the hourglass shaped Al₂O₃ nanochannels.

The process of APTES and N719 patterned onto the hourglass shaped Al_2O_3 nanochannels was shown in Figure S2. The inner surface of Al_2O_3 nanochannels with hydroxyl groups grafted the silane by APTES treatment, resulting in the nanochannels carried with amino groups. And then, a molecule of N719 was grafted with an amino group on the surface by its one carboxyl groups, resulting in the nanochannels carried with carboxyl groups. After APTES and N719 modification, the Al_2O_3 nanochannels realized pH response characteristic due to the protonation/deprotonation of the patterned amine and carboxyl groups upon solution pH variation. Furthermore, N719 was one kind of ruthenium complexes consisting of a ruthenium (II) atom coordinated by polypyridyl ligands and thiocyanate moieties in an octahedral structure. When the modified nanochannels were irradiated by light at a certain pH value, N719 molecule was excited by light and one electron from the molecular orbital t_{2g} distributed mainly on ruthenium (II) center, to an empty π^* molecular orbital mainly located on the bipyridyl ligand. So, the charge density of the freedom carboxylic groups increased due to the attached to the bipyridyl moiety. Therefore, the negative charges on the inner surface of N719-modified segment increased, while the surface charges on the APTES-modified segment had no change, realizing a response to light.



Nanochannels membrane treated by APTES

Figure S3. The schematic diagram of experimental setup used for N719 coating onto the channels.

Based on the theory of diffusion-limited patterning (DLP) of molecules in nanofluidic channels¹, different molecules exposing the channels can be patterned onto the surface by the bind to the surface. As shown in Figure S3, hourglass shaped Al₂O₃ nanochannels treated by APTES were mounted between the two chambers of the electrochemical cell, and one chamber was filled with N719 (0.3 mM ethanol solution) and the other was filled with ethanol. Therefore, the N719 molecule diffused along the nanochannel axis, and patterned onto the surface of nanochannels. Because of the narrow tip section of hourglass shaped Al₂O₃ nanochannels, the N719 molecule with large molecule volume diffused hardly through the tip section even though the diffusion time was further extended. So, N719 was successfully asymmetric modified onto one segment of the hourglass shaped Al₂O₃ nanochannels.



Figure S4. The schematic diagram of the experimental setup used for *I-V* measurement.

As shown in Figure S4, the nanochannels were mounted between the two chambers of the electrochemical cell filled with the 0.1mM KCl solution with adjusting pH values from 4 to 9. The ionic current was measured by a Keithley 6487 picoammeter. Ag/AgCl electrodes were settled in each cell to apply the desired potential and to measure the resulting ionic current, and the scanning voltage was applied from -2 V to +2 V. Each test was scanned for three times in dark and light state, respectively. The light source was the simulated visible light with an irradiance of 90 mW cm⁻², which was measured with a power meter (UV-A, Photoelectric Instrument Factory of Beijing Normal University). The testing temperature was the room temperature.



Figure S5. The photograph of unmodified and N719 modified hourglass shaped Al_2O_3 nanochannels.

The photograph of the unmodified and N719 modified hourglass shaped Al_2O_3 nanochannels was shown in Figure S5, and the area of the unmodified nanochannels was about 1 cm² (Figure S5a). The N719 modified area of the nanochannels was about 0.36 cm², and the color of the N719 modified area turned purple (Figure S5b).



Figure S6. (a-g) Schematic diagram of the process for decorating N719 onto one segment of symmetric hourglass shaped Al_2O_3 nanochannels. (a1-g1) The visible light images and (a2-g2) the

fluorescence images of symmetric hourglass shaped Al_2O_3 nanochannels with different N719 coating time, including (a1) 0 min, (b1) 10 min, (c1) 20 min, (d1) 30 min, (e1) 1 h, (f1) 2 h, (g1) 3 h. Scale bar was 20 μ m.

In the approach of DLP, the diffusion length and density of modified functional molecules on the channels can be affected by the reagent concentration and the diffusion time. As shown in Figure S6, the visible light and fluorescence images of symmetric hourglass shaped Al_2O_3 nanochannels illustrated the color change of the N719 modified segment in the N719 diffusion process. With the extended modification time, the length of N719 modified segment increased. When the modified time increased to 1 h, the N719 diffused at the half of the nanochannels, but the coverage of N719 on the surface was very little and not even, which was influenced by the short diffusion time and the low N719 concentration in the nanochannels. In order to obtain uniform coverage of N719 on the nanochannels, the modified time was increased to 3 h. Upon completion of 3 h diffusion, the purple of N719 segment was deepened, indicating that the N719 coverage of N719, the confined tip region of the hourglass shaped nanochannels could be blocked with the N719 diffusion time further extended.



Figure S7. The ionic transport characteristic of symmetric hourglass shaped Al_2O_3 nanochannels before and after modification. The nanochannels were measured in 0.1 mM KCl at pH 6 in the dark state and the light state.

As shown in Figure S7, the *I-V* curves of the unmodified and the APTES modified nanochannels were linear either in the light or dark state due to homogeneous charge distribution on inner walls at pH 6. Compared with unmodified nanochannels, the ionic current of the APTES modified nanochannels decreased which was attributed to wettability change of the channels. In contrast, after N719 modification the nonlinear *I-V* curve was observed, and the ion current of N719 modified nanochannels was further decreased. The nanochannels modified by N719 exhibited inhomogeneous charge distribution on inner surface at pH 6, which resulted in ionic selectivity transportation. In the light state, the negative charges on the N719 surface increased due to light induced electrons within N719 molecules, resulting in more remarkable ion selectivity transportation than that in the dark state.



Figure S8. *I-V* curves of symmetric Al₂O₃ nanochannels modified by APTES and N719 with pH values changing from 4 to 9 in dark state and light state. The N719 modification time was 3 h.

By comparison of the *I-V* curves of symmetric nanochannels modified by APTES and N719 between the dark and light state with pH values changing from 4 to 9, it was easy to find that under light state the ion currents increased at negative voltage compared with that of dark state, while the ion currents under positive voltage changed a little. Note that at the pH value of 6 a maximum ionic current change value was obtained. The increased ion currents of symmetric Al₂O₃ nanochannels modified by APTES and N719 in the light state could be attributed to the increased surface charge density on the inner walls of the N719 segment.

Reference

(1) Karnik, R.; Castelino, K.; Duan, C.; Majumdar, A., Nano letters 2006, 6 (8), 1735-1740.