Supporting Information

N3/Al_2O_3 Composite Nanochannels: Photoelectric and Photoelectric-and-pH Cooperatively Controlled Ion Gating

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1. Fabrication Schematic

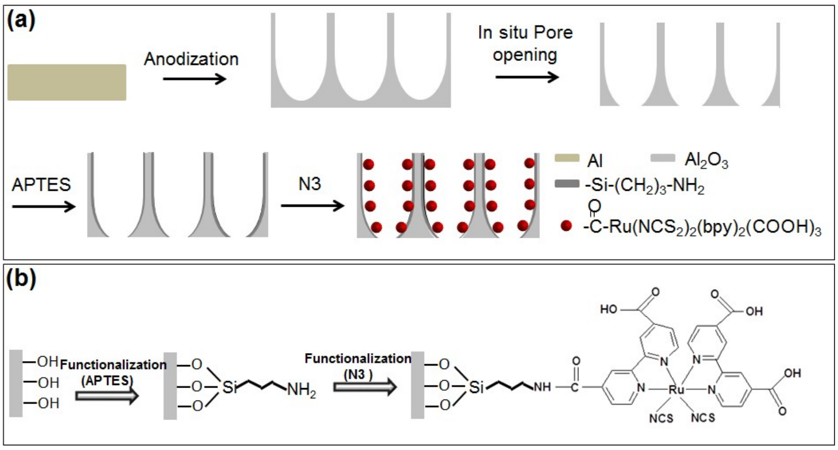

Figure S1 (a) Schematic illustration of the process for fabricating of N3 functionalized bullet shaped Al_2O_3 nanochannels for forming organic/inorganic composite nanochannels system. (b) Schematic illustration of the covalent modification process of APTES and then N3 molecules on Al_2O_3 nanochannels surface.

The process for fabricating N3 functionalized bullet shaped Al_2O_3 nanochannels as shown in **Figure S1**: (a) The bullet shaped Al_2O_3 nanochannels are prepared using a two-step anodization method combined with a time-controlled etching of the anodic barrier layer of Al_2O_3. The Al_2O_3 nanotubes with a barrier oxide layer at the bottom were firstly prepared using a two-step anodization method. After a time-controlled etching process upon the anodic barrier layer, the bullet shaped Al_2O_3 nanochannels with asymmetric geometry were built [1-3]. Then, the Al_2O_3 nanochannels were modified with APTES and N3 molecules in sequence for forming the functionalized nanocannels. (b) The covalent modification process: The as-prepared Al_2O_3 nanochannels with hydroxyl groups on surface reacted with APTES by a covalent grafted procedure resulting in the silanized Al_2O_3 nanochnnels carried with amino groups. After a N3 molecule was grafted with an amino group by its one carboxyl groups, the functionalized composite nanochannels were finally obtained and carried with several freedom carboxylic acid moieties on N3 molecular backbone.

2. Current-Voltage recordings device

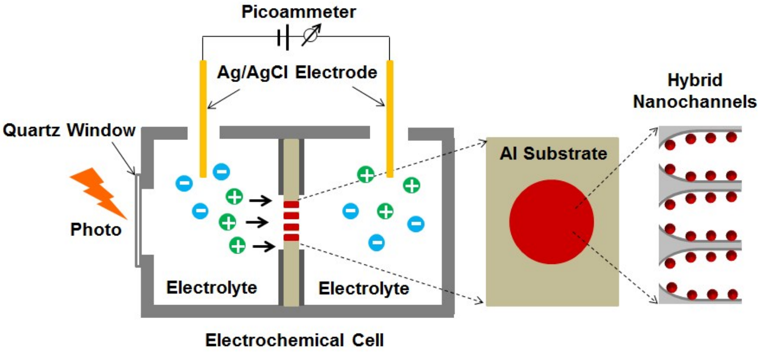

Figure S2 Schematic diagram of the custom-designed electrochemical cell with quartz window for the measurements of photo and pH modulated ionic transport properties of the N3/Al_2O_3 composite nanochannels.

3. SEM images of the bottom surface of porous Al_2O_3 samples

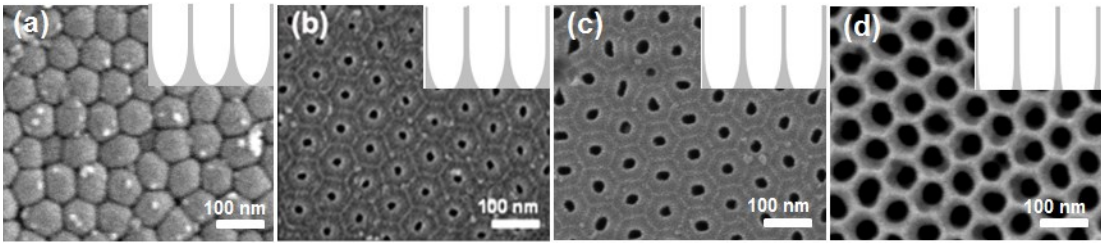

Figure S3 SEM images of the bottom surface of porous Al_2O_3 samples obtained with the different etching time of (a) 0, (b) 10, (c) 15, and (d) 30 min. The insets show the pore geometry evolution of the bottom view, which can be controlled from the closed hemispherical dome state to open state. The resulted alumina nanochannels via the time-controlled etching method can be modulated from asymmetry to symmetry structure.

4. Cross-sectional SEM image and Photograph of nanochannels

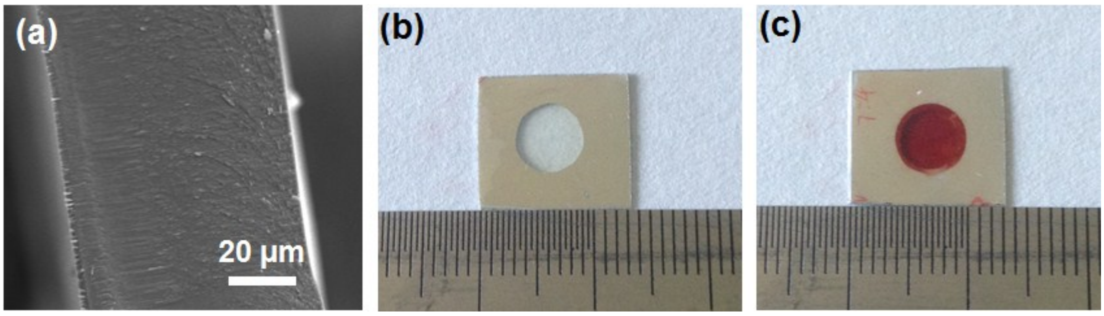

Figure S4 (a) Cross-sectional SEM image of the Al_2O_3 nanochannels. (b) Photograph of Al_2O_3 nanochannels membrane grown on Al substrate before and after N3 molecules modification.

5. UV-vis absorption spectra of nanochannels

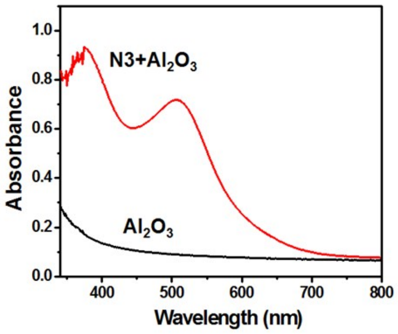

Figure S5 UV-vis absorption spectra of our bullet shaped Al_2O_3 nanochannels before (black curve) and after the modification with N3 molecules (red curve).

6. Ionic current-time traces of the composite N3/Al_2O_3 nanochannels

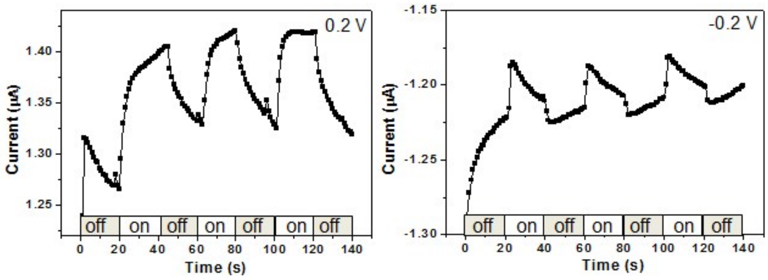

Figure S6 Ionic current-time traces of the composite N3/Al_2O_3 nanochannels when only the base side was exposed to light at ± 0.2 V.

As shown in Figure 2b, the N3/Al_2O_3 composite nanochannels show a nonlinear *I-V* curve and ionic transportation currents of the channels at negative voltage were higher than those at positive voltage. When the base side of the composite nanochannels was exposed to light, the ionic current increased with a responsive current of ~70 nA at + 0.2 V voltage, while the ionic current decreased with a responsive current of ~35 nA at - 0.2 V voltage (Figure S6). The light-induced surface charge contributed much linear current to the same measurement on the tip side of the composite nanochannels due to the larger pore diameter at base side.

7. I-V curves of the composite N3/Al_2O_3 nanochannels

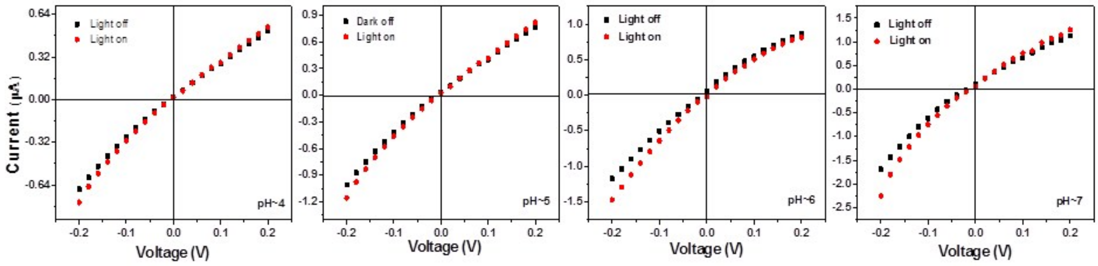

Figure S7 *I-V* curves of the composite N3/Al_2O_3 nanochannels with pH values changing from 4 to 7 at light on and off state. When photo is irradiated on the tip side with an irradiance of 11.5 mW/cm^2, the ionic current has an obvious increase at negative voltage at each pH value condition, while the ion current under positive voltage changes a little.