Supporting Information

For

A Flexible Ionic Synaptic Device and Diode-based Aqueous Ion Sensor Utilizing Asymmetric Polyelectrolyte Distribution

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Table of content:

Experimental section

Materials and Device Fabrication

Materials and Device Fabrication: ITO patterned glass and ITO patterned PET was purchased from Xiangcheng Technology. UV cured adhesive (NOV-81) was purchased from Norland Products, Inc. Poly(3,4-ethylenedioxythiophene): poly(styrenesulfonate) (PEDOT: PSS, CleviosTM_PH_1000) was purchased from Heraeus. Poly (Vinyl Alcohol) (PVA) with the molecular weight of 90000 was purchased from TCI Co., Ltd, and Poly (Styrene Sulfonic Acid) (PSS, 18wt% in water) with the molecular weight of 75000 which was purchased from Sigma-Aldrich Co., Ltd.

The ionic diodes were made using ITO patterned glass or PET as electrodes. Firstly, 80 μL PSS: PEDOT was drop-coated on the electrodes as buffer layer. PVA aqueous solution and PVA aqueous solution with different concentrations of PSS were drop-coated on the glass, followed by peeling off. Before assembling the device, the as-prepared PVA film of moderate size should be immersed in deionized water for 60 s. Subsequently, the pure PVA film was placed on the electrode coated with PSS: PEDOT. PSS hybrid PVA film was brought on the pure PVA film. Then the electrode was put on them. Finally, these two films are clamped by electrodes, followed by being sealed by NOA-81 adhesive. The ionic diode based pH sensor was made by the aforementioned structure with a punched hole on the PET electrode without PSS: PEDOT. And the synaptic device is made with one more PSS: PEDOT layer between PSS: PVA hybrid film and ITO patterned electrode.

Device characterization

The flexible performance of the device was measured when it was tightly bent around cylinders with different radii. The surface morphologies of Poly (Styrene Sulfonic Acid) film were observed by using AFM (SEIKO SPA-300HV) operated in tapping mode. XRD measurements of pure PVA, pure PSS, and their mixture film were carried out using DX-2700 X-ray diffractometer (Dandong Haoyunan Instrument Co. Ltd) with Cu Kα radiation (1.54 Å) at 40 kV and 50 mA. Infrared spectroscopy of PVA film, PSS film and PSS hybrid PVA film were characterized by using a Nicolet 380 FT-IR spectrometer. The electrical performances of the ionic diodes were characterized by electrochemical workstation (Chenhua, CHI660E).

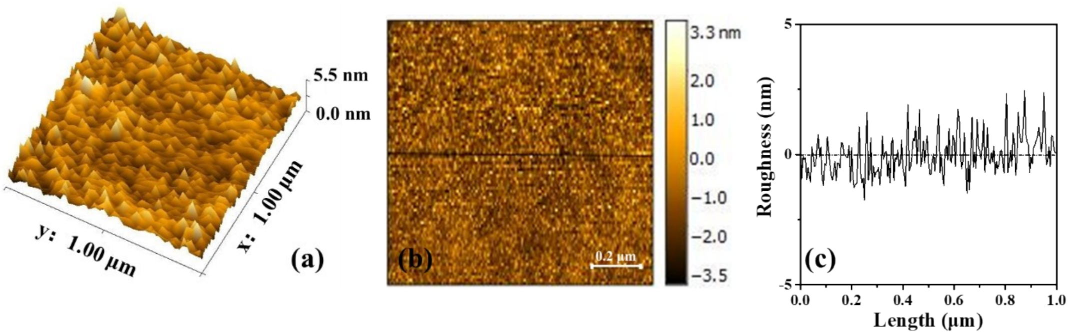

Figure S1. (a) and (b) AFM height image of the PSS hybrid PVA film. (c) AFM line scan of the film in (b).

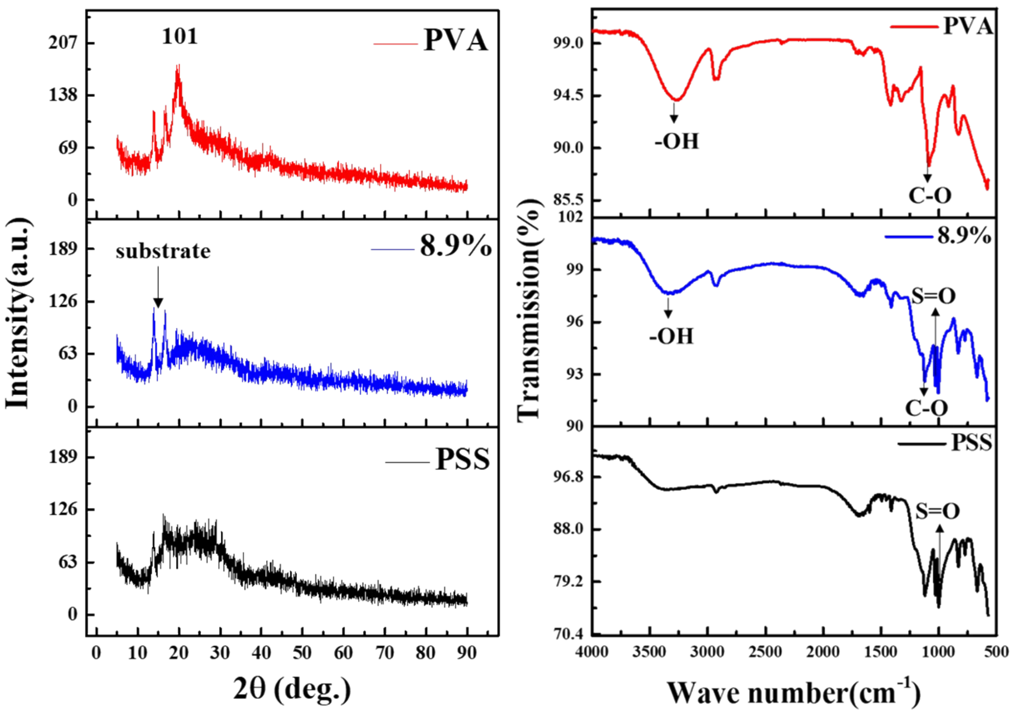

Figure S2. (a) XRD spectra of pure PVA, pure PSS and PSS hybrid PVA film. (b) Infrared spectroscopy of pure PVA, pure PSS and PSS hybrid PVA film.

The peak at 2θ = 19.4 corresponds to the (1 0 1) planes from the monoclinic unit cell of PVA.[1] The broad peak of PSS shows the disordered orientation of this polymer. The PSS hybrid PVA without peak exhibits that the presence of PSS destroys the crystallinity of PVA. And two small peaks in all films should be owing to the substrate.

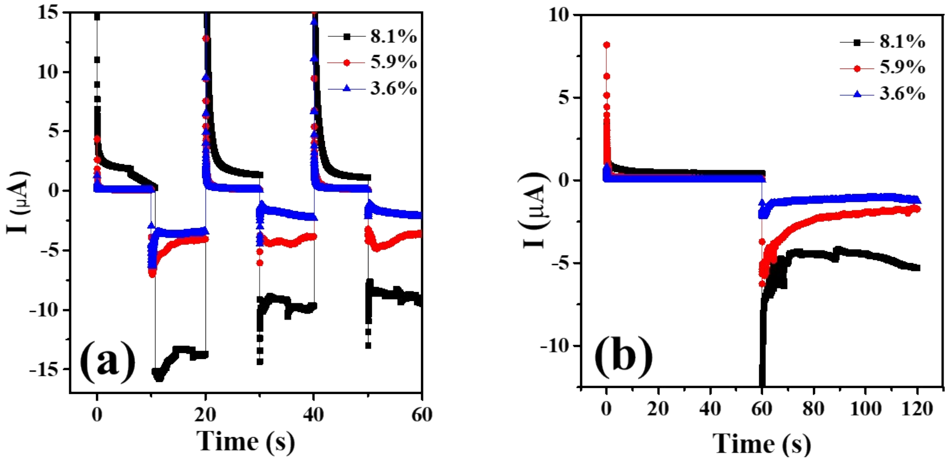

Figure S3. (a) Current responses of three diodes containing different PSS under AC field of 50 mHz with time. The repetitive biases applied are +2 V and -2 V. (b) Time dependence of current from diodes at constant forward (+2 V) and backward (-2 V) bias for long time.

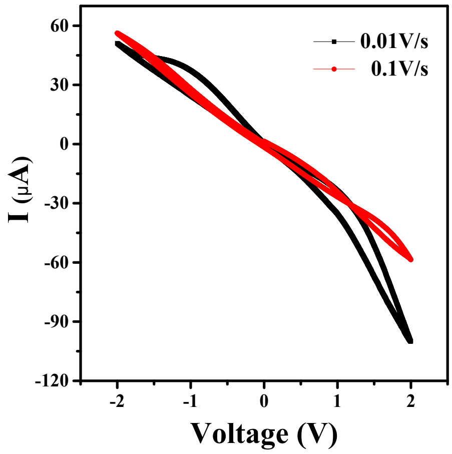

Figure S4. Working curves of the synaptic device under different scan rates.

Table S1. Comparison of the structures, principles and properties of ionic diodes reported in other literatures and our ionic device.

Structure	Rectification principles	Rectification Ratios	Operating voltage	Ref.
Nanopores stuffed DNA superstructures	Asymmetric nanofluidic geometries	~2	±2.0 V	2
Double-layers gels containing oppositely charged polyelectrolytes	Rectifying junction	~35	±5.0 V	3
oppositely charged heterogeneous membranes	Asymmetric heterojunction	~5	±2.0 V	4
Conical nanochannels with highly charged inner walls	Asymmetric geometries and charged surface of nanochannels	~10	±2.0 V	5
Double-layer polymer containing asymmetric polyelectrolyte	Asymmetric Polyelectrolyte Distribution	~15	±1.5 V	This work

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