Supporting Information

Integrated energy efficient electrochromic device for salt water purification

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Experimental Section

Chemicals and Reagents

3-Amino propyl trimethoxysilane (Sigma Aldrich), Ag foil (1 mm thick, Alfa Aesar), potassium ferrocyanide and potassium ferricyanide (Sinopharm Chemical Reagent Co., Ltd, China), hydrogen peroxide and ferric chloride hexahydrate ($FeCl_3.6H_2O$) from Macklin, China and sodium chloride and potassium nitrate from Kermel, China have been used in this study are analytical in grade, and used without further purification. Carbon cloth (CC) was purchased from Bio-Equip, China and MilliQ water (18.2 $M\Omega.cm^{-1}$) was used for solution preparation.

Synthesis of amine functionalized silsesquioxane polymer (PSQ)

The synthesis of silsesquioxane polymer with amine groups has been followed the procedure reported previously[1]. Initially, the pH of the monomer, 3-Amino propyl trimethoxysilane (100 mM in water, pH = 10.4) was adjusted to acidic condition (pH=2) using concentrated hydrochloric acid solution. Following this, the solution was stirred continuously for ~2h at room temperature to initiate the hydrolysis and condensation process. Finally, the above solution was heated at 60 ^oC for ~3h to obtain amine functionalized PSQ solution.

Redox polymer preparation (Anode)

A redox molecule, Ferrocyanide ($[Fe(CN)_6]^{4-}$) was immobilized into the primary amine functionalized silsesquioxane polymer by electrochemical method as reported by James's group[1]. The carbon cloth (1 cm^2) was washed thoroughly with deionized water before dipping in 1 mL of as-prepared polymer solution for 2h. After this step, the polymer modified carbon cloth was electrochemically cycled (30 cycles) in a solution containing 1 mM $K_3[Fe(CN)_6]$, 0.1 M KNO_3 and 10 mM HCl in the potential range between -0.2 V and 1 V vs Ag/AgCl. In this electrochemical test, the polymer modified carbon cloth was used as a working electrode, Ag/AgCl and platinum foil were used as the reference and counter electrode, respectively. After this electrochemical cycling process, the redox polymer modified carbon cloth electrode was taken out from the cell and washed with deionized water for further electrochemical characterization.

Prussian blue (PB) modified ITO preparation (Cathode)

A Prussian blue modified ITO cathode was prepared by chronoamperometry method. An indium tin oxide (ITO) working electrode was sequentially cleaned by water, acetone, ethanol solution with sonication before it was placed in a cell containing 3 mM of $K_4[Fe(CN)_6]$, 3 mM of $FeCl_3.6H_2O$ and 10 mM HCl solution along with a Ag/AgCl reference electrode and a platinum foil counter electrode. A potential of 0.4 V was applied on the working electrode for 400 seconds to deposit Prussian blue on ITO surface[2]. After that, the working electrode was taken out and washed with deionized water for further experiment.

Electrochromic desalination battery construction

Electrochromic desalination battery was constructed using Ag (1 cm^2) or redox polymer (1 cm^2) as anode, and PB|ITO as cathode (0.5 cm^2). Herein, Prussian blue acted as a Na^+ storage electrode as well as electrochromic display, and Ag or redox polymer could be chemically oxidized to generate electrons for the reduction of the cathode (PB). Initially, the two electrodes (anode and cathode) were placed in 0.6 M NaCl solution and connected with the external circuit. After that, 100 mM of hydrogen peroxide was added into the above container to oxidize the redox polymer or Ag foil. During this oxidation, electrons were generated from Ag or redox polymer to reduce PB by flow through an external circuit with color change from blue to colorless. At the same time, desalination was completed by ion storage process.

In the second step, the desalinated electrodes were subjected to salination in 100 mM KNO_3 solution where de-intercalation of ions could be realized by draining the energy from electrodes. For this, we have performed galvanostatic charge-discharge tests by applying a negative current of -3 μA to the cell.

Electrochemical characterization

Cyclic voltammetry (CV), linear sweep voltammetry (LSV), electrochemical impedance spectroscopy (EIS), galvanostatic charge-discharge (GCD) and open circuit potential (OCP) measurements were performed using a VERSASTATE F3 potentiostat. All the electrochemical characterization was carried out using a three-electrode system,

where the redox polymer, Ag foil and Prussian blue were used as working electrodes, Ag/AgCl (3 M KCl) and Platinum foil were used as reference and counter electrode, respectively, unless mentioned in this work. EIS measurement was performed in a two-electrode system at a biased formal potential ($E^{0'} = E_{pa}+E_{pc}/2$) of 160 mV for system 1 (PB//Redox polymer) and 120 mV for system 2 (PB//Ag) in a frequency range of 40000 Hz to 0.1 Hz at 10 mV amplitude. Energy dispersive X-ray (EDX) spectrometry was conducted by SEM (SEM, JSM-7500F, JEOL., Japan). X-ray powder di□raction (XRD) was carried out using a Bruker D8 Advance powder di□ractometer with Cu Kα radiation. UV-visible analysis of Prussian blue modified ITO film was done by UV-vis spectrophotometer (UV-2600, Kyoto, Japan). Fourier transform infrared spectra was recorded using FT-IR, Nicolet 170, USA. Conductivity measurement were performed by DDS-307 conductivity meter (Shangahai INESA & Scientific Instrument CO.LTD).

Conductivity Measurement

For system 1 (PB//redox polymer), we have measured conductivity of 0.1 M KNO_3 solution before and after salination process, because, we could not see a significant difference in the measuring of the conductivity of acidified 0.6 M NaCl solution before and after desalination. This may be due to the presence of high concentration of proton (H^+). However, for system 2 (PB//Ag), we have measured conductivity of 0.6 M NaCl solution before and after desalination.

Salt removal capacity calculation

Salt removal capacity = $\frac{(C0 - Ci)\ X\ V}{A}$, $C_0 - C_i$ is change in concentration before and after desalination or salination (mol/L), V = Volume of the solution and A= Area of the electrode[3].

Discharge Experiment

Discharge of both system 1(PB//redox polymer) and system 2 (PB//Ag) have been achieved by after applying of electrical energy (-3 μA) as well as the addition of 100 mM H_2O_2 (charging current was not applied in this case). For discharging process, -3 μA current was applied.

Figures

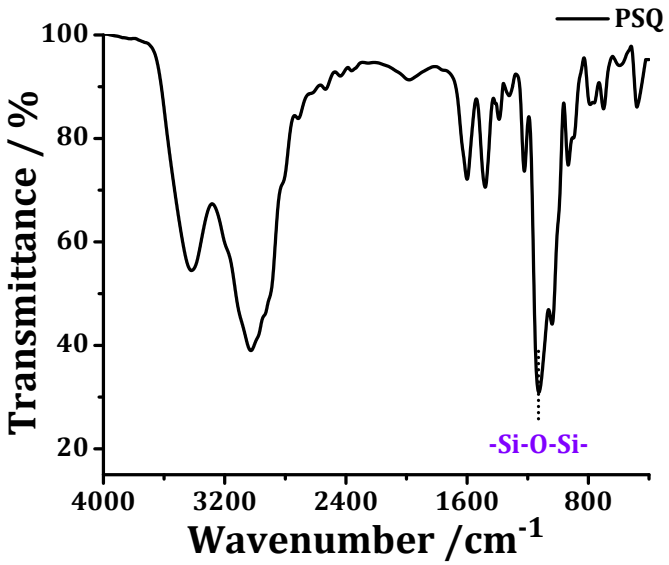

Fig. S1 FT-IR spectra of as-synthesized amine functionalized PSQ.

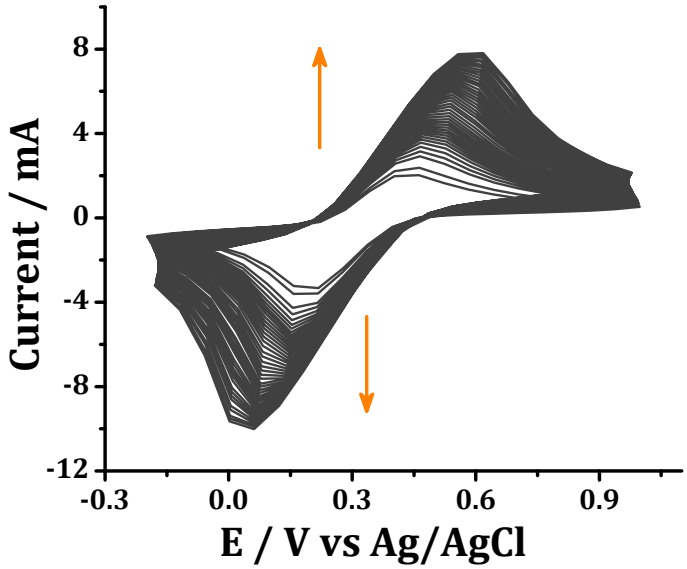

Fig. S2 Electrochemical cycling of PSQ film in 1 mM $K_3[Fe(CN)_6]$, 0.1 M KNO_3 and 10 mM HCl solution at a scan rate of 50 mV s^{-1}

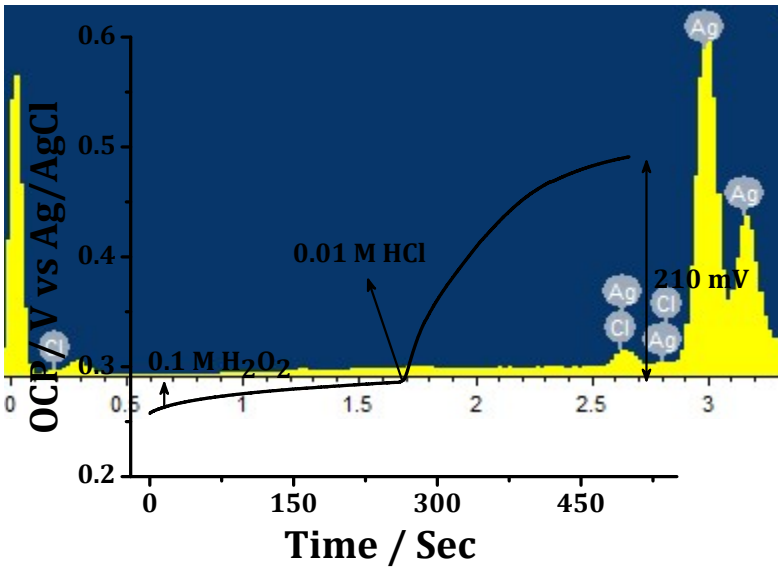

Fig. S3 OCP measurement of redox polymer film with the addition of 0.1 M H_2O_2 and 0.01 M HCl in 0.6 M NaCl solution.

Before salination | **After salination with $AgNO_3$ solution**

Fig. S4 Image of 100 mM KNO_3 solution before salination (Left) and 0.1 M KNO_3 solution after salination with addition of 10 mM $AgNO_3$ solution (Right).

Fig. S5 EDX spectra of Ag foil after H_2O_2 (0.1 M) treatment in 0.6 M NaCl solution.

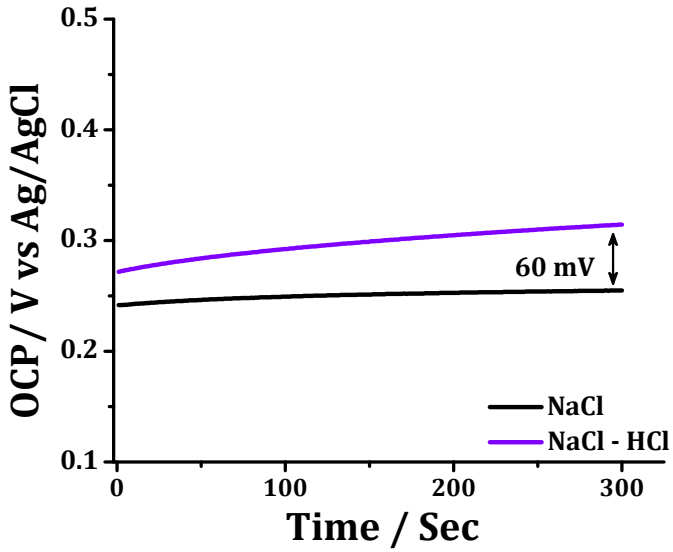

Fig. S6 OCP of redox polymer film in 0.6 M NaCl solution and acidified salt solution (10 mM HCl+0.6 M NaCl).

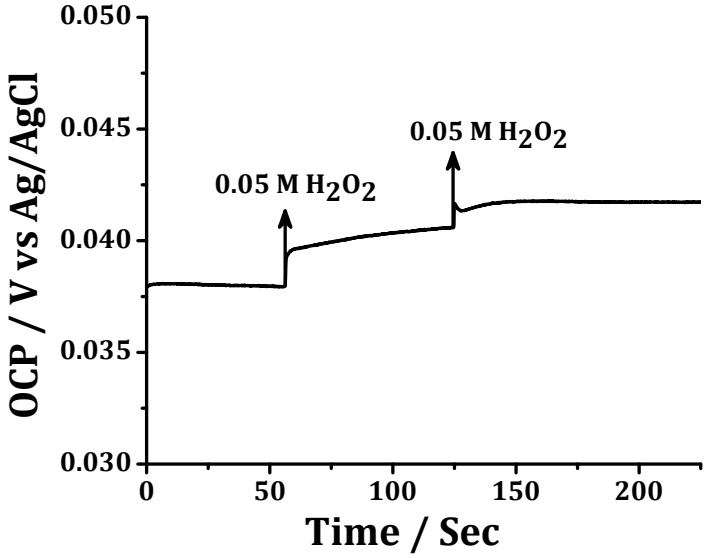

Fig. S7 OCP measurement of Ag foil with successive addition of H_2O_2 in 0.6 M NaCl solution

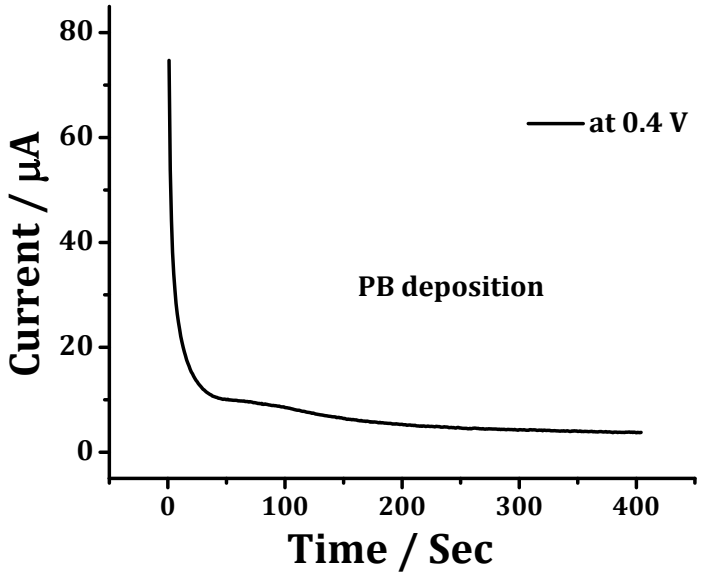

Fig. S8 Prussian blue (PB) deposition on ITO plate at 0.4 V vs Ag/AgCl.

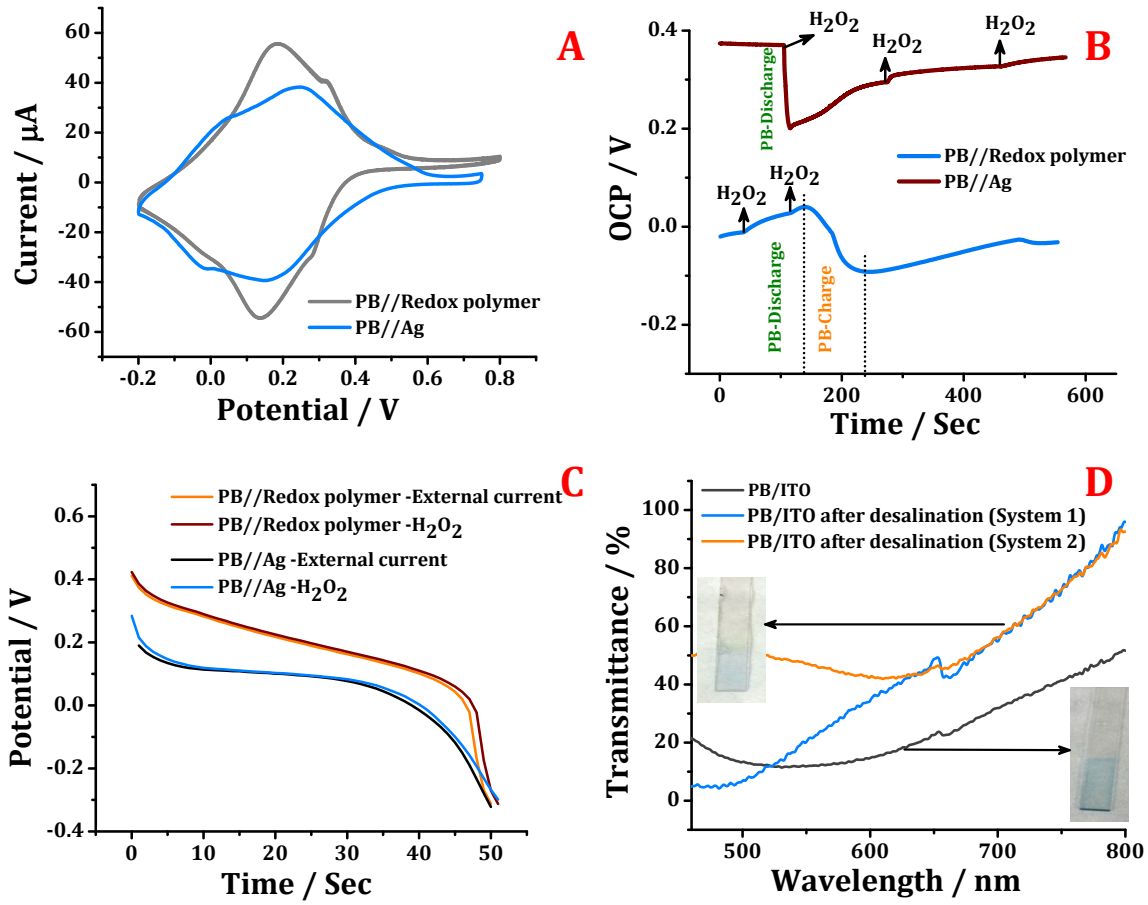

Fig. S9 A) Cyclic voltammogram of PB//Redox polymer and PB//Ag in 0.6 M NaCl; B) and its OCP measurement by continuous addition of 0.1 M H_2O_2; C) discharge profiles of PB//redox polymer and PB//Ag and; D) transmittance spectra of PB|ITO before and after desalination by H_2O_2 assisted electrochromic desalination battery.

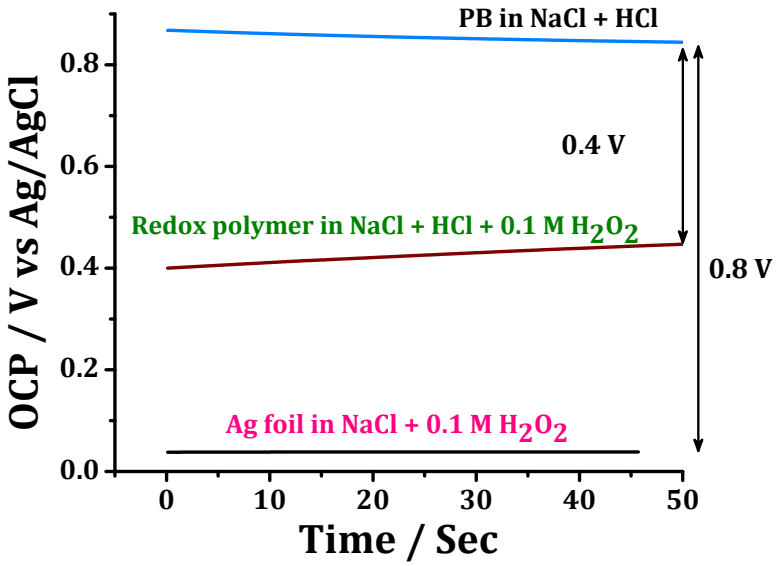

Fig. S10 Comparison of OCP values of PB|ITO (cathode), H_2O_2 oxidized redox polymer (anode) and H_2O_2 oxidized Ag foil (anode).

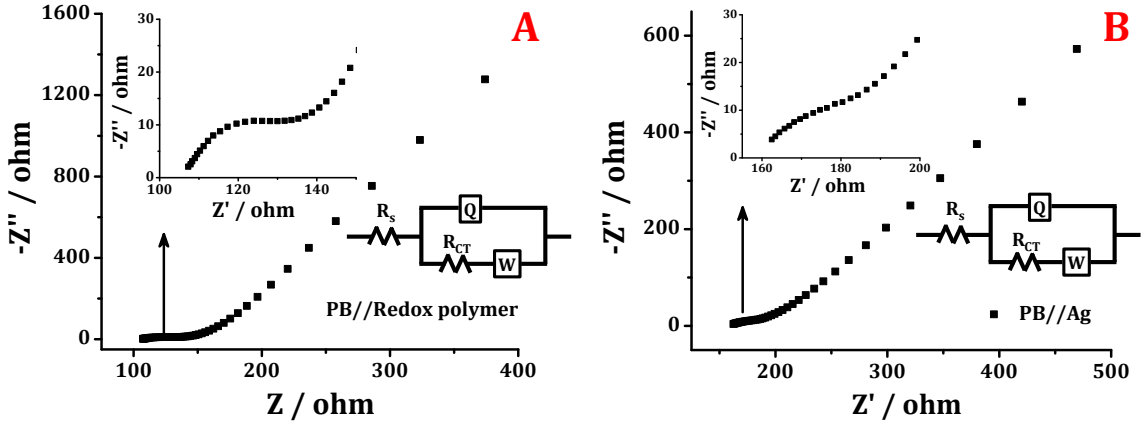

Fig. S11 A) Nyquist plots of PB//Redox polymer in acidified 0.6 M NaCl solution at 160 mV bias potential; and B) PB//Ag in 0.6 M NaCl solution at 120 mV bias potential.

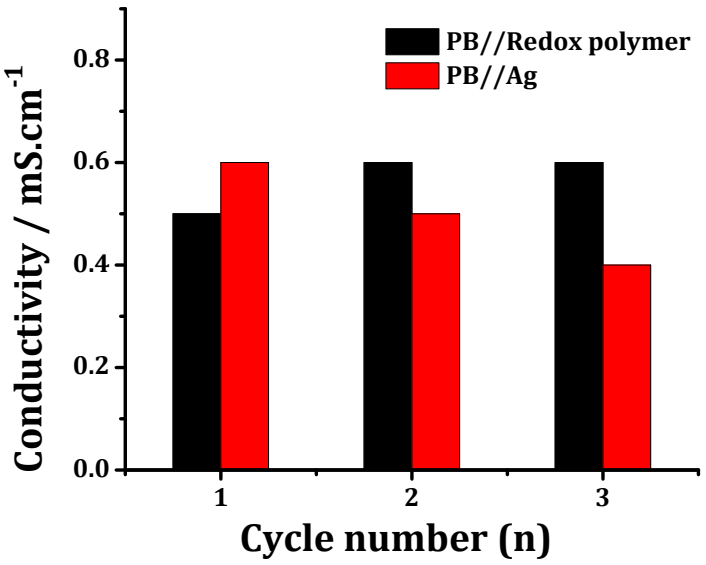

Fig. S12 Cyclic conductivity measurement of chemical assisted desalination battery.

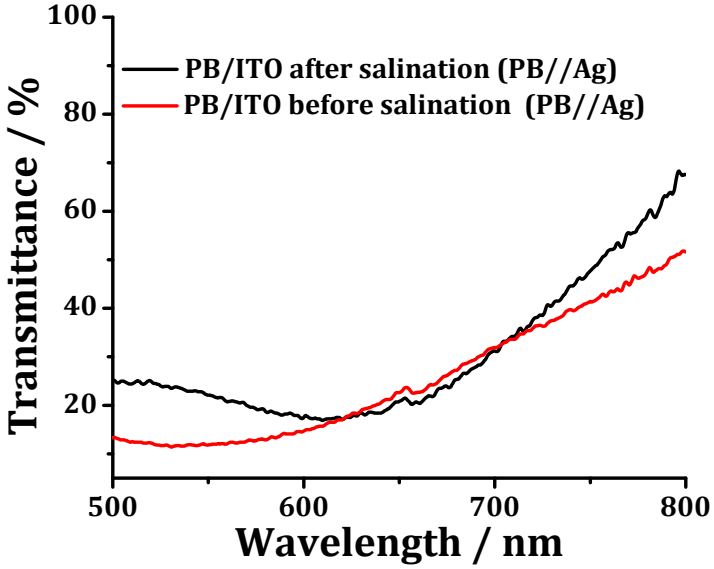

Fig. S13 Transmittance spectra of PB|ITO film before and after salination process of system 2 (PB//Ag).

References

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