

Supporting Information

Changeable critical state for switchable photocurrent direction via photo-electrochemical photocurrent polarity switching effect in BiFeO₃ nanoparticulate films

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1. Supplemental Methods:

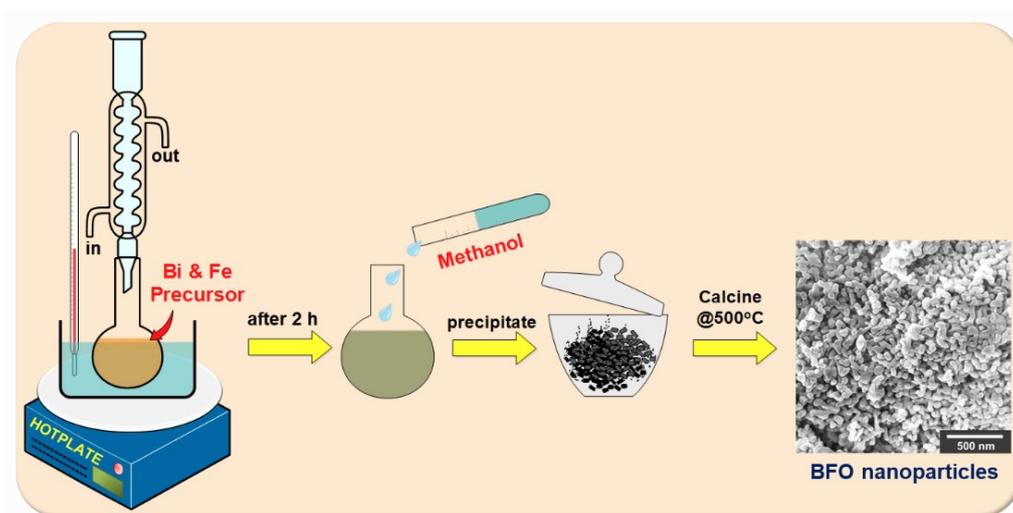
1.1 Materials and Chemicals: Iron (III) nitrate pentahydrate (Fe(NO₃)₃ · 5H₂O), bismuth (III) nitrate nonahydrate (Bi(NO₃)₃ · 9H₂O), ethylene glycol (98%), and ethanol, Potassium hydroxide (KOH), sodium sulphate (Na₂SO₄), sodium nitrate (NaNO₃) and sodium chlorate (NaClO₄) were procured from Merck India Pvt. Ltd. FTO-coated quartz substrates (7-8 Ω/sq) were procured from Sigma Aldrich. Before utilization, the substrates underwent a cleaning process involving ultrasonication successively with acetone, isopropanol, ethanol, and deionized water, followed by drying using compressed N₂ stream. All the chemicals used for the synthesis and electrochemical measurements were of analytical grade and were used as received without further purification.

1.2 Material Characterizations:

For the phase identification and structural elucidation, X-ray diffraction (XRD) measurements were carried out using a X-ray Bruker D8 Advance diffractometer (US) with Ni-filtered Cu K α radiation ($\lambda = 1.54 \text{ \AA}$, 40 kV, 40 mA) at an incident angle of 0.5° with a step size of 0.02° and step time of 3s. UV-vis absorption spectra were recorded in reflectance mode using a PerkinElmer Lambda 950 spectrometer equipped with an integrating sphere. X-ray photoelectron spectroscopy (XPS) measurements were performed using AXIS Supra (Kratos Analytical Ltd.). The spectra were fitted using CASA XPS software with a Shirley background subtraction and peak shape consisting of 30% Lorentzian-Gaussian ratio. The fitted spectra were further optimized by χ^2 minimization. Ultraviolet Photoelectron Spectroscopy (UPS) measurements were conducted using a Thermo Scientific NEXSA Surface Analysis system with a He I (21.2 eV) UV source under ultra-high vacuum ($<5 \times 10^{-9}$ mbar). The work function (Φ) was calculated from the secondary electron cutoff, and referenced with respect to gold standard. The work function was determined using:

$$\Phi = hv + E_{cutoff}$$

where $h\nu$ is the photon energy of the He I lamp (21.2 eV) and E_{cutoff} is the cutoff energy obtained from the UPS spectrum. All the spectra were referenced with respect to the adventitious carbon C 1s peak at 284.6 eV. Zeiss EVO50: ZEISS, Germany, was used for obtaining SEM and performing EDS measurements. The accelerating voltage for the scanning electron microscopy (SEM) and energy dispersive spectroscopy (EDS) measurements was 5 and 15 kV, respectively. Transmission electron microscopy (TEM) images were taken from TEM JEOL 1400 microscope (operating voltage 120 kV). A high-resolution TEM (HR-TEM) imaging was carried out using FEI Techni 20 with an accelerating voltage of 200 kV. The TGA thermograms were recorded using Perkin Elmer instrument (Pyris Diamond TG/DTA) in air with a heating rate of $10\text{ }^{\circ}\text{C min}^{-1}$ from room temperature to $800\text{ }^{\circ}\text{C}$.



Scheme S1: Synthetics of the methodology used for the synthesis of BFO NPs.

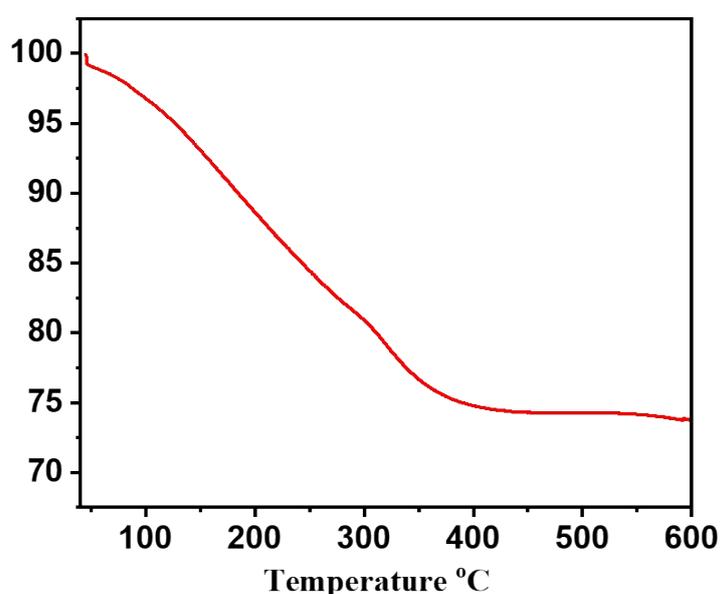


Figure S1 TGA plot of Bi-Fe Glycolate Precursor.

1.3 Photoelectrochemical Characterization:

All the PEC measurements were carried out in a standard three electrode single-compartment cell assembly using $Ag/AgCl/Cl^-$ (saturated with KCl) as a reference electrode, a Pt mesh as a counter electrode and FTO coated quartz substrates modified with the catalyst ink as a working electrode. The working electrode was fabricated by depositing a film of the sample on an FTO quartz substrate, for which the catalyst ink was prepared by mixing 1 mg of the sample with 100 μ L isopropanol. The mixture was sonicated for *ca.* 30 minutes, and then 10 μ L of the as prepared suspension was drop cast on a conducting side of an FTO coated quartz substrate with dimensions of 1.0 cm \times 1.0 cm (total geometrical area = 1.0 cm²) to make a thin film. The rest of the area was carefully masked with insulating resin. All the modified electrode substrates were allowed to dry completely under ambient conditions before using them for PEC measurements. All the PEC measurements were performed using a Zahner Zennium Pro 212 equipped with LED driver (450 nm, 0.65 A) with an intensity of 100 mW/cm². Electrochemical impedance spectroscopy (EIS) studies were performed within a frequency range of 1000 kHz to 100 mHz. To determine the charge carrier density of the materials, Mott–Schottky analysis was done in a potential range of -1.0 V to $+1.0$ V vs. Ag/AgCl reference electrode at an applied frequency of 1 kHz.

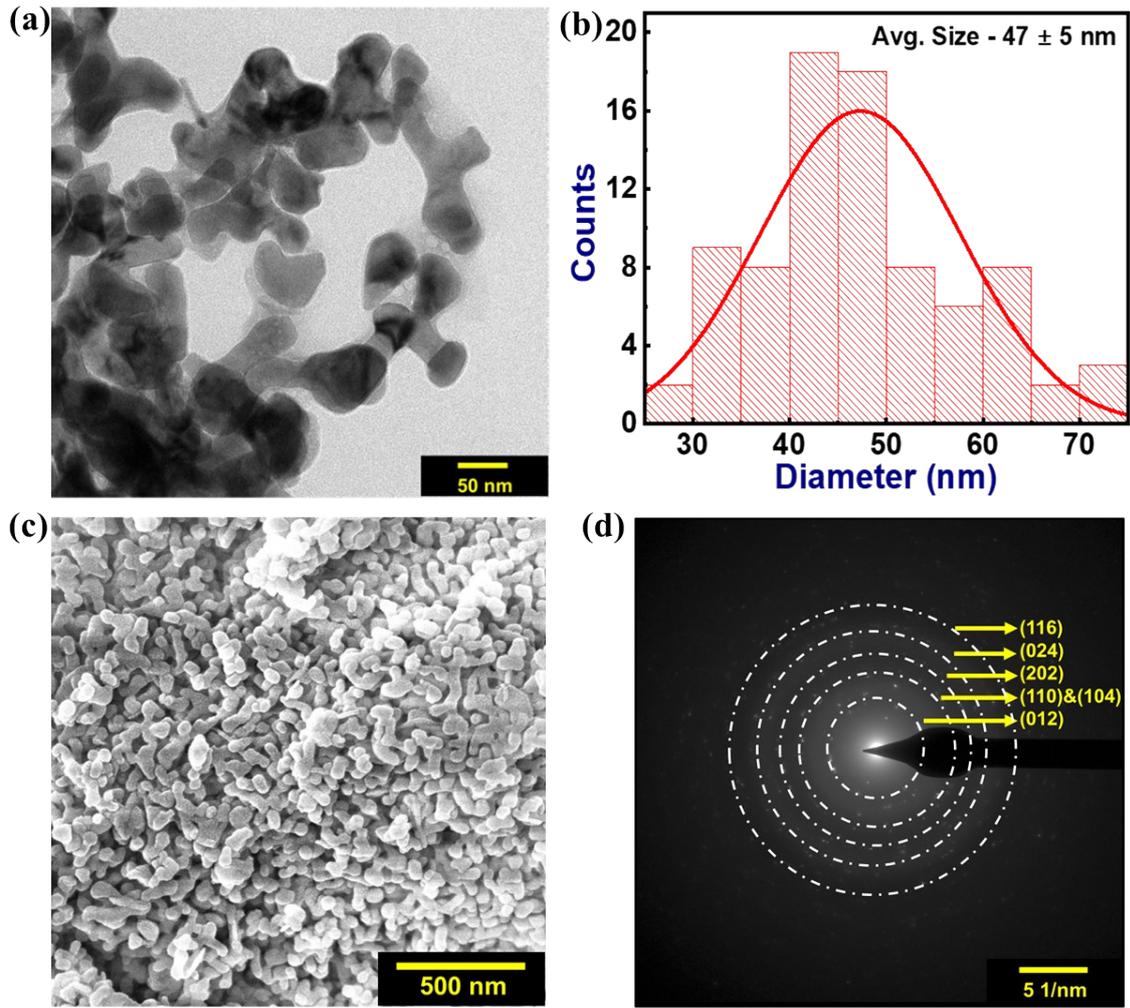


Figure S2: (a) TEM image (low magnification) of pristine BFO NPs, (b) size distribution profile (histogram), (c) FESEM image of pristine BFO NPs, (d) SAED pattern of BFO NPs.

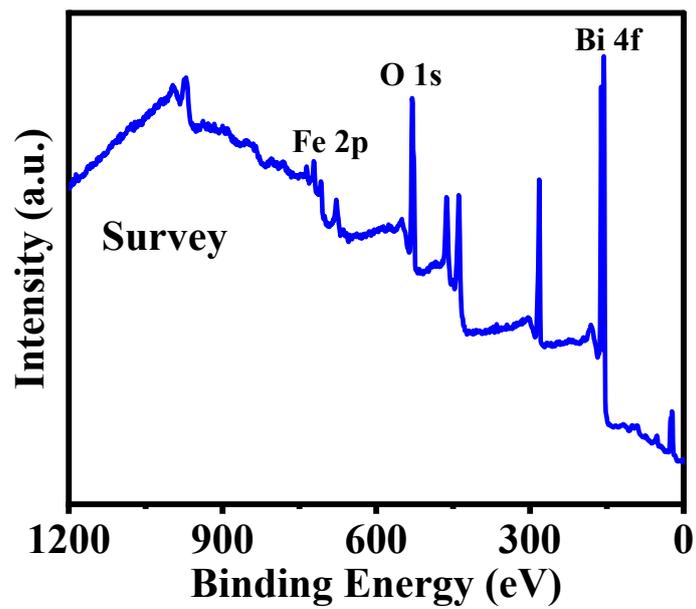


Figure S3: Survey XPS spectrum of pristine BFO NPs.

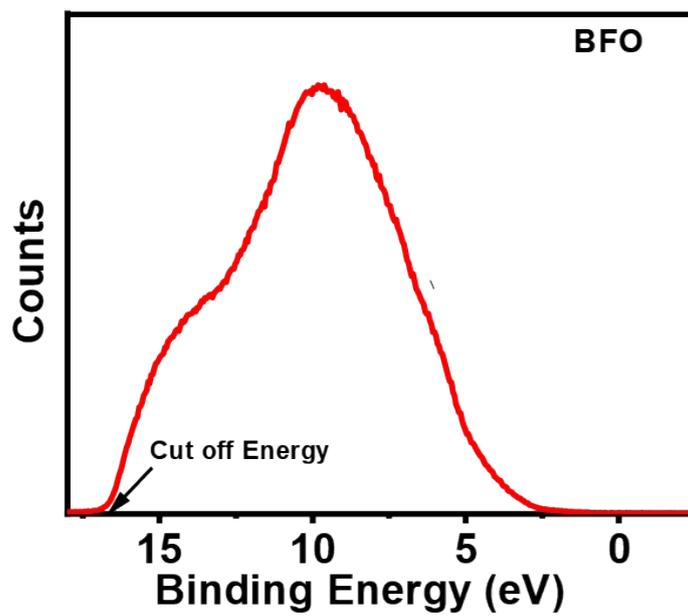


Figure S4: UPS survey scan of BFO NPs.

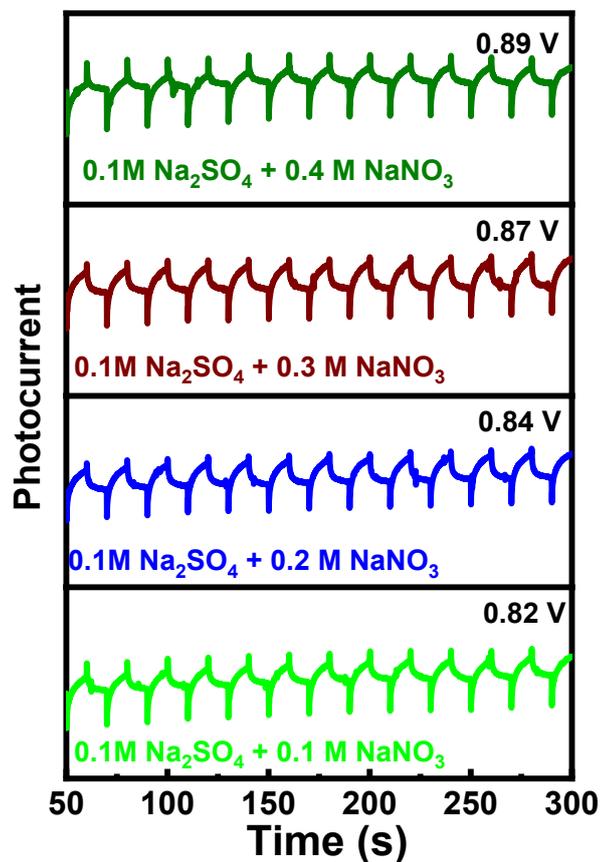


Figure S5 Critical state at switching potential for different ionic strengths.

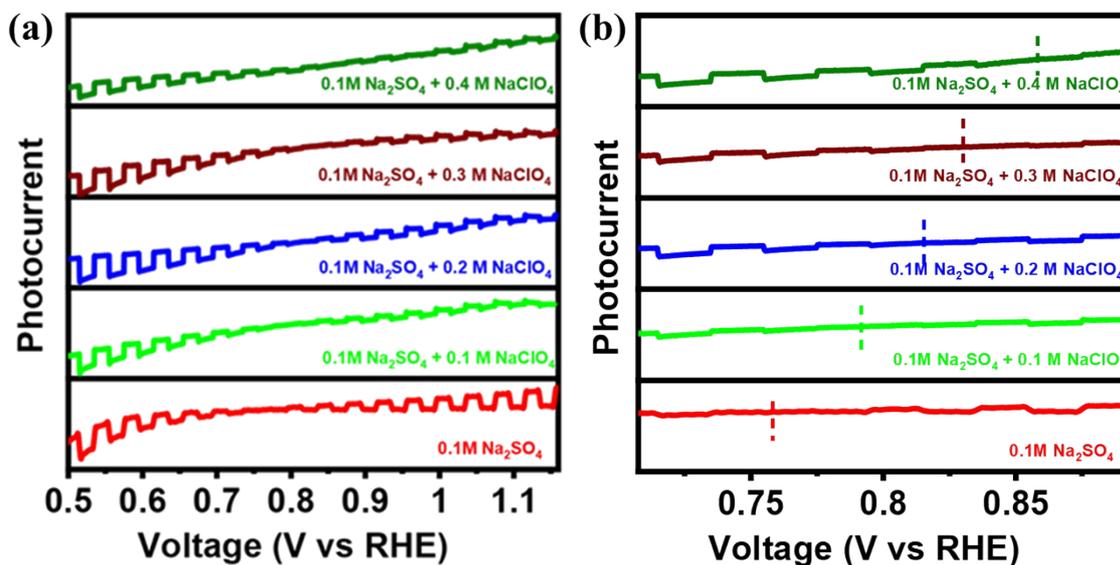


Figure S6: (a) Photocurrent vs voltage curves for BFO photoelectrode in different electrolyte compositions ($\text{Na}_2\text{SO}_4 + \text{NaClO}_4$), (b) enlarged portion of (a) showing the switching potential and shift in onset of photocurrent.

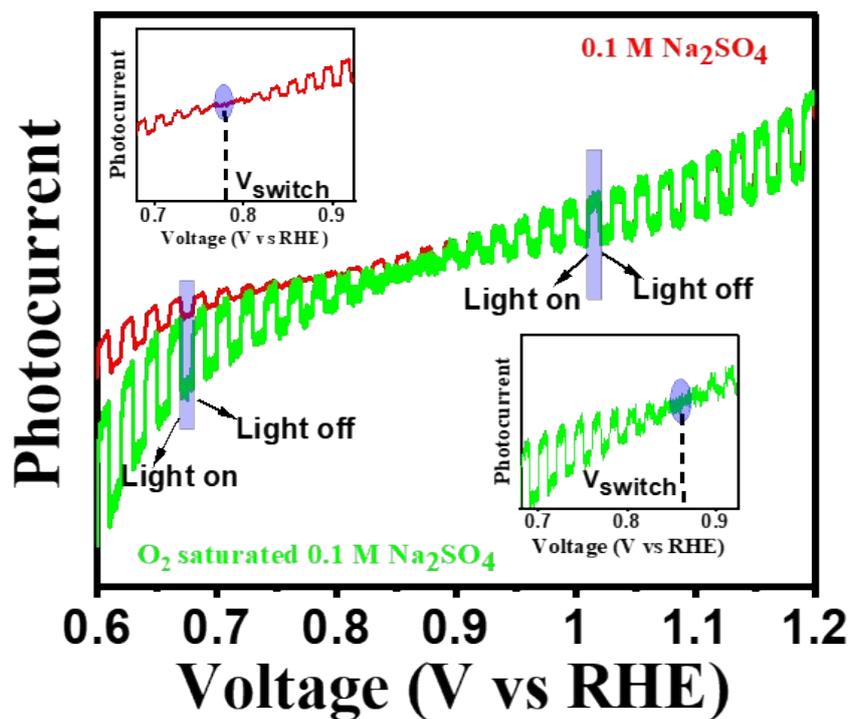


Figure S7. Photocurrent vs Voltage curves for BFO photoelectrode in 0.1 M Na₂SO₄ (red curve) and O₂ saturated 0.1 M Na₂SO₄ (green curve).

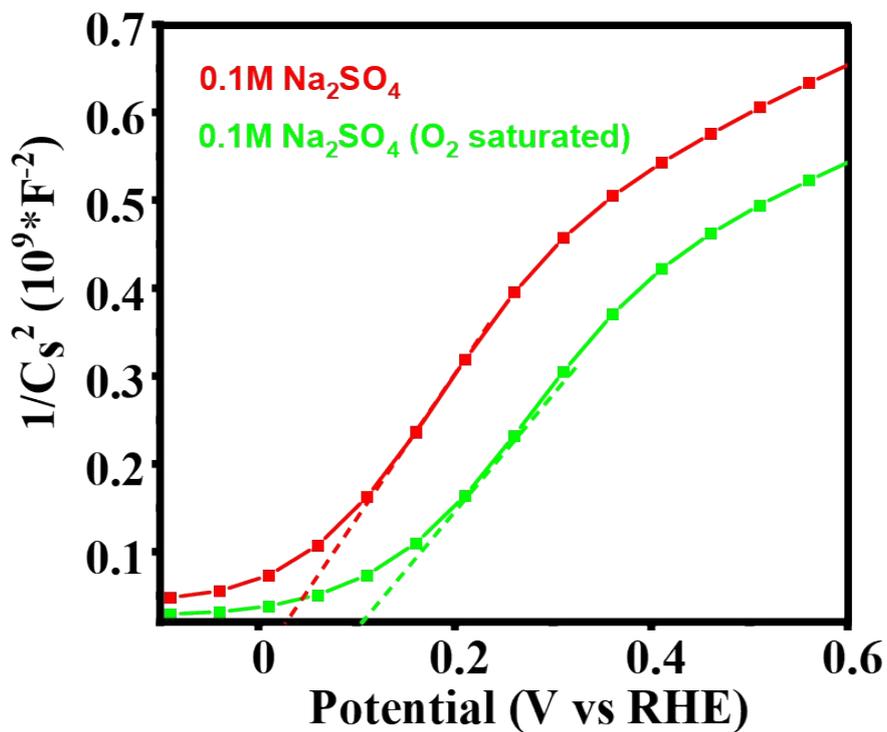


Figure S8 Mott-Schottky plots of BFO electrode in O₂ saturation and depletion conditions.

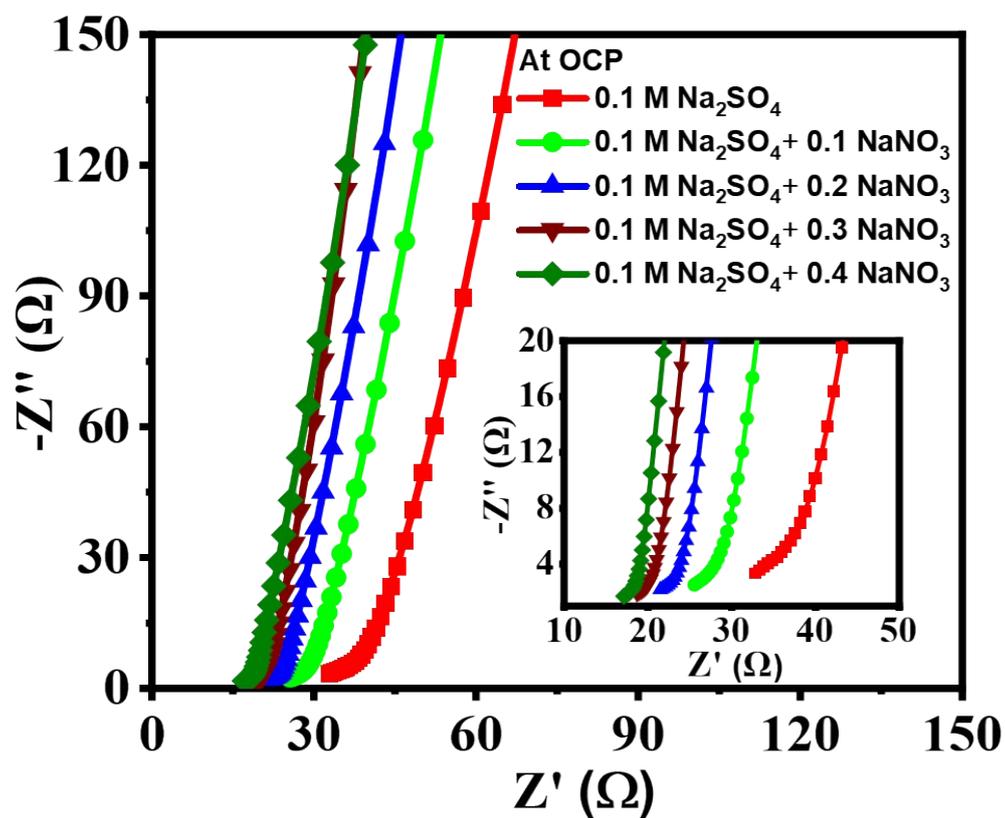


Figure S9 EIS plots at OCP for different electrolyte compositions.

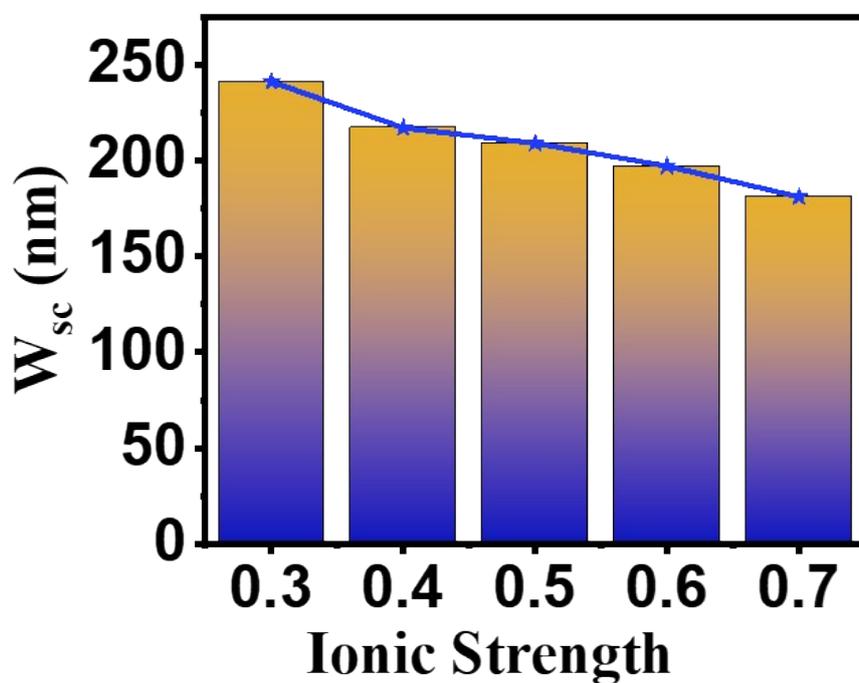


Figure S10 Variation in width of charge space layer as a function of ionic strength.