

Electronic supplementary information

Ion mediated Charge Carrier Transport in a Novel Radiation Sensitive Polyoxometalate-Polymer Hybrid

Abdus Salam Sarkar, Vishwanath Kalyani, Kenneth E. Gonsalves, Chullikkattil P. Pradeep and
Suman Kalyan Pal*

*School of Basic Sciences, Indian Institute of Technology Mandi, Mandi-175001, Himachal
Pradesh, India.*

*Corresponding Author: Tel.: +91 1905 267040; Fax: +91 1905 237924

E-mail: suman@iitmandi.ac.in

Materials and Measurements

Indium tin oxide (ITO) coated glass slides and aluminum (99.999%) were purchased from Sigma-Aldrich, USA. Hybrid polymer (POM-MAPDST) was synthesized and characterized following our previous report.¹ Phosphate buffer solution (PBS) and hydrochloric acid (HCL) were procured from Alfa Aesar, USA and Merck, India, respectively. Before device fabrication, ITO coated glass slides with a sheet resistivity of 8-12 Ω/\square were first patterned via chemical etching and then cleaned through ultra-sonication in DI water, acetone, and isopropyl alcohol. POM-MAPDST hybrid polymer (0.8 wt %) solution in acetonitrile was spin coated on ITO

coated glass substrates with a spinning rate of 5000 rpm for 60 s to achieve a thickness of about 70 nm. Finally, a 100 nm thick aluminum (Al) electrode was deposited via thermal evaporation under the chamber pressure of 1×10^{-6} mbar using a shadow mask. Film thicknesses were measured using NanoMap-LS stylus profilometer (Aep Technology, USA). Temperature dependent current-voltage (I-V) measurements were performed in a laboratory-made variable temperature cryostat using a programmable source meter (Keithley 2400). Electrochemical (LSV and EIS) measurements were performed on an electrochemical workstation (AutolabMetrohm). A conventional three electrode cell was used for all measurements, where POM-MAPDST or MAPDST coated ITO was used as a working, Ag/AgCl as a reference and Pt as a counter electrode. Solution pH was varied by changing the pH of 0.1M phosphate buffer solution with adding the appropriate amount of hydrochloric acid.

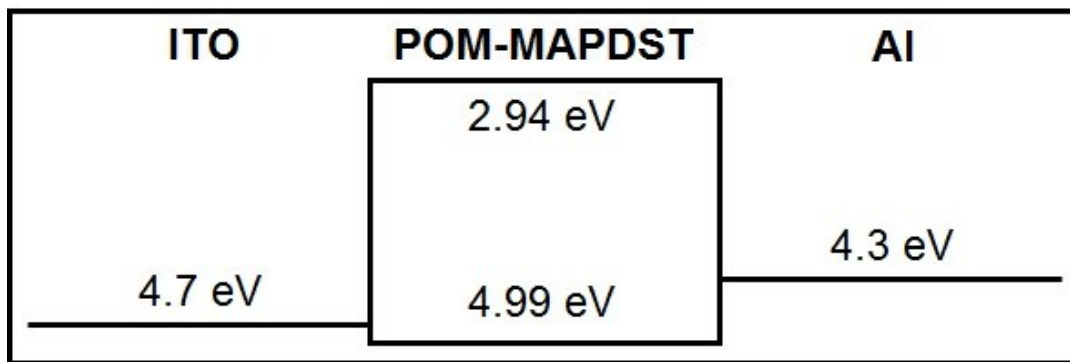


Fig. S1 Energy level alignment of ITO, POM-MAPDST and Al in the fabricated devices.

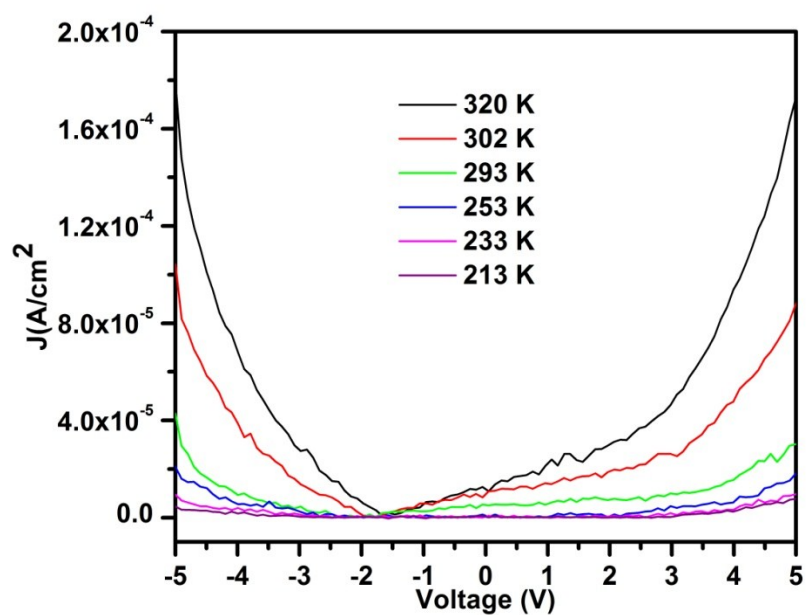


Fig. S2 Symmetric current density-voltage (J-V) characteristic of POM-MAPDST films at different temperatures.

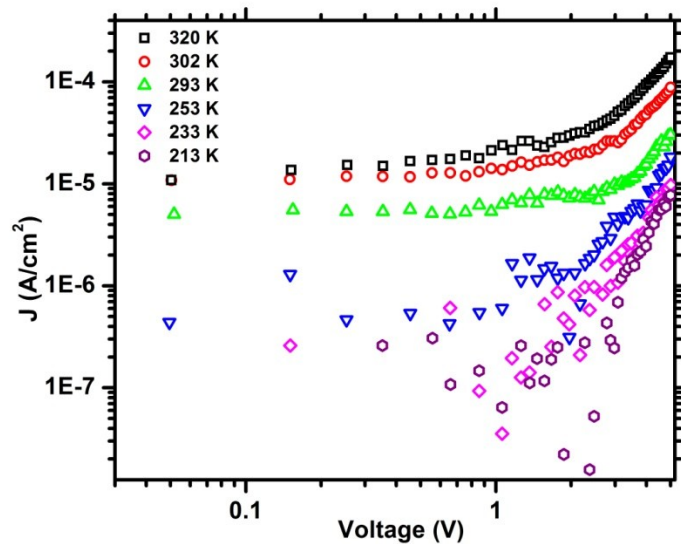


Fig. S3 Current density versus voltage (J-V) plots for POM-polymer hybrid films in log-log scale in the temperature range 302-213 K.

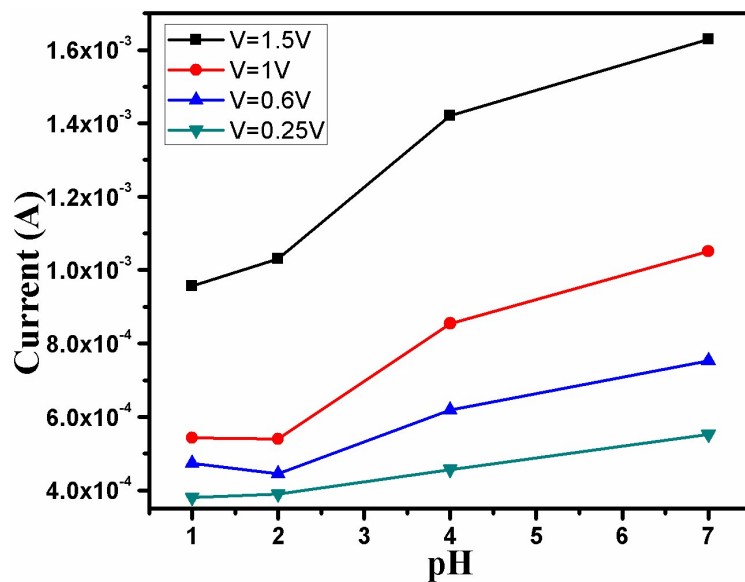


Fig. S4 Variation of current with pH for the POM-MAPDST working electrode at particular voltages.

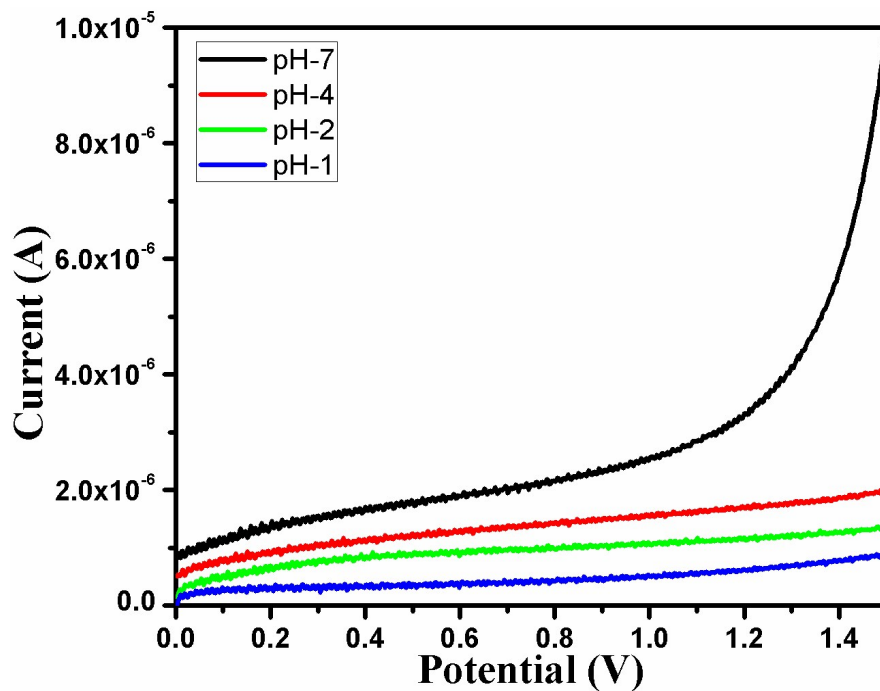
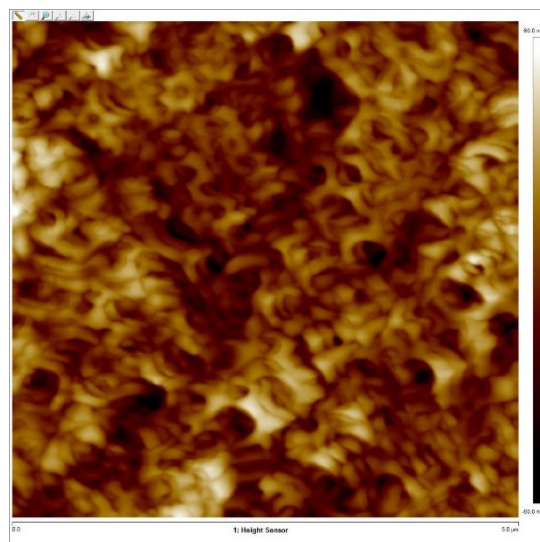
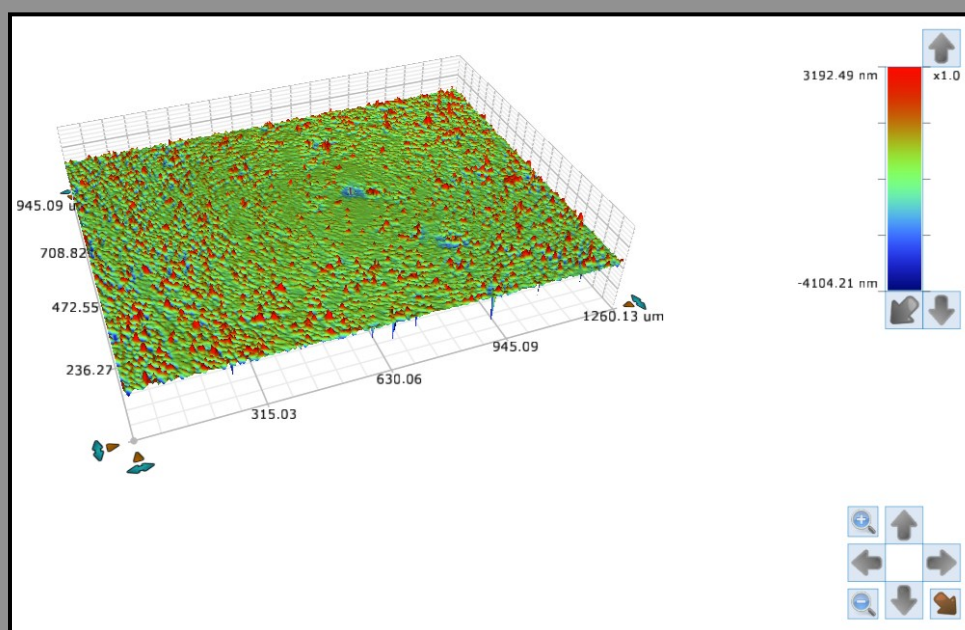


Fig. S5 Linear sweep voltammograms of MAPDST at different pH values.

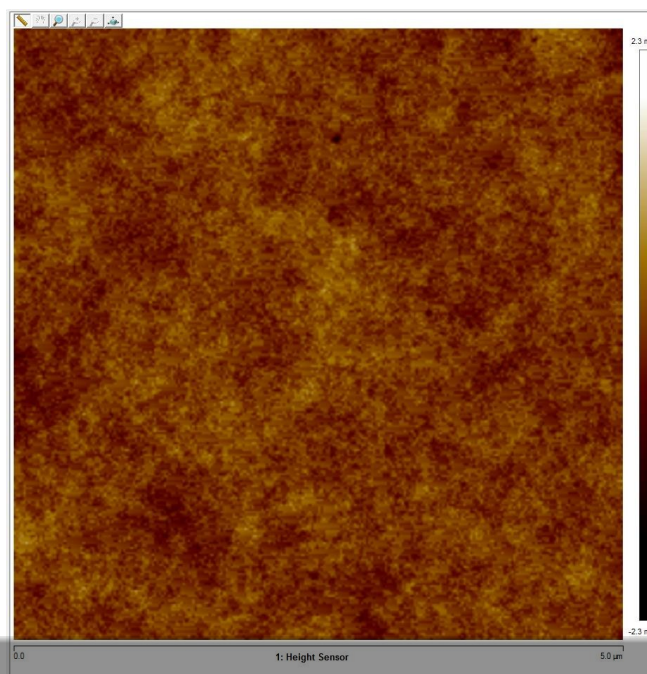


(a)

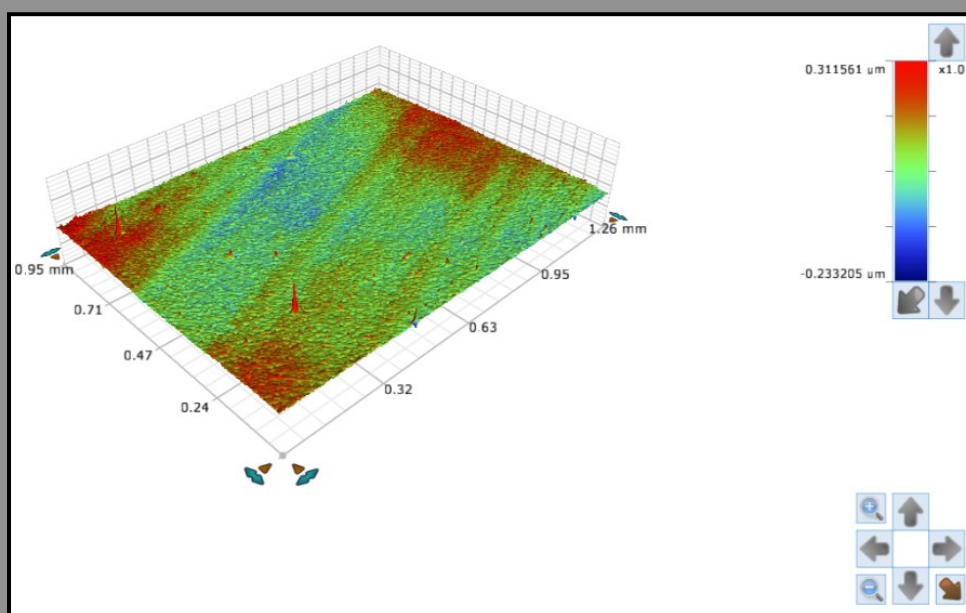


(b)

Fig. S6 (a) AFM and (b) 3D optical images of ITO/POM-MAPDST electrode surface.



(a)



(b)

Fig. S7 (a) AFM and (b) 3D optical images of ITO/MAPDST electrode surface.

Table 1: The parameters obtained from the fitting of impedance spectra using an equivalent circuit

pH value	R_s (Ω)	CPE (F)	R_{ct} ($K\Omega$)	Z_w
7	72.8	23.4	0.729	12.5 mMho
4	74.2	36.5	1.43	1.65 mMho
2	94.9	78.4	7.42	1.10 TMho
1	133	34.7	5.76	428 uMho

- ¹ V. Kalyani, V. Satyanarayana, A. S. Sarkar, A. Kumar, S. K. Pal, S. Ghosh, K. E. Gonsalves, and C. P. Pradeep, RSC Adv. **5**, 36727-36731 (2015).