Electronic Supplementary Material (ESI) for Analytical Methods.

Supplementary data

Monitoring of Drinking Water Quality: A Preliminary Approach by an Electronic Tongue based on Functionalized Polymer Membrane Electrodes

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I. Characterization of HDTC-PVA-PAA and Phosphorylated HDTC-PVA-PAA (P-HDTC-PVA-PAA) polymer membranes

UV-Vis absorption spectroscopy and XRD analysis

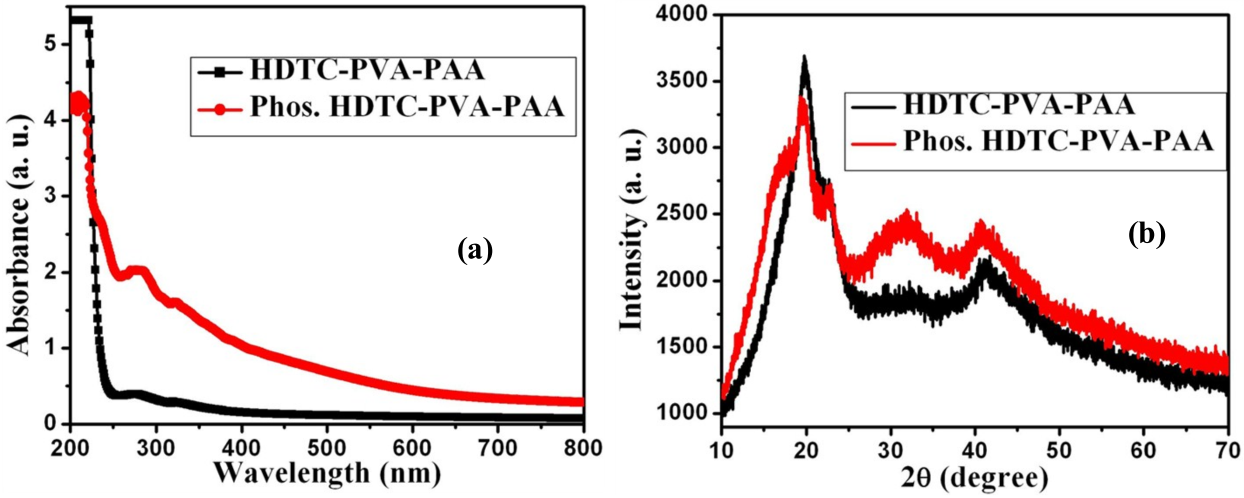

Fig. S1. (a) UV-vis. spectra and (b) X-ray diffractogram of HDTC-PVA-PAA and P-HDTC-PVA-PAA membrane respectively

UV-vis absorption analysis of HDTC-PVA-PAA and P-HDTC-PVA-PAA membranes were recorded on a SHIMADZU 2450 spectrophotometer. Typical absorption spectra of HDTC-PVA-PAA and P-HDTC-PVA-PAA membranes are shown in Fig. S1. (a).

As the spectra show both the membranes have absorption near UV-region which stem from the n to π* transition at ~330 nm for –OH groups and π to π* transition at ~280 nm for –C=O groups.

P-HDTC-PVA-PAA membrane shows higher absorptions due to phosphorylation. X-ray diffraction analyses of HDTC-PVA-PAA and P-HDTC-PVA-PAA membranes were done with PW 1710 X-ray diffractometer with a Cu-target (λ = 1.5418A°) and Ni-filter between 10° and 70° (2θ). X-ray diffractograms of both HDTC-PVA-PAA and P-HDTC-PVA-PAA membranes are shown in Fig. S1. (b).

It is observed that the intensity of the peak at 19.5° (2θ) is decreased after phosphorylation, indicating little decrease in crystallinity of the P-HDTC-PVA-PAA membrane. It is also observed that the intensity of peaks at 31.5° and 41° (2θ) are increased for P-HDTC-PVA-PAA membrane. This may be due to the increase in crystallite size of the material by the formation of phosphate diester after phosphorylation.

FT-IR spectroscopic analysis

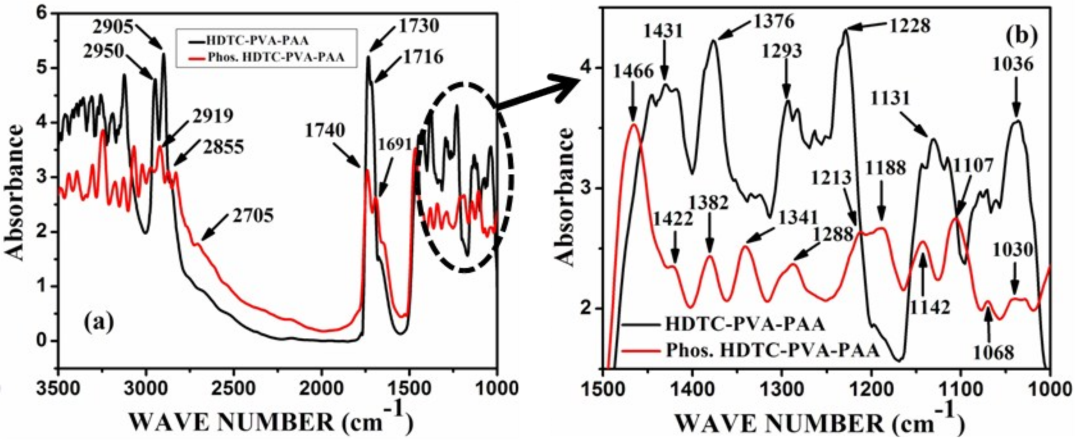

Fig. S2. FTIR spectra of HDTC-PVA-PAA and P-HDTC-PVA-PAA membrane, (a) 3500-1000 and (b) 1500-1000 cm^{-1}

For structural analysis, FT-IR study of HDTC-PVA-PAA and P-HDTC-PVA-PAA membranes were done to study the nature of chemical bonds present in both the membranes using Thermo Nicolet, NEXUS 870 FT-IR spectrophotometer. The spectra were recorded in absorption mode.

The spectra of HDTC-PVA-PAA and P-HDTC-PVA-PAA membranes are shown in Fig. S2. (a) and Fig. S2. (b). Assignments to FT-IR peaks of both the membranes are shown in Table S1 below.

Table S1. FTIR peak assignments for HDTC-PVA-PAA and P-HDTC-PVA-PAA membranes

S. No.	**HDTC-PVA-PAA (cm^{-1})**	**P-HDTC-PVA-PAA (cm^{-1})**	**Peak assignments**
1	2905, 2950	2855, 2919	Two types of –C-H asymmetric stretching vibrations are found due to the presence of $–CH_2$- and –CH (OH or COOH)- groups
2	-	2705	–O-H stretching of >P (=O)OH
3	1730	1740	>C=O stretching of –COOH and –COO- (ester functional group)
4	1716	1691	Methylene overtone or combination band
5	-	1466	P-O stretching of phosphate diester moiety
6	1431	1422	O-H bending vibrations of –COOH group
7	1376	1382	Bending vibration of $–CH_2$ moiety
8	1335	1341	Aliphatic O-H bending vibration
9	1293	1288	C-O asymmetric stretching of –C (=O)-O- moiety
10	1228	1213	CH_2 rocking vibration
11	-	1188	P=O stretching of phosphate diester moiety
12	1140	1142	C-O coupled vibration of –O-C (=O)-CH< (ester group) and $–CH_2$-HC-O- moieties
13	1131	1107	Out of plane bending vibration of –O-H bond of $–CH_2$-OH moiety
14	-	1068	P-OR (ester) stretching vibration
15	1036	1030	Coupled C-O stretching and O-H in-plane bending vibrations

II. Characterization of EVOH and P-C-EVOH polymer membranes

XRD analysis

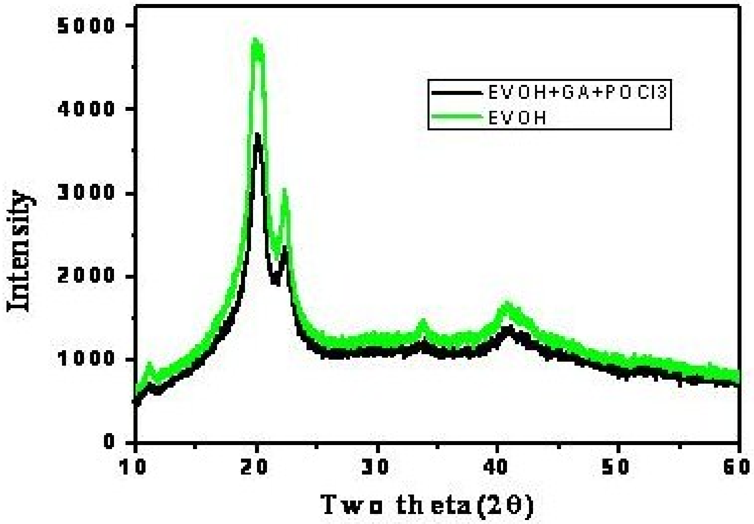

Fig. S3. XRD spectrum of EVOH and P-C-EVOH membranes

X-ray diffractograms of EVOH and P-C-EVOH (denoted as EVOH+GA+POCl3) are shown in Fig. S3. It is observed that the intensity of the peak at 19.5° (2θ) in EVOH is increased after cross-linking (with GA) and functionalization (using $POCl_3$) indicating better symmetrical orientation of the polymer chain leading to more crystalline state.

III. Characterization of PVA and P-C-PVA polymer membranes

FT-IR spectroscopic analysis

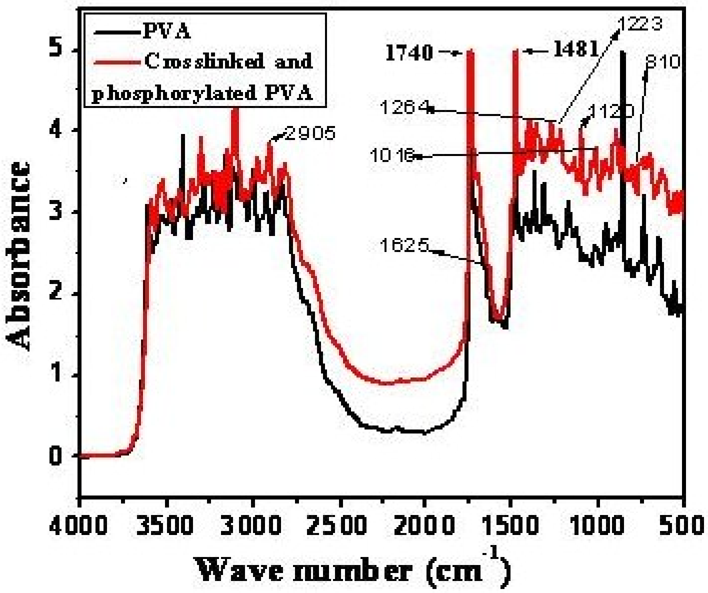

Fig. S4. FTIR spectra of PVA and P-C-PVA membrane

Fig. S4 shows the FTIR-spectrum taken in the frequency range of 4000–500 cm^{-1}. Absorption peaks at 1740 cm^{-1} for C=O stretching and at 1481 cm^{-1} are found due to P-O stretching of phosphate diester moiety in the phosphorylated and crosslinked PVA membrane which confirms the formation of phosphate diester group in between the poly (vinyl alcohol) chains.

XRD analysis

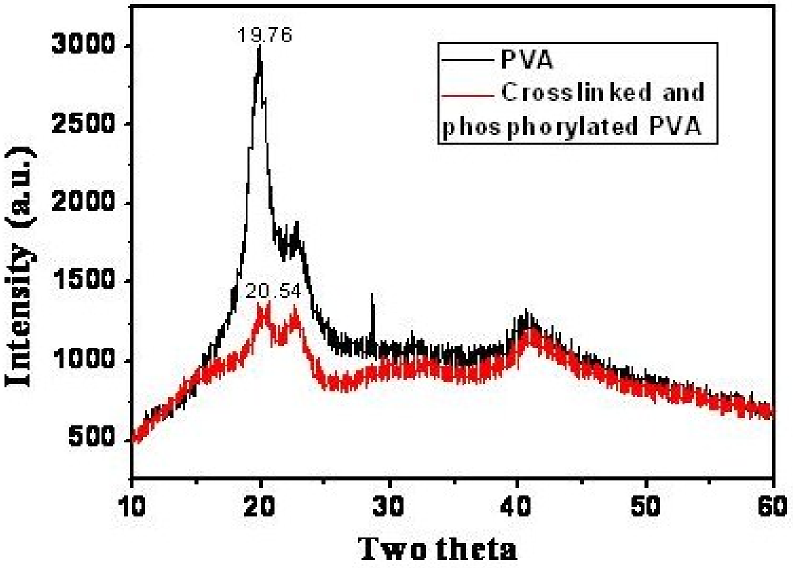

Fig. S5. XRD spectra of PVA and phosphorylated and crosslinked PVA (P-C-PVA) membrane

X-ray diffractograms of PVA and P-C-PVA (denoted as PVA+GA+$POCl_3$) are shown in Fig. S5. It is observed that the intensity of the peak at 20◦ (2θ) in EVOH is increased after cross-linking (with GA) and functionalization (using $POCl_3$) indicating better symmetrical orientation of the polymer chain leading to more crystalline state.

IV. Long-term stabilities of developed polymer membrane electrodes towards DW

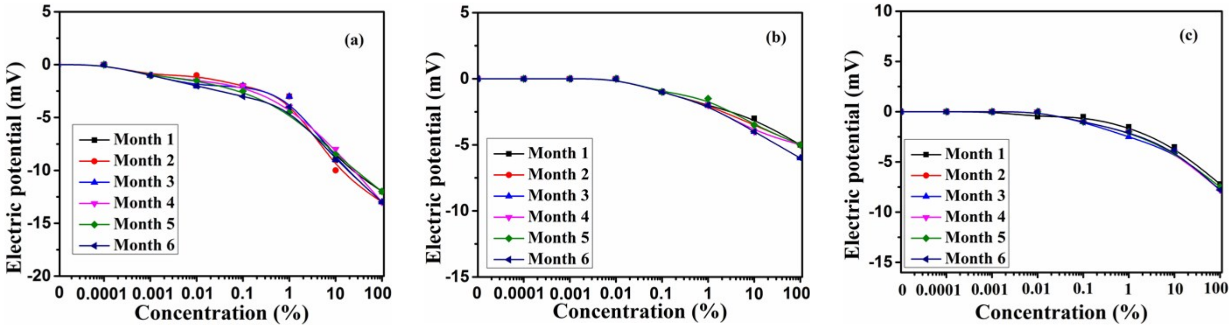

Fig. S6. Long-term stabilities of response potentials of (a) P-HDTC-PVA-PAA, (b) P-C-EVOH and (c) P-C-PVA polymer membrane electrodes towards Bislery solution