Prussian blue-based inorganic flexible electrochromism glucose sensor

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Abstract
Flexible inorganic Prussian blue (PB) containing electrode has been synthesised using a simple electrodeposition technique for dual functions in electronics (electrochromism) and biology (glucose sensing) applications. Structural and spectroscopic characterisations of the fabricated film have been done using electron microscopy and Raman spectroscopy. Flexible inorganic electrochromic device is one of its kind having promising features with colour contrast (50%), coloration efficiency (80 cm²/C) and robust stability for more than 400 s. The prototype device contains only PB electrode as active electrochromic material with gel electrolyte in a pre-designed device geometry that exhibits two primary colours, blue and green, with little amount of bias switching. Reversible redox processes have been found to be responsible for the electrochromism in PB containing flexible device. The same has been experimentally verified using spectroscopic and electrochemical techniques during device’s operation. Its additional use for glucose sensing purpose can be exploited for wearable electronics application. It is a first fully developed inorganic flexible device with superior electrochromic performance.

1 | INTRODUCTION
In this snowballed technological era, flexible electronics is an emerging class of nanotechnology that empower a wide range of applications such as bendable cell phone, flexible displays, wearable patches, sensor, electronic skin, e-paper etc. [1–3]. Flexible electrochromic devices are of utmost importance among flexible electronics due to their multifunctional applications in solar cell, resistive memory devices, energy storage device and glucose sensing while simultaneously functioning as an electrochromic device [4–9]. Electrochromic devices are known for reversibly changing their optical properties (reflectance/transmission/absorbance) under external applied bias and the materials exhibiting such properties are termed as electrochromic materials [10–13]. In addition to the multi-functional property, flexible electrochromic devices have an additional feature of deformation making them potentially useful in curved windows, military camouflage, etc [14–16].

Organic and inorganic materials are two major classes of materials spanning the world of electrochromism [12,17–21]. In recent years, many other compounds, for example, coordination [22], metallo-supramolecular [23,24], organometallic [25] etc. have also been used for electrochromic applications. Though the origin of electrochromism lies with the development of inorganic material, tungsten oxide (WO3), its application in electrochromism is limited due to complex processes involved [26,27]. On the other edge, organic materials have advantages of easy processability and low degradation, and thus have stronger footprints in the world of electrochromism. It would be of great interest to design flexible electrochromic devices incorporating inorganic materials while addressing the other issues related to inorganic materials. Prussian blue (PB) is

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one of the well-known inorganic materials known for its electrochromic performance since 1978 \cite{28}. It has been extensively useful in other applications of energy storage, sensors, hydrogen storage, fuel cells etc. including electrochromism as well \cite{29–32}. It is a coordinated 3D network of carbon, iron and nitrogen assembled in a cubic structure with lattice constant of 1.02 nm \cite{33}. It is blue in colour and changes its colour from blue to green (Prussian green, PG) on oxidation (positive bias) and to white (Prussian white, PW) on reduction (negative bias) \cite{34}. It has not been discussed largely for electrochromic properties due its other interesting applications as well \cite{35–37}.

However, the development of flexible inorganic electrochromic devices is restricted due to tedious fabrication processes and techniques involved in making inorganic electrochromic materials. Traditional high cost instruments including sputtering, physical-chemical vapour deposition methods are conventionally being used for making them \cite{1}. There is a growing need to develop inorganic materials using an easy and economic fabrication method in terms of technological and application-oriented perspective. Here, Prussian blue film on flexible indium doped tin oxide (ITO) coated polyethylene terephthalate (PET) substrates has been synthesised by a simple galvanostatic method. Flexible PB electrodes fabricated using simple electrodeposition method display outstanding electrochromic features with very good colour contrast, switching speed and power efficient performance which makes it superior in the field of known flexible electrochromic devices. It also makes the one of its kind of all inorganic flexible electrochromic devices possessing enhanced performance. The device has capability to switch between blue and green coloured states with bias triggering at $-1.5 \text{V}$ and $2.5 \text{V}$, respectively. The device does not contain any counter electrode to support its redox reaction and is entirely self-dependent and dependent on the electrolyte as well. The flexible PB electrode has also been used explored for glucose sensing and have been discussed individually as follows.

The fabricated PB films are characterised by once their compositional and structural properties are determined using Raman spectroscopy and SEM before exploring their applications. The Raman spectrum (Figure 1(a)) shows signature peaks (marked with *) at 274, 540, 2092 and 2154 cm$^{-1}$ \cite{46–50}. The typical morphology of the fabricated PB films has been characterised using SEM (Figure 1(b)), which clearly shows that film is deposited all over the electrode's surface. After establishing the composition of the fabricated film, electrochemical performance of the PB film is measured using cyclic voltammetry (CV) and has been studied and discussed in SI (Figure S1). Different fabricated PB electrodes have been used for dual application in flexible electrochromic device and glucose sensing and have been discussed individually as follows.

First, a flexible electrochromic device using PB as active material has been fabricated by following the recipe, along with representation of various steps involved (Figure S2), given in the SI. To observe various colour changes in the device, it has been appropriately connected to a power supply and variation in its optical states as a function of applied bias has been examined.

The as-fabricated inorganic flexible device has been tested for its electrochromic performance by connecting the active PB electrode (other electrode) with the positive (negative) terminal of the power supply (Figure 2). Initially when the device is unhooked from the power supply, that is, at $0 \text{V}$, it appears blue to the naked eyes as shown in Figure 2(a) due to the natural appearance of as fabricated PB film. As soon as a voltage of $2.5 \text{V}$ is applied to the device, as per the polarity arrangement shown in Figure 2(b), its appearance is changed from blue (Figure 2(a)) to green (Figure 2(b)), say ON state. This is likely due to the process of electrochemically initiated doping (dynamic doping \cite{38,51}) in PB, leading to variation in its optical property to transform to Prussian green (PG). Furthermore, with a bias of $-1.5 \text{V}$ to the device, keeping the bias polarity intact (Figure 2(c)), the device regains its original appearance of blue colour (OFF state) as shown in Figure 2(c). The reversible bias induced electrochromic behaviour possessed by PB (Figure 2) is the key reason of regaining back initial blue colour state by the device \cite{34,52}. The observed colour change by the flexible device can be easily understood from the following reaction \cite{33}

\[
\text{PB} \leftrightarrow \text{PG} + e^- ,
\]
From the above equation, one can appreciate the reversible electrochromic nature of PB by switching between PG and PB upon oxidation and reduction, respectively. This PB-based flexible inorganic electrochromic device switches between two primary colours, blue and green, with a very less applied bias signalling towards a better performing electrochromic device in kingdom of known flexible electrochromic devices. A comparison of this work with various known flexible electrochromic devices is given in Table S1 in the SI. Quantification of colour obtained from the device has been done experimentally, using in-situ UV-Vis spectroscopy, as discussed here.

To appreciate various colour appearances of the device under different bias conditions, in-situ bias dependent UV-Vis spectra of the device is considered (Figure 3(a)). Initially, in unbiased state, there is absorbance dip near 450 nm wavelength region corresponding to blue appearance of the device (dark blue curve, Figure 3(a)). With a bias of 2.5 V to the device (ON state), as per polarity arrangement depicted in Figure 2(b), absorbance spectra of the device changed as observed from the green curve in Figure 3(a). In this curve, there is minimum absorbance near 500 nm implying a maximum transmission of green colour wavelength and thus the device appeared green to the naked eyes. Furthermore, a bias of −1.5 V to the device makes it to regain its original appearance (OFF state) of blue colour by retracing the initial dark blue curve (blue curve, Figure 3(a)). The device shows a maximum colour contrast [53] of 50% at 450 nm between ON and OFF states. To verify the colour perceived from the device with the International standards of colour, CIE (Commission Internationale de l’Eclairage International Commission on Illumination) format 1976 has been given in Figure 3(b). It illustrates the actual photograph of the device in different states, ON and OFF, along with their (U′, V′) coordinates [54]. The CIE colour calculator has been used here to calculate CIE coordinates corresponding to different states of the device, that is, ON and OFF states of green and blue colour, respectively. Ability to switch using a small bias is not sufficient to assess the better electrochromic performance of the device. Therefore, various other performance parameters of the flexible electrochromic device have been measured to illustrate its better performance.

To investigate the spectro-electrochemical performance of the device at 450 nm wavelength, a potential square pulse switching between 2.5 V and −1.5 V with 3 s time interval has been applied to the device. Figure 4(a) shows switching of the device for longer than 390 s time interval with a very less change in absorbance of the device even after 350 s. Clear absorption switching between distinct coloured states of the device has been obtained with each bias switching for long duration of time (390 s), which indeed is a sign of better performance of inorganic flexible electrochromic device. One absorption switching cycle has been plotted (Figure 4(b)) to estimate time required by the device to switch between ON and OFF states. The device took 2.1 s to switch from its OFF (blue colour) state to ON (green colour) state at 2.5 V. On the bias reversal, it takes 2.4 s to revert back to its OFF state of original blue colour at −1.5 V such that there is 90% absorbance change in both conditions. The charge density of the device as a function of applied potential square wave has been estimated by measuring the amount of current flow through the device when the applied bias pulse is switched (Figure 4(c)). Colouration efficiency of the device [16], an essential parameter to rationalise the performance of electrochromic devices, is given by Equation (2).
where $\Delta OD = A_n - A_f$, with $A_n$ and $A_f$ are the values of absorbance in ON and OFF states, respectively, of the device and can be obtained from the UV-Vis spectra (Figure 4(b)), whereas ‘$Q$’ is the charge density. The obtained efficiency of $\sim 87 \text{cm}^2/\text{C}$ in this case (Figure 4(d)) from an inorganic yet flexible electrochromic device deposited using a simple electrodeposition method looks very promising because inorganic materials need tedious device fabrication method (Table S1) and still remain non suitable for flexible device applications. Apart from electronics, this flexible PB electrode has been further utilised for application in another area, biology, as glucose sensor. Glucose sensing is another additional biological application of this flexible PB inorganic electrode, and details are described below:

For carrying out CV analysis of the flexible PB electrode in a three cell electrochemical setup, the following were used: Ag/AgCl as the reference, platinum wire as the counter and active flexible PB as the working electrode with 1M aqueous KCl electrolyte [47]. In Figure 5(a), the CV curves have been recorded from the PB electrode by sweeping with different scan rates between 1 and 5mV/s. Arrow (Figure 5(a)) indicates the direction of scan. Its glucose sensing capabilities can be determined by looking at the dependence of CV curves after the addition of glucose solution to the electrolyte as shown in Figure 5(b). Pink curve in Figure 5(b) shows the electrochemical property of pristine PB electrode in the described three electrode electrochemical setup. With successive addition of glucose with varying concentration from 0.5 to 3.5mM, variation in the value of the current is clearly observed (Figure 5(b)). Figure 5 clearly shows that the flexible PB electrode is sensitive to addition of glucose by means of limiting the amount of current that flows through the electrode in an electrochemical cell. This confirms the use of flexible PB electrode for glucose sensing application as well. In summary, the fabricated flexible inorganic PB electrode has dual application properties namely, serving as an electrochromic device and the glucose sensing ability, thus making a significant impact in the area of flexible electronics.

**Figure 3** (a) In-situ UV-Vis absorbance spectra and (b) CIE diagram of the device under different bias conditions.

**Figure 4** Cyclic switching of the device to show its stability over the time (a) and zoomed portion of one cycle to estimate switching time of the device (b). Current flow through the device as a function of switching bias (c) and plot of change in optical density as a function of charge density for calculating colouration efficiency (d).
4 | CONCLUSIONS

A PB-based inorganic electrode, deposited on flexible substrates using a simple galvanostatic electrodeposition approach, shows dual application in electrochromism and glucose sensing. Two distinct primary colours, blue and green, were obtained from the flexible electrochromic device, designed in a modest way, with applied bias switching between −1.5 and 2.5 V, respectively. Excellent electrochromic feature with 50% colour contrast, nearly 87 cm²/C coloration efficiency and stability in absorbance switching cycles for nearly 390 s was acquired from the device. All these outstanding features and fast switching speed of the order of 2 s make this device stand apart in the realm of flexible electrochromic devices using an inorganic material. Electrochemical and spectroelectrochemical experiments reveal the fundamental processes responsible for displaying distinct colours, which is the redox switching from the flexible device. Moreover, flexible PB electrode is also useful for the glucose sensing purpose. The flexible inorganic electrode fabricated in a lucid manner is distinctive in the sphere of known flexible electrochromic devices that were typically fabricated with organic materials, addressing the drawback while delivering excellent performance, and also show biological importance when used for glucose sensing applications.

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