

# Calcium Ion-Sensor Based on Polyindole-Camphorsulfonic Acid Composite

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**ABSTRACT:** We hereby report a new conducting polymer-based calcium ion exchanger, namely polyindole-camphorsulfonic acid (PIn-CSA) composite, and its application in the development of calcium ion-selective electrode. The processable PIn-CSA composite is developed by homogenizing equimolar ratio of chemically synthesized PIn and CSA in tetrahydrofuran. The homogenized PIn-CSA composite is cast over the Pt disc electrode under ambient conditions. The ion-sensor exhibits near Nernstian response

for  $\text{Ca}^{2+}$  over a concentration range of  $2 \times 10^{-5}$  to  $1 \times 10^{-2}$  M with a response time of 8 s. The sensor can be used for a period of over 3 months without any major drift in its baseline potential. The useful pH range of the ion-sensor was found out to be 4.0–8.0. © 2012 Wiley Periodicals, Inc. *J Appl Polym Sci* 125: 2993–2999, 2012

**Key words:** composites; conducting polymers; ion exchangers; selectivity; sensor

## INTRODUCTION

The design of chemical sensors for selective detection of a specific analyte is a topic of considerable interest, due to their wide ranging application in the broad areas of chemistry and biology.<sup>1–6</sup> Selective determination of biologically important cations such as  $\text{Na}^+$ ,  $\text{K}^+$ ,  $\text{Mg}^{2+}$ , and  $\text{Ca}^{2+}$  is of prime significance. Among these, the detection of  $\text{Ca}^{2+}$  is important because it plays vital role in processes related to human biochemistry, such as in the cell shrinkage and shape formation,<sup>7,8</sup> synthesis and release of neurotransmitter,<sup>9</sup> nucleic acid metabolize,<sup>10</sup> and so on. Many physiological processes are triggered, regulated, or influenced by calcium ion.<sup>11,12</sup> Because of the importance of ionic calcium in biological processes; chemists have been interested in the design of chemical sensors for the specific detection of calcium ions. Standard methods for calcium determination are based on complexometric titrations<sup>13</sup> and other analytical techniques such as atomic absorption spectrometry. In contrast to these instrumental analytical techniques, which measure the total calcium concentration, ion-selective electrodes deter-

mine the activity of the biologically active calcium in ionic form i.e.,  $\text{Ca}^{2+}$ .

There has been considerable interest in the use of ion-selective sensors<sup>14–16</sup> for various purposes and particularly in the environmental, biological, and clinical areas. Accordingly, extensive studies have been made on the development of ion-selective electrodes (ISEs) based on unblocked (with conventional double barrel configuration) and blocked (coated wire electrode, CWE) interfaces. However, there are several known limitations associated with conventional ion-selective electrodes or ion-sensors. These drawbacks were minimized by using electroactive conducting polymers along with ion-sensing material preferably within plasticized PVC matrix or sol-gel protective membrane.<sup>17–23</sup> Conducting polymers are restricted for various applications due to their insolubility in most of the solvents, brittle nature of films and limitations of their electrochemical syntheses.<sup>24,25</sup>

Recently, conducting polymer composites have shown potential to overcome the problem of poor processability, stability, and mechanical properties of the conducting polymers.<sup>26</sup> However, most of the composites are limited to chemical synthesis or solution mixing routes only. Earlier we have reported electrochemical polymerization of indole and its derivatives in nonaqueous medium with excellent electrochemistry of polymer films.<sup>27–29</sup> More recently, the chemical synthesis of polyindole (PIn) is reported<sup>30</sup> and now composites of this polymer are also subject of intensive studies. We report here a

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new composite of PIn with camphorsulfonic acid (CSA) synthesized following chemical route and its application in the construction of calcium ion sensor without the use of any calcium selective chemical/ionophore/ion carrier. This configuration showed advantage over similar sensors reported earlier based on the use of conducting polymer composites or a single conducting polymer sensing layer, which is directly in contact with transducer. The new calcium ion sensor shows improved selectivity in the presence of a number of interfering ions which has been one of the important requirements of such sensor for practical applications.<sup>31</sup>

## EXPERIMENTAL

### Materials

Indole, ammonium peroxodisulfate, and  $\text{CaCl}_2 \cdot 2\text{H}_2\text{O}$  were obtained from Merck, India. CSA was obtained from HiMedia, India. All other chemicals used were of analytical grade. The aqueous solutions were made in double distilled water. All the experiments were performed at room temperature.

### Synthesis and characterization of PIn-CSA composite

PIn was prepared by the oxidative polymerization of indole using ammonium peroxodisulfate as described earlier.<sup>30</sup> The composite of PIn was made with CSA. Dried PIn was mixed with CSA in a mortar pestle in varying molar ratios of the two components. The molar ratio of PIn and CSA was varied from 3 : 1, 2 : 1, 1 : 1, 1 : 2 to 1 : 3. The PIn-CSA was dissolved by drop wise addition of THF resulting into a dark brown colored solution. The solution obtained by dissolving 6 mg PIn and 12 mg CSA in 1 mL THF was found to be optimum concentration for making the composite.

The UV-vis spectra of chemically synthesized PIn and that of the composite were recorded by dissolving them in dimethyl sulfoxide (DMSO) and tetrahydrofuran (THF), respectively using a Systronics UV-vis double beam spectrophotometer 2201. The scanning electron microscopy along with EDX analysis was carried out using FEI Quanta 200F scanning electron microscope.

### Construction of calcium ion sensor

Calcium ion sensor was constructed by casting 2  $\mu\text{L}$  solution of PIn-CSA in THF having optimum concentrations of PIn and CSA over Pt disc electrode (2 mm diameter). The solvent was allowed to evaporate for 12 h before being conditioned in 0.1M calcium chloride solution for 12 h. When not in use,

the modified electrodes were stored in a 0.001M calcium chloride solution at 25°C.

### Electrochemical measurements

Electrochemical experiments were performed on an Electrochemical Workstation Model CHI660B, CH Instruments, TX. Cyclic voltammetry was performed in an electrochemical cell containing 3 mL, 0.5M sulfuric acid equipped with PIn-CSA composite-modified Pt disc electrodes (2 mm diameter) as working electrode, an Ag/AgCl electrode (Orion, Beverly, MA) reference electrode and a platinum plate counter electrode.

The potentiometric experiments were performed in an electrochemical cell containing 3 mL, 0.01M Tris-HCl buffer solution pH 7.0 employing PIn-CSA composite-modified Pt disc electrode as working electrode and a double-junction Ag/AgCl reference electrode (Orion) containing 0.01M Tris-HCl buffer pH 7.0 in second junction, under stirred conditions. The measurements for different ions were carried out by stepwise addition of appropriate amount of standard solutions keeping the ionic strength and the pH constant. At base line potential, varying concentrations of different cations were added followed by measurement of steady-state potential.

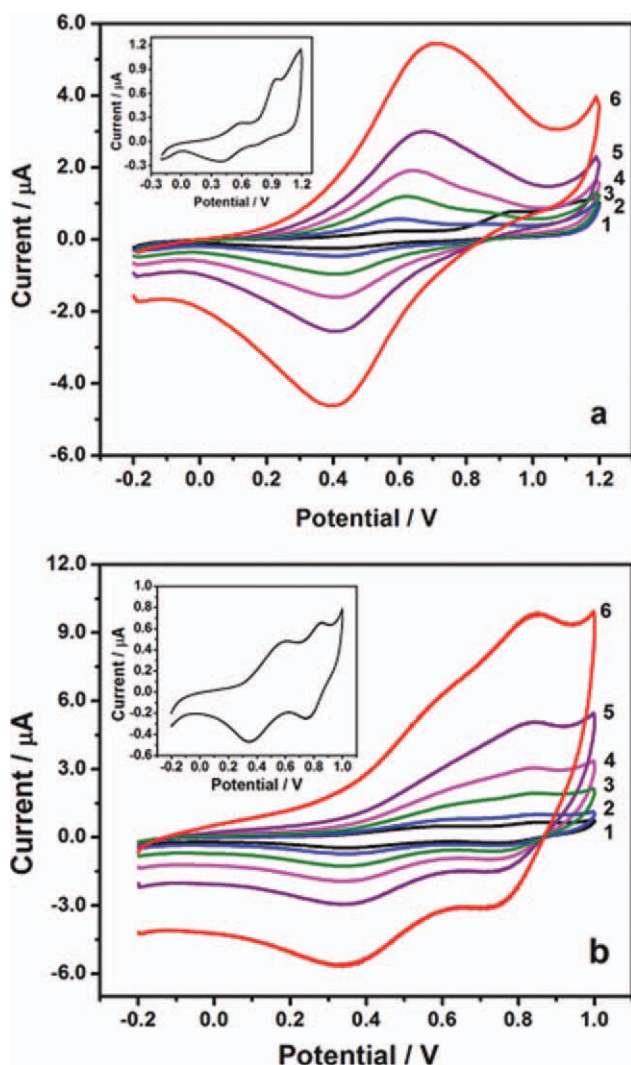
## RESULTS AND DISCUSSION

### Processable composite of PIn-CSA

For electrode modification it is a prerequisite that the chemical modifier can be tailored according to desired electrode shape. Chemically or electrochemically synthesized PIn does not dissolve in conventional solvents. So, it is difficult to process the same for sensor fabrication. To achieve this goal, a composite of PIn and CSA was prepared in varying proportions of the two components as mentioned in Experimental section. The optimization of the proportion of PIn and CSA in the composite for fabrication of ion-sensor was performed based on the potentiometric response of various compositions of the composite toward calcium ion. The composition containing PIn and CSA in equimolar ratio was found to be most suitable for preparation of modified electrodes.

### Cyclic voltammetry of PIn-CSA modified electrode

Cyclic voltammograms for chemically synthesized PIn and that of PIn-CSA were recorded in 0.5M  $\text{H}_2\text{SO}_4$  by modifying Pt disc electrode at various scan rates viz. 0.01, 0.02, 0.05, 0.10, 0.20, and 0.50  $\text{Vs}^{-1}$  as shown in Figure 1. In both the cases, the inset shows the voltammogram obtained at 0.01

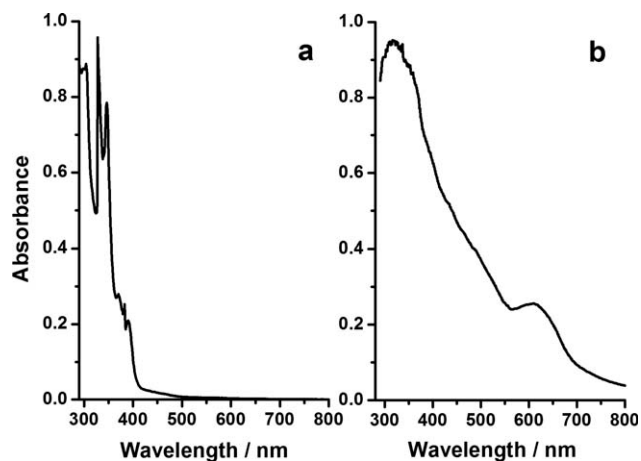


**Figure 1** Cyclic voltammograms of (a) PIn and (b) PIn-CSA in 0.5M H<sub>2</sub>SO<sub>4</sub> at different scan rates viz. 0.01, 0.02, 0.05, 0.10, 0.20, and 0.50 Vs<sup>-1</sup> (curves from lower to higher scan rates). [Color figure can be viewed in the online issue, which is available at [wileyonlinelibrary.com](http://wileyonlinelibrary.com).]

Vs<sup>-1</sup>. PIn showed anodic peaks (E<sub>pa</sub>) at 0.60 and 0.90 V, and cathodic peaks (E<sub>pc</sub>) at 0.41 and 0.77 V corresponding to change in the state of polymer. In PIn-CSA, again there are two redox couples with anodic peaks (E<sub>pa</sub>) at 0.58 and 0.84 V and cathodic peaks (E<sub>pc</sub>) at 0.34 and 0.74 V. But in this case there is a minor shift in the E<sub>pa</sub> and E<sub>pc</sub> values to the lower side. This indicates the formation of an electroactive composite of PIn with CSA. Also, it is quite clear that in PIn-CSA, the two redox couples can easily be distinguished even at higher scan rate.

#### UV-vis studies

Figure 2 shows the UV-vis spectra of PIn and PIn-CSA. Characteristic peaks of PIn are observed at 320, 367, and 398 nm. The spectrum of the composite is

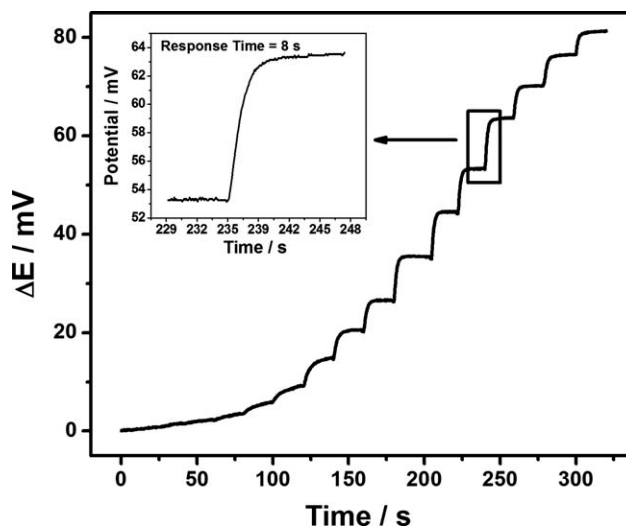


**Figure 2** UV-vis spectra of (a) PIn and (b) PIn-CSA.

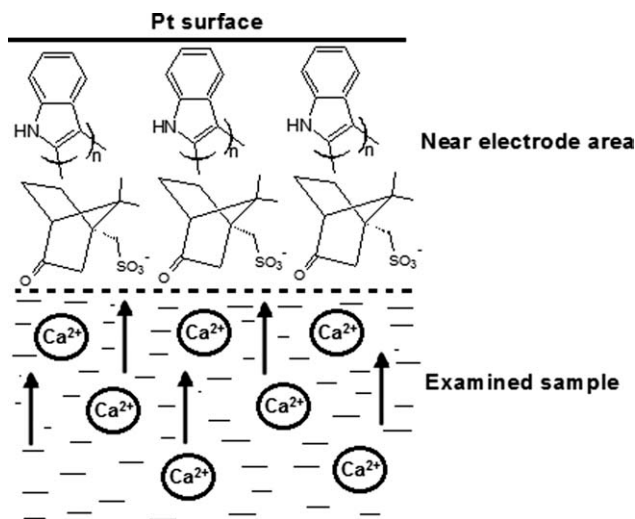
similar to that of PIn. However, a broad hump was observed at higher wavelength due to interaction of CSA with polymer chains.

#### Ion sensing behavior of PIn-CSA modified electrode

Figure 3 shows the typical potentiometric response of the ion-sensor on the addition of varying concentrations of Ca<sup>2+</sup>. The response is very fast with a detection limit of 5.0 µM. A schematic representation of the interaction of Ca<sup>2+</sup> with PIn-CSA modified Pt electrode is shown in Figure 4. A comparative study on the potentiometric response for Ca<sup>2+</sup> was carried out on electrodes modified with PIn and CSA alone (thereafter termed as Pt/PIn and Pt/CSA, respectively) as shown in Figure 5(b,c). Both of the electrodes showed poor responses toward Ca<sup>2+</sup> with the



**Figure 3** Typical potentiometric response of PIn-CSA modified electrode toward the addition of varying concentrations of Ca<sup>2+</sup> from 1 × 10<sup>-6</sup> M to 0.3 M in 0.01 M Tris-HCl buffer pH 7.0. The inset shows the response time.



**Figure 4** Interaction of  $\text{Ca}^{2+}$  with PIn-CSA film on Pt disc.

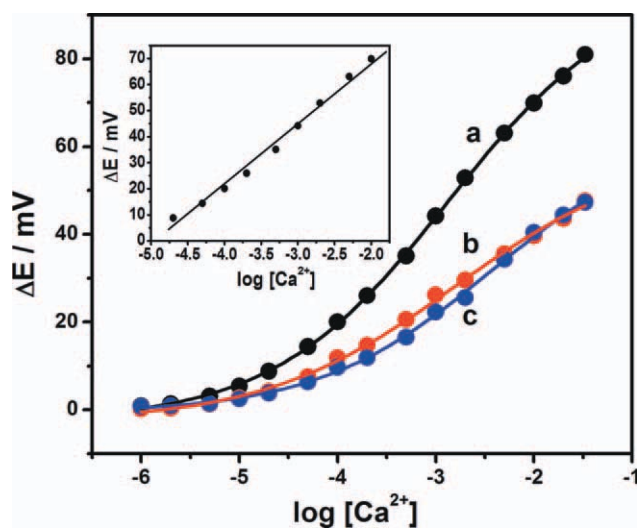
major problems associated with: (1) noise at the steady-state potential; and (2) sharp variation in a random order of the baseline potential. These two problems restricted the application of Pt/PIn or Pt/CSA electrodes for practical purpose. On the other hand, the PIn-CSA electrode [Fig. 5(a)] resulted in an improved reproducible response showing the advantage of present design.

It is also important to understand the sensing mechanism of PIn-CSA composite for calcium ions. It is believed that the presence of sulfonic acid along with indole residue generates ion-exchange property within polymeric domains for calcium ion. The presence of sulfonic acid in other polymeric domains has already been proved to exhibit calcium ion sensing properties.<sup>32,33</sup>

#### Sensitivity, response time, and storage stability of ion-sensor

The present sensor shows good sensitivity toward  $\text{Ca}^{2+}$ . The best dynamic range with the highest slope is greater than three decades. The slope for the potentiometric response of the sensor toward  $\text{Ca}^{2+}$  is calculated to be  $25.4 \pm 0.21$  mV within concentration range of  $2 \times 10^{-5}$  M to  $1 \times 10^{-2}$  M of  $\text{Ca}^{2+}$  as shown in the inset to Figure 5 for a freshly prepared electrode.

The response time of PIn-CSA-modified electrode was established by injecting desired concentrations of standard solutions into a stirred Tris-HCl buffer, pH 7.0. The response time of the sensor is measured as the time taken by the sensor to attain 95% of steady-state potential. The typical response curve is shown in Figure 3. The response time of the ion-sensor is found to be 8 s. The storage stability of the ion sensor was tested by measuring characteristic



**Figure 5** Comparative response curves for (a) PIn-CSA, (b) PIn, and (c) CSA modified electrodes toward varying concentrations of  $\text{Ca}^{2+}$  in 0.01 M Tris-HCl buffer pH 7.0. The inset shows the linear relationship between potential response and  $\log [\text{Ca}^{2+}]$ . [Color figure can be viewed in the online issue, which is available at [wileyonlinelibrary.com](http://www.interscience.wiley.com).]

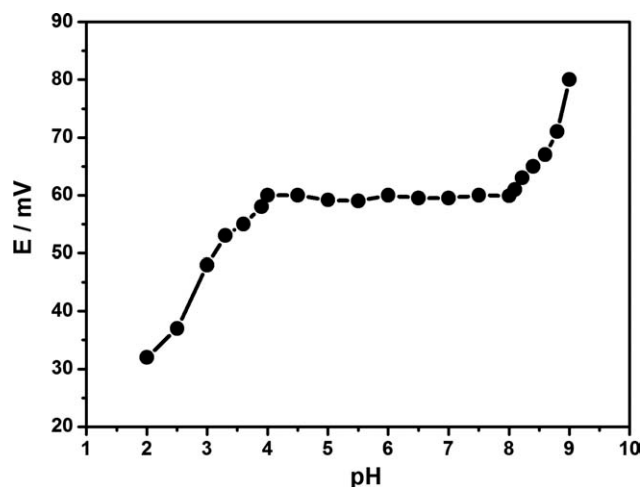
slopes systematically, usually after every 5 days. The lifetime for a typical ion-sensor is recorded in Table I. The sensor retains its response and lifetime over a period of 3 months without any significant change in the value of slope in the working concentration range. The drift in the baseline potential was in the order of  $<1\text{--}2$  mV in 30 days. This small drift in the baseline potential shows the potential application of the composite film for the construction of an ion-sensor suitable for practical application.

#### Dependence of potentiometric response on pH

The dependence of potentiometric response of PIn-CSA ion-sensor on pH was investigated within 2.0–9.0 pH range. To achieve this, 0.1M HCl or 0.1M NaOH were added to a solution containing 0.001M  $\text{Ca}^{2+}$ . After each addition of the acid or base, the solution's pH was measured while continuously monitoring the EMF of the system. Figure 6

**TABLE I**  
Lifetime and Drift in the Baseline Potential of a Typical  $\text{Ca}^{2+}$ -Sensor

Day	Limit of detection ( $\mu\text{M}$ )	Slope (mV/decade)	Baseline potential (mV)
1	5.0	25.4	50
10	5.1	25.2	50
20	5.3	25.0	50
30	5.5	25.0	49
50	5.9	24.8	49
70	6.3	24.8	48
90	7.0	24.6	47



**Figure 6** Effect of pH on the response of PIn-CSA modified electrode.

illustrates the dependence of EMF on pH obtained for the electrode. The electrode showed a good response to  $\text{Ca}^{2+}$  ions in the useful pH range of 4.0–8.0.

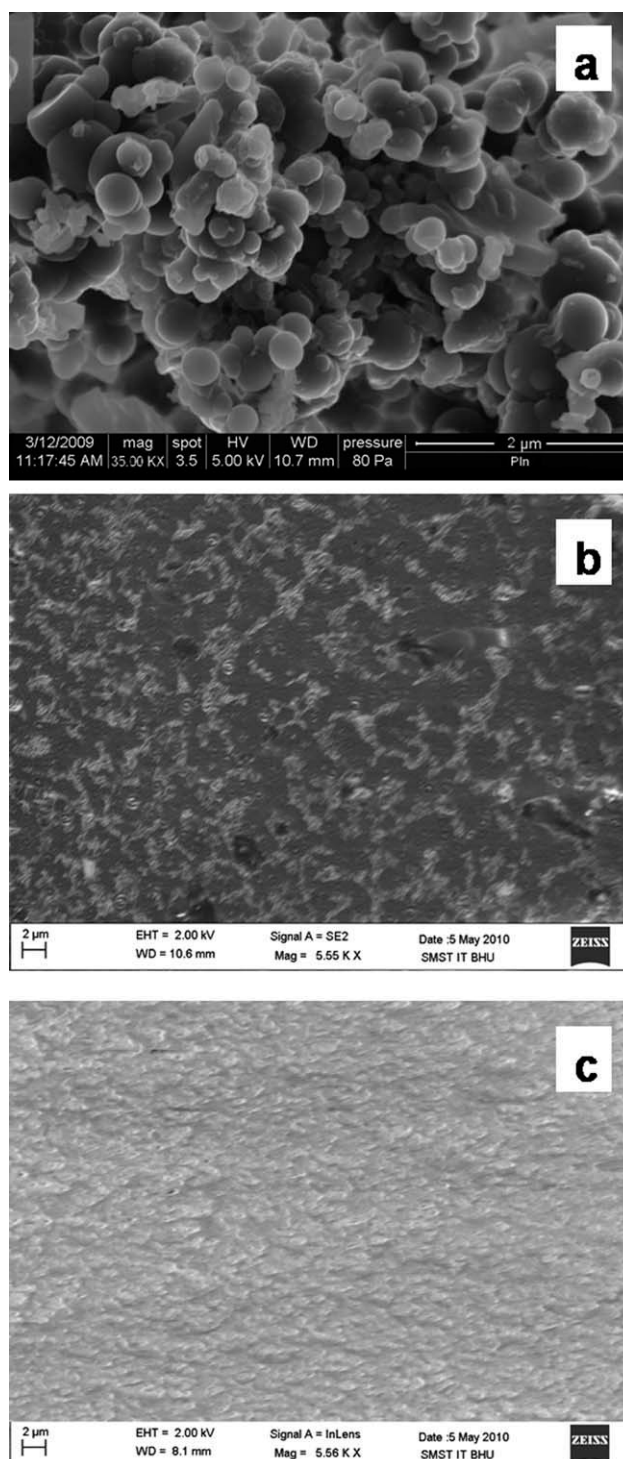
### Scanning electron microscopy

Scanning electron microscopy (SEM) revealed spherical morphology of PIn as shown in Figure 7(a). This is attributed to the formation of organic aqueous emulsion.<sup>30</sup> SEM of PIn-CSA was recorded by casting a thin film of the same over Pt surface. After evaporation of the solvent, the film was utilized for observing the morphology. The SEM image shows a uniform network like structure [Fig. 7(b)] attributable to change in the alignment of polymer chains due to their interaction with CSA. SEM of PIn-CSA was also performed after the sensing of  $\text{Ca}^{2+}$  to get an idea of the surface morphology of the composite after exposure to  $\text{Ca}^{2+}$ . The film was exposed to 0.2 M  $\text{Ca}^{2+}$  solution for 5 min. As is evident from Figure 7(c), the morphology of the PIn-CSA film changed significantly after interaction with  $\text{Ca}^{2+}$ .

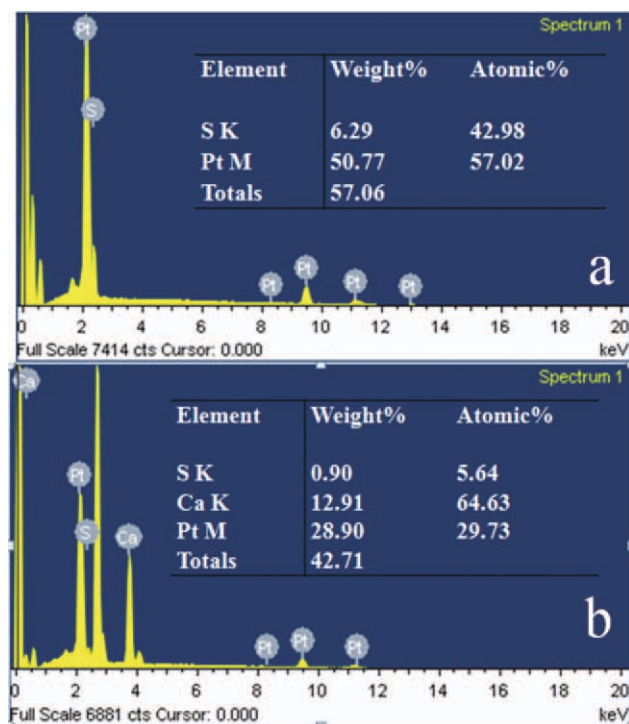
### Energy dispersive X-ray analysis

To have a clear picture of the composition of composite film, energy dispersive X-ray (EDX) analysis was performed both before and after the sensing of  $\text{Ca}^{2+}$ . For this purpose the same films that were used for SEM analysis were utilized. The results presented in the Figure 8 gives a qualitative idea of elemental composition of the PIn-CSA films. The presence of sulfur [Fig. 8(a)] indicates the presence of CSA groups in polymer network resulting in change in the morphology of same as evident from SEM above [Fig. 7(b)]. The film was exposed to 0.2 M

$\text{Ca}^{2+}$  solution for 5 min and after that analysis was again performed. The presence of  $\text{Ca}^{2+}$  in the results [Fig. 8(b)] indicates that the film has significantly taken up  $\text{Ca}^{2+}$  ions during its exposure to the standard solution of the cation.



**Figure 7** SEM images of PIn (a) and PIn-CSA film, before (b) and after (c)  $\text{Ca}^{2+}$  sensing (0.2 M).



**Figure 8** EDX patterns of PIn-CSA film, before (a) and after (b)  $\text{Ca}^{2+}$  sensing (0.2 M). [Color figure can be viewed in the online issue, which is available at [wileyonlinelibrary.com](http://wileyonlinelibrary.com).]

### Potentiometric selectivity

The potentiometric selectivity coefficient that indicates the relative response of a given sensor for the primary ion over other ions present in solution is

one of the most important characteristics of an ion-sensor. The selectivity of the proposed sensor was evaluated by establishing its selectivity coefficients in reference to some of the common interfering cations and the results are reported in Table II. The selectivity coefficients were determined by the matched potential method (MPM). In the MPM, the selectivity coefficient is defined as the activity ratio of the primary ion (A) and the interfering ion (B) that gives the same potential change in a reference solution. The interfering ion would be added to an identical reference solution until the same potential change is obtained. The selectivity coefficient  $K_{\text{Ca,B}}^{\text{pot}}$  is determined as:

$$K_{\text{Ca,B}}^{\text{pot}} = \frac{\Delta a_{\text{Ca}}}{a_{\text{B}}} = \frac{a'_{\text{Ca}} - a_{\text{Ca}}}{a_{\text{B}}}$$

where  $\Delta a = a'_{\text{Ca}} - a_{\text{Ca}}$ ,  $a_{\text{Ca}}$  is the initial primary ion ( $\text{Ca}^{2+}$ ) activity and  $a'_{\text{Ca}}$  is the activity of primary ion ( $\text{Ca}^{2+}$ ) in the presence of interfering ion, B, and  $a_{\text{B}}$  is activity of interfering ion. The initial activity of  $\text{Ca}^{2+}$  was fixed at  $5 \times 10^{-5} \text{ M}$  for measuring the selectivity coefficients using MPM and the magnitude of potential change was fixed at 15 mV. The values of selectivity coefficients are recorded in Table II including the values of the same obtained by other workers for  $\text{Ca}^{2+}$  ion-selective electrodes. As can be seen, the present ion-sensor shows excellent selectivity towards  $\text{Ca}^{2+}$  ions in comparison to the earlier reported ones indicating negligible interference in the sensor performance. It is indicated from Table II

**TABLE II**  
Selectivity Coefficient for the  $\text{Ca}^{2+}$  Sensitive Electrode

Interfering ion	Selectivity coefficients ( $-\log K_{\text{Ca,B}}^{\text{pot}}$ )									
	Reference No.									
	34	35	36	37	38	39	40	41	42	This work
$\text{Na}^+$	5.4	3.2	0.17	3.7	3.1	3.6	0.2	4.5	2.30	4.79
$\text{K}^+$	5.4	3.4	0.22	4.0	4.0	3.7	0.1	4.2	2.50	4.09
$\text{Mg}^{2+}$	4.4	1.4	0.3	4.9	4.6	4.2	0.4	4.4	2.15	4.79
$\text{Li}^+$	4.3	—	—	—	2.5	—	0.4	3.4	2.65	4.38
$\text{NH}_4^+$	5.1	3.2	—	—	—	—	—	4.6	2.44	6.09
$\text{Ba}^{2+}$	—	—	—	—	3.1	—	0.2	4.3	—	4.39
$\text{Sr}^{2+}$	—	—	—	—	3.5	—	0.2	3.5	2.25	3.24
$\text{Al}^{3+}$	—	1.5	—	—	4.5	—	1.9	2.4	2.52	3.01
$\text{Fe}^{3+}$	—	3.0	—	—	—	—	1.6	2.3	1.92	2.42
$\text{Cu}^{2+}$	—	1.5	—	—	—	—	—	2.6	2.05	3.54
$\text{Mn}^{2+}$	—	2.6	—	—	3.2	—	—	2.2	1.25	2.27
$\text{Co}^{2+}$	—	—	—	—	—	—	0.6	2.1	2.30	2.24
$\text{La}^{3+}$	—	—	—	—	3.6	—	—	4.8	—	—
$\text{Ce}^{3+}$	—	—	—	—	4.6	—	—	4.9	—	—
$\text{Ag}^+$	—	—	—	—	—	—	—	—	1.92	4.78
$\text{Cr}^{3+}$	—	—	—	—	—	—	—	—	1.58	2.67
$\text{Hg}^{2+}$	—	—	—	—	—	—	—	—	1.55	2.54
$\text{Pb}^{2+}$	—	—	—	—	—	—	—	—	2.25	2.53
$\text{Zn}^{2+}$	—	—	—	—	—	—	—	—	2.20	2.84
$\text{Cd}^{2+}$	—	—	—	—	—	—	—	—	2.25	3.07

that selectivity coefficients obtained for the present sensor are nearly equal to or even greater than in comparison to the earlier reported ones for calcium ion-sensors.

### CONCLUSIONS

The present investigation relates to the development of a calcium ion sensor based on processable PIN-CSA composite. The composite was synthesized following facile chemical method followed by its characterization using UV-vis, SEM, EDX, and cyclic voltammetric measurements. The processable electroactive composite was utilized for construction of a highly sensitive, low cost, user friendly calcium ion-sensor. The ion-sensor showed excellent response for calcium ion with high stability, reproducibility, and negligible drift of the baseline potential. The slope of the present ion sensor was calculated to be  $25.4 \pm 0.21$  mV per decade. Various cations were selected for interference studies; however, negligible interference was observed when other cations were less than 0.01M concentration. The limit of detection for present sensor was found to be 5  $\mu$ M.

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