

Hydrogen peroxide sensing properties of PVA/TiO₂/I₂ nanocomposite-based free standing membranes

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ABSTRACT: The nanocomposite of titanium-di-oxide (TiO₂)/iodine (I₂) in polyvinyl alcohol (PVA) matrix has been explored to be used in hydrogen peroxide (H₂O₂) sensing applications for the first time. The proposed nanocomposite can be easily casted in the form of thin film on glass substrates as well as free standing membranes. These nanocomposite films and membranes exhibit reduced resistance values and easily observable colour changes in the presence of H₂O₂. The films also exhibit significant quenching in photoluminescence emission properties upon H₂O₂ exposure. These sensor responses have been attributed to redox reactions at nanocomposite films and H₂O₂ interface. This study indicates an easy to fabricate, flexible and environmental friendly sensing platform for H₂O₂. © 2015 Wiley Periodicals, Inc. *J. Appl. Polym. Sci.* **2015**, *132*, 42257.

KEYWORDS: hydrogen peroxide; nanocomposite; PVA; TiO₂; I₂; sensors and actuators; surfaces and interfaces; synthesis and processing

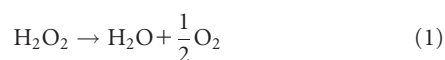
Received 22 November 2014; accepted 23 March 2015

DOI: 10.1002/app.42257

INTRODUCTION

Hydrogen peroxide (H₂O₂) holds marked significance in variety of fields, for example, environmental, food manufacturing, pharmaceuticals, clinical and cosmetic applications.¹ It is used as a disinfectant, antiseptic, bleaching agent, oxidizing agent, and rocket propellant.^{2–4} Most of these applications are dependent on the strong oxidation properties of this compound. However, H₂O₂ being a strong oxidizer can also corrode many materials and its high concentrations generally affect the environment adversely. Moreover, many enzymatic reactions inside living organisms produce H₂O₂ as an end-product. Consequently, a measurement of its concentration is required for proper monitoring of these biological reactions.⁵ Therefore, simple, selective and sensitive detection measures of hydrogen peroxide are necessary for its practical applications.

A number of techniques have been reported in literature for its detection. These techniques are usually based on the measurement of a noticeable property on exposure to H₂O₂. In general, H₂O₂ is thermodynamically unstable and decomposes slowly but spontaneously to form water and oxygen gas as:



Hydroxyl radicals formed during the decomposition of H₂O₂ act as strong oxidizing agents. This decomposition reaction can be observed by different changes. These include for example,

color changes, changes in electrochemical potential of the redox reaction or an increase in heat energy resulting from the exothermic nature of the reaction. Furthermore, changes in some optical properties can also be utilized in sensor applications for example, refraction and absorption properties. Particularly, in chemical sensors, the incorporation of enzymes is required to be used as a catalyst for the reduction of H₂O₂. However, sensors based on enzymatic reactions generally require complex techniques for immobilization of these enzymes thereby affecting the overall sensor output in terms of lifetime as well as cost.⁶ Furthermore, these enzymes can also get denatured in applications requiring high concentrations of peroxide, making the sensor ineffective. Therefore, nonenzymatic sensors with sufficiently high stability, simplified fabrication procedures and low cost are a better alternative.⁷

In recent years, nanoparticles have gained a significant interest due to their easily controllable size dependent electronic properties which can also be explored in sensing applications.⁸ A number of inorganic catalysts are reported in literature for example, metal oxide nanoparticles based on copper,^{9,10} manganese¹¹ and iron,¹² etc. Depending on their intrinsic properties, these oxides get reduced or oxidized in the presence of H₂O₂, and exhibit an amperometric or potentiometric response while regaining their original redox state. In addition, conductometric sensors have also been reported in literature as a successful means to detect

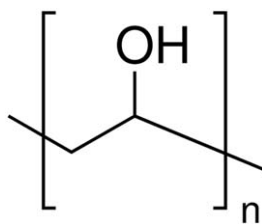


Figure 1. Molecular structure of polyvinyl alcohol.

H_2O_2 . Conductometric sensors are generally simple and low-cost as they do not need a reference electrode. Such type of sensors can be easily fabricated using thin film materials and enzymatic optimizations. These sensors are based on the measurement of conductivity changes taking place due to different mechanisms.¹³ However, a significant impact of the buffering capacity of the aqueous solutions has limited their applications.

Among these varied examples, titanium dioxide (TiO_2) nanoparticles have many distinct properties that can be efficiently utilized to function as active component of sensors based on polymers. When hydrogen peroxide is present on the TiO_2 film, it is reduced. This produces OH^- radicals, which injects holes into the semiconductors valence band.¹⁴ Its sensor response towards H_2O_2 vapors can be intensified by the use of commonly known iodine molecules as in titration-based sensing solutions. Firstly proposed by Kingzett *et al.*, these methods are based on the oxidation of iodide to iodine by H_2O_2 in the presence of a catalyst. Prilled iodine, being a shiny, grey nonmetal and the fourth member of the halogens is also quite easy to handle. It sublimates easily to produce a beautiful purple vapor. However, the integration of nanoparticles in the form of thin films along with the iodine molecules is generally difficult to achieve. Furthermore, a practical H_2O_2 sensor should be able to work quickly as well as accurately. In addition, for application of the device as a commercial product, it should be economical and uncomplicated also. It is well known that the addition of nanoparticles like TiO_2 ,¹⁵ CNT,¹⁶ in polymeric matrices to form nanocomposites can be easily accomplished to enhance their permeability properties and retain the selectivity properties as well. In the present work, thin films based on TiO_2 and I_2 have been explored to be used in H_2O_2 sensing applications. The nanocomposite film surface acts as a sensing platform for the analyte (H_2O_2 in the present case). The key properties which greatly affect the sensor response of the overall composite are the morphology, particle size and the effective surface area of the sensing platform. Furthermore, the adsorption capability and electron-transfer properties of the composite also play a significant role. Therefore, these key attributes have been investigated in detail by fabricating TiO_2/I_2 nanocomposite in PVA matrix in the form of thin film on glass substrate as well as in the form of thin flexible membranes. The resulting nanocomposite exhibited interesting changes on exposure to different concentrations of H_2O_2 .

EXPERIMENTAL

Figure 1 shows the chemical structure of polyvinyl alcohol (PVA). PVA is a polymer based on ethanol monomers as repeat-

Table I. Concentration of Iodine in the Samples 1–5

Sample no.	Iodine concentration (%)
1	100
2	50
3	20
4	15
5	0

ing units. The presence of alcohol group imparts hydrophilic nature to the material and its linear structure is responsible for its high crystallinity, tensile strength and flexibility. These characteristics are desirable in obtaining films as well as membranes when PVA is used as a matrix. High glass transition temperature of PVA ($T_g = 85^\circ\text{C}$) is responsible for its high thermal stability. Furthermore, its resistance towards oil, organic solvents and most of the natural gases makes it an ideal candidate for sensor applications. Different samples of PVA/ TiO_2/I_2 nanocomposite were prepared as follows: A known quantity of PVA powder (7 wt. %) was mixed with distilled water by constant stirring at constant temperature of 40°C for 3 h until a homogeneous dispersion of polymer is obtained. This dispersion was then utilized to form a stock solution, to which different concentrations of I_2 (100, 50, 20, 15, and 0 wt. % termed as sample 1, 2, 3, 4 and 5, respectively) were mixed and again stirred continuously for 3–4 h. Table I shows the concentration values of iodine in all the samples.

The obvious change in colour of materials even before mixing can also be seen in Figure 2.

A separately prepared dispersion of a known quantity of TiO_2 (20 wt % of PVA) in distilled water was slowly and carefully added to these concentrations while stirring. A homogeneous suspension was observed after the addition of TiO_2 nanoparticles which did not sediment noticeably in several hours and settled into a gel like material. The gel so obtained in each case was spread on a glass plate and kept for 24 h in dark, at room

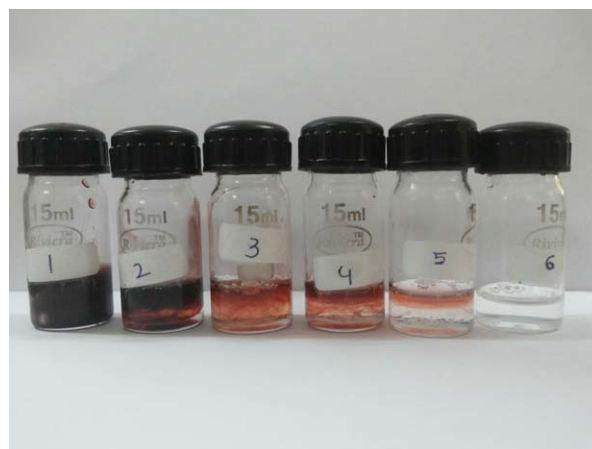


Figure 2. A photograph showing PVA-based dispersions with different concentrations of iodine. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]



Figure 3. A digital image showing the nanocomposite-based flexible membrane.

temperature, until all the water evaporated. This drop casting technique enables the formation of dense and thin polymeric layer. The PVA membranes adhered to the glass support were then peeled off the glass plates. Figure 3 shows the picture of flexible membrane so formed. For the fabrication of samples on plain glass plates, the materials with similar concentrations could be made with lower PVA content to enhance the conductivity and hence increased sensor response towards hydrogen peroxide vapors. These samples formed were analyzed in their original state and after H_2O_2 exposure for different intervals of time. Electrical characterizations were performed by making ohmic contacts on the films using highly conducting silver paste. After the contacts were suitably allowed to dry, the films were placed one by one inside a homemade sensor characterization system as shown in Figure 4. The samples were subjected to an exposure to a known volume of H_2O_2 already mixed with inert Argon gas at repeated time intervals and with different concentrations of H_2O_2 . Photoluminescence spectra of the thin films of composites were studied using Shimadzu spectrofluorometer RF-5301PC. Fourier transform infra red spectroscopy (FTIR) analyses were performed using Nicolet 6700 thermo-scientific instrument. Size and morphology of these thin films and membranes were characterized by using Carl Zeiss Scanning electron microscope (SEM). The change in electrical resistance of the films on exposure to hydrogen peroxide was observed using a Keithley electrometer (Model: 6514).

RESULTS AND DISCUSSION

The morphology of TiO_2/I_2 nanocomposites was observed with scanning electron microscope (SEM) image analysis by examining the cross section of nanocomposite film prepared by drop casting. Figure 5(a) shows the SEM image of iodine thin film on plain glass substrate. The films exhibited quite uniform particle distribution. The iodine dispersion in water when mixed (20 wt. %) with TiO_2 nanoparticles' dispersion, forms a uniformly distributed thin film in nanometric dimensions as shown in Figure 5(b). The inset shows the enlarged view of the same film. These structures are highly desirable for sensor applications as they provide a large surface area for efficient and quick redox reactions between sensing surface and the material to be sensed. These nanocomposites (diameter in the range of 20–50 nm) were used to form relatively

uniform dispersion throughout the whole polymer matrix. The thin flexible membrane so formed exhibited high orders of uniformity indicating a good adhesion between organic and inorganic phases. The transport of gases to be sensed is greatly facilitated by the high capacity of PVA to swell. The addition of TiO_2 nanoparticles are known to induce the presence of voids and disruption of chain packing in PVA which are responsible for high degree of gas permeation.¹⁷ TiO_2 as a hydrophilic nanomaterial inside the PVA/ TiO_2/I_2 nanocomposite also facilitates the formation of a homogeneous dispersion.¹⁸ However, an optimized amount of TiO_2 is required as high concentrations can lead to increased thickness of the skin layer, suppressing the presence of voids, increased viscosity and finally decreased solvent/solute rate exchanges.^{18,19}

To explore the sensing mechanism of the nanocomposite so formed, detailed optical studies were also carried out. Photoluminescence (PL) response of the polymeric membranes doped with TiO_2 nanoparticles and different concentrations of I_2 in initial state as well as after exposure to H_2O_2 vapors were measured. Figure 6 shows the response of sample 3 (with 20 wt. % TiO_2 and 20 wt. % I_2) at different excitation wavelengths. At an excitation of 410 nm as shown in Figure 6(a), the response of TiO_2 nanoparticles towards H_2O_2 vapors was studied. It can be easily seen from the figure that PL intensity was slightly quenched exhibiting a very small response of nanoparticles towards vapors. However, the excitation of the same sample at a wavelength of 350 nm to study the response of I_2 exhibited quite interesting results as shown in Figure 6(b). The PL intensity was significantly quenched exhibiting the strong response of I_2 towards H_2O_2 vapors. The results signify the fact that even after the formation of composite membranes or films, sensor response of I_2 towards H_2O_2 is retained and even enhanced due to the presence of TiO_2 nanoparticles. The PL peak of I_2 is actually quenched by the products of the decomposition reaction [eq. (1)] that is, water and oxygen. This quenching was easily observable in the PL spectra. These measurements were performed ex-situ by exposing the film(s) to H_2O_2 vapors under controlled environment and then loading it in the sample holder of the PL spectrophotometer in exactly similar controlled environments inside the clean room. In this way, the presence of contributions from any physisorbed species was assumed to be similar in all the samples. Therefore, changes observed in PL spectra have been attributed solely due to H_2O_2 exposure.

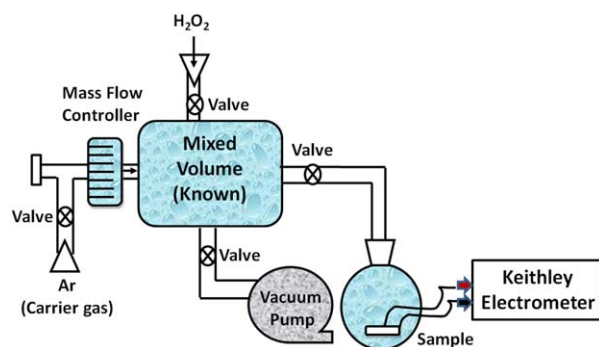


Figure 4. Schematic of the electrical characterization system for sensing films. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

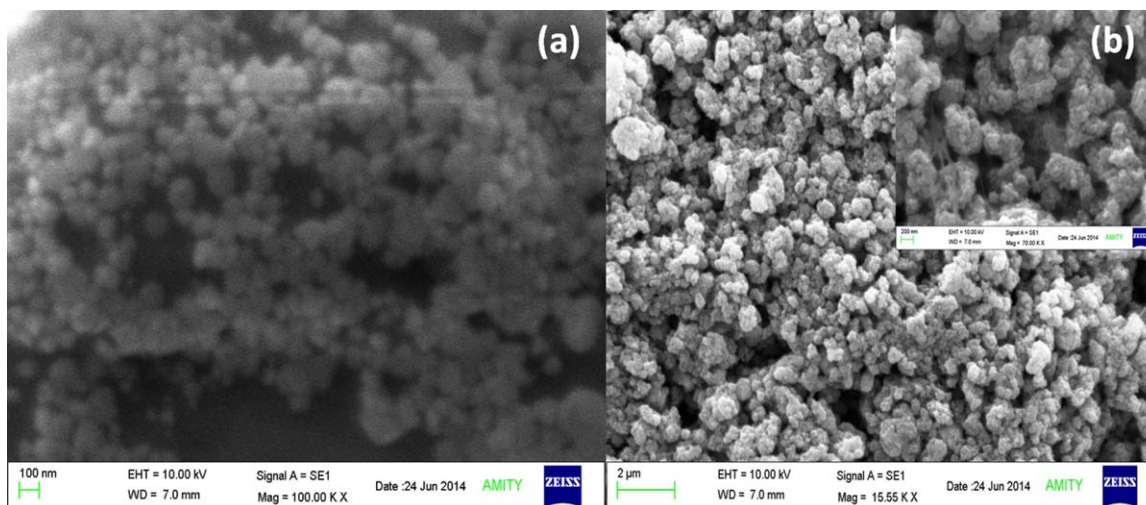


Figure 5. SEM micrographs of (a) I_2 and (b) TiO_2/I_2 thin films without PVA on glass substrates. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

The fundamental physico-chemical processes taking place on the exposure of H_2O_2 were analyzed using FTIR spectroscopy. As shown in Figure 7, the broad and strong absorption in

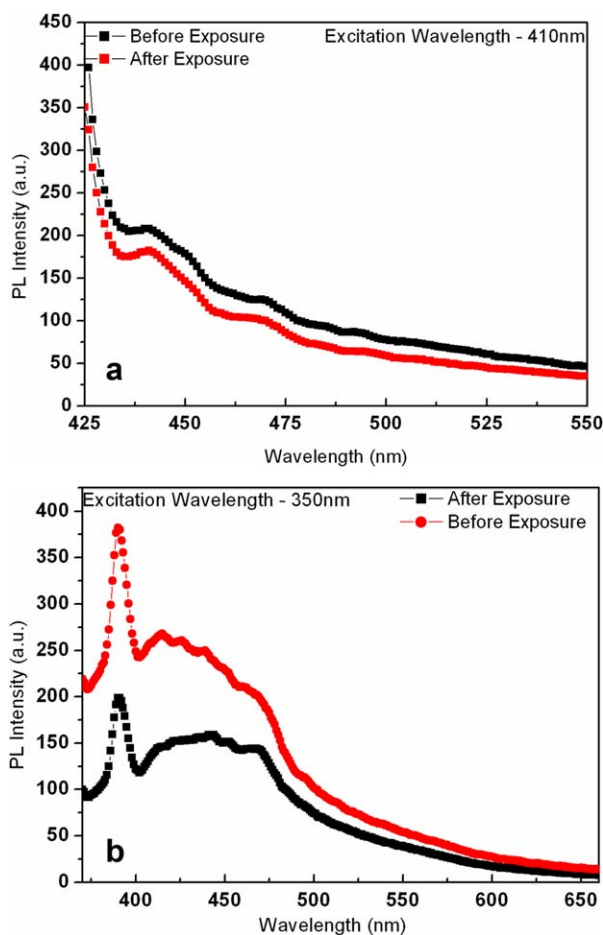


Figure 6. PL spectra of the PVA/ TiO_2/I_2 nanocomposite thin film at an excitation wavelength of (a) 410 nm and (b) 350 nm. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

3000–3700 cm^{-1} range can be attributed to symmetric stretching vibration of O-H group in PVA. This O-H stretching is sensitive to inter/intra chain hydrogen bonding interaction among PVA chains. This bonding is also responsible for the formation and mechanical flexibility of the nanocomposite membrane. Iodide (I^-) catalyzed decomposition of hydrogen peroxide results in the formation of H_2O and O_2 . The formation of O_2 is manifested by the occurrence of FTIR peaks at 608 and 950 cm^{-1} .²⁰ Therefore, as the samples are exposed to H_2O_2 , iodide is oxidized to iodine. The formation of these water molecules is indicated by the IR absorption for free O-H stretching in the range of 3610–3640 cm^{-1} observed only in presence of H_2O_2 . However, in the presence of H_2O_2 , this O-H stretching peak in PVA chains (2961–3040 cm^{-1}) is enhanced indicating the presence of hydrogen bonding interaction between hydroxyl group on PVA chain and oxygen from water molecule. This interaction is also exhibited by the defining peak at 1561 cm^{-1} representing the O-H group vibration deformation with the

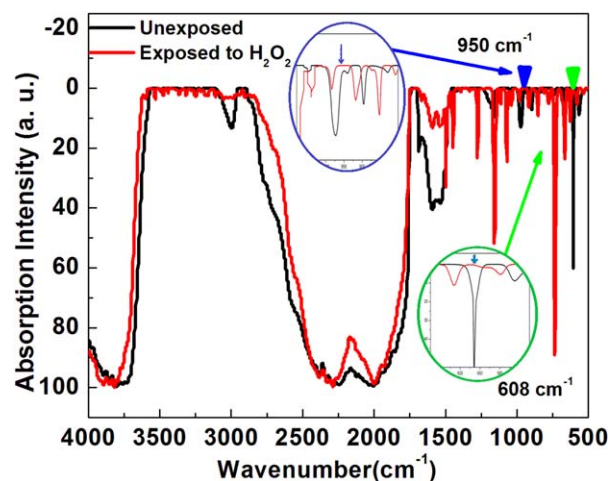


Figure 7. FTIR absorption spectra of the PVA/ TiO_2/I_2 nanocomposite thin film in the absence and presence of H_2O_2 . [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

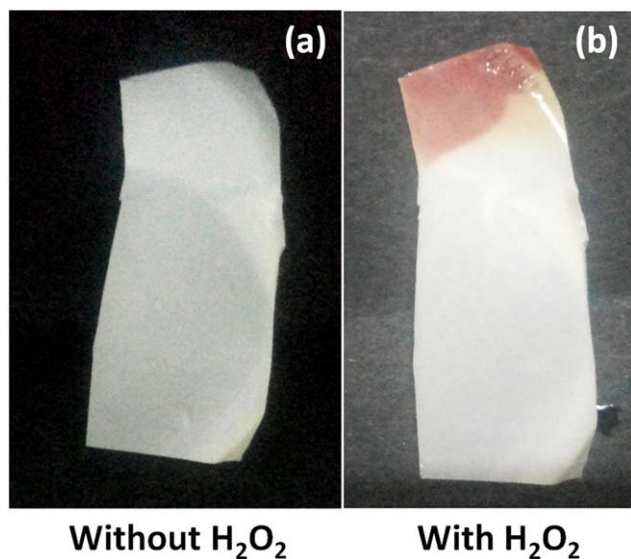


Figure 8. Pictures showing changes in color of the sample 3 (intermediate concentration with 20 wt. % TiO₂ and 20 wt. % I₂) (a) without and (b) with H₂O₂ exposure. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

hydrogen bonding.²¹ Furthermore, C=O stretching peak at 1668 cm⁻¹ is enhanced in the presence of H₂O₂.²² The reusability of the nanocomposite is therefore affected by the presence of surplus H₂O as explained above. Moreover, the interaction between titanium ionic species and polymeric matrix results in the molecular rearrangement of PVA skeleton due to the ion energy input. This results in aromatization of PVA chains repre-

sented by the absorption peaks in 2155–2161 cm⁻¹ range.²³ The exposure of H₂O₂ results in further modification causing enhanced absorption in this region.

The colour changes in the films were also observed carefully on exposure to H₂O₂. The self-assembled polymer-based nanocomposites change colour from white to dark pink when oxidized in the presence of H₂O₂. Figure 8(a,b) show the changes in colour of the sample 3 (intermediate concentration with 20 wt. % TiO₂ and 20 wt. % I₂) on H₂O₂ (30% w/v) exposure.

The regeneration of this oxidized state is achieved by the TiO₂ nanoparticles present in the composition when the films are sufficiently dried again. The response and recovery times for PVA/TiO₂/I₂ nanocomposite thin films with different concentrations of iodine were carefully studied as shown in Figure 9. In the presence of H₂O₂ vapors, the electrical resistance of the samples decreases sharply. The nanocomposites formed with different concentrations of iodine were quite stable even after many cycles of detection and recovery which was not the case with pristine iodine films. The response and recovery times were found to be comparatively faster for higher concentrations of iodine as compared to lower ones. The on/off ratio for nanocomposite thin films with 0, 15, 20, 50, and 100 wt. % iodine concentrations were found to be 1.3, 1.7, 1.9, 2.04, and 2.4, respectively. The pristine iodine films were also investigated for sensor response, but they become nonfunctional just after two cycles. The sensor response of the films was also found to improve with the increase in concentration of iodine. However, the dense polymeric films or membranes, based on PVA/TiO₂/I₂ nanocomposite, with higher concentrations of iodine also result in reduced dispersion properties which stimulate the formation

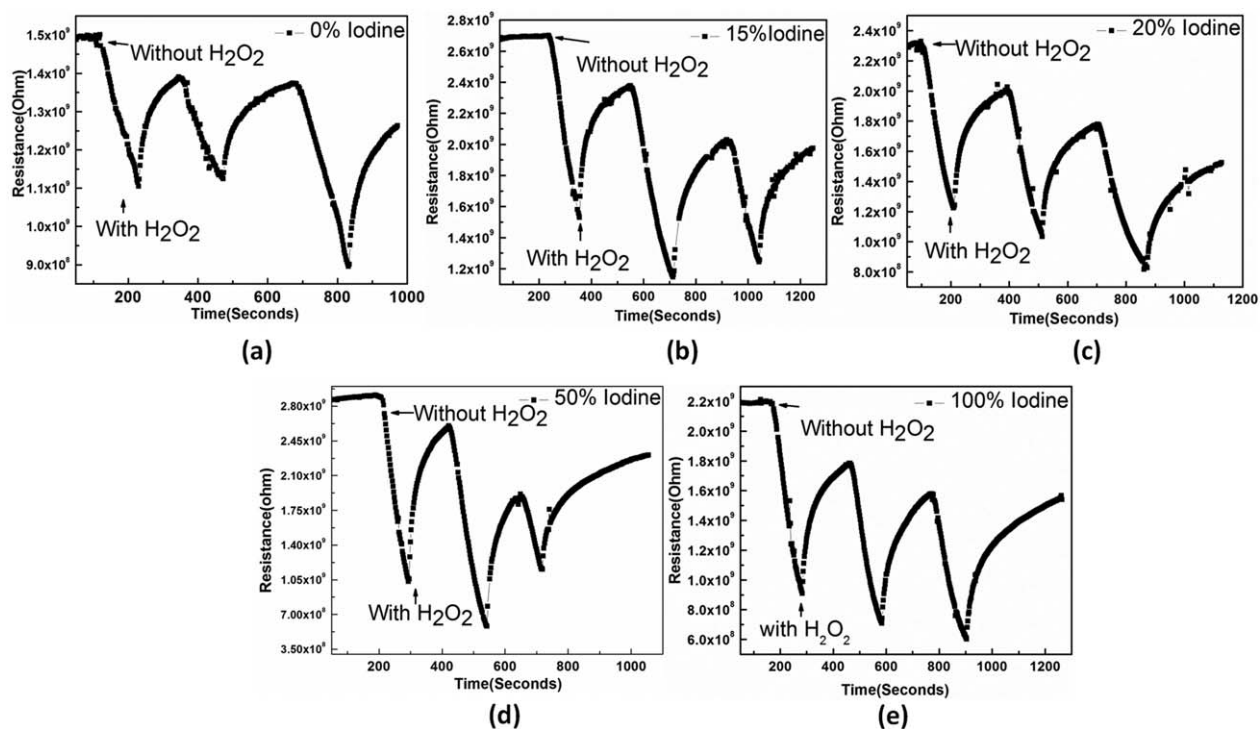


Figure 9. Resistance vs. H₂O₂ exposure time characteristics of nanocomposite thin films with (a) 0 wt. %, (b) 15 wt. %, (c) 20 wt. %, (d) 50 wt. %, and (e) 100 wt. % iodine concentrations, respectively.

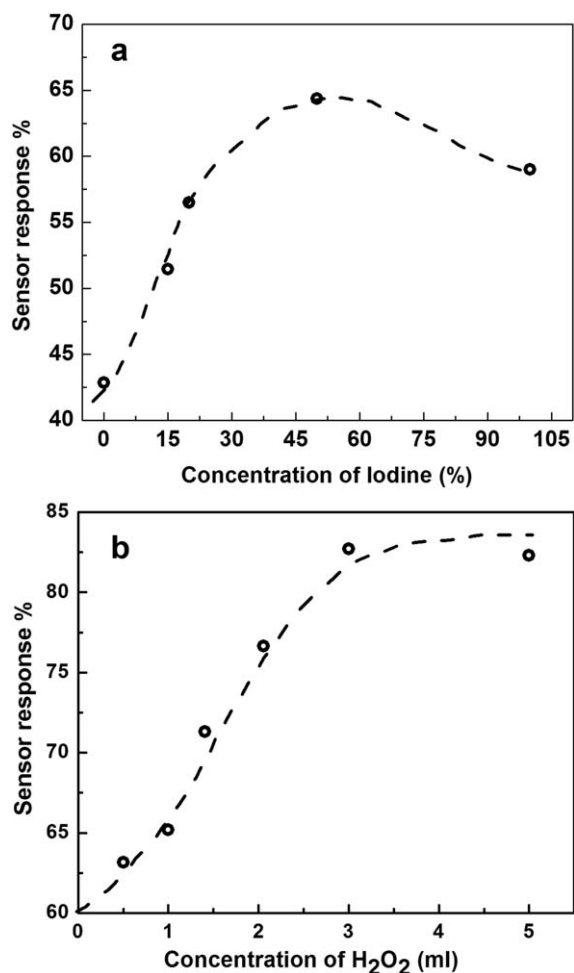


Figure 10. Sensor responses of the PVA/TiO₂/I₂ nanocomposite thin films as a function of concentration of (a) iodine and (b) H₂O₂.

of aggregates.¹⁷ These dense films with reduced porosity result in decreased sensor response at 100 wt. % iodine concentration as shown in Figure 10(a). Figure 10(b) shows the sensor response of the films for different concentrations of H₂O₂. The films exhibited increased sensor response with the increase in concentrations of H₂O₂ in the mixing chamber (as shown in the sensor setup) with a saturation type of behavior. The thin flexible membranes were observed to bear the fatigue of H₂O₂ exposure two to three times. On the other hand, thin film on glass substrates could work up to four to five times. Moreover, the repeatability of the films towards H₂O₂ sensing was found to reduce as the iodine concentration was increased beyond 20% in the nanocomposite. Based on these results, the mechanism of resistance or colour changes in the nanocomposite films can be understood as follows. As the samples are exposed to H₂O₂, iodide is oxidized to iodine. The iodine so formed is then reduced back to iodide due to the presence of TiO₂ nanoparticles in the film which facilitate the recovery of the redox process. This reaction was monitored by observing a distinguishable colour change in the films before and after H₂O₂ exposure. In this reaction progression, the presence of TiO₂ nanoparticles not only assists the redox process of iodine and iodide, but also changes the conductivity of the thin films. This

conductometric change is therefore, an additional measurable quantity for the sensing of H₂O₂, as well as a specialization of the proposed nanocomposite. The enhanced sensor response of the nanocomposite films can be attributed to their enhanced effective surface area. The films with higher iodine concentrations in PVA as a matrix exhibited fast response but the repeatability of the films towards H₂O₂ sensing was found to reduce as the iodine concentration was increased beyond 20 wt. % in the nanocomposite. Therefore, overall performance of the films with 20% iodine concentration was found to be better.

The sensing films also exhibited significant selectivity to H₂O₂, with no measurable response for other analytes like alcohol, acids and urea. This study demonstrates an easy to fabricate and flexible sensing platform for H₂O₂ with key advantages of portability, low price, low power consumption, adequate sensor response and selectivity.

CONCLUSION

PVA/TiO₂/I₂ nanocomposite thin films have been investigated to be used in H₂O₂ sensing applications. The nanocomposite could be casted in the form of thin films or free standing membranes. These samples showed easily observable colour change from white to dark pink, quenching in photoluminescence emission and reduced resistance values on exposure to H₂O₂. These samples exhibited long term stability in continuous operation with fast response times and negligible warm-up time. Moreover, these films are insensitive to ambient temperature with reproducible characteristics.

ACKNOWLEDGMENTS

The authors are thankful to DRDO (Project: ERIP/ER/1103029/M/01/1448) for financial assistance. The authors are also thankful to Dr. Ashok K. Chauhan, Founder President and Dr. V. K. Jain, Distinguished Scientist and Professor, Amity University, Noida, India for their continuous encouragements and Mr. Pramod Kumar for providing technical help.

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