



Nanoporous cerium oxide thin film for glucose biosensor

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ABSTRACT

Nanoporous cerium oxide (CeO₂) thin film deposited onto platinum (Pt) coated glass plate using pulsed laser deposition (PLD) has been utilized for immobilization of glucose oxidase (GOx). Atomic force microscopy studies reveal the formation of nanoporous surface morphology of CeO₂ thin film. Response studies carried out using differential pulsed voltammetry (DPV) and optical measurements show that the GOx/CeO₂/Pt bio-electrode shows linearity in the range of 25–300 mg/dl of glucose concentration. The low value of Michaelis-Menten constant (1.01 mM) indicates enhanced enzyme affinity of GOx to glucose. The observed results show promising application of the nanoporous CeO₂ thin film for glucose sensing application without any surface functionalization or mediator.

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1. Introduction

Biosensors have recently gained much attention to estimate analytes of clinical importance due to selectivity and best response time and accuracy (Wei et al., 2006; Singh et al., 2007; Ekanayake et al., 2007; Matharu et al., 2007; Pandey et al., 2007). In the realization of a biosensor with improved response, enzyme attachment and its compatibility with a solid surface are crucial parameters. Further, chemistry involved in the immobilization of desired biomolecules on an electrode surface need to be as mild as possible since enzymes are highly sensitive and may undergo denaturation under harsh conditions. A number of immobilization schemes and materials have been investigated for biosensor application (Rogers, 1997; Arya et al., 2008).

Glucose biosensor is an intensely investigated bio-electronic device due to its clinical importance in the treatment of diabetes mellitus and importance in environment and food industry (Zhao et al., 2007). Till date the most commonly used amperometric glucose sensors use the specific recognition of glucose by glucose oxidase (GOx). Though a large number of matrices like thiolated gold nanoparticles (Pandey et al., 2007), TiO₂ (Viticoli et al., 2006), Woodceramics (Qian et al., 2004), carbon nano tubes (Liu and Lin, 2006) and thin film matrices of ZnO (Wei et al., 2006; Wang et al., 2006), ZrO₂ (Kim et al., 2006), iron oxide (Kaushik et al., 2008)

have been used for glucose biosensor fabrication. However, investigations are being conducted for search of new matrices to achieve better stability and functionality of enzyme (GOx) for *in-vitro* and *in-vivo* (Yu et al., 2006) glucose measurement.

Semiconducting oxide materials owing to high ionic conductivity, capacitive action, catalytic properties and high isoelectric point (IEP) have gained considerable interest in the fields of biosensors as alternate matrices (Singh et al., 2007; Wei et al., 2006; Kouassi et al., 2005). A number of inorganic matrices such as TiO₂ (Viticoli et al., 2006), SnO₂ (Liao et al., 2006), ZrO₂ (Kim et al., 2006) have been used for the immobilization of biomolecules. Recently, zinc oxide (ZnO) has been identified as a potential material for biosensor applications (Singh et al., 2007; Wei et al., 2006). However, ZnO based glucose sensors necessitate operation at a high potential (0.7 V) to obtain sensing response that may cause other analytes (ascorbic acid, uric acid, etc.) to interfere (Wei et al., 2006; Wang et al., 2006). On the other hand, the ability of cerium oxide (CeO₂) to act as a redox couple makes it a promising material to act as a matrix for the fabrication of a mediator-less amperometric biosensor. Further, owing to its high IEP (~9.0) (Lee et al., 2000), CeO₂ is suitable for adsorption of enzymes having low IEP like glucose oxidase (GOx) having IEP 4.2 (Wei et al., 2006), without any harsh chemical treatment. Moreover, the excellent electronic conductivity makes CeO₂ an attractive matrix for biosensor application (Rodriguez et al., 2007; Andersson et al., 2007; Suzuki et al., 2002). The recent interest in implantable glucose sensor and compatibility of CeO₂ with existing silicon technology warrants its application to develop MEMS based implantable glucose sensor. CeO₂ has already been exploited extensively for various applications such as electrolytes

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for fuel cells (Murray et al., 1999), ultraviolet absorbents (Goubin et al., 2004), oxygen sensors (Gerblinger et al., 1995), solar cells (Corma et al., 2004) and as catalysts (Avellaneda et al., 2008).

In this work, successful attempts have been made towards the fabrication of a mediator-less amperometric glucose biosensor by immobilization of GOx enzyme on the nanoporous surface of CeO₂ thin film deposited on platinum coated glass slide using pulsed laser deposition (PLD) technique. PLD is a well known reproducible technique to grow metal oxide films with controlled stoichiometry at relatively low process temperature and used extensively for the preparation of nanostructures (Gupta et al., 2006). Owing to the fact that the CeO₂ has been deposited by PLD, the matrix is compatible with solid state devices which could lead to its application to implantable biosensors.

2. Experimental

2.1. Materials

D-Glucose, GOx (200 U/mg), horseradish peroxidase (HRP) (200 U/mg), *o*-dianisidine were purchased from Sigma-Aldrich. Sodium phosphate monobasic anhydrous and sodium phosphate dibasic dihydrate were obtained from Sisco chemical, India. CeO₂ powder (99.9% purity) acquired from Cerac, inc., USA was used for making targets for PLD. All chemicals were used without further purification. Deionized water was used for the preparation of aqueous solutions.

2.2. Preparation of solutions

Phosphate buffer saline (PBS) 50 mM, pH 7.0 (0.9% NaCl) solution was prepared by adjusting the proportion of monobasic sodium phosphate solution and dibasic sodium phosphate solution and then adding 0.9% NaCl to the solution. GOx (1 mg/ml) solution and HRP solution (1 mg/ml) were freshly prepared in PBS buffer of pH 7.0. Different concentrations of glucose solution and solution of *o*-dianisidine (1%) were freshly prepared in deionized water.

2.3. Preparation of CeO₂ film and immobilization of GOx

The CeO₂ films were deposited by PLD onto platinum (Pt) coated corning glass plates. The Pt coating (~0.2 μm thick) on corning glass was done by RF-sputtering under Ar gas ambient using Pt metal target (99.99% pure). To prepare the target for PLD, CeO₂ powder was crushed in a pastel mortar, pressed into pellet and sintered for 4 h at 1400 °C. The films were prepared by ablating the ceria target with Nd-YAG laser at a fluence of 1.2 J/cm² in 10 mT oxygen pressure.

Prior to immobilization of GOx, CeO₂/Pt electrode is electrochemically pre-treated at 0.8 V to get rid off any other oxidizing species and to obtain active CeO₂ surface. Immobilization of GOx onto CeO₂ matrix is achieved via electrostatic interaction of positively charged CeO₂ and negatively charged GOx enzyme at pH 7.0. For immobilization of GOx, 30 μl of the freshly prepared GOx solution was dropped on the CeO₂ film and was kept at 4 °C overnight followed by extensive washing with buffer to remove any unbound GOx. The electrodes were dried under nitrogen flow and kept at 4 °C when not in use.

2.4. Measurement and apparatus

The CeO₂/Pt electrode and GOx/CeO₂/Pt bioelectrodes were investigated using fourier transform infrared (FTIR), atomic force microscope (AFM), differential pulse voltametric (DPV) techniques. Thickness measurements were done using Dektak IIA surface

profiler. FTIR spectra were recorded using Perkin Elmer (Model Spectrum BX) spectrophotometer to study the formation of desired CeO₂ films and GOx immobilization. AFM studies, using Veeco DCP2 instrument, were carried out in non-contact mode to examine the modification of surface morphology after GOx immobilization. The images were analyzed by SPM Lab Analysis software. DPV measurements were carried out on an Autolab Potentiostat/Galvanostat (Eco Chemie, Netherlands) using a three-electrode cell configuration with Ag/AgCl electrode as a reference electrode and Pt foil as a counter electrode in 10 ml of phosphate buffer saline (PBS) solution (50 mM, pH 7.0, 0.9% NaCl). The apparent enzyme activity of bio-electrode was studied using UV–vis spectrophotometer (Perkin Elmer lambda 35). For UV–vis measurements bio-electrode was dipped in the 3 ml PBS solution containing 20 μl of dye (*o*-dianisidine, 1% in H₂O), 50 μl of HRP and 100 μl of substrate (glucose). After 1 min of incubation of bio-electrode, absorbance corresponding to the oxidation of *o*-dianisidine, was measured at 500 nm for monitoring the enzyme kinetics.

3. Results and discussion

The CeO₂ thin films (110 nm thick) deposited by PLD were found to be smooth, transparent and strongly adherent to the substrate. The X-ray diffraction study (data not shown) shows the growth of an amorphous film at room temperature on Pt coated glass substrate. The growth of amorphous nature during deposition is attributed to unavailability of minimum energy required for the nucleation of grain along a particular growth direction.

3.1. UV–vis studies

For UV–vis characterization CeO₂ film was deposited on fused quartz substrate under similar deposition condition and was found to be highly transparent (>80%) in the visible region. The transmission curve of the CeO₂ film in the UV region shows a sharp fall at ~325 nm corresponding to the onset of fundamental absorption edge (see supplementary data). This curve has been used to obtain band gap using Tauc plot and its value has been found to be 4.09 eV that is slightly at higher side reported for CeO₂ by various workers (Miao et al., 2005; Patsalas et al., 2002) suggesting the formation of disordered CeO₂ thin film (Dewan et al., 2007).

3.2. FTIR studies

Fig. 1(a) and (b) shows the FTIR spectra for CeO₂/Pt electrode and GOx/CeO₂/Pt bio-electrode respectively. Deposition of CeO₂ film on a Pt surface has been indicated by the presence of sharp and intense bands at 542 and 441 cm⁻¹ (Fig. 1(a)) wherein 542 cm⁻¹ peak may be attributed to the T_{1U} longitudinal phonon frequency and the 441 cm⁻¹ peak to the T_{2G} triply degenerate phonon frequency of CeO₂ (Verma et al., 2006). In the FTIR spectra of GOx/CeO₂/Pt bio-electrode (Fig. 1(b)), appearance of additional absorption bands at 1547, 1659 and 3285 cm⁻¹ corresponding to the amide bond present in glucose oxidase indicate the immobilization of GOx on the CeO₂ surface.

3.3. AFM studies

In Fig. 2(a) and its inset, AFM image of the as-deposited CeO₂ thin film reveals the formation of rough surface morphology with uniformly distributed nanopores. The roughness of the film surface (average root mean square roughness), an important parameter for sensing application that plays a basic role in the charge transfer capacity (Avellaneda et al., 2008) has been estimated for CeO₂ film and has been found to be about 3 nm. The value of the observed

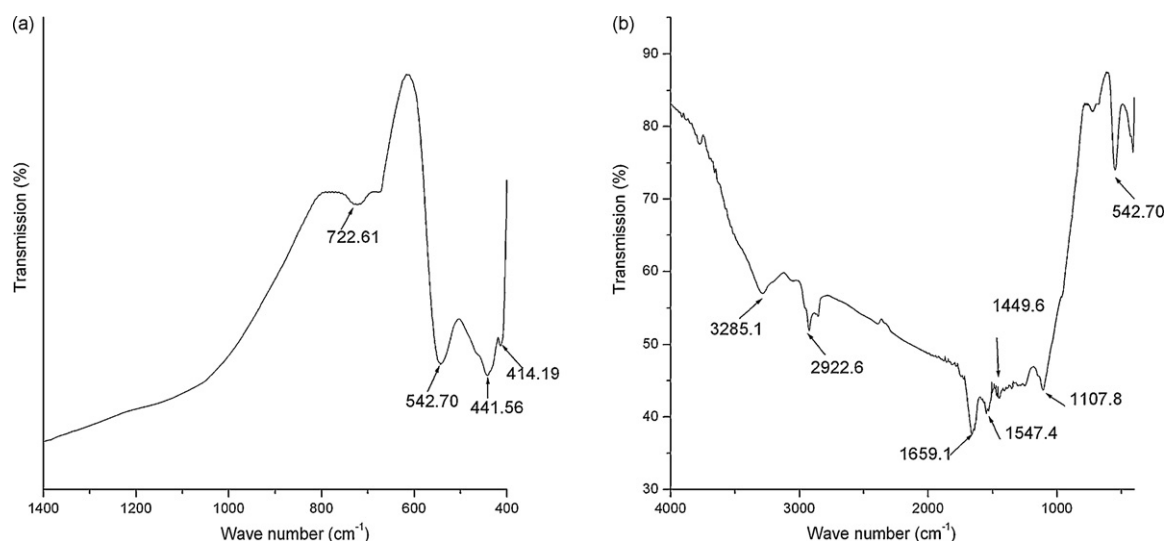


Fig. 1. FTIR spectra of (a) CeO_2 film and (b) GOx/CeO_2 film.

roughness indicates nanoporous morphology of the film. Further the single slope observed in the curve of bearing ratio plot (not shown) reveals homogenous morphology in the CeO_2 film. In the AFM micrograph of $\text{GOx/CeO}_2/\text{Pt}$ bio-electrode (Fig. 2(b)) and its inset, presence of uniformly distributed globular structure in prepared $\text{GOx/CeO}_2/\text{Pt}$ bio-electrode along with an increase in its average rms roughness to ~ 30 nm indicates the successful immobilization of GOx on the disordered surface of CeO_2 film.

3.4. DPV studies

The DPV voltammogram was recorded for CeO_2/Pt electrode after the pretreatment (inset Fig. 3(a)). An oxidation peak is observed at 0.33 V, which is found to be invariant with repeated scans and even on addition of different concentrations of glucose in the buffer solution. The oxidation peak may be attributed to the redox property of CeO_2 (Chettibi et al., 2006). However, when glucose oxidase (GOx) was immobilized on the CeO_2 matrix the oxidation current was found to decrease due to the non-conducting nature of the macro-molecular enzyme (inset Fig. 3(a)).

For estimation of glucose concentration DPV studies of $\text{GOx/CeO}_2/\text{Pt}$ bio-electrode have been carried out in PBS buffer (50 mM, pH 7.0) in the voltage range 0–0.65 V (Fig. 3(a)). The bio-electrode is kept for about 20 s in glucose solution for enzymatic

reaction prior to recording the DPV voltammogram. An oxidation peak is observed at 0.33 V, which is stable with repeated number of scans and the oxidation current is found to increase continuously with an increased glucose concentration over the range 0–300 mg/dl. The absence of peak for H_2O_2 and the observation of oxidation peak at 0.33 V suggest the two possible mechanistic pathways for electron generation (Scheme 1). The mechanism in path A depends on the interesting redox property of CeO_2 . Oxygen atoms in the CeO_2 unit leave the lattice site easily giving rise to a large variety of non-stoichiometric oxides with the two limiting cases CeO_2 and Ce_2O_3 . Ceria is able to change reversibly from Ce^{4+} to Ce^{3+} under reducing condition and vice versa (Chettibi et al., 2006). Moreover, the absence of oxidation peak of H_2O_2 clearly suggests that the CeO_2 matrix is acting as a better electron acceptor, over molecular oxygen, from the reduced enzyme (Matharu et al., 2007). As shown in path A (Scheme 1), CeO_2 might be acting as direct electron acceptor from the reduced enzyme. On electron acceptance CeO_2 gets reduced, that on re-oxidation during DPV scan, results in the peak at 0.33 V. In the other pathway i.e. path B, the electron generation might be taking place via H_2O_2 production. The generated H_2O_2 react with cerium oxide, causing its reduction. The reduced CeO_2 results in an oxidation peak at 0.33 V during DPV scan. However, the reaction of CeO_2 with H_2O_2 is known to occur in highly acidic media (Sigler and Masters, 1957). In the present study

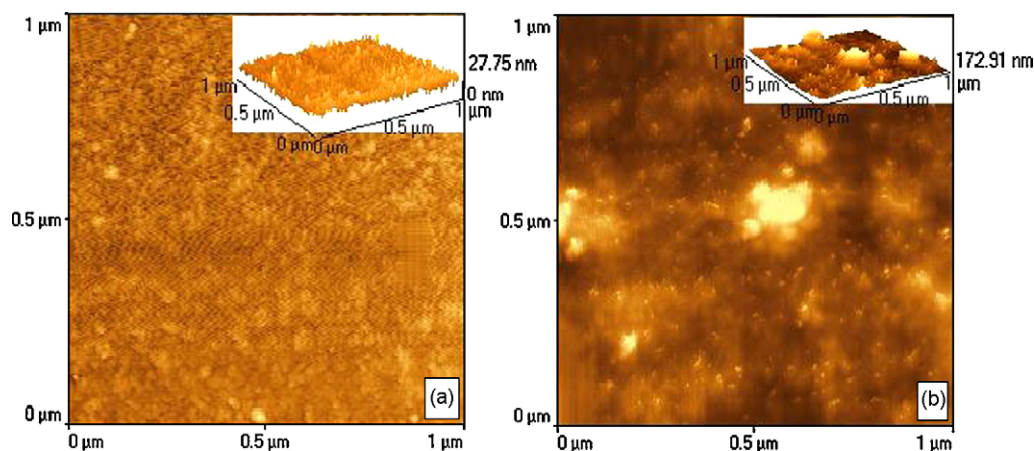


Fig. 2. AFM micrographs of (a) CeO_2 thin film ($1\ \mu\text{m} \times 1\ \mu\text{m}$), (b) GOx immobilized on CeO_2 matrix ($15\ \mu\text{m} \times 15\ \mu\text{m}$) with respective three dimensional picture as inset.

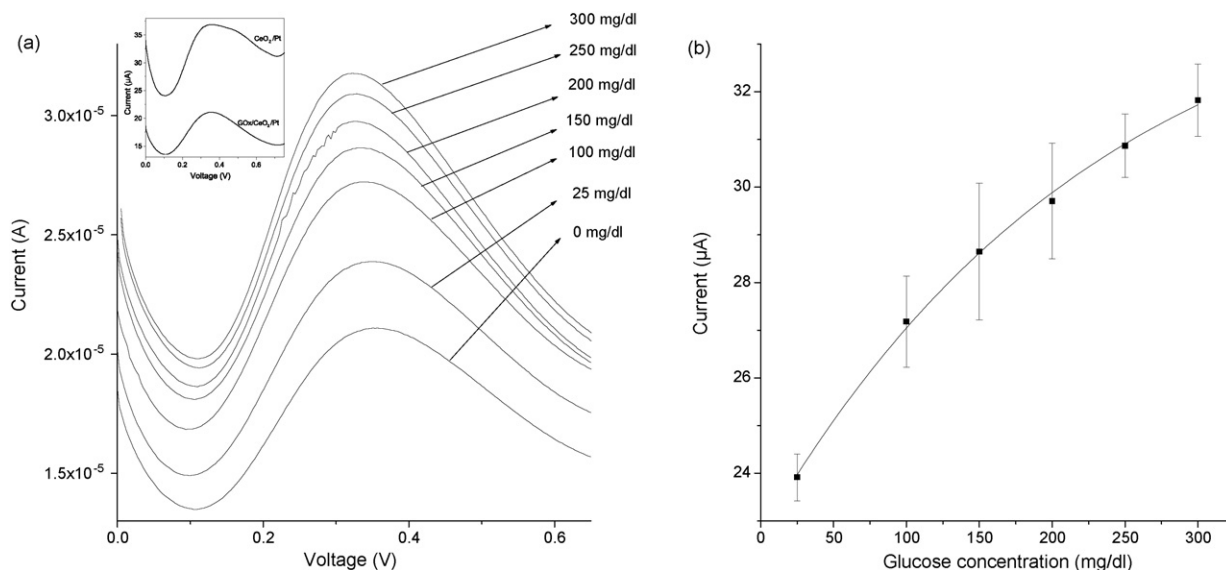


Fig. 3. (a) Amperometric response of GOx/CeO₂/Pt bio-electrode with glucose concentration (inset: DPV voltammogram of CeO₂/Pt and GOx/CeO₂/Pt electrodes) (b) Linear curve of GOx/CeO₂/Pt bio-electrode with glucose concentration.

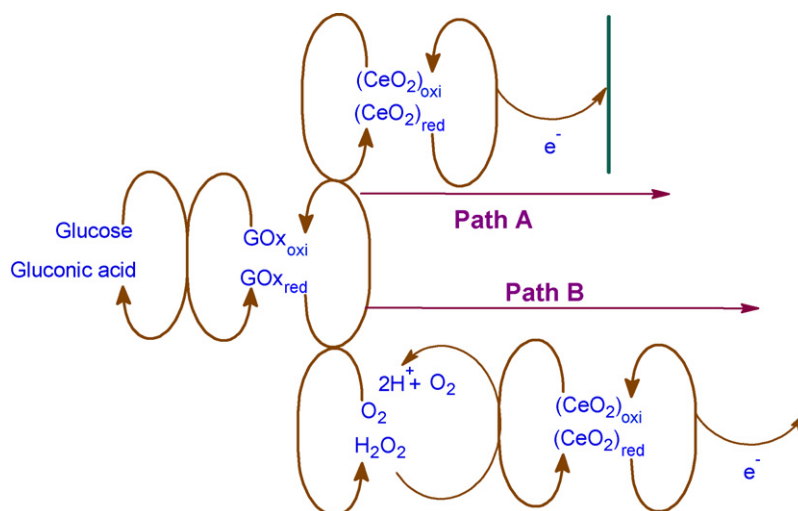
the experiments have been carried out in PBS buffer at pH 7.0 and therefore the possibility of path B is negligible. Thus it appears that reaction occurs via path A with PLD deposited CeO₂ acting as the electron acceptor over the oxygen and helping in the fabrication of the mediator less glucose biosensor.

Fig. 3(b) shows the variation of oxidation current measured at a fixed voltage of 0.33 V as a function of glucose concentration. The observed linear response as a function of glucose concentration indicates that the prepared bio-electrode can be efficiently used to detect glucose over the concentration range 25 to 300 mg/dl. The results of triplicate sets indicated by error bars (Fig. 3(b)) reveal the reproducibility of measurements within $\pm 5\%$, and show the higher reliability of prepared bio-electrode for glucose detection.

3.5. Estimation of Michaelis-Menten kinetic parameters (K_m^{app})

The Michaelis-Menten kinetic parameter (K_m^{app}) of enzymatic reaction, that determines the affinity of enzyme for its substrate, has been estimated using Hanes plot i.e. graph between [substrate concentration] and [substrate concentration/current]

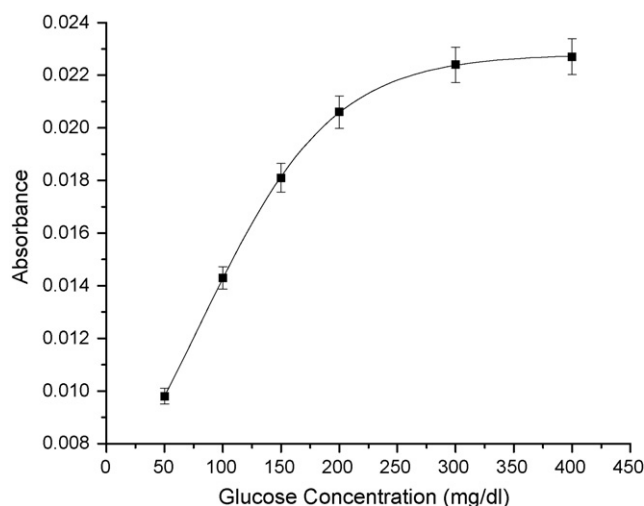
(Walker, 2000). The value of K_m^{app} is found to be about 1.01 mM for the immobilized GOx and depends on various factors such as matrix and the method of immobilization of enzymes, that could bring different conformational changes in the enzyme structure as the enzyme kinetics is environment sensitive (Singh et al., 2007; Kouassi et al., 2005). The small K_m^{app} value indicates increased affinity of GOx for its substrate. The observed low value of K_m^{app} in the present investigations for glucose (Table 1) indicates the advantage of nanoporous CeO₂ matrix as compared to other oxides or polymer matrices for enzyme immobilization and can be attributed to direct electron transfer through Ce³⁺/Ce⁴⁺ redox couple and to the favorable conformational changes in enzyme. Being a nanostructure the matrix provides high electron communication between the enzyme's active site and the electrode along with high surface area providing a suitable microenvironment that helps in effective immobilization of enzyme in large amount on the surface of the matrix. Moreover most of the matrices used in biosensors require cross-linkers for enzyme immobilization. This is not a necessity for oxide matrices, used in the present study, owing to their high IEP which make them suitable for physical immobilization. It may be



Scheme 1. Schematics of the Biochemical reaction at the GOx/CeO₂/Pt bio-electrode.

Table 1Comparison of the GOx/CeO₂/Pt bio-electrode with other matrices.

S. no.	Immobilization matrix	Method of immobilization	Linearity (mM)	K (mM)	Shelf life	References
1	ZnO nanorods	Physical	0.01–3.45	2.9	–	Wei et al. (2006)
2	Polypyrrole nanotubes	Physical	0.5–10	7.01	<2 week	Ekanayake et al. (2007)
3	Gold nanoparticles	Covalent	15	3.74	6 months	Pandey et al. (2007)
4	ZnO nanocomb	Physical	0.02–4.5	2.19	–	Wang et al. (2006)
5	CeO ₂	Physical	1.39–8.33	1.01	10 weeks	Present work

**Fig. 4.** UV-vis response as a function of glucose concentration.

noted that most of the oxide matrices like ZnO, TiO₂ require a mediator for electrochemical sensing. However, CeO₂ matrix is found to be advantageous for realization of mediator-less biosensor due to its excellent redox property.

3.6. Photometric response studies

UV-vis studies have been performed to calculate the apparent enzyme activity of GOx/CeO₂/Pt bioelectrode. The difference between the initial and the final value of the absorbance at 500 nm corresponding to the oxidation of dye, is plotted as a function of concentration of glucose (Fig. 4). It is clear that the GOx/CeO₂/Pt bio-electrode shows linearity from 50 to 300 mg/dl glucose concentration. The apparent enzyme activity has been calculated using the equation $a_{app}^{enz} (U\ cm^{-2}) = AV/\epsilon ts$, where A is the difference in absorbance before and after incubation, V is the total volume (3.17 cm³), ϵ is the millimolar extinction coefficient (7.5 for *o*-dianisidine at 500 nm), t is the reaction time (min) and s is the surface area (cm²) of the electrode. The apparent enzyme activity has been found to be $1.89 \times 10^{-2} U\ cm^{-2}$, indicating that 1.89×10^{-2} units of GOx are actively working on unit electrode surface area (1 cm²).

UV-vis measurements have been carried out to determine the shelf life of GOx/CeO₂/Pt bioelectrode. The shelf life studies carried out at regular interval of week for 10 weeks with 200 mg/dl glucose concentration (data not shown) indicate that the prepared bio-electrode retain about 80% of activity even after 10 weeks.

4. Conclusion

Nanoporous CeO₂ thin films deposited onto Pt coated glass by PLD have been used for immobilization of glucose oxidase, and successfully exploited for glucose biosensing. The prepared bio-electrode (GOx/CeO₂/Pt) using DPV studies shows a linear increase

in oxidation current at 0.33 V with increasing glucose concentration upto 300 mg/dl indicating the potential of PLD deposited CeO₂ matrix for realization of a mediator-less biosensor. The relatively low value of Michaelis-Menten constant (1.01 mM) shows enhanced enzymatic activity of GOx onto CeO₂/Pt surface. The shelf life of the prepared bio-electrode is found to be more than 10 weeks suggesting that nanoporous CeO₂ thin film provides an attractive matrix for fabrication of stable biosensor. The results clearly indicate that PLD deposited CeO₂ matrix is efficient for the realization of mediator-less glucose biosensor. The higher value of IEP of CeO₂ is advantageous and does not require any linker or functionalization for immobilization of enzymes. Further, the biocompatibility of CeO₂ nanoporous film deposited by PLD, and its possible integration with existing micro-electronics technology could lead to development of MEMS and ISFET based biosensors.

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Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.bios.2008.10.032.

References

- Andersson, D.A., Simak, S.I., Skorodumova, N.V., Abrikosov, I.A., Johansson, B., 2007. Appl. Phys. Lett. 90, 031909.
- Arya, S.K., Datta, M., Malhotra, B.D., 2008. Biosens. Bioelectron. 23, 1083–1100.
- Avellaneda, C.O., Berton, M.A.C., Bulhões, L.O.S., 2008. Sol. Energy Mater. Sol. Cells 92, 240–244.
- Chettibi, S., Wojcieszak, R., Boudjennad, E.H., Belloni, J., Bettahar, M.M., Keghouche, N., 2006. Catal. Today 113, 157–165.
- Corma, A., Atienzar, P., Garcia, H., Ching, J.Y.C., 2004. Nat. Mater. 3, 394–397.
- Dewan, N., Gupta, V., Sreenivas, K., Katiyar, R.S., 2007. J. Appl. Phys. 101, 084910.
- Ekanayake, E.M.I.M., Preethichandra, D.M.G., Kaneto, K., 2007. Biosens. Bioelectron. 23, 107–113.
- Gerblinger, J., Lohwasser, W., Lampe, U., Meixner, H., 1995. Sens. Actuators, B 26, 93–96.
- Goubin, F., Rocquefelte, X., Whangbo, M.H., Montardi, Y., Brec, R., Jobic, S., 2004. Chem. Mater. 16, 662–669.
- Gupta, V., Bhattacharya, P., Yuzuk, Y.I., Sreenivas, K., Katiyar, R.S., 2006. J. Cryst. Growth 287, 39–43.
- Kaushik, A., Khan, R., Solanki, P.R., Pandey, P., Alam, J., Ahmad, S., Malhotra, B.D., 2008. Biosens. Bioelectron. 24, 676–683.
- Kim, H., Yoon, S.H., Choi, H.N., Lyu, Y., Lee, W., 2006. Bull. Kor. Chem. Soc. 27 (1), 65–70.
- Kouassi, G.K., Irudayaraj, J., McCarty, G., 2005. J. Nanobiotechnol. 3, 1–9.
- Lee, T.W., Paik, U., Choi, S., Lee, S.H., Lim, H.S., Kim, C.J., 2000. J. Kor. Phys. Soc. 37, 721–725.
- Liao, C.W., Chou, J.C., Sun, T.P., Hsiung, S.K., Hsieh, J.H., 2006. IEEE Trans. Biomed. Eng. 53 (7), 1401–1408.
- Liu, G., Lin, Y., 2006. Electrochem. Commun. 8, 251–256.
- Matharu, Z., Sumanam, G., Arya, S.K., Singh, S.P., Gupta, V., Malhotra, B.D., 2007. Langmuir 23 (26), 13188–13192.
- Miao, J.J., Wang, H., Li, Y.R., Zhu, J.M., Zhu, J.J., 2005. J. Cryst. Growth 281, 525–529.
- Murray, E.P., Tsai, T., Barnett, S.A., 1999. Nature 400, 649–651.

- Pandey, P., Singh, S.P., Arya, S.K., Gupta, V., Datta, M., Singh, S., Malhotra, B.D., 2007. *Langmuir* 23, 3333–3337.
- Patsalas, P., Logothetidis, S., Metaxa, C., 2002. *App. Phys. Lett.* 81, 466.
- Qian, J., Suo, A., Yao, Y., Jina, Z., 2004. *Clin. Biochem.* 37, 155–161.
- Rodriguez, J.A., Ma, S., Liu, P., Hrbek, J., Evans, J., Perez, M., 2007. *Science* 318, 1757–1760.
- Rogers, E., 1997. *Handbook of Biosensors & Electronic Noses Medicine, Food, and the Environment*, 1st ed. CRC Press, USA.
- Sigler, P.B., Masters, B.J., 1957. *J. Am. Chem. Soc.* 79, 6353–6357.
- Singh, S.P., Arya, S.K., Pandey, P., Malhotra, B.D., Saha, S., Sreenivas, K., Gupta, V., 2007. *Appl. Phys. Lett.* 91, 063901.
- Suzuki, T., Kosacki, I., Anderson, H.U., 2002. *J. Am. Ceram. Soc.* 85, 1492–1498.
- Verma, A., Bakshi, A.K., Agnihotri, S.A., 2006. *Sol. Energy Mater. Sol. Cells* 90, 1640–1655.
- Viticoli, M., Curulli, A., Cusma, A., Kaciulis, S., Nunziante, S., Pandolfi, L., Valentini, F., Padeletti, G., 2006. *Mater. Sci. Eng., C* 26, 947–951.
- Walker, J.M., 2000. *Principles, Techniques of Practical Biochemistry*, 5th ed. Cambridge University Press, UK.
- Wang, J.X., Sun, X.W., Wei, A., Lei, Y., Cai, X.P., Li, C.M., Dong, Z.L., 2006. *Appl. Phys. Lett.* 88, 233106.
- Wei, A., Sun, X.W., Wang, J.X., Lei, Y., Cai, X.P., Li, C.M., Dong, Z.L., Huang, W., 2006. *Appl. Phys. Lett.* 89, 123902.
- Yu, B., Long, N., Moussy, Y., Moussy, F., 2006. *Biosens. Bioelectron.* 21, 2275–2282.
- Zhao, Z.W., Chen, X.J., Tay, B.K., Chen, J.S., Han, Z.J., Khor, K.A., 2007. *Biosens. Bioelectron.* 23, 135–139.