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Short communication

A novel non-enzymatic zinc oxide thin film based electrochemical recyclable strip with device interface for quantitative detection of catechol in water

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ABSTRACT

Catechol, one of the major effluents released by various chemical and metal processing industries, causes severe pollution of groundwater. Monitoring of catechol in water using cost-effective, handheld sensor is demanding for the safety of the environment. In this work, non-enzymatic zinc oxide thin film based electrochemical strip sensor is developed on conducting glass substrate for detection of catechol. The preparation of strip without employing standard Pt or Ag/AgCl electrodes and simply depositing ZnO through wet chemical process represents a cost-effective innovative technique. The ZnO thin film is characterized using field emission scanning electron microscope (FESEM), energy dispersive X-ray spectroscopy (EDS), atomic force microscopy (AFM) and grazing incidence X-ray diffractometer (GIXRD). Catechol is electrochemically detected by means of cyclic voltammetry and amperometry. A prominent redox peak of the developed strip attributed to the detection of catechol is observed at −0.26 V in cyclic voltammetry. The strip is integrated with readout meter and an algorithm is built based on the experimentally observed linear variation of amperometric current with catechol concentration. The quantitative detection performance is demonstrated by testing 0.1–12 ppm catechol solutions.

1. Introduction

Handheld electrochemical strip sensors are attractive as affordable, sensitive devices for instant monitoring of organic/inorganic/metallic analytes present in body fluids or in wastewater (Yang and Gao, 2018; Nie et al., 2010; Zhang and Liu, 2016; Xiao et al., 2016). Typical electrochemical strip sensors usually consist of working electrode (WE), counter electrode (CE) and reference electrode (REs) on single platform. The challenging part of developing electrochemical strip sensor is to identify as well as accommodate WE, CE and REs on an appropriate conducting substrate, which can produce a distinguishable signal under measurement. Several research efforts have already been undertaken to study the electrochemical interactions of diverse WEs with different target analytes. These WEs are mostly prepared by immobilizing sensing materials on metallic/standard conducting substrates (e.g. glassy carbon electrode (GCE)/Platinum (Pt)/Gold (Au) etc.) (Sheng et al., 2012; Sugita et al., 2013; Li et al., 2014; Zhang et al., 2004). The performances of these discrete WEs are usually studied with respect to standard reference (e.g. Ag/AgCl) and counter (e.g. Pt) electrodes within an electrochemical chamber (Wang et al., 2014; Maikap et al., 2016, 2018). In order to develop strip sensor, integration of discrete electrodes needs their dimensional, compositional and handling compatibility suitable for producing stable signal when exposed to target analyte. The development of strip sensors enabling detection of liquid phase analyte have been described elsewhere (Hossain et al., 2011; Tao et al., 2017). Recently, Tehrani and Bavarian have developed direct laser engraved graphene based strip for the detection of glucose in blood sample (Tehrani and Bavarian 2016). Pei et al. have reported copper-based microchip sensor for determination of zinc in blood serum (Pei et al., 2014). Zhang et al. have developed titania nanoparticle modified gold strip sensor for the determination of arsenic (III) (Zhang et al., 2016). Nevertheless, the sophisticated fabrication of microchip sensors, achieved mostly by using clean-room facilities, is rather expensive and requires the involvement of trained personnel (Ribeiro et al., 2010; Olney et al., 2014).

Phenolic contaminants are known as major effluents produced by various chemical and metal processing industries and cause severe pollution of groundwater (Rao et al., 2015). The acute exposure of

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catechol in humans may cause irregular breathing, muscle weakness and tremors, loss of coordination and even respiratory arrest at lethal doses (Mandani et al., 2013; Maleki et al., 2017). Therefore, the monitoring of catechol becomes of fundamental importance for the safety of the environment. The detection of phenolic compounds usually requires sophisticated and costly spectro-photometric techniques (Nagaraja et al., 2001). Alternatively, enzyme immobilized WEs for the detection of phenolic hazards (including catechol) have been also studied (Rodríguez-Delgado et al., 2015; Gul et al., 2017; Maleki et al., 2017; Zhao et al., 2009; Yue et al., 2015; Lu et al., 2006; Whyte et al., 2014; Hill et al., 2003). Nonetheless, the development of non-enzymatic WEs for the electrochemical detection of phenolic hazards is also found elsewhere (Han et al., 2014; Yin et al., 2011). As compared to non-enzymatic sensors, enzymatic sensors are usually less stable at room temperature and as a consequence enzyme immobilized electrodes are not appropriate for field application.

In the present work, a simple technique is employed allowing the preparation of a three-electrode (WE, CE, RE) platform on single fluorine doped tin oxide (FTO) based conducting glass substrate. Subsequently, the developed three-electrode platform is used to prepare a non-enzymatic ZnO WE based strip sensor for the detection of catechol. The performances of developed non-enzymatic strip sensors are studied through cyclic voltammetry (CV) and amperometry. The strip is integrated with readout meter and an algorithm is built based on the experimentally observed linear variation of amperometric current with catechol concentration. The sensor can quantitatively detect (0.1–12 ppm) catechol in water sample. The strips can be easily recycled by wet chemical treatment. The detection of catechol using ZnO and conducting glass based strip sensor described in this work, represents a novel and promising approach, since no electrochemical strip for catechol detection have been implemented up-to-date.

2. Material and methods

Three-electrode platforms are prepared on commercial FTO coated glass substrates (Resistivity 7 Ω/sq, FTO layer thickness 150–160 nm procured from Dyesol, Australia). In order to prepare the strip, a typical FTO coated glass substrate (2 cm × 2 cm) is separated in three sections for preparing WE (1 cm × 2 cm), CE (0.5 cm × 2 cm) and RE (0.5 cm × 2 cm) by creating in between line scratches for physically separating the electrical connection.

A schematic representation of the fabrication procedure of ZnO-WE based strip is shown in Fig. 1. ZnO thin layer is grown on the pre-selected section (WE part) of FTO substrate using a dip coater (Xdip-SV1, Apex Instruments, India) at 200 mm/min dipping and withdrawing speed, in a solution (concentration: 0.5 M) prepared by dissolving zinc acetate dehydrate and triethanolamine in 2-methoxy ethanol. The film is slowly dried up and kept at 100 °C for 10 min. Subsequently it is heated at 200 °C for 2 h. During the coating procedure, a teflon tape is used as mask for a selective deposition of the film. Bare FTO surface is used as CE and RE. A photograph of the prepared strip along with the optical microscope image of the area in proximity of the line scratch (width ~50 μm) are shown in Fig. 1.

The surface morphology of thin ZnO layer is assessed by using Field Effect Scanning Electron Microscope (FESEM) (Sigma HD, Zeiss, Germany) and atomic force microscopy (AFM) (Nanosurf C3000, Switzerland). The crystalline nature of the film is investigated by Grazing incidence X-ray Diffractometer (GIXRD) (X-PERT PRO Panalytical, Netherland).

The electrochemical response of the developed strip is investigated through Cyclic voltammetry (CV), amperometry and electrochemical impedance spectroscopy (EIS) employing an electrochemical workstation (SP150, Biologic instruments, France).

3. Results and discussion

Fig. 2(a) and (b) show the FESEM image and the energy dispersive X-ray spectrum (EDS) of ZnO layer grown on FTO based substrate respectively. FESEM image highlights a homogenous surface of ZnO layer, with minimum porosity. EDS confirms the presence of Zn and O in the film. The peak of 'Sn' in EDS originates from FTO based glass substrate. The X-Ray diffraction pattern of the ZnO layer coated over FTO substrate is presented in Fig. 2(c). The characteristic XRD peaks for ZnO (representing (100) (002) (101) planes) and FTO (marked '*') are shown in the figure. Fig. 2(d) represents 2D and 3D AFM images of the developed films. As observed in the developed ZnO film is characterized by a surface roughness within the range of 90–120 nm.

Electrochemical impedance spectrum (EIS) of the bare FTO and ZnO coated FTO is used to confirm alternatively the presence of ZnO film over the FTO substrate. Fig. 2(e) shows the Nyquist plots of EIS for the bare FTO and ZnO coated FTO in presence of 4 μM catechol solution. The lower resistance of ZnO coated FTO as compared to the bare FTO in EIS indicates the presence of ZnO layer on the FTO substrate. The CV plot in Fig. 2(f) compares the electrochemical response of the developed strip in the absence and presence of catechol kept within phosphate buffer medium (pH~7). In absence of catechol, no distinguishable redox peak is observed. However, when exposed to a catechol solution the strip shows prominent redox peak at −0.26 V. The redox interaction of catechol on ZnO surface has been discussed in our published article (Maikap et al., 2016), where we reported that ZnO catalyzes the oxidation of catechol to o-quinone. Furthermore, other groups have shown a similar catalytic activity of ZnO for the electrochemical transformation of organics (Nair et al., 2011).

Here, the concentration (2, 4 and 6 μM) of catechol is varied by the successive addition of fixed amount (50 μL) catechol solution into the phosphate buffer. It is worth noticing that by increasing the catechol concentration, the intensity of redox peak current at first increases, but decreases at higher concentration (shown in inset of Fig. 2(f)).

The amperometry experiments are carried out by applying threshold voltage (−0.26 V) in the reference electrode. Fig. 2(g) represents the amperometric response of the developed strip when the catechol concentration is varied from 0 to 8 μM. As determined from the plot, a linear response is observed when the concentration of catechol remains within ~6 μM. However, such a linear trend is not followed when the concentration of catechol is increased (~8 μM). The interaction of slightly basic zinc oxide with acidic catechol may deteriorate the performance of the strip since it is exposed in catechol solution for a long time during CV and amperometry. We have recycled the used strip by keeping it in 2 N HCl solutions for 5 h followed by rinsing with distilled water and successive growth of a ZnO layer as WE. The recycled strip shows similar redox potential (at −0.26 V) as obtained from the original test strip (shown in Fig. 2(h) when kept within 4 μM catechol solution.

The developed non-enzymatic ZnO thin film based strip is interfaced to a readout meter for quantitative real time detection of catechol. The readout meter is calibrated in accordance to the experimentally observed linear variation of amperometric current with catechol concentration.

A microcontroller with a 2.8″ touch shield display (Arduino, Italy), programmed using a C++ code, is used to implement the read out meter.

Fig. 3 shows the schematic sketch (a) and the digital image (b) of the developed assembly of the typical electrochemical strip and readout meter. The working and counterpart of the strip are connected with analogue to digital (ADC) and ground (GND) ports of the controller respectively. The reference part of the strip is employed to apply the redox potential. In order to detect catechol in water, chemical activation of the strip is achieved by applying redox potential and a constant current of 100 mA. A 12 Voltage supply is partitioned into two ports to provide power supply to the display-controller assembly (9 V) and

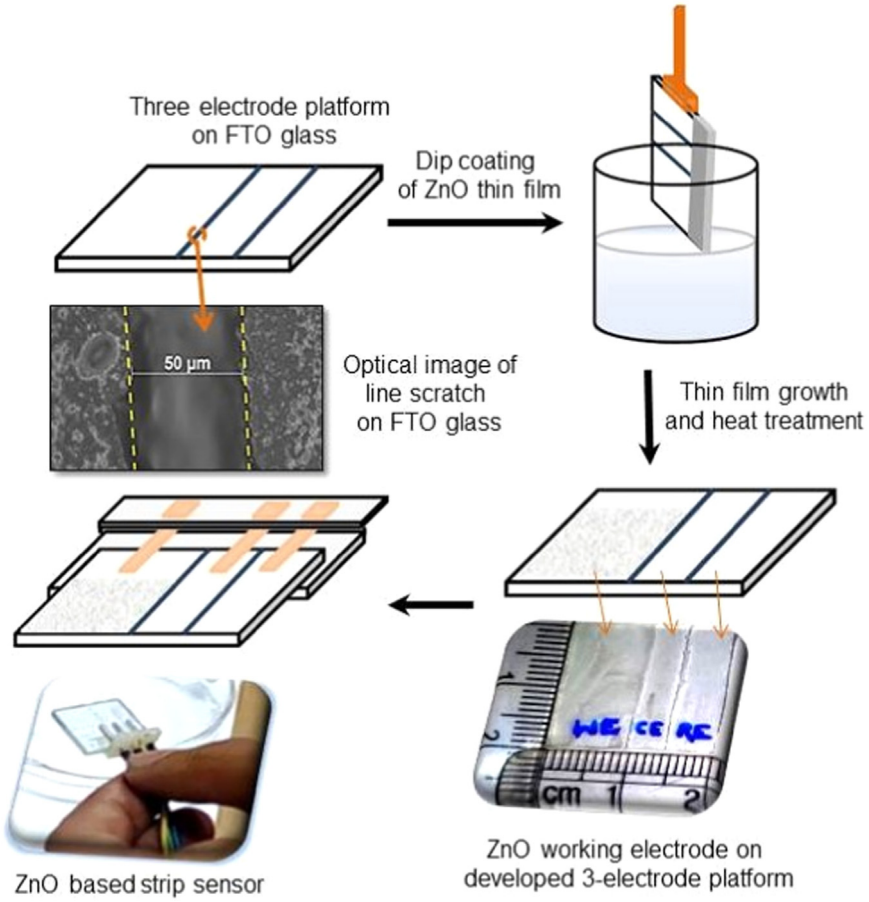

Fig. 1. Schematic procedure to prepare sensing strip along with optical image of line scratch on FTO glass and digital image of the developed strip.

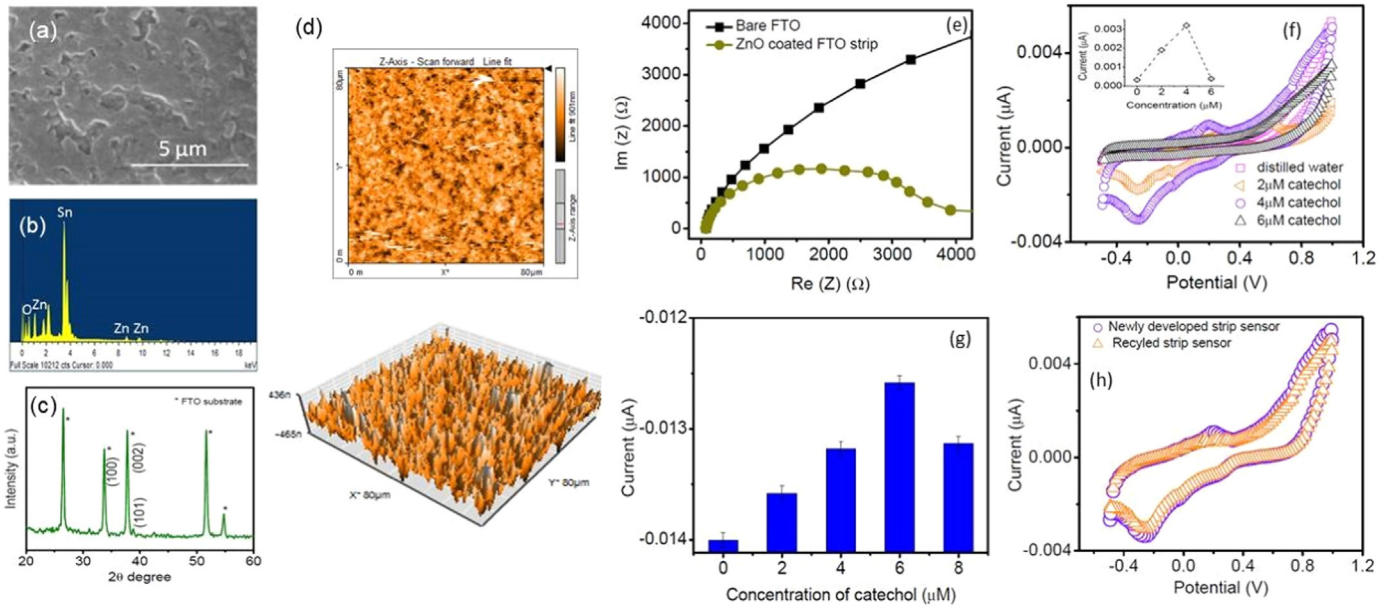

Fig. 2. (a) FESEM (b) EDS (c) XRD (d) AFM of the ZnO film coated on FTO substrate. (e) EIS of bare FTO and ZnO coated FTO substrate (f) CV plot of developed strip in presence of distilled water and catechol solution. Inset shows the variation of redox peak current with catechol concentration. (g) Amperometric response of the strip with the variation of catechol concentration. (h) CV of new and recycled test strip in presence of 4 µM catechol.

activation potential to the strip.

Fig. 3(c) shows the real-time test results of the developed sensing device in presence of distilled water and different known concentrations (0.1–12 ppm) of catechol solutions. We summarize in Table S1 of Supplementary information the real-time experimental results, for the freshly prepared strips, prepared in eight different batches, under the exposure of 0.1, 2, 5, 10 and 12 ppm catechol. The relative standard deviations (RSD) are found ~19, 6, 3, 2, 6% for 0.1, 2, 5, 10, 12 ppm

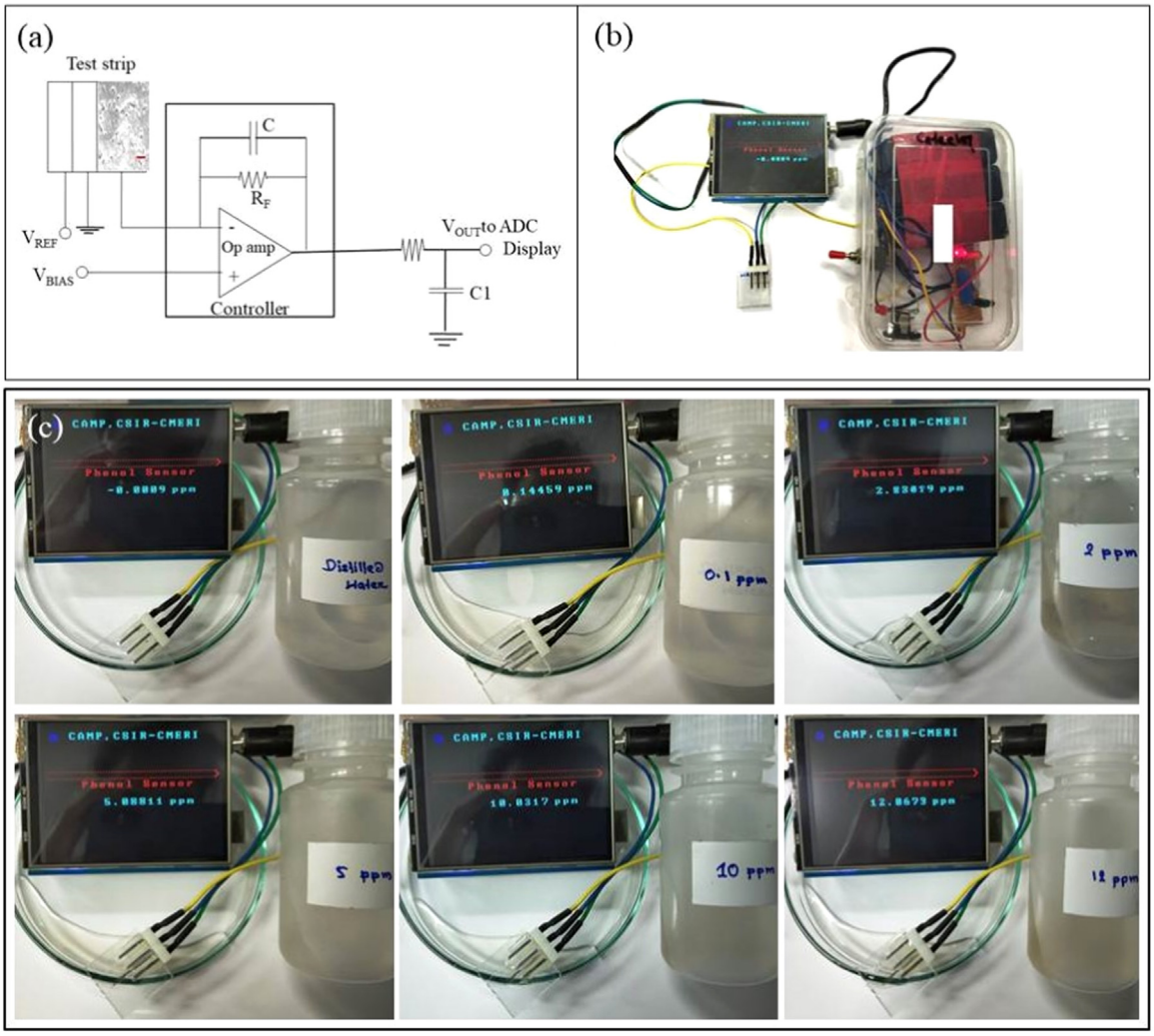

Fig. 3. (a) Schematic assembly of the electrochemical strip and readout meter. (b) Digital image of the integrated strip and readout meter. (c) Real-time test results of the developed typical sensing device in presence of distilled water and known concentrations (0.1, 2, 5, 10 and 12 ppm) of catechol.

catechol. As observed, the RSD value for detection of 0.1 ppm catechol is considerably higher than the other studied concentrations. It has also been found that the RSD value for the experimental results increases for 12 ppm catechol. We have compared the performance of freshly prepared and recycled strip sensor for the detection of 5 ppm catechol (summarized in Table 2 of Supplementary information). It is worth noticing that the performance of the strip consecutively recycled for 4 times is coherent (RSD value 8%) with the freshly prepared sensor.

An extensive comparison with the developed sensor and other enzymatic and non-enzymatic electrochemical sensor for the detection of catechol (summarized in Table S3) is provided in the Supplementary information. It can be stated that majority of the existing sensors, unlike ours, are fabricated on standard GCE and employ standard Pt counter and Ag/AgCl reference electrode (Han et al., 2014; Aravindan et al., 2017; Apetrei et al., 2013; Portaccio et al., 2010; Wang et al., 2008; Chen et al., 2015; Nazari et al., 2015). Due to an altogether better receptor and transduction properties, some of the reported implementations exhibit a superior catechol detection limit compared to the present work. Although, the developed system combined with readout meter and the recyclable, non-enzymatic strip is advantageous as a portable alternative to current sensors for ppm level detection of catechol present in water.

4. Conclusions

Zinc oxide based non-enzymatic and recyclable strip sensor for the electrochemical detection of catechol in water is developed on conducting glass supporting a three-electrode configuration. The performance of the developed sensor is verified through standard electrochemical techniques like cyclic voltammetry and amperometry. In cyclic voltammetry, the strip shows distinguishable redox peak at −0.26 V which is used as input for amperometry. The linear dependency of amperometric current with catechol concentration is used to calibrate the algorithm, thus enabling the integration of the strip with read-out meter. Functional activities of the integrated strip is verified by testing various concentrations (0.1–12 ppm) of catechol. The detection limit of the developed sensor can be further enhanced by using other different suitable materials employing similar conducting glass based strip hereby reported.

CRediT authorship contribution statement

A. Maikap: Conceptualization, Data curation, Formal analysis, Software, Validation, Visualization, Writing - original draft. **K. Mukherjee:** Conceptualization, Investigation, Supervision, Methodology, Writing - review & editing, Funding acquisition. **B. Mondal:** Funding acquisition, Resources, Supervision, Writing - review & editing. **N. Mandal:** Resources, Funding acquisition, Writing - review & editing. **A.K. Meikap:** Supervision, Writing - review & editing.

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Declaration of interests

None.

Appendix A. Supporting information

Supplementary data associated with this article can be found in the online version at doi:10.1016/j.bios.2018.12.033.

References

Apetrei, I.M., Rodriguez-Mendez, M.L., Apetrei, C., de Saja, J.A., 2013. Sens. Actuator B Chem. 177, 138–144.
Aravindan, N., Preethi, S., Sangaranarayanan, M.V., 2017. J. Electrochem. Soc. 164 (6), B274–B284.
Chen, X., Li, D., Li, G., Luo, L., Ullah, N., Wei, Q., Huang, F., 2015. Appl. Surf. Sci. 15, 444–452.
Gul, I., Ahmad, M.S., Naqvi, S.M.S., Hussain, A., Wali, R., Farooqi, A.A., Ahmed, I., 2017. J. Appl. Biol. Biotechnol. 5, 72–85.
Han, H.S., You, J.M., Seol, H., Jeong, H., Jeon, S., 2014. Sens. Actuator B Chem. 193, 623–629.
Hill, H.A.O., Wong, L.L., Xie, W., Jones, J.P., 2003. US Patent. US6511592B1.
Hossain, M.M., Faisal, S.N., Kim, C.S., Cha, H.J., Nam, S.C., Lee, H.J., 2011. Electrochem. Commun. 13, 611–614.
Li, H., Li, R., Worden, M.R., Barton, C.S., 2014. ACS Appl. Mater. Interfaces 6, 6687–6696.
Lu, Y., Chen, Y., Zhang, Z., 2006. US Patent. US7989851 B2.
Maikap, A., Mukherjee, K., Mondal, B., Mandal, N., 2016. RSC Adv. 6, 64611–64616.
Maikap, A., Mukherjee, K., Mandal, N., Mondal, B., Meikap, A.K., 2018. Electrochim. Acta 264, 150–156.
Maleki, N., Kashanian, S., Maleki, E., Nazari, M., 2017. Biochem. Eng. J. 128, 1–11.
Mandani, P., Desai, K., Highland, H., 2013. ISRN Toxicol. 397524.
Nagaraja, P., Vasantha, R.A., Sunitha, K.R., 2001. J. Pharm. Biomed. Anal. 25, 417–424.
Nair, M.G., Nirmala, M., Rekha, K., Anukaliani, A., 2011. Mater. Lett. 65, 1797–1800.
Nazari, M., Kashanian, S., Rafipour, R., 2015. Spectrochim. Acta A Mol. Biomol. Spectrosc. 145, 130–138.
Nie, Z., Nijhuis, C.A., Gong, J., Chen, X., Kumachev, A., Martinez, A.W., Narovlyansky, M., Whitesides, G.M., 2010. Lab Chip 10, 477–483.
Olney, D., Fuller, L., Santhanam, K.S.V., 2014. Sens. Actuator B Chem. 191, 545–552.
Pei, X., Kang, W., Yue, W., Bange, A., Heineman, W.R., Papautsky, I., 2014. Anal. Chem. 86, 4893–4900.
Portaccio, M., Tuoro, D.D., Arduini, F., Lepore, M., Mita, D.G., Diano, N., Mita, L., Moscone, D., 2010. Biosens. Bioelectron. 25, 2003–2008.
Rao, C.V., Rivenson, A., Simi, B., Reddy, B.S., 2015. Cancer Res. 55, 259–266.
Ribeiro, C., Brogueira, P., Lavareda, G., Carvalho, C.N., Amaral, A., Santos, L., Morgado, J., Scherf, U., Bonifácioi, V.D.B., 2010. Biosens. Bioelectron. 26, 1662–1665.
Rodríguez-Delgado, M.M., Alemán-Nava, G.S., Rodríguez-Delgado, J.M., Dieck-Assad, G., Martínez-Chapa, S.O., Barceló, D., Parra, R., 2015. Trends Anal. Chem. 74, 21–45.
Sheng, Z.H., Zheng, X.Q., Xu, J.Y., Bao, W.J., Wang, F.B., Xi, X.H., 2012. Biosens. Bioelectron. 34, 125–131.
Sugita, T., Hiramatsu, K., Ikeda, S., Matsumura, M., 2013. ACS Appl. Mater. Interfaces 5, 2580–2584.
Tao, L.Q., Zhang, K.N., Tian, H., Liu, Y., Wang, D.Y., Chen, Y.Q., Yang, Y., Ren, T.L., 2017. ACS Nano 11, 8790–8795.
Tehrani, F., Bavarian, B., 2016. Sci. Rep. 6, 27975.
Wang, C., Du, J., Wang, H., Zou, C., Jiang, F., Yang, P., Du, Y., 2014. Sens. Actuator B Chem. 204, 302–309.
Wang, S., Tan, Y., Zhao, D., Liu, G., 2008. Biosens. Bioelectron. 23, 1781–1787.
Whyte, L., Sloss, S., Whitehead, N., McColl, D. Smith, A., 2014. US Patent. US 8877023 B2.
Xiao, F., Wang, L., Duan, H., 2016. Biotechnol. Adv. 34, 234–249.
Yang, Y., Gao, W., 2018. Chem. Soc. Rev. https://doi.org/10.1039/c7cs00730b.
Yin, H., Zhang, Q., Zhou, Y., Ma, Q., Liu, T., Zhu, L., Ai, S., 2011. Electrochim. Acta 56, 2748–2753.
Yue, W., Zhiqiang, Z., Cuiping, W., Yong, C., Fei, L., Hongmin, J., Qingtao, M., 2015. China Patent. CN104391021A.
Zhang, D., Liu, Q., 2016. Biosens. Bioelectron. 75, 273–284.
Zhang, M., Smith, A., Gorski, W., 2004. Anal. Chem. 76 (17), 5045–5050.
Zhang, X., Zeng, T., Hu, C., Hua, S., Tian, Q., 2016. Anal. Methods 8, 1162–1169.
Zhao, J., Wu, D., Zhib, J., 2009. Bioelectrochemistry 75, 44–49.