



Optical fibre based non-enzymatic glucose sensing over Cu²⁺-doped polyaniline hybrid matrix

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ABSTRACT

The opto-chemical glucose sensing over cupric ion doped polyaniline (Cu²⁺/PANI) hybrid polymer matrix coated glass rod based optode has been demonstrated. Cu²⁺/PANI hybrid matrix was synthesized by *in situ* chemical polymerization of intrinsically functionalized aniline. Furthermore, developed optode has been explored for direct oxidation of glucose on Cu²⁺/PANI hybrid matrix for non-enzymatic glucose sensing employing O-dianisidine indicator system. The proposed glucose sensor works well in range of 50 mg/dL–200 mg/dL with response time of 15 s in artificial as well as in biological samples along with 40 days of lifespan.

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1. Introduction

The glucose monitoring is an essential need of clinical diagnostics for proper treatment of diabetes mellitus and various damaged body organs like heart, kidney, eyes, and blood vessels [1–3]. It also requires in biotechnology and food processing industries for control of product quality and optimization of a processes [4]. As result, development of reliable, responsive and selective glucose sensor has attracted huge attention of scientists and many approaches like optical [5,6], electrical [7–9] and luminescence [10] are still in progress, while, development of glucose sensor has been focused area of research since 1960s.

Generally glucose sensors employ glucose oxidase (GOx) to catalyses the oxidation of b-D-glucose to d-gluconolactone and successively produces hydrogen peroxide and hydronium ion [11,12]. But greatest drawback of this sensor is lack of stability due to the intrinsic nature of enzymes [13,14]. GOx loses activity at high temperature (above 40 °C) and after exposure to hard chemicals like strong acid and base [15,16]. To address this problem, many attempts have been made to develop enzyme free glucose sensors [17,18]. The nonenzymatic sensors works on direct oxidation

of glucose on different metal catalysts, which changes electrical and optical properties, The different catalysts reported in this regards are platinum [19], gold [20], nickel [21], copper [22], CuO [23] and carbon cloth [24]. The limitation of enzyme-free sensor is poor sensitivity, selectivity, biocompatibility and chemical poisoning due to adsorbed species [25]. Chen et al. reported that the use nano materials improve the sensitivity and selectivity of non enzymatic sensor [26]. The limitation can be also overcome by using metallic alloy (Pt₂Pb), since the alloys are insensitive towards interfering radical and shows better catalytic properties than pure metals [27,28]. Gerard et al. has reviewed the biocompatible behaviour in conducting polymer suitable for bio-device, which indicates that combining the metallic centres with polymeric matrix may improve the technique [29]. On the other hand, use of supports materials enhance the electron transfer ability, stabilisation of oxidation state, increase the surface area and controls the agglomeration [30]. Furthermore, polyaniline have attracted intensive interest due to its excellent electronic properties, stability such as π-conjugated backbone facilitating electron transfer and dopant dependent electrical and catalytic properties [31,32]. Kaushik et al. [33] has used metal polyaniline composite for efficient electrocatalysis of glucose for glucose estimation but many parameters has been not reported. The chemically modified polyaniline has been also used for oxidation of methanol, ethanol, ascorbic acid and other C-1 molecules for different applications [34].

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In this context, optical methods of sensing bears many advantageous features like immunity to electromagnetic interference, multiplexing, remote sensing capabilities and does not requires a reference electrode [35–38]. Optical sensing also bears certain exclusive advantages like monitoring of glucose in the case of patient with heart pacemaker under the interaction of strong electromagnetic field used in cancer therapy. Optical method also enabled to sense in deeper lying or less accessible region of the body [3,39]. Muley et al. [40] has modified optical fibre by coating polyaniline as support matrix due to its proton coupled redox chemistry and its resulting pH dependent properties. The modified optical fibre was used for glucose sensing as enzyme electrodes after immobilization GOx [41]. Here, the present paper combines selective catalytic behaviour of copper with polyaniline to generate well arranged glucose catalytic sites. The catalytic property of hybrid polymeric matrix was used for oxidation of glucose. The quantity of oxidized products were monitored using dyes based indicator system to sense the glucose in prepared aqueous solution as well as biological fluid. It was found that optical fibre based sensor reported here could provide efficient responses for glucose sensing with favourable selectivity and reliability to commercial sensor.

2. Experimental

2.1. Material

Aniline (99.5%), cupric nitrate (99.5%), ammonium per sulphate (99.5%) and glucose were purchased from E-Merck and used without any further purification. Further, doubled distilled water and AR grade solvents were used during entire investigation.

2.2. Synthesis of $\text{Cu}^{+2}/\text{PANI}$ composites

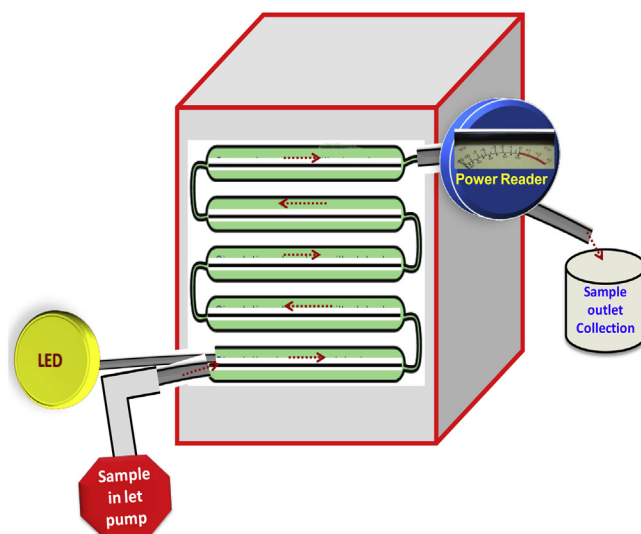
Initially 500 mg $\text{Cu}(\text{NO}_3)_2 \cdot 3\text{H}_2\text{O}$ was mixed in 5 mL aniline solution in 25 mL methanol. The resulting mixture was stirred for 30 min at room temperature on a magnetic stirrer. In thus obtained solution 0.5 M aqueous ammonium per sulphate (APS) solution was added drop by drop with constant stirring at ($\sim 5^\circ\text{C}$) temperature maintained by ice bath. Finally, dark blackish green colour precipitate was obtained. The precipitate was filter using watt man no. 1 filter paper and dried in vacuum oven at 60°C . The obtained matrix was purified for oligomers by chemical extraction method.

2.3. Characterization

The prepared samples were characterized by Fourier Transform Infrared spectrometer (FTIR, Bruker, model Alpha) in KBr phase and X-ray diffraction (XRD) technique using Rigaku Rotaflex, RAD/Max–200 B instrument at a scanning rate of 2° per min. SEM photographs were taken with the help of Hitachi-3700, Scanning Electron Microscope (SEM) after coating with gold. The UV–vis spectra were recorded on UV-260, Shimadzu UV spectrometer.

2.4. Catalytic behaviour of composite

Glucose oxidizing behavior of $\text{Cu}^{+2}/\text{PANI}$ was studied by recording the UV–vis spectra of glucose solution as such and after treating with prepared composite. For this purpose stock solution of glucose with 150 ppm concentration was made in triple distilled water. Five mL of this solution was kept in two beakers of 25 mL capacity and labelled as beaker A and B. In beaker A, a pellet of $\text{Cu}^{+2}/\text{PANI}$ with 13 mm diameter and 0.2 mm thickness prepared by hydraulic press applying pressure of 10 tons was dipped for 5 min. However, beaker B was considered as a reference solution. Further, 01 mL glucose

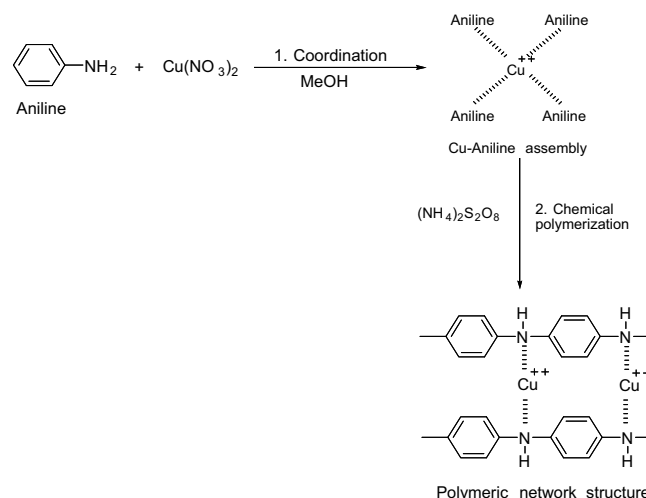


Scheme 1. Cartoon demonstration of material synthesis.

solution was pipette out from both the beaker and UV spectra were recorded.

2.5. Device fabrication

The $\text{Cu}^{+2}/\text{PANI}$ was coated on a U-shaped pyrex glass rod by dip coating method and then fixed on the wall of a glass chamber ($2.5 \times 5 \text{ cm}^2$) via two holes. The both end of rod were projected outside the box and coupled with optical fiber. The optical fiber was a standard single mode optical fiber at 1300 nm with core and cladding diameters of 8.5 and 12.5 μm , respectively (cable type OFNR from Optical Cable). One LED (white emission) was attached from one end of the fiber and the other end with photo-detector. In order to sense the glucose, the glucose solution was passed along with *o*-dianisidine (100 ppm) in the chamber. The LED has been switched on to introduce light through optical fiber and the output intensity was measured at the other end. In this step, the stock solution of glucose was diluted in different concentration. The intensity of absorption was measured for different concentration of glucose and curve between concentration and absorbance recorded as calibration curve. It can be used for determination unknown concentration of glucose solution. The complete experimental setup



Scheme 2. Block diagram of proposed synthesis of $\text{Cu}^{+2}/\text{PANI}$ composite materials.

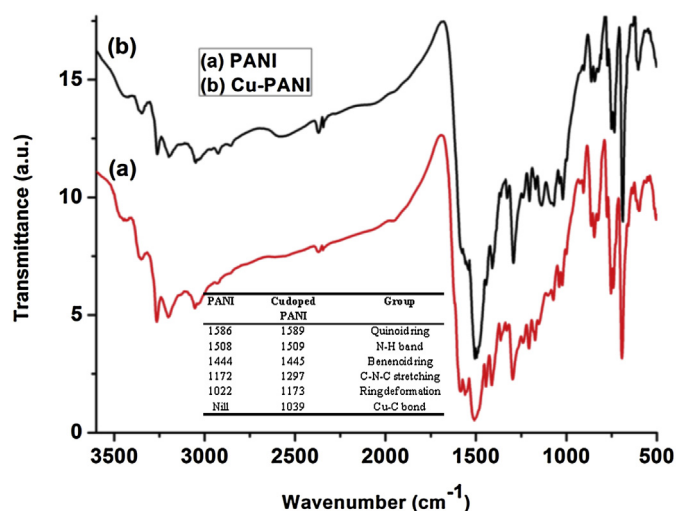


Fig. 1. FT-IR spectra of PANI and Cu/PANI.

is shown in Scheme 2. All measurement were conducted at room temperature ($\sim 25^\circ\text{C}$), with the same triplicate experiments.

In order to determine the feasibility of the proposed sensor for glucose analysis in real samples, the glucose concentration of serum of human blood was examined in identical manner. The samples were collected from the local medical diagnostic laboratory. The samples were also analyzed with commercial method used in local medical laboratory for comparison.

3. Results and discussion

3.1. Chemical characterization

Scheme 1 sketches the entire process for the preparation of Cu^{+2} /PANI composite material. The synthesis strategy is, first, to form coordination between Cu^{+2} and aniline monomer. It is because the acidic nature cupric ion and basic nature of aniline. This step also functionalises the aniline to make it prone for polymerisation. This is the key step to control the internal structure of the composite material. The second step involves chemical polymerization of

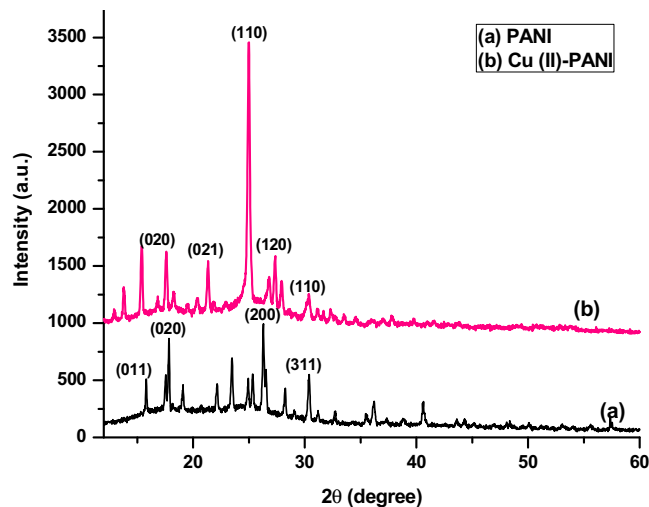


Fig. 2. XRD spectra of PANI and Cu/PANI.

this functionalized aniline monomer in the presence of APS. Vibrational spectroscopy provides insight about the interaction of the Cu^{+2} and aniline. Fig. 1 shows FTIR spectra of PANI and Cu^{+2} /PANI and important peaks are given in inset Fig. 1. Data exhibit characteristic signals of PANI appearing at 1586 cm^{-1} (Quinoid ring), 1508 cm^{-1} (N-H band), 1444 cm^{-1} (Benzenoid ring), 1295 cm^{-1} (C-N-C stretching), and 1172 cm^{-1} (N-Q-N). On comparing the IR peaks of PANI to Cu^{+2} /PANI composite it is found that IR spectra of composite shows hypochromic shift due to the loosening of matrix because presence of metal [42]. For instance, while ring deformation of PANI was observed at 1022 cm^{-1} , the signal is shifted to 1039 cm^{-1} in the presence of Cu^{+2} in the PANI system, which indicates the chemical interaction of aniline monomeric residue and Cu^{+2} . In addition to the characteristic vibrational bands of PANI, a signal at 586 cm^{-1} appears in the spectrum of Cu^{+2} /PANI system. This newly formed signal upon the interaction of PANI with Cu can be attributed to the formation of linkage between polyaniline and Cu^{+2} centre ion.

The crystal structure of the prepared materials was studied by XRD (Fig. 2). Fig. 2(a) presents x-ray diffraction spectra of neat PANI and Fig. 2(b) of Cu^{+2} /PANI. XRD of PANI is showing most of the

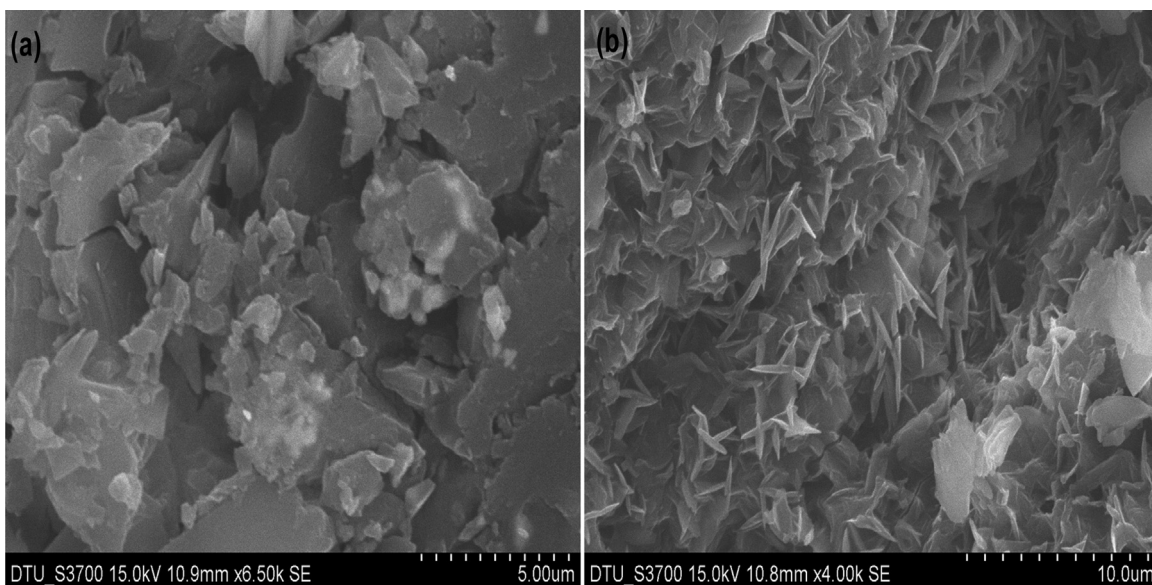


Fig. 3. SEM photographs of PANI and Cu/PANI.

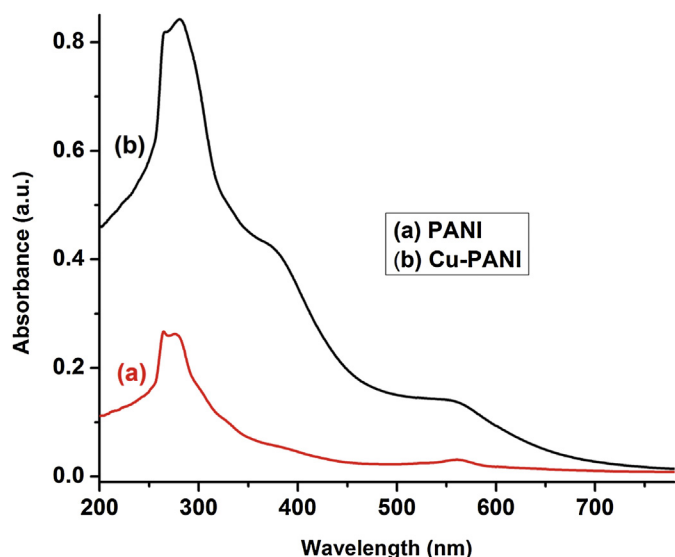


Fig. 4. UV spectra of red of glucose and black for glucose treated with Cu/PANI. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

prominent peaks below 40° . However, $\text{Cu}^{+2}/\text{PANI}$ is also showing more additional intense peaks at 2θ values of 16° , 21° , 25° , 27° and 30° due to presence copper [JCPDS 04-0836] [43]. The peaks of $\text{Cu}^{+2}/\text{PANI}$ are more intense compared to the ones of neat PANI. Higher intensity infers the presence of higher crystallinity due the presence of Cu ion. Crystallinity in composite is compared with strongest reflection of PANI and found that crystallinity of composite increases by 1.65 than pure PANI. It may be because the doping of metal increases the crystallinity due controlled polymerization [9,44].

Better crystallinity in the presence of Cu^{+2} is also supported by Scanning Electron Microscopy (SEM). Fig. 3 presents SEM photographs for neat PANI and $\text{Cu}^{+2}/\text{PANI}$ system. The micrograph of pure PANI is showing different morphology than composite matrix. The cu doped PANI is showing binary type flakes plate like structure, which may provide excess active sites and absorption capacity due porous structure, which is visible in micrograph.

3.2. Catalytic behavior of $\text{Cu}^{+2}/\text{PANI}$

The UV spectra of pure glucose and glucose after being treated with $\text{Cu}^{+2}/\text{PANI}$ are shown in Fig. 4. The spectra of treated glucose is showing an additional peak at 330 nm. It reveals the formation of gluconic acid along with hydrogen peroxide due to oxidative interaction between glucose and Cu^{+2} ions present in PANI matrix. Further, amount of hydrogen peroxide controls the efficiency of glucose sensors by providing electrical response in electrical sensor and oxidizing a dye in opto-chemical sensor. Thus, generated H_2O_2 oxidises *o*-dianisidine redox dyes, which controls the efficiency of the proposed $\text{Cu}^{+2}/\text{PANI}$ based optode. The degree of oxidized *o*-dianisidine was monitored by UV spectra. The spectra shown in Scheme 3, clearly indicates a peak at 418 nm due to oxidation of *o*-dianisidine along with appearance of light red colour. This colour transition works as an indicator to detect various biomolecules in bio fluid [45]. It also generates complimentary optical response in opto-chemical sensor. The change in optical response is proportional to the glucose concentration, optode activity and the time of reaction. The time of reaction correlates with response time of proposed sensor [46–48]. The reaction mechanism is illustrated in Scheme 3 with help of Eqs. (1) and (2).

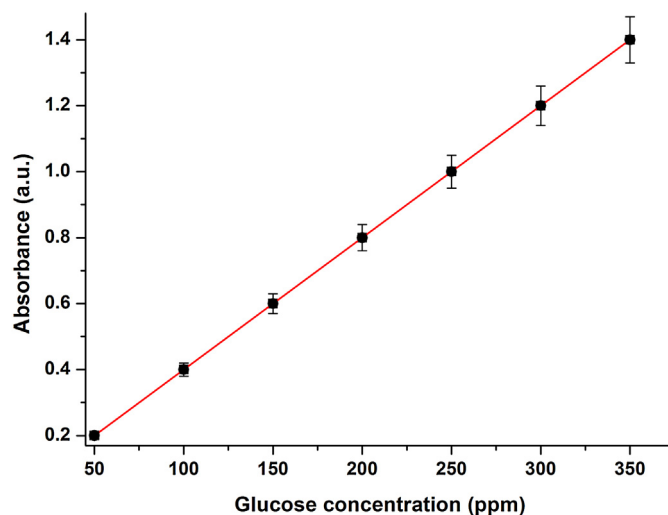


Fig. 5. Change in optical response with glucose concentration.

3.3. Glucose sensing

Further, the trend in absorbance with the concentration of glucose is given in Fig. 5. It reveals the regular increase in absorbance with increase in glucose concentration. The linearity in the change in absorbance confirms its suitability for glucose sensing. The optical response was very stable and recorded with time. The data is shown in Fig. 6, it reveals to reach the 90% steady-state in 15 s, which is response time. The optical response of the present sensor at higher concentration shows a linear response for a wide range of concentrations of glucose (50–350 mg/dL) with the detection limit of 2 ppm. All the data from this sensor reveal the properties of high sensitivity, detection limit and fast response time, attributed to the fact that $\text{Cu}^{+2}/\text{PANI}$ can greatly increase the catalytic active areas and promote the oxidation of glucose. Six successive glucose sensing measurements were performed in 50 mg/dL solution and reproducible results were observed with relative standard deviation (RSD) of 0.25%. It demonstrates the optode was not poisoned during glucose oxidation and can be used repeatedly. Further, experiment were also performed by measuring the absorbance of 50 mg/dL glucose concentration using six different $\text{Cu}^{+2}/\text{PANI}$ optodes and result yields the RSD of 0.261 percent, inferring the reliable behaviour of developed methods.

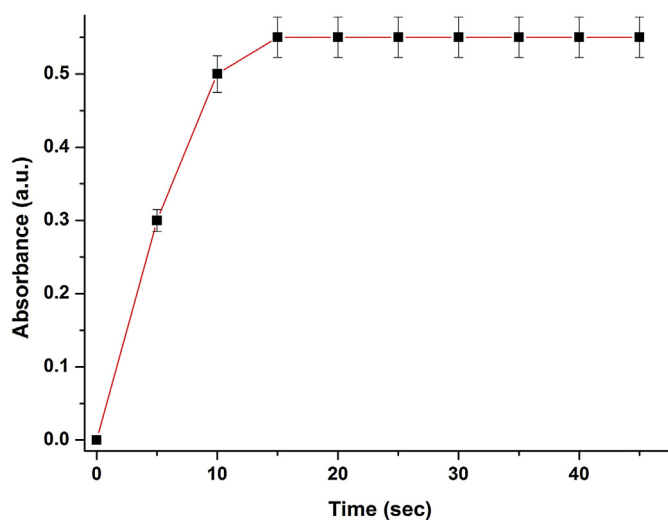
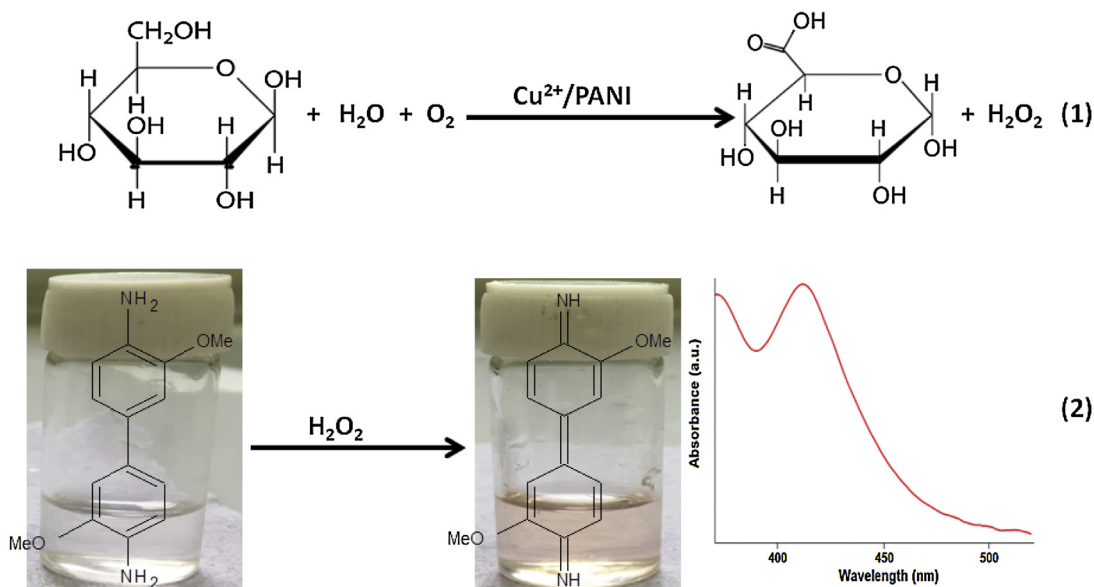


Fig. 6. Optical response of fabricated optode versus time.



Scheme 3. Schematic mechanism and involved chemical reactions.

3.4. Interference effects

The selectivity of developed sensor was also investigated against the possible coexisting interfering bio-molecules such as ascorbic acid (AA), p-acetamide phenol (AP), uric acid (UA), fructose, galactose, lactose, ribose and maltose [49,50]. Considering that the concentration of glucose is about 30 times higher than interferents. Adequate amount of interfering molecules were added, and optical response of the prepared optode was examined (Fig. 7). The results show that no significant optical response changes change due to the interfering molecules. The high selectivity may be attributed to the presence of Cu^{2+} in PANI matrix, since the negatively charged PANI centres of hybrid film repels AA, UA, AP and non-catalysing to fructose and maltose. It seems that presence of Cu^{2+} in interaction with PANI makes as non-interactive substrate for common interferences.

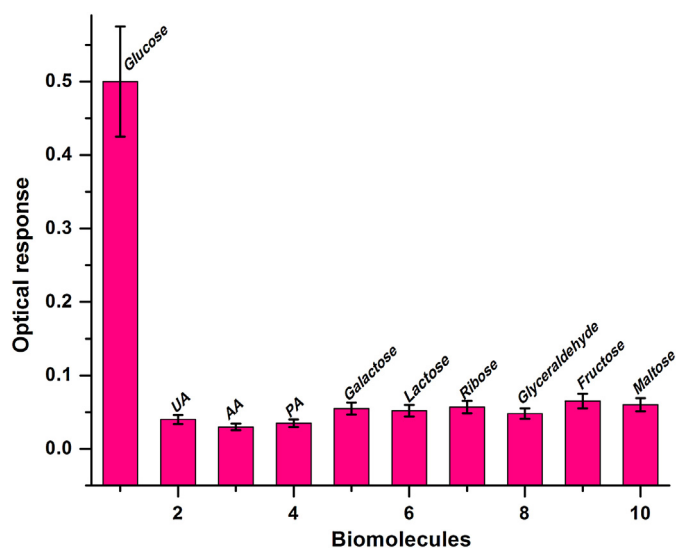


Fig. 7. Optical response of the PANI/Cu against the glucose, AA, UA, PA, galactose, lactose, ribose, glyceraldehydes, fructose and maltose.

3.5. Reproducibility and stability

The reproducibility of response time of the sensor was investigated by comparing the response absorbance of five identically prepared opto-electrodes. The relative standard deviation (RSD) was found 2.8% at a glucose concentration of 50 mg/dL. The chemical stability of opto-electrodes was not changed by the oxidation product and can be used repeatedly for the detection of glucose. The sensing element was stored in air at ambient conditions and its sensitivity was tested every 40 days. The result demonstrated that the sensitivity was constant after being stored for 40 days. The good reproducibility and long-term stability of the sensor are desirable for most routine analysis.

3.6. Real sample analysis

The concentrations glucose in human serum samples were also measured by the developed nonenzymatic glucose optodes and results are shown in Table 1. The RSD was calculated found 0.431 percent. Thus, results are confirming that the observed results and methods are in agreement with the result obtained by the commercial glucose biosensor used in local hospital. It implies that the sensing ability of our glucose sensor is not only limited to the standard glucose samples but also it can be used to test on real human serum samples with a good reliability.

Table 1
Comparison of glucose detection test for real samples of present method to hospital method.

Sample	Hospital method (mg/dL)	Present method (mg/dL)
1	70.51	70.52
2	75.22	75.21
3	80.71	80.68
4	83.25	83.26
5	90.72	90.70
6	95.49	95.50
7	98.42	98.43
8	105.18	105.17
9	120.10	120.12

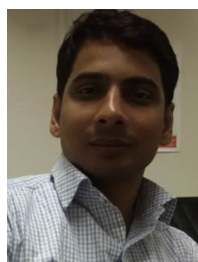
4. Conclusion

The nonenzymatic glucose sensor has been proposed using optical fiber approach. The chemistry of preparative route and glucose sensing has been explained on basis of experimental results. The glucose sensing behaviour has been compared with available glucose sensors in term of sensitivity, selectivity and life of use. The prepared hybrid has been characterized to understand the effect of copper metal on the structure and properties of polyaniline. The proposed enzyme-free sensor can detect glucose selectively and reliably, and it is a great promising device for practical glucose monitoring.

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