

Development of a Low-Cost Hemin-Based Dissolved Oxygen Sensor With Anti-Biofouling Coating for Water Monitoring

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Abstract—Conventional electrochemical dissolved oxygen (DO) sensors are expensive as they use platinum in their construction. In addition, these sensors biofoul when used in natural or waste water, which leads to reduced sensitivity and variable performance. Here, we solve these problems by: 1) replacing platinum with hemin as the low-cost alternative for electrocatalysing the oxygen reduction reaction and 2) using silicone rubber [poly(dimethylsiloxane) (PDMS)] functionalized with polyethyleneglycol (PEG) as the anti-biofouling gas permeable membrane to provide selectivity with an increased lifetime. This DO sensor has a sensitivity of $20.7 (\mu\text{A}/\text{cm}^2)/(\text{mg}/\text{L})$ of DO in a concentration range of 2–7 mg/L. In addition, the common interferences, such as phosphates and nitrates, show minor influence in the DO detection. Furthermore, the PEG functionalization of PDMS membrane reduced biofouling and increased the lifetime of the sensor by 20 times in accelerated biofouling conditions.

Index Terms—Dissolved oxygen, water monitoring.

I. INTRODUCTION

DISSOLVED oxygen (DO) in water is essential for aquatic life. Marine creatures require a DO concentration of at least 5 mg/L to survive [1]. DO is also important for the sustenance of healthy water bodies. Low DO concentration causes

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excessive growth of anaerobic bacteria which can damage the water system permanently. More importantly, low DO concentration is indicative of a variety of contaminants, making DO one of the most important parameters in determining the health of water bodies. Usually, DO sensing/measurement is performed using chemical, optical or electrochemical methods. In the chemical method, DO is sensed by chemical titrations that produce color/intensity change in response to concentration. However, this method is labour intensive, uses reagents and requires specially trained personnel to perform it [1]. In the optical method, the DO concentration is rapidly (< 60 s) detected by its ability to quench fluorescence intensity of Ruthenium (Ru) complex immobilized on an oxygen permeable film [2]. Although fast, the complexity of the optical system (light source, detector, and optical filter) and the photobleaching of the DO sensing complex makes this method expensive and difficult to implement. The electrochemical method relies on the electrocatalytic reaction of oxygen on platinum: the sensor based on this reaction is known as the “Clark electrode” [3]. The Clark electrode has three essential components: a platinum (Pt) working electrode, a silver/silver chloride (Ag/AgCl) reference electrode, and a gas-permeable teflon membrane. During sensing, a -0.7 V (vs Ag/AgCl) electrical potential is applied to the Pt electrode. The oxygen reduction reaction (ORR) occurs on the Pt electrode surface at this potential to produce a current proportional to the local DO concentration. The teflon membrane is used to separate the oxygen from other interfering species that may be present. Because of its simple working principle and high accuracy, the Clark electrode is the best available sensor for continuous DO measurement. It is, however, limited in the following aspects: (i) the Pt catalyst is expensive [4]; (ii) the teflon membrane has low oxygen permeability thus limiting the sensitivity; and (iii) biofouling remains a serious problem.

Transition metal N4-macrocyclic compounds such as metalloporphyrin complexes have been extensively studied as candidates for the ORR catalysts in fuel cells because of their high catalytic activities [4]. Among these complexes, hemin (chloro(protoporphyrinato) iron(III)) is a promising alternative to platinum because it is inexpensive, has a high catalytic rate for the ORR, (porphyrin with iron center has the highest ORR catalytic activity among all porphyrin groups [5]) and can be easily incorporated on the sensing electrode [6].

Liang *et al.* developed a hemin-coated carbon electrode as the ORR catalyst and found that its catalytic activity increased with increasing hemin content [7]. Ye *et al.* developed a hemin-modified carbon nanotube (CNT) electrode as a DO sensor [8]. Due to the high surface area of CNT, this electrode showed a high current response (2 mA/cm^2) while sensing DO, but the high cost of CNT and interference due to the interaction of CNT with other ionic species in water limited its effectiveness. Furthermore, since hemin was applied using a layer-by-layer deposition process, it produced fragile films.

Recently, electrodes prepared by the electropolymerization of hemin have been used for nitric oxide sensing [9]. Electropolymerization gives a strong adhesive bond at the substrate/hemin interface and allows for increased concentration of hemin [10]. However, due to poor current collection capacity, electropolymerized films with higher hemin loading do not produce proportionally higher current or increased sensitivity. In a related development, copolymerized pyrrole and cobalt porphyrin films have been used to significantly enhance the catalytic capacity for fuel cell electrodes [11]. We follow a similar strategy here by co-electropolymerizing hemin and pyrrole to fabricate the electrode and use it for the first time in an oxygen sensing application.

Conventionally, Teflon membrane with the thickness ranging from 25 to 50 μm is used in Clark type electrodes as a gas permeable barrier to prevent interfering species from interacting with the electrode. Teflon has good mechanical and chemical stability but low gas permeability (3 Barrer- O_2 and 13–40 Barrer- H_2O), thus limiting the sensitivity of the Clark electrode. Poly(dimethylsiloxane) (PDMS) is an excellent alternative to teflon because of its high gas permeability (400–800 Barrer- O_2 and 32000 Barrer- H_2O). However, since it is strongly hydrophobic, PDMS is prone to foul via the adsorption of proteins and other components in environmental samples [12].

Various surface modification methods have been proposed to alleviate biofouling on PDMS. These include gas plasma treatment [13], ultraviolet irradiation [14], metal coating [15], dynamic surface modification, which involves ionic liquids or surfactants [16], and polyethylene glycol (PEG) grafting by wet chemical methods. Among the methods available, PEG grafting is a relatively simple and effective method [17] and is used in present work to minimize fouling on PDMS.

In this paper, we report the development of the first, low-cost DO sensitive electrode for water monitoring using polyhemin rather than platinum as the ORR catalyst. A new electropolymerization method incorporating hemin, polypyrrole (ppy) and silver has been developed to achieve sufficient sensitivity for environmental DO sensing needs. Highly oxygen permeable PDMS thin films have been incorporated with anti-biofouling coating that provides selectivity while also preventing deterioration in performance.

II. MATERIALS AND DESIGN

A. Reagents

Chloro[3,7,12,17-tetramethyl-8,13-divinylporphyrin-2,18-dipropanoato(2-)] iron(III) (hemin) 98%, pyrrole (98%),

silver nitrate (AgNO_3 , 99%), poly(ethylene glycol) dicarboxylic acid (PEGDA) (MW=600, >96%), N,N'-dicyclohexylcarbodiimide (DCC) (>99%), 3-aminopropyltriethoxysilane (APTES) (99%) and yeast extract were purchased from Sigma-Aldrich (St. Louis, Missouri). Polydimethylsiloxane (PDMS) Sylgard 184 was purchased from Dow Corning (Midland, MI). Sulfuric acid (H_2SO_4 , 98%) was purchased from Calden (Georgetown, Ontario).

Phosphate buffer solution (PBS) (10 \times) was purchased from Bioshop (BioShop Canada Inc, Burlington, Ontario). All reagents were of analytical grade and were used without further purification. Nitrogen gas (99.9999% pure) was purchased from Alphagaz (Montreal, Quebec). Milli-Q grade water (18.2 $\text{M}\Omega\cdot\text{cm}$) was used to prepare all solutions, unless otherwise noted.

B. Electrode Fabrication

Indium tin oxide (ITO) substrates of 200 nm thickness were made by plasma sputtering (Torr Compact Research Coater CRC-600 manual planar magnetron sputtering system, New Windsor, New York) on a soda-lime glass substrate. The sputtered glass substrates were diced into 5 mm \times 10 mm pieces for further processing.

C. Electropolymerization and Electrochemical Characterization

All electrochemical depositions and characterizations were performed using an EmStat2 electrochemical workstation (PalmSens, Utrecht, The Netherlands) and a standard three-electrode setup. The electrochemical system consisted of an Ag/AgCl reference electrode, a platinum wire counter electrode, and the fabricated hemin DO sensor as the working electrode. The control of electrochemical workstation and data collection were all performed by PS tracer 3.0.

D. Sensor Design

Three design configurations of DO sensors are proposed. As shown in Fig. 1 (a), each design has four layers: a conductive layer, a DO sensitive layer, a PDMS membrane layer and an anti-biofouling layer. ITO thin film serves as the bottom conductive substrate in all the designs due to its low cost and stability. The major difference between three designs is the composition of the DO sensitive layer which are pure hemin (Fig. 1 (b)), hemin/polypyrrole co-deposition complex (Fig. 1 (c)), and hemin/polypyrrole/silver co-deposition complex (Fig. 1 (d)).

Hemin is used as a replacement of platinum as the oxygen reduction reaction catalyst. Due to its carboxyl end groups, hemin is amenable to electrochemical polymerization which simplifies the synthesis procedure of DO sensitive electrode since other porphyrin-based DO sensitive electrodes are usually synthesized via layer-by-layer method that requires multiple coating and washing processes [19]. Furthermore, electropolymerization also increases the loading density of hemin on the electrode, as compared to layer-by-layer

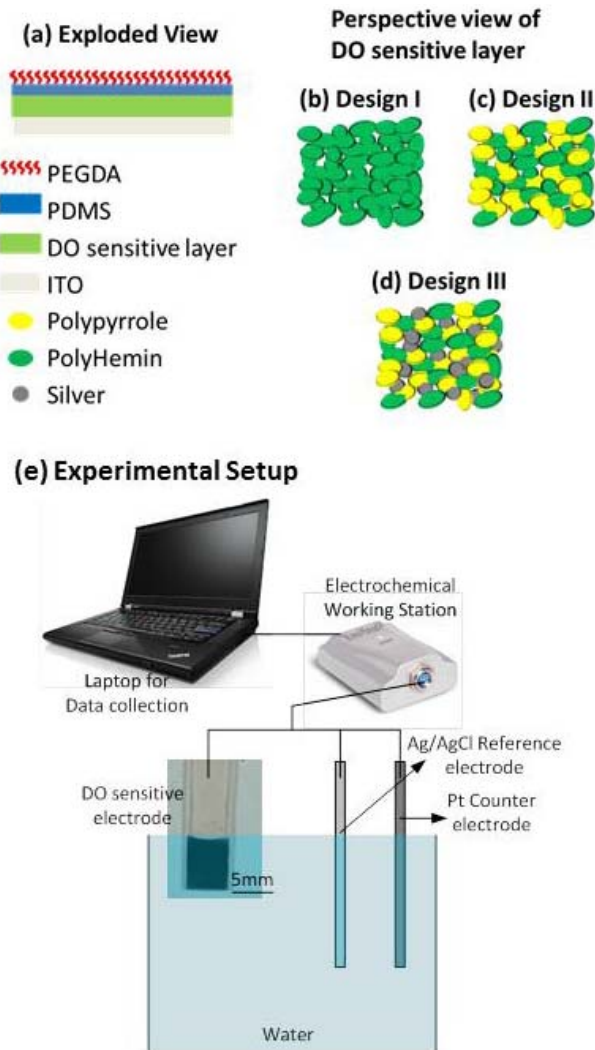


Fig. 1. Schematic of DO sensitive electrode: (a) the exploded view; and the different designs of the DO sensitive layer, (b) electrodeposited pure hemin (c) co-deposited hemin/polypyrrole complex, (d) polyhemin/polypyrrole/silver co-deposited complex, and (e) the experimental setup of DO sensing.

deposition. Thus, the electropolymerized hemin is chosen as the DO sensitive layer of the first design (Fig. 1(b)). However, electropolymerized hemin may be not sufficiently conductive and unable to produce higher current despite the higher loading. Co-polymerization with a conductive polymer such as polypyrrole (ppy) has been shown to improve the current collection capacity of cobalt porphyrin electrodes and therefore was co-deposited in the second design (Fig. 1 (c)). In addition, co-deposition of cobalt porphyrin with transition metal oxides have been found to enhance its ORR catalytic properties [20], [21] which motivated co-deposition with silver [22] in the third design (Fig. 1 (d)). The sensitivity of each design is tested the results are presented in the results and discussion section. The third layer is a thin PDMS film (20 μm in thickness) that serves to isolate the electrode from interfering species such as nitrates and phosphates while allowing oxygen and water vapor to permeate freely.

Finally, the top most layer is a single monolayer of surface functionalized poly ethylene glycol (PEG) used to prevent biofouling of the PDMS surface. PDMS is susceptible to the

adhesion of proteins, cells and other biological materials due to its strongly hydrophobic character. This leads to fouling that isolates the sensor from its environment and ultimately causes failure of the device. To prevent fouling, PEG chains were grafted on the PDMS surface. Hydroxyl groups were first formed on the surface by air plasma treatment (HARRICK PLASMA, Ithaca, NY). A layer of APTES was then formed by reaction of the ethoxy groups of APTES (5% solution, 80 $^{\circ}\text{C}$, 30 min) with the hydroxyl groups on the PDMS surface [16]. The PDMS-APTES surface was then treated with PEGDA (20 mM in tetrahydrofuran, 24 h) containing 20 mM N,N'-dicyclohexylcarbodiimide (DCC). The PEG with free carboxyl end groups is chemically attached to the PDMS by reaction with the amino groups of PDMS-APTES. The water contact angle was shown to decrease from 100 $^{\circ}$ before grafting to 20 $^{\circ}$ after grafting indicating that the PEG is successfully grafted onto PDMS surface reducing its hydrophobicity. Protein adsorption experiments were conducted to assess the fouling resistance of the modified PDMS [23]. The image of a fully fabricated electrode is shown as an inset in the depiction of the experimental setup for characterization of the sensor (Fig. 1(e)). Based on this design, the material cost alone was reduced by a factor of 17. In addition, this solid state electrode does not need further assembly or reference solution filling as the conventional Clark electrode that will further reduce the cost.

E. DO Sensing

All DO sensing experiments were performed using the chronoamperometry method at a fixed potential of -0.7 V for 200 seconds to obtain a stable current. The three electrode system was used for the chronoamperometry experiments (Fig. 1(e)). The electropolymerized DO sensitive electrodes were connected to the working electrode of electrochemical workstation. Tap water was used as the “test sample” for DO concentration measurement. During sensing, DO sensitive electrodes were submerged into water and the desired electrical potential was applied to trigger the ORR while recording the current. The DO concentration was varied by nitrogen purging [18]. A calibration curve of oxygen concentration versus N_2 purging time was obtained using a commercial dissolved oxygen meter (U-21ex, HORIBA). All experiments were carried out at room temperature. The average of three replicate measurements was used.

III. RESULTS AND DISCUSSION

A. DO Sensing Electrode Performance

To evaluate the system's performance, electro polymerization was performed in solutions with the key components in the different combinations (each component at 0.1 M) by applying a potential of 0.9 V for 100 s. The catalytic property of these DO sensitive electrodes was tested in 0.1 mM PBS solution by cyclic voltammetry (CV) method over the range of 0.5 V to -1 V with a 0.1 V/s scan rate. The CV results are shown in Fig. 2. The CV of bare ITO electrode showed that no electrochemical reaction occurred spontaneously in this potential range. The CV of polyhemin immobilized electrode

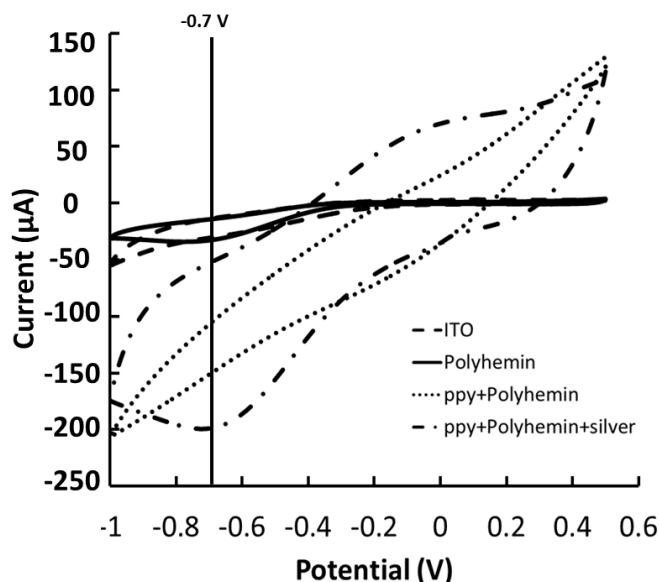


Fig. 2. Cyclic voltammogram (CV) for DO sensitive electrodes of varying composition in tap water. CV scans were conducted over a range of 0.5 V to -1 V at a 0.1 V/s scan rate. The area of the DO-sensitive material was 25 mm^2 .

showed a peak at -0.7 V [24] during the reverse scan while there was no obvious peak in the forward scan. The pure polyhemin coated electrode showed a small but definite ORR current ($100 \mu\text{A}$) as compared to the bare ITO electrode.

The CV of the polyhemin+polypyrrole co-deposited film showed a nearly linear response in current over the measurement range. Although the current was higher it did not show a characteristic peak at the ORR potential of poly hemin. It is possible that the conductivity of the polypyrrole is still not large enough and polypyrrole reacts with the reactive oxygen species generated to produce this behavior.

The CV of the electrode produced by co-deposition of silver with polypyrrole and polyhemin shows the highest current response. A clear ORR peak can be observed at -0.7 V during the reverse scan indicating not only that the ORR reaction occurs on the electrode but also that the current thus produced is effectively collected from it. This deposition condition and material combination was used in all subsequent experiments as the optimized configuration for the electrode.

Next, chronoamperometry measurements were performed on the DO sensing electrodes in 0.1 mM PBS solution with various DO concentrations (2–6.8 mg/L) at a polarization potential of -0.9 V. As shown in Fig. 3 (a), the initial current density is high but falls rapidly and reaches a steady state value which depends on the concentration of the DO in the solution. This behavior is expected as initially the concentration of the dissolved oxygen near the electrode is high, producing a high current. Once the oxygen in the vicinity of the electrode is consumed, a diffusion layer is established close to the electrode and the rate of the reaction is controlled by the mass transfer of oxygen across the diffusion layer. As the diffusion layer grows, the rate becomes smaller, eventually reaching a steady state. At steady state, the current is proportional to the concentration gradient across the diffusion layer and hence to the bulk concentration of DO in the solution.

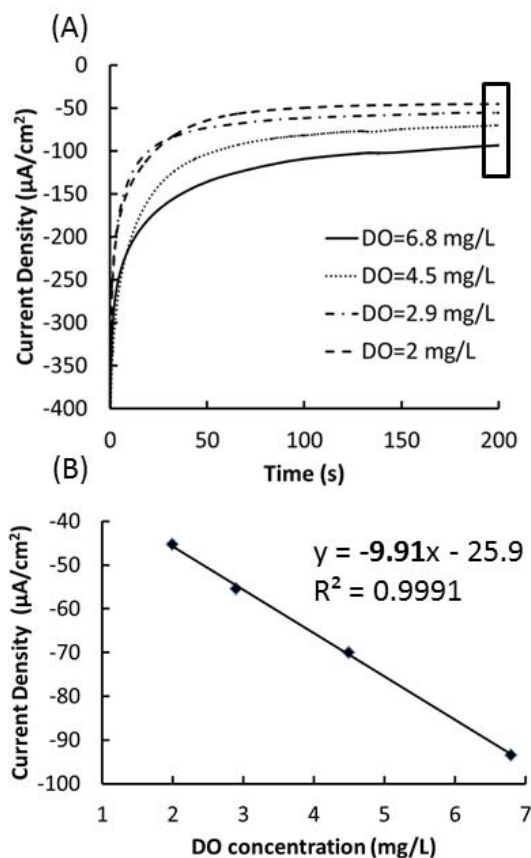


Fig. 3. (a) Chronoamperogram of DO sensor (hemin+ppy+silver) in water with DO concentration 6.8 mg/L, 4.5 mg/L, 2.9 mg/L and 2 mg/L. The current at steady state (200s) is taken. (b) Plots of currents in steady state of different DO concentration which shows a linear relationship. The sensitivity of the sensor is calculated as the slope of fitted line.

The relationship between current and DO concentration in a mass transfer controlled case can be expressed by following equation:

$$I = 4 \times F \times P_m \times A \times P(O_2)/b \quad (1)$$

where I is the response current during DO sensing, F is the Faraday's constant, P_m is the gas permeability of the membrane, A is the surface area of DO sensitive material coverage on working electrode, $P(O_2)$ is the partial pressure of oxygen and b is the thickness of the membranes. The concentration of DO then can be obtained from $P(O_2)$ by Henry's law:

$$X = K_{O_2} \times P(O_2) \quad (2)$$

where X is the concentration of DO, and K is Henry's constant. Fig. 3 (b) shows the steady state current density plotted against the DO concentration and shows a linear relationship as expected from theoretical considerations. The sensitivity of this electrode is then defined as the slope of the regression line fitting the data.

In order to determine the best electropolymerization conditions for the DO sensitive electrodes, various preparation conditions were tested and their sensitivities compared with electrodes prepared by layer-by-layer electropolymerization as

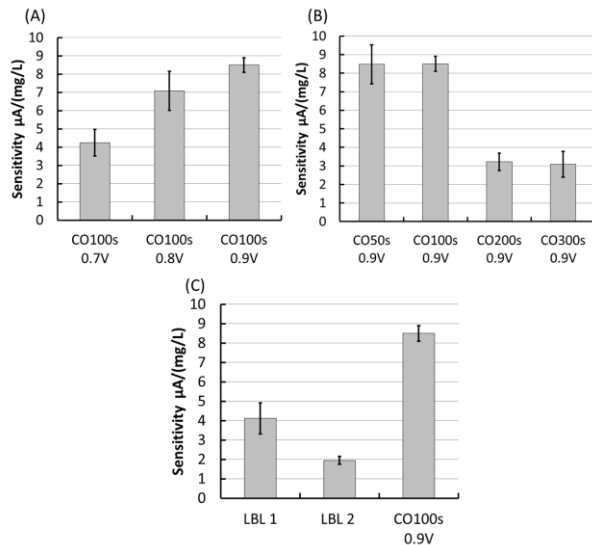


Fig. 4. Comparison of the sensitivity of DO sensors prepared under different conditions: (a) copolymerization at different potential; (b) copolymerization for different duration; and (c) comparison between one and two layers of layer-by-layer polymerization as well as copolymerization. The sensitivity values are: 4.12 (LBL 1), 1.95 (LBL 2), 8.48 (CO50s), 8.5 (CO100s), 3.22 (CO200s), 3.09 (CO300s), 7.08 (0.8 V) and 4.25 (0.7 V). All DO sensing experiments were done by chronoamperometry with the potential fixed at -0.7 V for 200 s to achieve stable current. Data are means \pm SD, $n = 3$ CO = coelectropolymerization; LBL=layer-by-layer in separate solutions in the order, number refers to the number of layer of each component: silver, ppy, polyhemin. The potential was 0.9 V for all experiments except CO 100s (0.8 V) and CO 100s (0.7 V).

shown in Fig. 4. First, the potential at which the electropolymerization was carried out is varied from 0.7V to 0.9V while maintaining the deposition time at 100s. Fig. 4 (a) shows that the sensitivity of DO electrodes increases with the increase in the deposition potential. This is expected and can be explained as follows. Pyrrole electropolymerization occurs at 0.2V while silver is at 0.6V and electropolymerization of hemin occurs at 0.7 V. Therefore, it is expected that the amount of hemin polymerized on the electrode will be smallest at 0.7 V and the largest at 0.9V corresponding to the sensitivities observed. The potential of copolymerization cannot be increased over 0.9 V as polypyrrole oxidation occurs, leading to a drastic reduction in its conductivity [20]. Therefore, 0.9V was identified as the optimal deposition potential.

Next, the duration of the electropolymerization was varied from 50 – 300 s while maintaining the deposition potential at 0.9V. The sensitivities of the DO electrodes thus prepared are shown in Fig. 4 (b). It shows that a copolymerization time of ≤ 100 s gave the highest sensitivity. Electron microscopy of the deposited layer shows a thickness of ~ 350 nm at 100s deposition in this condition. Reduced sensitivity was observed at durations longer than 100s where the deposited layer becomes too thick, perhaps restricting the electron transfer from the top surface to the substrate electrode. Therefore, 100s electropolymerization was chosen as the optimal time for electrode preparation.

Fig 4(c) shows the comparison between the electrode formed by electropolymerization at the best condition as identified in the previous experiments and the conventional layer by layer electropolymerization method.

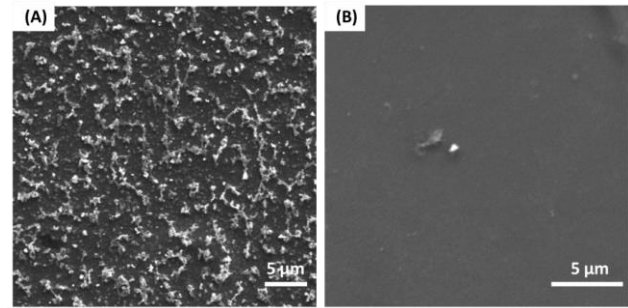


Fig. 5. The SEM images of the DO electrode surface (A) coelectropolymerization 100s (CO100s) and (B) layer-by-layer (LBL1).

The layer-by-layer electrodes showed 50–75% lower sensitivity than co-polymerized electrodes indicating the higher loading of hemin and better conductivity of the polymer in the electropolymerized case. It should be noted that the electrodes copolymerized for 100s at 0.9V (CO100s-0.9V) have the smallest variation in sensitivity ($0.4 \mu\text{A}/(\text{mg}/\text{L})$) as compared with all other conditions, indicating that this synthesis condition of electrodes was optimal and has good reproducibility.

Fig. 5 shows the SEM images of the surface of the electropolymerized (CO100s) and layer-by-layer (LBL 1) DO electrode which are significantly different from each other, indicating that the arrangement and topography of the electrode could play a part in the increase in sensitivity. For instance, it can be seen that the co-polymerized electrode has a distribution of silver nanoparticles on the co-polymerized hemin-pyrrole matrix which could enhance the conductivity and current collection. Furthermore, the sensitivity was reduced as the numbers of layers were increased from one layer (LBL 1) to two layers (LBL 2), indicating that even with the increased hemin loading, the loss of charge collection capability leads to a lower response and sensitivity.

B. Life Time

The life time of the DO sensitive electrode was determined by repeatedly sensing DO concentration in a tap water sample for 120 times. The DO sensor was placed in water with stir bar set at 200 rpm to ensure a constant mass transfer rate of DO towards the electrodes. Measurements were performed repeatedly for durations of 200 s with interval between the measurements was set as 10 s. The electrode is stable for over 60 measurements ($<1\%$ deviation) and has a deviation of ($\sim 25\%$) at 120 measurements.

C. Interference and PDMS Membranes

Many ionic species such as phosphates and nitrates that may be present in natural water can alter the response of a bare DO electrode. Experiments were performed by measuring the current responses of four individual DO sensor electrodes in the solutions with and without the interfering species but the same concentration of DO ($6.8 \text{ mg}/\text{L}$). The concentrations of interfering species were chosen as 0.01 M which is close to the upper limit of the range of concentration of these species present in surface and waste water [25]. The presence of

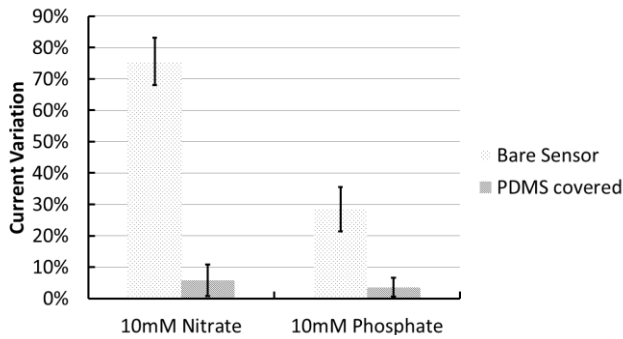


Fig. 6. Current response of DO sensors in the presence of interfering species nitrates and phosphates with and without 20 μm PDMS overlay. Bare electrode without PDMS coating shows significant changes in current due to presence of nitrates and to a lesser extent phosphate. However, PDMS coating allows only DO and water vapor to permeate and shows no influence on the current due to presence of nitrates and phosphate. ($n = 4$).

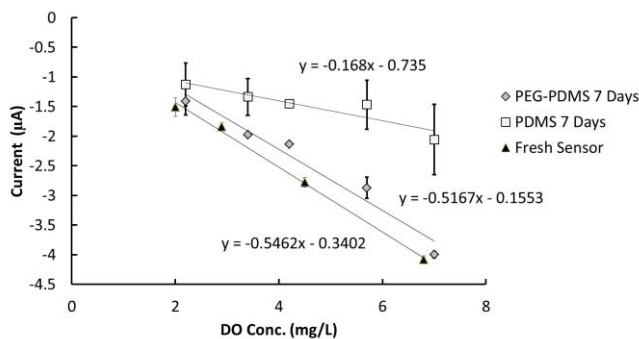


Fig. 7. DO data for sensors after exposure to accelerated biofouling environment for 7 days. ($n = 4$).

these species increases the current response and their effect is measured as the difference in the current with and without the interfering species normalized to the current without them. Experimental results (Fig. 6) show that addition of 0.01 M nitrate and phosphate to 0.1 mM PBS buffer with 6.8 mg/L DO causes about 30% and 70% current variation respectively in the response of the bare DO sensor. This large variation will have a significant impact on the accuracy of the sensor.

However, if a gas permeable PDMS membrane was used as a protective barrier, it allows the DO and water vapor to permeate through it while minimizing the transport of interfering species such as nitrates and phosphates. In this case, PDMS was applied to the DO sensor by spin coating at 4000 rpm for 60 s. This process produces a PDMS coating of 20 μm in thickness. As expected, the PDMS membrane can effectively reduce the current variation to less than 5% for both nitrate and phosphate (Fig. 6).

D. Accelerated Bio-Fouling Test

Biofilms were grown on both modified and unmodified DO sensitive electrodes under laboratory conditions by using nutrient solutions prepared by adding 1% yeast extract to tap water to accelerate the biofouling [26]. The sensing results of both sensors after 7 days of biofilm growing and fresh (day zero) sensors are shown in Fig. 7. It can be seen that the bare electrode does not respond as well to the variation in DO concentration after 7 days due to biofouling. The film

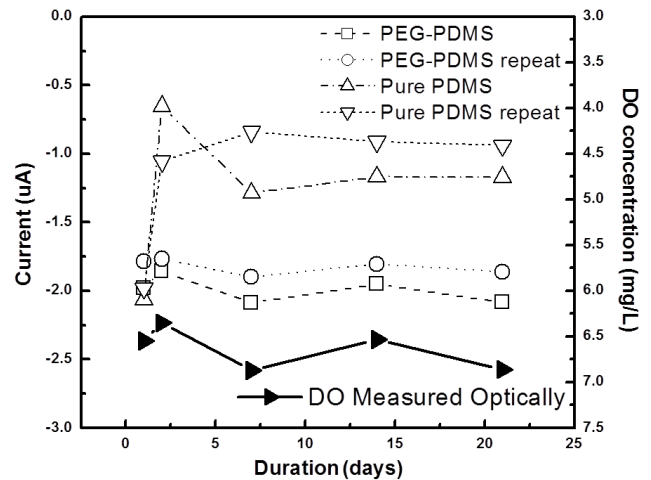


Fig. 8. Response current of sensors in tap water after 1, 2, 7, 14, and 21 days. The solid triangular symbols indicate the corresponding DO concentration measure by a commercial optical DO sensor (HORIBA).

developed on the surface of the electrode does not allow permeation of oxygen through it and hence the sensitivity of the sensor is lost. However, the surface modified sensor even after 7 days in accelerated biofouling environment shows a linear response to variation in DO concentration indicating that the biofilm formation has been reduced and the sensor can still function despite being immersed in an accelerated biofouling environment.

In order to further examine the antifouling capacity of both sensors, we recorded the response current of both DO sensors to fresh tap water after 1, 2, 7, 14, and 21 days of accelerated biofouling process and the results are shown in Fig. 8. The actual DO concentration in these samples were measured using a commercial optical DO sensor which was clean and not in the accelerated biofouling environment. The duration of the test was chosen to be 21 days as the commercially available DO sensor membranes biofoul within 14 days in this accelerated environment [27]. The results show that the bare PDMS coated sensors lose their sensitivity within a day while the PEG grafted PDMS coating is able to withstand accelerated biofouling environment for over 21 days and still measure the DO concentration accurately.

IV. CONCLUSION

In summary, we demonstrate an inexpensive, anti-fouling DO sensitive electrode based on co-electropolymerization of hemin and pyrrole with silver and with sufficient sensitivity for environmental monitoring. In addition, a PDMS membrane was used to prevent interference and showed less than 10% of the current change in presence of phosphate and nitrate. The PDMS was modified with PEG to minimize biofouling. The modified sensor maintained its sensitivity under accelerated bio-fouling conditions while the bare PDMS sensor lost function within one day. The DO sensing electrode had a sensitivity of 20.7 ($\mu\text{A}/\text{cm}^2$)/(mg/L) over a DO concentration range of 2–7 mg/L, i.e the usual range encountered in water monitoring (4–7 mg/L). Although this sensor has a lower sensitivity (20 $\mu\text{A}/(\text{mg/L})$) as compared to commercially

Clark electrodes ($60 \mu\text{A}/(\text{mg}/\text{L})$) it is sufficient enough for environmental sensing application. The main advantages of this sensor are its lower cost for manufacture and its longer lifetime. In addition, since this is a solid state sensor, it could be miniaturized and integrated with a microfabricated reference electrode such as those that have been recently published [28]–[30] to form a complete sensing system at a very low cost.

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