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Pencil-Drawn Chemiresistive Sensor for Free Chlorine in Water

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Abstract—Free chlorine concentration in drinking water is an important control parameter throughout the distribution network, since both too low and too high concentrations can lead to health hazards, with 0.5 to 2 ppm being a typically acceptable range. Although colorimetric and electrochemical methods exist for measuring free chlorine, they require either addition of chemicals during manual sampling or maintenance-heavy instrumentation such as reference electrodes. We have previously demonstrated a simple, reliable, reagent-fee solid state chemiresistive sensor for continuous monitoring of aqueous free chlorine concentrations based on a functionalized carbon nanotube film. Here we show that the same sensing principle can be translated to lower cost materials – as simple as a line drawn between two contacts using a free IKEA pencil. While IKEA (HB grade, about 70% graphite) pencils work well enough for quantitative free chlorine sensors, the use of 9B grade pencils (90%+ graphite) results in higher sensitivity. Bare pencil line sensors show a non-selective response to a wide range of aqueous species; Pencil lines functionalized with a redox-active aniline oligomer (PCAT, phenyl-capped aniline tetramer), however, are highly selective to oxidant species, namely free chlorine, in a demonstrated range of 0.06 to 60 ppm. The resulting sensors are very low cost, durable, resettable, reusable and resistant to fouling. In contrast to electrochemical sensors, they do not require the use of a reference electrode. They can be operated continuously on-line for drinking water quality monitoring.

Index Terms—Drinking water quality, free chlorine, nanocarbon doping, solid-state sensors.

I. INTRODUCTION

Free chlorine is a strong oxidizing reagent and has been widely used as a disinfectant in water treatment systems for drinking water, water used for recreational purposes and for waste water that is discharged into the environment. In drinking water treatment and distribution, the concentration of free residual chlorine (dissolved chlorine) must be tightly controlled so that it is between 0.5 - 2 ppm [1]. At low concentrations, chlorine is not effective at killing pathogenic microorganisms such as bacteria and viruses [2]; while at high levels free chlorine reacts with natural organic material that may be dissolved to produce trihalomethane and other harmful (potentially carcinogenic) by-products [3]. In addition, the concentration of free chlorine decreases as the residence time of water in the distribution network increases. Therefore, it is imperative to monitor the free residual chlorine concentration in drinking water at several locations along the distribution network so that adequate concentrations are maintained to ensure safety. Free chlorine concentration is typically determined through one of several methods that use colorimetric (using color change associated with reaction of free chlorine with N-N-diethyl-p-phenylenediamine (DPD)) [4-7], chemiluminescent [8, 9], liquid chromatographic [10], or electrochemical [11-14] detection. All these techniques require reagents or use of reference solutions/electrodes for calibration which require maintenance and refill and are therefore unsuitable for continuous, low-cost, autonomous monitoring of free-chlorine concentrations.

An alternative approach is the use of solid state sensors (e.g. chemiresistors) that change their electronic properties (e.g. film resistance) in response to changes in their chemical environment (e.g. oxidant concentration). Previously, we have developed a free chlorine sensor [15] based on thin films composed of single-walled carbon nanotube percolation networks [16] that were decorated with phenyl-capped aniline tetramer (PCAT) molecules. PCAT is redox-active and can be converted from its reduced to its half-oxidized or oxidized states using aqueous free chlorine (e.g. bleach). The oxidized form, due to its more highly conjugated structure, has a smaller gap between its highest occupied molecular orbital (HOMO) and its lowest unoccupied molecular orbital (LUMO), making it a suitable p-dopant for the carbon nanotube films [17,18]. The reduced form does not discernably dope carbon nanotubes. This sensor operates continuously and reagent-free using only a very small amount of electrical power. Its main drawback is the use of carbon nanotubes, which are available either only with large amounts of ill-defined (and often redox-active) impurities or at a prohibitive price. Recently, pencil dawn electronic devices [19], including gas sensors [20], have been popularized for their ease of use and low cost of fabrication [21].

Here we demonstrate that reliable and selective aqueous free chlorine sensors can be manufactured using widely available and low-cost 9B pencils or even HB pencils (e.g. as provided at IKEA stores

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[22]). The resulting sensors were tested for quantitative sensing of aqueous free chlorine in the 0.06 to 60 ppm range, for resettability, for reproducibility, for selectivity, and for fouling resistance.

II. RESULTS AND DISCUSSION

A. Materials and device fabrication

The 9B pencil used in this work was manufactured by Bruynzeel Holland while the IKEA pencil was collected from a nearby store. Typical compositions of pencil lead are >90% graphite, <5% clay and 5% wax for 9B, and 68% graphite, 26% clay and 5% wax for HB (such as IKEA pencil) [23]. PCAT was synthesized and purified according to published procedures [24]. Ammonium persulfate (98.0% pure, Sigma Aldrich), L-ascorbic acid (99.0% pure, Caledon), and methanol (anhydrous, Comalc) were used as received. The free chlorine samples were prepared by diluting a commercially available hypochlorite bleach solution (LAVO, Montreal).

The sensing device comprises two parallel gold electrodes sputtered on a glass slide with a thin layer of graphite between them forming a chemiresistor. Chromium (20 nm) and gold (200 nm) were sputter-deposited onto a frosted glass and patterned using a contact mask. The two gold electrodes were connected with pencil graphite by writing with a 9B or HB pencil producing a total resistance in the range of 0.2 – 1.5 KΩ. The number of lines written with the pencil was used to control the resistance of the graphitic layer, with a typical thickness of 1µm as shown in the cross-section in Fig. 1d extracted from a 50x 3D reconstructed optical image (Fig 1c), taken with a N-STORM Nikon microscope. A polydimethylsiloxane (PDMS) channel (15 mm long, 2 mm high, 2 mm wide) is bonded on top of the glass substrate by air plasma to prevent contact between the analyte and the gold electrodes, see schematic (Fig. 1a) and photograph (Fig. 1b) of the device. Some sensors were fabricated by attaching the PDMS to the glass slide using a double-sided adhesive tape (Kapton, Capliq Corp.) with a rectangular (2 mm x 10 mm) opening to expose the graphite layer. No difference in performance was noted between the two channel fabrication methods. The adhesive tape withstood exposure to aqueous analytes for several weeks.

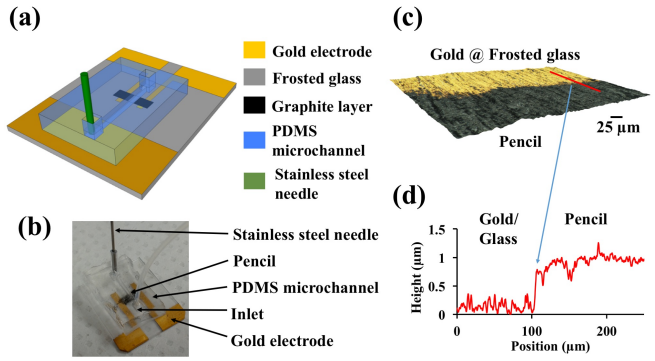

Fig 1. Graphite solid-state sensor. (a) Schematic diagram of the device; (b) Fabricated sensor device; (c) 3D reconstructed optical micrograph and (d) cross-section of the pencil line on gold on frosted glass.

A methanolic solution of PCAT was flowed through the channel for 5 minutes, after which measurements were performed by flowing analyte solution through the channel using a syringe pump and measuring the current at a fixed potential using a Keithley 2636 source meter. The data presented in this work was collected from numerous devices, resulting in somewhat different measured currents due to variation in film fabrication, but also demonstrating robustness and repeatability. The sensor data can be analysed in different ways. For consistency, in this work we plot the relative change in conductivity 500 seconds after exposure to the analyte.

B. Detection of aqueous free chlorine using IKEA pencil

First we quantify the effect of free chlorine concentration in water samples on the oxidation of the PCAT bound on the surface of the graphitic film fabricated using an IKEA pencil and the resultant change in conductivity. Four different concentrations 0.06 ppm, 0.6 ppm, 6 ppm, and 60 ppm of free chlorine samples in DI water were investigated, covering the relevant range for drinking water. For each test, 2 mL of the sample solution were flowed through the channel for 10 minutes at a flow rate of 0.2 mL/min. The current through the PCAT coated graphitic film (16 KΩ) was measured at an applied potential of 100 mV. The low applied potential ensured that there were no electrochemical side-reactions at the graphite-water interface. The current was recorded before introducing the sample solution and found stable just above 6.0 µA in methanol. When the graphite-PCAT film is exposed to free chlorine in the sample solution, the current across the film increases significantly (Fig. 2). When a sample solution of 60 ppm free chlorine in DI water was flowed through the sensor, the current increases rapidly at first followed by a slower increase until it reaches a stable value 2.24 µA above the baseline in 500 sec. Similarly, the change in current for 6 ppm, 0.6 ppm, and 0.06 ppm was recorded as 2.12 µA, 0.85 µA, and 0.25 µA, respectively. This allows the construction of a calibration curve, although the sensor shows signs of saturation above 6 ppm (Fig. 2b).

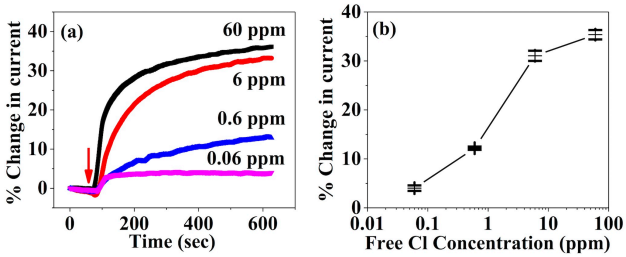

Fig. 2. Detecting free chlorine using PCAT-graphite (IKEA HB pencil). (a) The current vs time plot for exposure to different concentrations; (b) Calibration curve from data in (a).

C. Detection of aqueous free chlorine using 9B pencil

The sensor was also fabricated using a very soft pencil (9B) in order to compare it with the ordinary HB (IKEA) pencil based sensor device. The proportion of graphite to clay is higher in 9B pencil as compared to HB. Therefore, the resistance of the device fabricated using 9B pencil was lower (about 5 times compared to the HB), and it was possible to apply a lower potential of 10 mV across the electrodes during the measurement, further minimizing the danger of electrochemical interferences. All the other operating conditions were the same as described before. The device made with the 9B pencil performed in a similar fashion as the HB pencil (Figure 3). An increase in current was observed within seconds upon exposure to dilute free chlorine of sub ppm (0.06 and 0.6 ppm) to 60 ppm (Figure 3a). The change in current for 500 sec. for four free chlorine solutions

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60 ppm, 6 ppm, 0.6 ppm, and 0.06 ppm are 6.47 µA, 5.82 µA, 2.70 µA, and 0.70 µA, respectively (Figure 3a). The current is seen to increase with concentration (Figure 3 b). Subsequently, experiments were performed in the concentration range of interest in drinking water applications (0 - 10 ppm) and the relationship between the change in current with log concentration was found to be approximately linear (Figure 3 c). These results indicate that the amount of free chlorine in the solution is directly related to the degree of oxidation of the PCAT species which is associated with the degree of doping graphite sites that in turn leads to changes in the resistance of the graphite-PCAT hybrid system. The current can thus be used to quantify various free chlorine concentrations present in the sample. The linear range of the sensor covers the whole range of relevant chlorine concentrations (0.5 – 2 ppm) in drinking water. The sensor appears to approach saturation near 60 ppm. The sensitivity of the device fabricated with 9B pencil is significantly higher than the sensitivity of the device fabricated with HB pencil due to higher graphite content in 9B pencil, but functional devices can be produced with pencils of different hardness. For clarity, all following measurements in this work were conducted with 9B pencil devices.

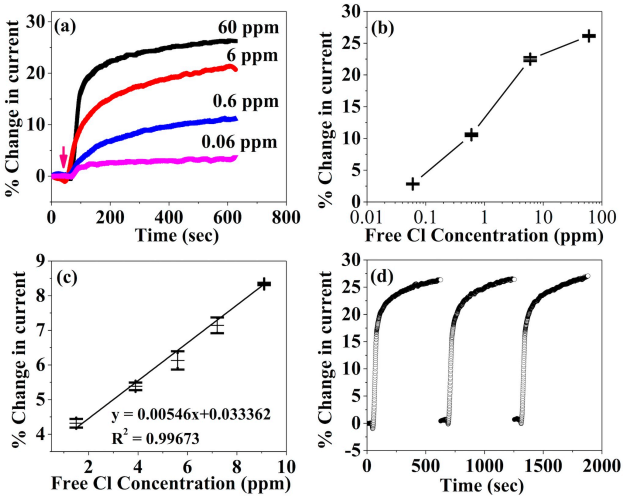

Fig. 3. Detecting free chlorine using PCAT-graphite (9B pencil). (a) The current vs time plot for exposure to different concentrations; (b) Calibration curve from data in (a); (c) Calibration curve showing linear relationship in the 1.5 to 9 ppm range; (d) Three times successive resetting of the device by applying -0.8V across one of the gold electrodes relative to the steel counter electrode after exposure to 60 ppm free chlorine.

Once the sensor has been used for detection of free chlorine, the PCAT is in an oxidized state. It will slowly equilibrate chemically with its environment and over time return to a more reduced state if in contact with a lower free chlorine concentration. This process can be accelerated, however, through chemical or electrochemical resets. It is possible to electrochemically reduce the oxidized PCAT so that the sensor is restored to its original state and the sensor can be used repeatedly. The "reset" of the sensing device was performed by applying -0.8 V for 5 min between one of the gold electrodes connected to the graphitic film and a steel counter electrode placed in the outlet of the channel which was filled with methanol. The reset reduces PCAT species resulting in un-doping the graphite film which restores the current across the sensor film to the baseline. The sensor was reset more than 25 times (three of which are shown in Fig. 3d) and the resistance of the sensor was found to settle into the original value indicating the stability, robustness, and reproducibility of the device. Thus, the resistance of the device can be switched back and forth from residual (high) level to oxidized (low) level by resetting and sensing free chlorine, respectively. We have also investigated the reset of the sensor in tap water itself rather than methanol in order to make it reagent free. It was possible to reset the sensor in tap water, but due to the presence of some residual free chlorine, the PCAT gets re-oxidized and consequently, the current increases immediately to reach a stable value corresponding to the residual concentration. Nevertheless, this experiment demonstrates that the sensor can be reset both in methanol as well as in water.

D. Fouling resistance

To test for interference of organic carbon species and fouling resistance, sensors were exposed to waste water and humic acid (Fig. 4). Deionized water samples (DIW) and waste water samples (WW, collected from the Dundas Waste Water Treatment Plant, Hamilton, Canada) spiked with 0.06 ppm, 0.6 ppm, and 6 ppm of free chlorine were flown through one device, with a negligible change in response (Fig. 4a). In order to determine whether the sensor would foul when used with surface waters, another device was exposed to a flow of DIW with 2 ppm of humic acid as a model contaminant for 30 min. A 0.6 ppm free chlorine in DIW sample was measured before and after humic acid exposure, with no noticeable change in response (Fig. 4b), indicating no degradation/fouling effect on the device.

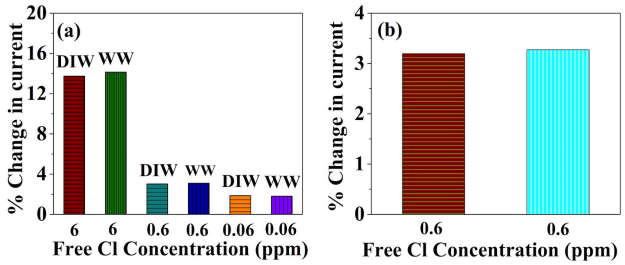

Fig. 4. Effect of waste water and humic acid solutions (a) The histogram demonstrates no significant change in current in graphite-PCAT device for free chlorine sample of 6, 0.6, and 0.06 ppm prepared with waste and DI water, (b) Change in current signal for 0.6 ppm free chlorine before and after humic acid flow over the device.

E. Effect of interfering species

As a control experiment, two sensors were fabricated with 9B pencil. One sensor was functionalized with PCAT while the other was left bare. The sensitivity was tested by flowing DI water at the rate of 0.2 ml/min for 15 minutes followed by 2 ppm hypochlorite solution for 15 minutes. The change in current upon exposure to 2 ppm sodium hypochlorite is reported is shown in Fig. 5. The PCAT functionalized sensor exhibits a greater change in current compared to the bare pencil sensor. The effect of interfering species (nitrate, phosphate and sulfate) was tested on the same sensors using the appropriate sodium salts. First, DI water was flowed over both sensors for 15 minutes followed by water containing 10 ppm nitrate for 15 minutes. The sensors were also exposed to phosphate (0.03 ppm) and sulfate (500 ppm) at concentration levels that are the maximum allowable in surface waters according to government regulations [25][26]. The PCAT functionalized sensor showed a lower response to the

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interfering species as compared to the bare sensor. The effect of the interfering species on the sensor performance was evaluated by comparing the sensor response to the maximum concentration of the interfering species to the response to 2 ppm of free chlorine. The inset (Fig. 5) shows that the PCAT functionalization reduced the response of the sensor to interfering species anywhere between 2.4 to 4.5 fold in comparison to its response to free chlorine. From this data it is evident that PCAT functionalization improves both the sensitivity and specificity of the pencil electrode sensors.

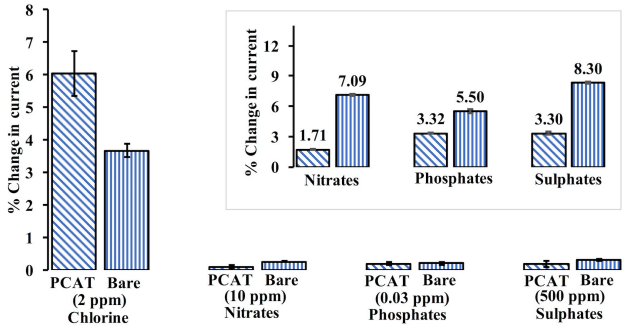

Fig. 5. Effect of interfering species. Change in current for sensors with and without PCAT. PCAT functionalization resulted in higher sensitivity to chlorine and better discrimination against nitrate, phosphate and sulphate. Inset compares the efficiency of the sensors, calculated as the ratio of current for interfering species to current for free chlorine.

III. CONCLUSION

A solid state chemiresistive sensor based on a graphitic film fabricated by drawing with a pencil has been demonstrated for measuring aqueous free-chlorine concentrations. The device operates over a wide range from 0.06 to 60 ppm to guarantee safe levels (0.5 to 2 ppm) of free chlorine in drinking water. The response is approximately linear within a 1 to 10 ppm range and largely unaffected by species that commonly interfere with free chlorine measurements in drinking water at their maximum allowed concentrations. Our sensor is based on the redox-activity of oligoanilines that are non-covalently attached to the graphitic film. Free chlorine is detected due to the interconversion of PCAT between different forms that cause distinct doping states of their graphite host films. Since the sensing mechanism does not rely on electrochemistry, a reference electrode is not required for operation. The pencil base sensor is easy to fabricate, robust, selective, and much lower in cost compared to other existing sensors. It provides an effective way to measure free chlorine in a reagent free manner. It is expected that this sensor will find widespread application in resource poor settings where there is a critical need to quantitatively measure fee chlorine to determine effective treatment of drinking water.

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