Crumpled graphene oxide decorated SnO₂ nanocolumns for the electrochemical detection of free chlorine

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Abstract A crumpled graphene oxide–SnO₂ nanocolumn (CGO–SnO₂) composite electrode was fabricated using aerosol-based techniques. First, SnO₂ nanocolumn thin films were fabricated using an aerosol chemical vapor deposition (ACVD) technique. The surface of the nanocolumn was then decorated with CGO by electrospray deposition. The CGO–SnO₂ electrode was utilized for the electrochemical detection and determination of the free chlorine concentration in aqueous solutions using linear sweep voltammetry (LSV) and amperometric *i*–*t* curve techniques. The CGO–SnO₂ electrodes worked through the direct electrochemical reduction of hypochlorite ions (ClO[−]) on the surface of the electrode, which was used to determine the free chlorine concentration. The electrodes operate over a wide linear range of 0.1–10.08 ppm, with a sensitivity of 2.69 $\mu\text{A } \mu\text{M}^{-1} \text{ cm}^{-2}$. Further, selectivity studies showed that these electrodes easily conquer the electrochemical signals of other common ions in drinking water distribution systems, and only shows the electrochemical reduction signals of free chlorine. Finally, the CGO–SnO₂ electrodes were successfully employed for the detection of free chlorine in tap water solutions (St. Louis, MO 63130, USA) with a sensitivity of 5.86 $\mu\text{A } \mu\text{M}^{-1} \text{ cm}^{-2}$. Overall, the sensor fabricated using simple and scalable aerosol-based techniques showed a comparable performance to previous

studies on amperometric chlorine sensing using carbon-based electrodes.

Keywords Graphene oxide · SnO₂ · Chlorine detection · Aerosol chemical vapor deposition

Introduction

The quality of drinking water has to be monitored continuously to avoid waterborne diseases including cholera, diarrhea, and typhoid fever in many developing nations. Chlorine is the most commonly used disinfectant for the treatment of various water resources including drinking water, waste water, and swimming pools. The environmental protection agency (EPA) requires water supply utilities to maintain a residual disinfectant concentration throughout the distribution system to inhibit microbial re-contamination of treated drinking water. The addition of NaOCl as a chlorine source in water generates both hypochlorite ions (ClO[−]) and hypochlorous acid (Qin et al. 2015).

High levels of chlorine can have negative health effects such as eye/nose irritation, stomach discomfort, anemia, and nervous system affects in some infants (Chowdhury et al. 2014). In the ecosystem, excess chlorine residuals can interact with organic matter to form disinfection by-products (DBPs). These DBPs are toxic and pose a threat to the health of consumers. The EPA has established maximum contaminant levels (MCLs) for DBPs, which apply to both large community water systems and non-transient, non-community water systems that add disinfectant. Small communities are particularly vulnerable to compliance failures with regulatory standards for DBPs, which can be largely attributed to the limited resources available for monitoring (Sinha et al. 2006; Hall et al. 2007).

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Due to this, different types of analytical methods are being used to monitor free chlorine residuals. The most common methods include, spectrophotometric monitoring (Moberg and Karlberg 2000; March and Simonet 2007; He and Yu 2015), interferometry (Xu et al. 2011), colorimetry (Lou et al. 2011) and electroanalytical methods (Soldatkin et al. 1997; Campo et al. 2005; Kishioka et al. 2005; Kodera et al. 2005; Thiagarajan et al. 2011). Among these, electroanalytical methods are advantageous in their robustness, low cost, ease of use, and real-time monitoring capabilities. One of the most commonly used techniques for online free chlorine (part of chlorinated water not reacted with any contaminants) monitoring is amperometric sensing. Prussian blue electrodes (Salazar et al. 2015), gold thin film microelectrodes (Olivé-Monllau et al. 2009), and nano-Au film electrodes (Thiagarajan et al. 2011), have been applied as amperometric chlorine sensors; however, these devices have high costs due to the use of expensive noble metals as electrode materials (Hall et al. 2007).

To overcome this hurdle, simple, low-cost materials must be developed for the real-time detection and determination of free chlorine in water distribution systems. Recently, graphene-based nanomaterials have shown promise as an electrochemical, optical, and biological sensing material (Kochmann et al. 2012). More specifically, carbon-based composite materials, including carbon nanotube composite electrodes (Olivé-Monllau et al. 2011), carbon nanotube–epoxy composites (Olivé-Monllau et al. 2010), multi-walled carbon nanotube/epoxy with CuO nanoparticles (Muñoz et al. 2015), and chemically modified graphite-based electrodes, were used for free chlorine sensing (Pan et al. 2015). Further, graphene and metal oxide nanocomposites have been successfully utilized for electrochemical biosensing applications. For example, graphene/SnO₂ nanocomposite-modified electrodes (Sun et al. 2013; Nurzulaikha et al. 2015), and octahedral SnO₂ nanocrystals bounded by reduced graphene oxide nanosheets for the electrochemical determination of dopamine were reported (Ma et al. 2015). In addition, quantum sized SnO₂-conjugated reduced graphene oxide nanocomposite were applied as non-enzymatic glucose sensors (Ye et al. 2014; Mohd Yazid et al. 2014; Fu et al. 2015). Typically, the fabrication process for these electrodes is complex, requiring multiple steps where each material is synthesized independently and combined in additional steps with limited control over the final morphology (McCreery 2008; Muñoz et al. 2015).

Herein, we focus on the development of metal oxide–graphene nanocomposite sensors using aerosol-based synthesis routes—*aerosol chemical vapor deposition (ACVD)* and *electrospray deposition* (Shah et al. 2012; Kavadiya et al. 2016, 2017)—for the electrochemical detection of free chlorine. Aerosol-based synthesis routes are

advantageous due to their scalability and low cost while still maintaining precise control and flexibility in deposition (Pratsinis 2010; Jiang et al. 2016, 2017). For electrode fabrication, SnO₂-nanostructured columns were produced using ACVD and functionalized with crumpled graphene oxide (CGO) using electrospray deposition (Shah et al. 2015). The main advantage of these aerosol-based techniques is the single step synthesis and deposition of the material on the substrate in the desired morphology (Zhan et al. 2010). The two-step synthesis approach of the electrode offers precise control over the material ratio and maintains the chemical composition and morphology of the individual structures. We have demonstrated the electrode performance for the detection of free chlorine using linear sweep voltammetry (LSV) and amperometric techniques in neutral pH conditions and in real water resources (tap water, St. Louis, MO 63130, USA). In both cases, the CGO–SnO₂ electrodes showed a robust performance for the electrochemical detection and determination of free chlorine.

Methods

Electrode fabrication

The SnO₂-nanostructured thin films were prepared on 25 × 50 mm Corning alkaline earth boro-aluminosilicate glass coated with Indium Tin Oxide (ITO, 0.7 mm thickness, Delta Technologies, Limited, Loveland, CO) using ACVD, described in detail in previous work (Thimsen et al. 2008a, b; An et al. 2009; Chadha et al. 2014). In brief, the precursor (in vapor phase) is introduced into the reactor zone and converted to metal oxide particles. As the particles travel through the reactor via convective flow, growth occurs through coagulation and coalescence. The particles are eventually deposited onto the ITO substrate by diffusion in the boundary layer, along with any unreacted precursor vapor (Kulkarni and Biswas 2004). Following deposition, particle sintering and further growth on the substrate occurs as the deposited particles interact with the unreacted precursor vapor and the subsequently deposited particles. For the growth of the SnO₂ nanocolumns in the ACVD system, tetramethyl tin (TMT, Sigma-Aldrich, MO, USA) was used as the precursor. The precursor was delivered via a bubbler at a rate of 11 ccm with nitrogen (N₂) as a carrier gas and oxygen was used as a dilution flow, delivered at a rate of 100 ccm. For this study, the substrate temperature was fixed at 600 °C, the distance between the feeding tube and substrate was fixed at 1 cm, and the deposition time was 30 min. All the parameters used for the growth of SnO₂ nanostructure were optimized based on the framework developed in previous studies (An et al. 2010).

Following the deposition of nanostructured SnO₂ thin films, the surface was decorated with CGO. First, graphene oxide sheets were synthesized using Hummer's method (Hummers and Offeman 1958; Wang et al. 2012a, b). The solution was sonicated for 1 h prior to the electrospray process to ensure the exfoliation of the GO sheets was maintained. A precursor solution containing GO sheets was then prepared by adding 3 mM of ammonium acetate to a 0.31 mg ml⁻¹ of GO solution. Using an electrospray deposition system, the GO sheets were aerosolized to yield a crumpled structure and deposited on the SnO₂ thin films in a single step. Electrospray is an atomization technique to generate nanoparticles from a liquid solution at ambient conditions using an electric field (Fig. 1). The electrospray technique has been described and used previously to self-assemble molecules and deposit on metal oxide thin films (Shah et al. 2015; Kavadiya et al. 2016). Moreover, electrospray can be used to crumple GO sheets via evaporation induced crumpling. Briefly, GO precursor solution is pumped at a flow rate of 1 $\mu\text{L min}^{-1}$ through a capillary needle. An electric field is applied in the deposition chamber by connecting the needle to a high voltage source and the substrate to the ground. The electrospray system was operated in the Taylor cone-jet mode to obtain monodisperse droplets. Through the evaporation of the solvent, the GO sheets in the droplet are converted into crumpled GO particles, which then deposit on the substrate. The spray solution properties and electrospray conditions used for these sensors are detailed in Table 1.

Material characterization

The thickness and morphology of the deposited SnO₂ columns were characterized using scanning electron microscopy (SEM, FEI NovaNanoSEM 230, OR, USA), carried out at 15 kV. The crystallinity of the film was characterized using X-ray diffraction (XRD, Bruker d8 Advance, MA, USA), with Cu K α radiation ($\lambda = 1.5406 \text{ \AA}$) and operated at 40 kV and 40 mA. The growth direction and crystal structure of the individual nanocolumns were confirmed using high-resolution transmission electron microscopy (HRTEM, JEOL JEM-2100F, MA, USA), carried out at 200 kV. The morphology of the

CGO particle was imaged using transmission electron microscopy (TEM, FEI Transmission Electron Microscope, OR, USA). The elemental composition and purity of the thin films was analyzed using X-ray photoelectron spectroscopy (XPS, Physical Electronics 5000 Versa Probe II Scanning ESCA MN, USA).

Electrochemical testing

All the electrochemical and electroanalytical experiments were carried out using a three-electrode setup, with the synthesized composite material on ITO as the working electrode, Ag/AgCl as the reference electrode, and platinum wire as the counter electrode. A CHI 760 bipotentiostat (CH Instruments, Austin, USA) was used for all the electrochemical measurements (cyclic voltammetry (CV), linear sweep voltammetry (LSV), and amperometric $i-t$ curve). All the electrochemical solutions were prepared using ultra-pure deionized water. The experiments were performed using a phosphate buffer solution (PBS, pH 7.4) and purged with ultra-pure nitrogen gas. The CV and LSV measurements were carried out in a voltage range of 0.8 to -0.8 (V) , scanned at a rate of 100 mV s^{-1} . We also employed the amperometric $i-t$ curve technique, where the potential was fixed at -0.45 V and the current response was measured as a function of time. Following the electrochemical characterization of the electrode, the selectivity of the electrode for free chlorine was tested. An amperometric $i-t$ curve was studied to determine the interference of different species including Na⁺, K⁺, Ca²⁺, NO₃⁻, and SO₄²⁻. At the fixed potential range (-0.45 V), the current response was measured with the addition of interfering compounds including, KCl (1.02 mM), KNO₃ (1 mM), CaSO₄ (0.98 mM), NaSO₄ (0.96 mM), and NaCl (0.95 mM). All of these compounds were added at concentrations similar to those found in tap and recreational water sources. (Muñoz et al. 2015) Finally, Saint Louis City tap water (MO, 63130 USA) was used to analyze the performance of the electrode under real-world conditions.

Results and discussion

Material characterization and film fabrication

The SnO₂ nanocolumns of the films deposited via ACVD had an average height of $4.8 \mu\text{m}$ and an average cross-section of 140 nm (Fig. 2c). XPS analysis was used to confirm the purity of the SnO₂, and only showed a small carbon impurity peak that can be attributed to surface carbon (Fig. 2a). The XRD patterns obtained for the bare SnO₂ films are consistent with that expected for cassiterite (PDF 01-071-5323), as shown in Fig. 2b. The pattern

Fig. 1 Deposition procedure for the construction of CGO-SnO₂ nanocomposites

Table 1 Process parameters for the crumpling and deposition of graphene oxide using electrospray

Spray solution properties					Electrospray conditions			Droplet properties
Solvent	Dielectric constant	Ammonium acetate concentration (mM)	Graphene oxide concentration (mg ml ⁻¹)	Solution conductivity (μS cm ⁻¹)	Flow rate (μL min ⁻¹)	Cone-jet voltage (kV)	Deposition time (min)	Mean droplet size ⁱ (nm)
Water	80	3	0.15	357	1	5.9–7	30	613

Fig. 2 Physicochemical characterization: **a** XPS spectra of the as-deposited SnO₂ nanocolumn thin films on Si wafer, demonstrating the surface purity of the prepared sensing elements. **b** XRD of SnO₂ nanostructured thin films grown for 30 min at 600 °C. Reference PDF#01-071-5323 (RDB). Cross-sectional SEM images of **(c)** SnO₂ nanostructured thin films and **(d)** CGO–SnO₂ composite films. **e** High

magnification SEM images of the CGO sheets attached to the surface of SnO₂ nanocolumn. Top-view SEM images of **e** and **f** TEM image of individual crumpled graphene oxide sheet. The arrow shows the tip of uncoated SnO₂ nanostructure **(c)** and coated SnO₂ nanostructure with CGO **(d–e)**

indicates preferential growth along the (211) plane, which is a high index plane that should have improved catalytic activity due to increased density of dangling bonds (Tian et al. 2007; Han et al. 2009).

The graphene oxide sheets were crumpled using electrospray and then deposited onto the SnO₂ nanostructured thin film, with the composite film shown in Fig. 2d. The voltage is adjusted to create a stable Taylor cone-jet at the tip of the needle, resulting in the production of monodispersed droplets. The charged droplets then travel in the electric field towards the substrate. As the droplet travels towards the substrate, the solvent evaporates causing a confinement (capillary) force that crumples the GO sheets. The solvent is completely evaporated before reaching the

substrate. The crumpled nanoparticles deposit and adhere to the nanostructured SnO₂ thin films via van der Waals forces. The CGO nanoparticle, shown in Fig. 2f had an average diameter of around 200 nm. The total amount of CGO deposited on the electrode was about 4.5 μg. The SnO₂ base films decorated with CGO were characterized by SEM (Fig. 2c–e). The base columnar structure of the thin films remained the same before and after CGO deposition, with some breakage of the columnar structure upon CGO loading. As shown by the high magnification SEM images, the CGO coated the surface of the nanocolumns (Fig. 2e). The use of CGO increases the surface area as compared to GO sheets by preventing sheet aggregation due to pi–pi interactions. In addition, the SnO₂ base layer

acts as a template for the graphene material, which further increases the available surface area as compared to crumpled sheets deposited on a surface.

Electrochemical detection of free chlorine

To investigate the electroanalytical performance, the CGO–SnO₂-modified electrodes were tested for the detection of free chlorine in a three-electrode electrochemical cell setup in a PBS solution (pH 7.4) using cyclic voltammetry (CV). Figure 3a shows the CV response of the bare ITO electrode in the presence of 1.20 ppm NaOCl in pH 7.4 PBS solution, which shows a null detection response. Figure 3b and c shows the electrochemical reduction peak for free chlorine at the SnO₂ and CGO electrodes, respectively. The SnO₂ electrode shows an electrochemical reduction peak at -0.42 V with the current increment of 44.25 μ A. The strong reduction peak can be attributed to the large surface area and superior electrical properties of the nanocolumn thin films. The nanostructured columns not only result in a large surface for reaction but also minimize the charge barriers for electrons and increases electron lifetime (Thimsen et al. 2008a, b; Wang et al. 2012a, b; Chadha et al. 2014). The CGO electrode also shows a reduction peak at around -0.42 V, with the current increment of 5.7 μ A. Because graphene oxide is an insulator, the moderate reduction peak is a function of the extent of surface reactions such as adsorption, which are facilitated by CGO's large surface area and, potentially, by the functional groups on the surface. Finally, the CGO–SnO₂ composite electrode (Fig. 3d) shows the best electrochemical reduction response at -0.44 V, with a current increment of 60.80 μ A. This result clearly shows that the combination of SnO₂ nanocolumns and CGO has a superior electrocatalytic performance

compared to the individual SnO₂ and CGO films for the detection of free chlorine in the pH 7.4 PBS, which can be attributed to the synergistic effects of the composite material. The CGO on the surface of the nanocolumns results in increased surface reactions, and the single crystal nanocolumns allow for efficient electron transfer for these reactions at the electrode surface.

The electrochemical reduction mechanism of NaOCl at CGO–SnO₂ electrodes, which has been shown to occur at roughly -0.42 V (Kodera et al. 2005; Olivé-Monllau et al. 2010, 2011; Thiagarajan et al. 2011; Kiss et al. 2014; Senthilkumar and Zen 2014; Tang et al. 2014; Muñoz et al. 2015; Salazar et al. 2015; Wang and Anzai 2015) is as follows:

To study the effect of analyte concentration on the electrocatalytic activity of SnO₂–CGO, LSV was employed for the detection of free chlorine (Fig. 4). The concentration of NaOCl in the electrolyte was increased from 0.1 to 10.08 ppm and the corresponding change in current was measured. Figure 4 shows the LSV responses of the CGO–SnO₂ electrode at six different concentrations of NaOCl (0, 0.1, 0.9, 4.01, 8.05, 10.08 ppm, increasing from a to f). Here, the LSV shows a well-defined electrochemical reduction peak for the detection of free chlorine at around -0.45 V. Further the reduction peak intensity increases along with the concentration of ClO[−]. This result confirms that CGO–SnO₂ electrode has high sensitivity within the tested concentration range (of 0.1–10.08 ppm), which encompasses the concentration of chlorine found in drinking water distribution systems. Furthermore, the calibration curve (Fig. 4, inset) was plotted from the LSV response at the reduction peak and

Fig. 3 CV studies for the electrochemical reduction of NaOCl (23.3 μ M (1.20 ppm)) in pH 7.4 PBS. CV response of **a** ITO, **b** SnO₂, **c** CGO, and **d** CGO–SnO₂ electrode

Fig. 4 LSV response of CGO–SnO₂ electrode in pH 7.4 PBS for the electrochemical reduction of NaOCl (NaOCl concentration: **a–f** 0, 0.1, 0.9, 4.01, 8.05, 10.08 ppm)

the sensitivity of the electrode was calculated to be $2.69 \mu\text{A } \mu\text{M}^{-1} \text{cm}^{-2}$.

To study the effect of interfering compounds on the performance of the electrode, an amperometric $i-t$ curve was produced (Fig. 5). While there was no change with the addition of each interfering compounds (KCl, KNO_3 , CaSO_4 , NaSO_4 , NaCl), a slight decrease in the current magnitude was observed overall. Following the addition of interfering compounds, upon further addition of NaOCl (0.1 mM), the proposed electrode clearly shows a large, stepwise increment in the current response for the electrochemical reduction of ClO^- , even at this low concentration. This behavior confirms that the CGO– SnO_2 electrode overcomes the interference effect of various ions at relatively high concentrations (1 mM). Finally, the results validate the application of the CGO– SnO_2 electrodes for the selective, real-time sensing of free chlorine.

Detection of free chlorine in tap water

To validate the potential real-time sensing response, we have examined the electrocatalytic properties of CGO– SnO_2 electrode to detect free chlorine in tap water. Saint Louis city tap water (MO, 63130 USA) was collected and used to directly prepare the stock solutions with NaOCl at various concentrations. The LSV technique, with a potential window of 0.8 to -0.8 V and a scan rate of 100 mV s^{-1} , was again employed to determine the free chlorine concentration in PBS solution. Figure 6 shows the LSV response of the CGO– SnO_2 electrode for various concentrations of ClO^- ions. For increasing concentrations of ClO^- , the corresponding reduction peak increases linearly. This confirms that the proposed electrode successfully detects free chlorine in tap water samples. The linear range of detection for free chlorine is 0.1–10.08 ppm. The

Fig. 5 Amperometric response of the CGO– SnO_2 electrode for each sequential addition of **a** NaOCl (0.1 mM), **b** KCl (1.02 mM), **c** KNO_3 (1 mM), **d** CaSO_4 (0.98 mM), **e** NaSO_4 (0.96 mM), **f** NaCl (0.95 mM) in pH 7.4 PBS

Fig. 6 LSV response of CGO– SnO_2 electrode for electrochemical reduction of NaOCl in pH 7.4 PBS. (NaOCl concentration in tap water: **a–f** 0, 0.1, 0.9, 4.01, 8.05, 10.08 ppm)

inset of Fig. 6 shows the current vs. concentration plot for the detection of free chlorine in the tap water. From the calibration curve, the sensitivity of the CGO– SnO_2 electrode for the detection of free chlorine was found to be $5.86 \mu\text{A } \mu\text{M}^{-1} \text{cm}^{-2}$. These electroanalyses studies clearly show that the CGO– SnO_2 electrode effectively detects free chlorine in real water resource samples. Further, the linear range of this electrode falls within the acceptable limit to detect free chlorine (0.1–10.08 ppm) set by the various monitoring agencies. We also compared the results of CGO– SnO_2 electrodes with other electrode materials reported in the literature. Table 2 shows the comparison studies of the present electrodes for the detection and determination of free chlorine. We can see that the electrode possesses a reasonable linear range of detection for free chlorine sensing (0.1–10.08 ppm) compared to other electrode materials.

Stability studies

The stability of the proposed electrode was examined before and after the detection of free chlorine. After the electroanalytical studies, the CGO– SnO_2 electrode was tested in a pH 7.4 PBS solution using CV at a scan rate of 100 mV s^{-1} and the background response was recorded (Fig. 7, curve a). The electrode was then stored in open air under ambient conditions (25°C) for 5 days. On the fifth day, the electrode was re-examined using the same procedures to determine the background current response in pH 7.4 PBS (Fig. 7, curve b). From Fig. 7, curve b, we observe that there is only a slight shift in the reduction scan but no large drop in the background current response. Based on this result, we can conclude that the CGO– SnO_2 electrode is electrochemically sensitive, selective, and stable at standard temperature and pressure conditions and could be reused for the multiple analyses.

Table 2 Comparison table for the detection of free chlorine at various electrode materials

Electrode	Potential (V)	pH	Linear range (ppm)	References
Prussian blue	−0.2	5.5	0–10	Salazar et al. (2015)
PolyMnTAPP-nano-Au	−0.1	10.4	0.087–37.97	Thiagarajan et al. (2011)
Polymelamine	0.125	7.0	0.035–24.81	Senthilkumar and (Zen 2014)
Boron-doped diamond	1.1	8.0	0.1–2	Murata et al. (2008)
PEDOT-gold	0	7.0	0.0035–3.30	Tsai et al. (2011)
Platinum	0.15	7.0	0–1.5	Ordeig et al. (2005)
Gold	0.15	5.0–8.0	0–0.4	Campo et al. (2005)
Silver	–	5.8	1–100	Jović et al. (2015)
CNT composite ceramic analyzer	−0.10	5.5	0.2–4	Olivé-Monllau et al. (2011)
CNT composite	−0.10	5.5	0.02–4	Olivé-Monllau et al. (2010)
CNT-epoxy-CuO nanoparticles	−0.35	5.5	–	Muñoz et al. (2015)
Graphite	0.1	7.0	–	Pan et al. (2015)
SnO ₂ -CGO	−0.45	7.4	0.1–10.08	This work

Fig. 7 Background scan of CGO–SnO₂ electrode in pH 7.4 PBS. Curve a is the background response immediately after the experiment in tap water, curve b shows the background response after 5 days

Conclusion

We have successfully fabricated CGO–SnO₂ nanocomposite electrodes using ACVD and electrospray deposition techniques. As-prepared CGO–SnO₂ electrodes were successfully employed for the detection of free chlorine in the pH 7.4 PBS and in real tap water. In both cases, the CGO–SnO₂ electrodes showed excellent sensitivity for the detection of free chlorine within the acceptable linear range (ppm). In addition, these electrodes overcome the interference effects of other ions commonly found in tap water and only shows selective electrochemical response for the detection-free chlorine. These electrodes, deposited via a highly simplified deposition approach had a chlorine sensing performance comparable to those previously reported in the literature for more complex and extensively

optimized processes. The electrode fabrication procedure for sensor applications is novel, cost effective, and scalable. Furthermore, this method of electrode fabrication could be optimized and expanded for other electrochemical biosensing, and environmental sensing applications.

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