



# Amperometric bromate-sensitive sensor via layer-by-layer assembling of metalloporphyrin and polyelectrolytes on carbon nanotubes modified surfaces

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## ABSTRACT

A novel amperometric sensor for bromate ( $\text{BrO}_3^-$ ) was developed using the layer-by-layer (LbL) assembly process of iron(III)-porphyrin (Fe(III)P) and polyelectrolytes alongside oxidized multiwall carbon nanotubes (OMWCNTs) on a disposable screen-printed carbon electrode (SPCE). Positively charged Fe(III)P and negatively charged poly(sodium 4-styrenesulfonate) (PSS) were used as structure blocks for LbL assembly on the OMWCNTs modified SPCE. The electrocatalytic response by Fe(III)P from the amperometric LbL sensor for determining  $\text{BrO}_3^-$  concentration was characterized using cyclic voltammetry. Critical experimental parameters affecting the sensor's performance were optimized, including the number of assembled layers, pH of the buffer solution, and concentration of Fe(III)P immobilized on the electrode surface. A linear response from 100 nM to 2.5 mM of  $\text{BrO}_3^-$  in 0.2 M SAB solution with a sensitivity of  $115.2 \mu\text{A mM}^{-1}$  and a detection limit of 43 nM were achieved with good selectivity. As a final demonstration, the proposed LbL sensor,  $[\text{Fe(III)P-PSS}]_1\text{-Fe(III)P-OMWCNTs/SPCE}$ , was applied to analyze  $\text{BrO}_3^-$  concentrations in tap water and mineral water samples.

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## 1. Introduction

Chlorination and ozonation have emerged as two of the most promising methods for disinfection of drinking water [1,2]. However, these disinfection methods tend to oxidize the bromide ( $\text{Br}^-$ ) present in natural water, such as seawater and freshwater, to bromate ( $\text{BrO}_3^-$ ), which presents a potential human health problem. The  $\text{BrO}_3^-$  is a bromine-based oxyhalide formed as a disinfection byproduct during chlorination or ozonation in water containing  $\text{Br}^-$  [3–5].  $\text{BrO}_3^-$  has also been classified as a group B2 carcinogen and has an acceptable maximum contaminant level of 10  $\mu\text{g/L}$  for  $\text{BrO}_3^-$  in global drinking water regulations to prevent the consumption of excess  $\text{BrO}_3^-$  [6–8]. Moreover, the significantly high concentration of  $\text{BrO}_3^-$  has been recently detected in natural water due to a chemical reaction of  $\text{Br}^-$  with sunlight and chlorine [9,10].

Several studies have been carried out to determine the concentration of  $\text{BrO}_3^-$  in water samples using ion chromatography (IC) [11,12], IC with inductively coupled plasma mass spectrom-

etry [13,14], liquid chromatography-mass spectrometry [15], gas chromatography-mass spectrometry [16], and spectrofluorometry [17]. However, these techniques require many pre-treatment procedures such the preparation of high levels of chloride in the sample matrix exchange sites [18], and the need to operate with complicated and expensive instruments. Therefore, the development of new methods for the simple, rapid, and inexpensive determination of  $\text{BrO}_3^-$  is required for environmental samples. Hence, electrochemical techniques have been introduced as reasonable, uncomplicated, and fast procedures to detect a wide range of  $\text{BrO}_3^-$  in water samples [19–23].

Iron(III)-porphyrin (Fe(III)P), the metalloporphyrin compounds of which have excellent electrocatalytic properties, has been applied in the detection of several major analytes, such as biocatalysts, molecular materials, and chemical mediators [24–26], due to their unique structural and electronic properties. However, most of the modified electrodes composed of Fe(III)P complexes have shown a number of problems such as loss of electron transfer mediators and short-term stability [21].

The incorporation of metalloporphyrin (i.e. Fe(III)P) into electrode materials has previously been shown to enhance the sensitivity of electrochemical sensors for various chemical com-

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pounds [21,25,27–29]. For instance, Fe(III)P and multiwalled carbon nanotubes composites on glassy carbon electrodes have been employed to detect ascorbic acid, dopamine, uric acid, and nitrite at concentrations as low as 3, 0.09, 0.3, and 0.5  $\mu\text{M}$ , respectively [25]. Since pristine multiwalled carbon nanotubes (MWCNTs) on the surface are stable, it is somewhat difficult to modify their surface directly. Hence, the oxidized multiwalled carbon nanotubes (OMWCNTs), which are inserted branches on the surfaces of the MWCNTs, significantly increase the surface activity of MWCNTs, which increases the linkage between some functional groups (such as carboxylic acid groups) and MWCNTs for modification of the MWCNTs [30]. Thus, the OMWCNT is a promising material as it possesses excellent interchangeability and electrochemical conductivity, and is able to immobilize various substances on its external and internal surfaces [31,32].

In this paper, we introduce a newly developed, novel, and highly sensitive amperometric sensor design based on the layer by layer (LbL) assembly technique of Fe(III)P and polyelectrolytes for resolving the disadvantages of Fe(III)P. We then demonstrate its usefulness in the sensitive and selective detection of  $\text{BrO}_3^-$ . Carballo et al. determined the LbL assembly is utilizing metalloporphyrin in combination with a polyelectrolyte on an electrode surface [33]. However, there has not been any reported research done on the Fe(III)P with polyelectrolytes and OMWCNTs on a disposable SPCE for developing bromate sensor.

In our approach, negatively charged OMWCNTs were assembled on a SPCE, followed by sequential electrostatic adsorption of positively charged Fe(III)P and negatively charged poly(sodium 4-styrenesulfonate) (PSS) electrolytes. The performance of the LbL sensor for detecting  $\text{BrO}_3^-$ , including its sensitivity, reproducibility, and long-term stability, were evaluated using cyclic voltammetry (CV). In this study, the design parameters are optimized and include the number of Fe(III)P layers and the concentration of Fe(III)P. In addition, a comparison is given with the LbL assembled on SPCEs. Finally, the Fe(III)P and the polyelectrolyte integrated with the LbL sensor were employed to analyze  $\text{BrO}_3^-$  concentrations in chlorinated water (i.e. tap water) and ozonated water (i.e. mineral water) samples. The result was validated using ultraviolet-visible (UV-vis) spectroscopy measurements.

## 2. Experimental

### 2.1. Reagents

The MWCNTs with 90% purity (5–20 nm diameter) and <10  $\mu\text{m}$  length were obtained from local company (Carbon Nanomaterial Technology Co., Ltd, Korea). Fe(III)P and PSS were purchased from Sigma-Aldrich (St. Louis, USA) and used without further purification. Analytical grade potassium bromate ( $\text{KBrO}_3$ ) was also purchased from Sigma-Aldrich (Missouri, USA). A predetermined concentration of  $\text{BrO}_3^-$  solutions was completed with the supporting electrolyte (0.2 M sodium acetate buffer (SAB), pH 7) for the daily preparation. De-ionized (DI) water (resistivity > 18  $\text{M}\Omega\text{ cm}^{-1}$ ) produced by the NANOpure Diamond Ultrapure water system (Barnstead, Newton, MA, USA) was used for preparing all aqueous solutions and for rinsing. Nitrogen ( $\text{N}_2$ ) gas (high purity grade, 99.99%) was used for  $\text{O}_2$  reduction reaction of Fe(III)P. Hydrochloric (HCl) acid and sodium hydroxide (NaOH) were used for pH adjustment.

### 2.2. Apparatus

The electrochemical analysis data were obtained using a computer controlled potentiostat (Autolab PGSTAT302N, Netherland), managed by GPES (version 4.9) software for characterization of

the amperometric LbL sensors. SPCEs were custom made by The BIO Co. Ltd. (Republic of Korea) and consisted of a carbon working electrode (geometric working area: 0.028  $\text{cm}^2$ ), a carbon counter electrode, and an Ag/AgCl reference electrode. A sensor connector was used to connect the SPCE with the potentiostat. All electrochemical measurements for  $\text{BrO}_3^-$  were performed at room temperature. A 0.2 M SAB solution (pH 7.0) was used as a reference, and the different concentrations of  $\text{BrO}_3^-$  were added to 10 mL of the SAB for quantitative analysis of the  $\text{BrO}_3^-$ . For CV, a scan rate of 50  $\text{mV s}^{-1}$  was employed unless otherwise specified. The morphology of the modified electrodes was characterized by field emission scanning electron microscopy (FESEM, JSM-7600F, JEOL Ltd, Japan) and atomic force microscopy (AFM, Dimension 3100, Bruker, USA).

### 2.3. Preparation of the oxidized multiwalled carbon nanotubes

The MWCNTs were treated by ultrasonication in a 40 mL mixture of concentrated sulfuric ( $\text{H}_2\text{SO}_4$ ) and nitric acid ( $\text{HNO}_3$ ) (v/v = 3:1) for 3 h at 55  $^\circ\text{C}$  and then for 5 h at 80  $^\circ\text{C}$  [34]. After this treatment, the mixture was washed with distilled water and filtrated through a polycarbonate filter (Millipore, pore size 0.4  $\mu\text{m}$ ). Subsequently, the suspension was rinsed thoroughly with distilled water until neutralized. The MWCNTs were then dried at 70  $^\circ\text{C}$  for 24 h. During this process, the surface of each MWCNT was oxidized and then functionalized with hydroxyl ( $-\text{OH}$ ), carbonyl ( $-\text{C}=\text{O}$ ), and carboxylic ( $-\text{COOH}$ ) groups [35].

### 2.4. Fabrication of amperometric $\text{BrO}_3^-$ sensor by LbL assembly on an SPCE

The fabrication procedures of Fe(III)P, PSS, and the OMWCNTs modified SPCE are illustrated in Fig. 1. A suspension of 1  $\text{mg mL}^{-1}$  of the OMWCNTs in 0.01 wt% Nafion solution (80/20%, v/v, absolute ethanol/DI water) was sonicated for 1 h. Then, 10  $\mu\text{L}$  volumes of this suspension were directly dropped onto the surface of the working electrode and dried to immobilize the OMWCNTs at 70  $^\circ\text{C}$  for 10 min in an oven. The LbL multilayer formation proceeded as follows: the OMWCNTs modified SPCE was alternately dipped in 2 mM Fe(III)P and 2 mM PSS solution for 30 min each, followed by rinsing with 0.2 M SAB solution (pH 7.0) and drying under  $\text{N}_2$  gas. The process was repeated to deposit from one to four layers of Fe(III)P with PSS on the OMWCNTs modified SPCE. Fresh Fe(III)P solution and PSS solution were used each time. Prior to any electrochemical measurements, each  $[\text{Fe(III)P-PSS}]_n\text{-Fe(III)P-OMWCNTs/SPCE}$  ( $n = 0, 1, 2, 3$ ) was thoroughly rinsed with 0.2 M SAB solution (pH 7.0) and stored in a dark condition. All the  $\text{BrO}_3^-$  determination experiments were carried out under a dark condition at 25  $^\circ\text{C}$  to avoid the occurrence of photolysis of Fe(III)P in a visible light condition [36–38].

### 2.5. Analysis for photolysis of Fe(III)P

The photodegradable activity (or photolysis) of Fe(III)P was measured by exposure of  $[\text{Fe(III)P-PSS}]_1\text{-Fe(III)P-OMWCNTs/SPCEs}$  to light for different radiation durations (0.5, 1, 5, 10, and 30 min) at room temperature. A 36 W portable lamp was used as a source of visible light [39].

### 2.6. Detection of $\text{BrO}_3^-$ in real water samples using the proposed LbL sensors and conventional method

The  $[\text{Fe(III)P-PSS}]_1\text{-Fe(III)P-OMWCNTs/SPCEs}$  were employed to analyze the  $\text{BrO}_3^-$  concentrations in real water samples, and the result was validated by taking simultaneous measurements with a UV-vis spectrophotometer (DR6000, HACH, USA) [40,41]. Various concentrations (60 nM – 2 mM) of  $\text{BrO}_3^-$  solution (20 mL) were

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