ABSTRACT: Heavy metal pollution is posing a severe health risk on living organisms. Therefore, significant research efforts are focused on their detection. Here, we developed a sensing platform sensor for the selective detection of lead(II) acetate. The sensor is based on self-assembled polyethyleneimine-functionalized carbon nanotubes (PEI-CNTs) and graphene oxide films deposited onto gold interdigitated electrodes. The graphene-based nanostructure showed a resistive behavior, and the fabricated layer-by-layer film was used to detect Pb(II) acetate in an aqueous solution by comparison of three electrochemical methods: impedance spectroscopy, amperometry, and potentiometry stripping analysis. The results obtained from different methods show that the detection limit was down to 36 pmol/L and the sensitivity up to 4.3 μAL/μmol, with excellent repeatability. The detection mechanism was associated with the high affinity of heavy metal ions with the functional groups present in the PEI-CNTs and GO, allowing high performance and sensitivity. The achieved results are important for the research toward integrated monitoring and sensing platforms for Pb(II) contamination in drinking water.

1. INTRODUCTION

Non-essential heavy metals such as mercury (Hg), arsenic (As), lead (Pb), and cadmium (Cd) are cumulative, non-biodegradable, and highly toxic, causing serious health problems on living organisms as they are prevalent even at very low concentrations.1 Briefly, Pb and Pb-based compounds are widely known as hazardous environmental pollutants and toxic agents that can cause severe environmental damage and diseases in animals and humans.2-5 Moreover, Pb ions are a common soil contaminant that causes a decrease in soil biological activity.6 Pb ions can enter the human body through inhalation, ingestion, or consumption of contaminated food and water and accumulate in different tissues and distinct vital organs. Several diseases, such as those associated with memory deterioration in children, reduced fertility in men, intellectual deficit, adverse effects on the central nervous, gastrointestinal, and immune systems, and producing mitochondrial degradation and DNA damage, have been reported.7-10 Lead acetate (PbAc), also known as lead (II) acetate, is a lead-based component widely used in the processing of various commercial products. For example, PbAc is used to manufacture cosmetics, pesticides, water repellents, mildew protection products, and so on.10,11 On the whole, several adverse health problems in living beings are associated with prolonged exposure to lead acetate.12,13 Consequently, researchers are highly keen on developing new materials that are highly sensitive and capable of determining these ions in an aqueous solution.

In recent years, graphene-based nanostructures appeared as an emerging class of materials in many applications, from environmental monitoring to human health issues.14,15 Graphene is an atomic monolayer of sp² hybridized carbon atoms arranged in a hexagonal pattern and considered a semimetallic material with zero band gap, high electronic mobility (200,000 cm² V⁻¹ s⁻¹), surface-to-volume ratio (2600 m² g⁻¹), optical transmission (~97.7%), mechanical strength (130 GPa), and high electrical and thermal conductivities.16,17 It naturally arouses interest in different areas; however, pristine graphene is not favorable for sensing applications despite the exceptional properties.18 In this sense, various approaches have
been employed to functionalize graphene-based materials to expand sensing platforms’ applications.

Graphene-based materials modified with organic compounds containing functional groups have the natural ability to improve the mechanisms of adsorption of heavy metal ions through electrostatic forces, chelation, and hydrogen bonds, thus facilitating their detection. Graphene oxide (GO) and carbon nanotubes (CNTs) are of graphene-based materials, with GO having differently oxygenated groups (hydroxyl, epoxide, carbonyl, and carboxyl) at the edges and in the basal plane, making it an advantageous material to form stable solutions in water and other organic solvents. These oxygenated groups serve as active sites for adsorbing heavy metal ions, making GO a strong candidate for sensing due to adsorption of various heavy metal pollutants. In contrast, CNTs have extraordinary hydrophobic performance, it being impossible to study their properties through solution-based techniques. Recently, polyelectrolymeime (PEI), a polymeric cation rich in amine groups that contains a nitrogen atom with a lone pair, demonstrated outstanding ability in the functionalization of CNTs. Besides, PEI is widely known for its chelating metal properties; after the functionalization of CNTs with PEI, it allows the possibility of introducing active sites in CNTs for heavy metal adsorption. Polyethyleneimine-functionalized carbon nanotubes (PEI-CNTs) have shown efficiency in technological applications such as solar cells, removal of pollutants, and an excellent electrochemical sensing platform for silver nanoparticles, chromium ions, and promethazine hydrochloride. Nevertheless, it has been little explored for detecting heavy metal ions and even less regarding the PEI-CNT/GO composites. In particular, Huang et al. reported an electrochemical sensor using a glassy carbon electrode (GCE) modified with three-dimensional GO-CNT hybrid nanocomposite for the simultaneous detection of Pb\(^{2+}\) and Cd\(^{2+}\) ions using anodic stripping voltammetry. Shuping Wu et al. developed an electrochemical sensing platform integrating a hierarchical nanostructure (CNT/graphene/gold nanoparticle (AuNP)/Nafion) on the surface of a GCE electrode for the sensitive detection of Pb\(^{2+}\) in water and milk samples, exhibiting rapid response and high sensitive Pb\(^{2+}\) detection. In contrast, different nanocomposites containing graphene-based materials have been widely used to determine trace amounts of heavy metal ions. Hui et al. have developed an electrochemical sensor for the detection of copper (Cu) and zinc (Zn) ions based on a Au electrode modified through layer-by-layer (LbL) assembly of titanium carbide (Ti\(_3\)C\(_2\)T\(_x\)) and CNT composites. The sensitivity of the sensor was attributed to a synergistic effect between Ti\(_3\)C\(_2\)T\(_x\) and CNTs, which decreases the resistance of electron exchange during the redox process. Zhou et al. fabricated a field-effect transistor (FET) device-based sensor to specifically detect Pb\(^{2+}\) ions in water using a reduced graphene oxide (rGO)/AuNP hybrid structure, rGO being used as the semiconducting channel material and AuNPs being used to improve the performance of the sensor.

In this study, we report a highly sensitive platform for detecting Pb(II) acetate in an aqueous solution. An easy strategy was implemented to prepare a PEI-CNT, designed to be a positive polyelectrolyte. Our functionalization process is based on wrapping CNTs with a PEI polymeric chain. It has been shown that PEI can act as a good supramolecular complex to adsorb on the CNT’s surface via intermolecular forces. Therefore, it paves the way to manufacture a nacre-like structure with GO onto gold interdigitated electrodes (IDEs) in a straightforward, versatile, low-cost, and functional way through the LbL technique. PEI-CNTs were characterized by UV–vis and XPS spectroscopy. The fabricated sensor was used to detect Pb(II) acetate in an aqueous solution by impedance spectroscopy (IS), amperometry, and potentiometric stripping analysis (PSA). The detection mechanism was associated with the high affinity of heavy metal ions with functional groups present in the PEI-CNTs and GO, allowing high performance and sensitivity.

2. RESULTS AND DISCUSSION

2.1. Stable Aqueous Solution of the PEI-CNT Composite. The CNT functionalization process is based on a supramolecular complexation method using PEI to wrap the CNTs, as illustrated in Figure 1a. A black water-stable solution is obtained, remaining stable after 15 days of preparation (see Figure 1b). It is a non-covalent approach to functionalize CNTs through π−π interactions, hydrogen bonding, and van
der Waals forces. In this way, it is possible to synergistically combine PEI-CNTs with GO for high affinity with heavy metal ions, thus allowing an increase in the sensitivity of sensors through the strong electrostatic interaction with Pb ions in lead acetate.

2.2. UV−Vis and XPS Characterizations of the PEI-CNT Composite. The successful functionalization of CNTs with PEI is certified by UV−vis and XPS spectroscopy. Figure 2a shows the UV−vis absorption spectra obtained from the aqueous dispersions of GO, PEI-CNTs, and PEI. The spectrum of the GO aqueous solution displays a characteristic absorption band at 230 nm characteristic of the π−π* transitions due to the C−C bonds from the sp2 hybridization regions, and a small shoulder at 300 nm due to the n−π* transitions of C=N bonds present in sp3 hybridizations. The UV−vis spectrum of the as-prepared PEI-CNT suspensions shows an absorbance band around 270 nm, commonly attributed to the π−π* transitions of the aromatic C−C bonds of a graphitic structure. Besides, it can be seen from Figure 2a that the complexation of CNTs does not inhibit the PEI absorption response.

The XPS data were recorded before and after the functionalization of CNTs with PEI. Figure 2b shows the XPS survey spectra of unmodified CNTs and PEI-functionalized CNTs, showing relatively intense peaks that indicate the presence of C and O in both non-functionalized and functionalized samples. At the same time, N is only present in PEI-CNTs. Additional peaks are observed in the survey XPS spectrum of PEI-CNTs generated from the Si substrate. The high-resolution band associated with the electron C 1s core-level of unmodified CNTs and PEI-functionalized CNTs are shown in Figure 2c,d, respectively. The band related to the C 1s electron of the unmodified CNTs displays the main peak near 284.3 eV, which can be resolved mainly by deconvolution into two peaks, generally attributed to sp3 (284.2 eV) and sp2 (284.9 eV) hybridized graphitic carbon atoms. The peak at 286 eV can be due to C−O−C bonds from impurities. The C−C maximum peak of PEI-CNTs shows a significant up-shift from 284.3 to 285.0 eV compared to that of CNTs (Figure 2d), indicating rehybridization of sp3 carbon to sp2 carbon. It was deconvoluted into four peaks at 284.3, 285.0, 285.7, and 286.9 eV, commonly assigned to the sp2, sp3, C−N amine, and −N−C==O bondings, respectively. After PEI functionalization, an additional peak appears in the N 1s region, showing PEI’s presence after the surface modification of the wrapped CNTs. Deconvolution of the N 1s signal reveals peaks at 399.9, 400.8, and 402.1 eV, associated with interactions between the CNT surface and amine groups through the N−C, N==C, and N−C==O bonds, respectively.

2.3. LbL Self-Assembled Multilayer Films of PEI-CNTs and GO and Their Electrical Properties. The LbL assembly was employed in the growth of the film onto IDEs, consisting of spontaneous organization and sequential adsorption of PEI-CNTs and GO. It is mainly driven by van der Waals forces, hydrogen bonds, π−π stacking, and electrostatic interactions. Figure 3a illustrates the scanning electron microscopy (SEM) images of as-deposited (PEI-CNTs/GO)25 films onto Au IDEs. As shown in Figure 3b, the coating film is all over the IDE region, composed of randomly clustered GO nanoplatelets (see Figure 3c,d). The electrical properties of (PEI-CNTs/GO)25 multilayered films were analyzed by I−V

Figure 2. (a) UV−vis absorption spectra of GO aqueous solution, PEI-functionalized CNTs, and PEI. (b) XPS survey spectra of unmodified CNTs and PEI-functionalized CNTs. High-resolution C 1s core-level spectra of (c) unmodified CNTs and (d) PEI-functionalized CNTs. (e) High-resolution N 1s spectrum of PEI-functionalized CNTs.

Figure 3. SEM images of the as-deposited (PEI-CNT/GO) film onto IDEs. (a) Representative top view of the LbL film onto Au IDEs. (b) Zoomed view of the image (a). Surface morphology of the LbL film: (c) on the Au finger and (d) between a finger pair.
characteristic curves and electrical impedance measurements (see Figure 4). In Figure 4a, it can be seen that the electrical $I-V$ response of the (PEI-CNTs/GO)$_{25}$ LbL film has linearity similar to that of a resistor behavior. The real and imaginary parts of impedance are associated with an Ohmic resistance ($Z' = R$) and capacitance ($Z'' = 1/j\omega C$), respectively, and related through $Z = Z' + Z''$. It is well-known that the phase ($\theta$) represents the angle between impedance components in the complex plane (inset Figure 4b), giving $-90$, $0$, or $90$° when the electrical response presents a capacitive, resistive, or inductive behavior, respectively.\(^{43}\) Figure 4b shows the Bode plots for the phase before and after the LbL nanostructuration on the IDEs. Bare IDEs have a phase of $-90$° in almost the whole frequency regions analyzed, and after the LbL formation, it becomes approximately 0° from 1 to 10 kHz. For frequencies above 10 kHz, the response is not purely resistive because of the capacitive effects from the design of the IDEs.\(^{43}\) Similarly, the capacitive behavior of the bare IDEs is shown in Figure 4d in the frequency range where $\theta = -90$°.

So far, we have shown a straightforward approach through a non-covalent method for CNT functionalization using PEI. Also, the combination of the individual properties of PEI-CNTs and GO through the LbL technique is advantageous for the formation of a graphene-based nanostructure with suitable and ideal properties for a sensing platform.

### 2.4. (PEI-CNT/GO) LbL Film as a Platform Sensing of Pb(II) Acetate

Different strategies were approached to study the capacity of the (PEI-CNT/GO)$_{25}$ LbL film as a detection platform. IS and amperometry were used to investigate the LbL film’s ability to operate as an impedimetric or chemiresistive sensor to detect different analytes and distinguish different lead acetate concentrations. Additionally, the PSA was performed aiming at the specific detection of Pb(II) acetate.

The detection mechanism of an impedimetric sensor is based on changes produced in the sensing layer and detected through impedance measurements.\(^{44}\) A close comparison of the data obtained from impedance measurements is shown in Figure 5. The impedance magnitude and the real and complex parts of the impedance show the device’s ability to differentiate all samples analyzed (see Figure 5a–c). A clear difference between impedimetric responses is observed from 1 kHz to 1 MHz. The Nyquist plot shows a tendency to form a semicircle (Figure 5d). Where the diameter of the formed semicircle can be related to the film’s electrical resistance. Therefore, the decrease in the semicircle can be related to the reduction in the interfacial electrical resistance. When ionic charges in the solution increase, the electrical resistance of the (PEI-CNT/GO)$_{25}$ LbL film submerged in ultrapure water, 0.1 M HCl, and 7.4 μM Pb(II) acetate in 0.1 M HCl solution. (a) Impedance magnitude vs frequency, (b) real part vs frequency, (c) imaginary part vs frequency, and (d) Nyquist plots.

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The GO$_{25}$ LbL film decreases due to the affinity between ions in the solution and functional groups (i.e., hydroxyl, carboxyl, epoxy, carboxyl, and amine groups) in both GO and PEI-CNTs. Ions are attracted to the solid–liquid interface, and the charge transport properties of the LbL film are then strongly altered.

Impedance measurements were also taken by successively adding a 100 μmol/L Pb(II) acetate stock solution into the 0.1 mol/L HCl solution under continuous stirring. The lowest measured concentration was 100 nmol/L, without significant changes observed in the impedimetric response of the sensor at lower concentrations.

Figure 6. Impedimetric response of the (PEI-CNT/GO)$_{25}$ LbL film for the successive addition of Pb(II) acetate in 0.1 mol/L HCl solution. (a) Relative impedance modulus ($Z/Z_0$) vs frequency. (b–d) Calibration plots obtained from the impedance module, real and imaginary impedance at a fixed frequency value of 10 kHz. The inset of (d) shows the behavior of $Z''$ at concentrations below 1 μmol/L.

Figure 7. Amperometric response of the (PEI-CNT/GO)$_{25}$ LbL film for the successive addition of lead(II) acetate in 0.1 mol/L HCl solution. The voltages of (a) −0.3, (b) −0.4, (c) −0.6, and (d) −0.8 V were applied to evaluate the performance of the device in the detection of Pb(II) acetate. (e) Stabilized current response vs concentration of Pb(II) acetate for −0.3, −0.4, −0.6, and −0.8 V. (f) Sensitivity vs applied voltage of chemiresistive sensor.
correlation coefficient \( R = 0.99 \) for the both impedance module and real impedance. The imaginary impedance exhibits a linear behavior \( R = 0.96 \) from 1 to 7.4 \( \mu \text{mol/L} \) and hyperbolic below 1 \( \mu \text{mol/L} \) (see Figure 6 and inset Figure 6d). It is important to highlight that the impedimetric sensor’s sensitivity is derived from the affinity of functional groups in the sensing layer with ionic charges in the analyte. The oxygen- and nitrogen-containing functional groups, such as hydroxyl (\(-\text{OH}\)), carboxyl (\(-\text{COOH}\)), epoxy (\(-\text{COC}\)), carbonyl (\(-\text{C}==\text{O}\)), and amine (\(\text{N}==\text{H}\)), contribute to improved sorption performance and serve as active sites for Pb ion adsorption. This strongly affects the electrical properties and the charge carrier mechanisms in the \((\text{PEI-CNT/GO})_{25}\), LbL film. Consequently, the detection of Pb(II) acetate is facilitated in impedance measurements.

The detection mechanism of chemiresitive sensors is based on changes in the electrical conductivity of the sensing layer when the concentration of impurities in the aqueous solution is modified.\(^{45}\) Figure 7 shows the amperometric current response of a \((\text{PEI-CNT/GO})_{25}\) chemiresistor obtained after the successive addition of Pb(II) acetate stock solution in 0.1 \( \text{mol/L} \) HCl under continuous stirring. The figures also compare previous results with the electrical response obtained in ultrapure water (black line) and 0.1 \( \text{mol/L} \) HCl (red line). The voltage was set at \(-0.3\), \(-0.4\), \(-0.6\), and \(-0.8 \text{ V}\) to find the most sensitive condition and ensure an optimal chemiresitive sensor performance (see Figure 7a–d). The choice of negative voltages is due to the stripping peak current of lead ions in that region.\(^{46}\) For all voltages analyzed, a clear difference was observed in the electrical response obtained in pure water and 0.1 \( \text{mol/L} \) HCl solution. The significant changes between measurements made by varying the Pb(II) acetate concentration from 500 \( \mu \text{mol/L} \) to 7.4 \( \mu \text{mol/L} \) are more noticeable from \(-3 \text{ V}\). Moreover, the difference in the amperometric current response increases as the voltage becomes more negative. This is attributed to improvements in the kinetics of Pb(II) cations attracted to the interface at negative voltages and also to its affinity with oxygenated groups in GO. Figure 7e shows the amperometric current response of the chemiresitive sensor as the Pb(II) acetate concentration increases, with the current fixed for a particular time after the measurements stabilize. A linear behavior can be observed between the electric current and the Pb(II) acetate concentration at all applied voltages. When comparing the current–concentration plots corresponding to each voltage, it can be seen that the difference lies in the slope of each figure, being greater as the voltage becomes more negative. Figure 7f illustrates the sensitivity versus Voltage plot; the straight-line response was obtained between \(-0.3 \text{ and } -0.8 \text{ V}\), obtaining a sensitivity of up to 4.3 \( \mu \text{A.L}/\mu \text{mol} \), comparable to the values reported in the literature.\(^{47}\)

Moreover, the PSA technique needs concentrations above 500 \( \mu \text{mol/L} \) to get a response from the device, and then we set a deposition potential at \(-0.8 \text{ V}\) during 30 s. With the PSA technique, it was necessary to use concentrations above 500 \( \mu \text{mol/L} \) to obtain a response from the device. Figure 8 shows the PSA measurements for the successive increase in the concentration of Pb(II) acetate under stirring. A well-defined stripping signal was found around \(-0.64 \text{ V}\), associated with the Pb\(^{2+}\) ions present in Pb(II) acetate.\(^{48}\) The analytical signal was an exponential function of the Pb(II) acetate concentration within the 520–1200 \( \mu \text{mol/L} \) range, with a correlation coefficient of \( R = 0.98 \) (inset Figure 8). These results suggest strong interactions between Pb(II) acetate and the \((\text{PEI-CNT/GO})_{25}\) LbL film, which might be the origin for the sensitivity of the layer sensing to Pb(II) acetate due to the electrostatic attraction of Pb\(^{2+}\) ions to the solid–liquid interface.

2.5. Analytical Performance of the Proposed Sensing Platform. So far, three different techniques have been used to detect Pb ions. Then, the performance of the sensor will be assessed from the limit of detection (LOD). The LOD was calculated by taking a signal-to-noise ratio of 3, with calculations presented in the Supporting Information. The corresponding calibration plots displayed good linearity between the electrical response and the Pb(II) acetate concentration from the different methods used here, with a correlation coefficient of 0.9999 (see Figure S1). The LODs for impedimetric and amperometery sensors for Pb ions were 36 \( \text{pmol/L} \) and 78 \( \text{nmol/L} \), respectively. When using the PSA technique, the LOD for Pb ions was \( \sim 25 \text{ \mu mol/L} \).

Under optimal experimental conditions, the \((\text{PEI-CNT/GO})_{25}\) LbL film was highly sensitive (LOD = 36 \( \text{pmol/L} \)) toward Pb ions and significantly lower than the guideline value of 72 \( \text{nmol/L} \) for drinking water given by the Environmental Protection Agency.\(^{48}\) A comparison of the performance of Pb ion detection using different techniques and materials is summarized in Table 1. It can be seen that the proposed sensing platform has advantages in the detection of Pb ions.

Finally, the repeatability of the proposed sensing platform was investigated after 15 detection replicates of 0.5 \( \text{mmol/L} \) Pb(II) acetate under the same working conditions using IS. All impedimetric responses are shown in Figure S2, and all curves obtained were identical with an acceptable standard deviation of 1.8%. The results obtained are satisfactory in terms of repeatability, making the proposed sensor platform attractive, with great potential to determine trace levels of Pb ions.

3. CONCLUSIONS

CNTs have been successfully functionalized with PEI through an easy and environmentally friendly methodology. The idea consists of wrapping CNTs with a PEI polymeric chain through a sonication process. It is a non-covalent approach to functionalize CNTs in a stable aqueous solution easily. The attachment of PEI to CNTs was confirmed by UV–vis and XPS spectroscopy. All graphene-based thin films were successfully obtained by LbL films formed by the sequential
addition of PEI-CNTs and GO. The electrical characterizations show the resistive behavior of the (PEI-CNT/GO)_{25} LbL film. On the other hand, we have shown the ability of the LbL film as a sensing platform for the detection of Pb(II) acetate.

The detection mechanism associated with the electrochemical techniques studied with the functionalization of the microelectrodes allows us to obtain a LOD of down to 36 pmol/L and a sensitivity up to 4.3 μA/L/μmol, with excellent repeatability. This is possible due to the high affinity of heavy metal ions with the functional groups present in PEI-CNTs and GO, allowing us to obtain a high-performance and sensitive detection platform.

### 4. EXPERIMENTAL SECTION

#### 4.1. Materials and Composite Fabrication

The CNTs used here are multi-walled CNTs having 95 wt % of purity, lengths of 10–20 μm, and diameters of ~100 nm, acquired from CNT Co., Ltd., Seol, Korea. Poly(ethyleneimine) (50 wt % in water) solution and lead (II) acetate were purchased from Sigma-Aldrich. Graphene oxide water dispersion with a concentration of 0.4 wt % (4 mg/mL) was obtained from Graphenea Inc. A Pb(II) acetate (0.01 M) stock solution was prepared with HCl (0.1 M) solution, and Pb(II) acetate working solutions were prepared by successive dilutions of the stock solution with HCl (0.1 M) solution. PEI-CNTs were prepared by adding 10 mg of PEI in 10 mL of ultrapure water and sonicating for 30 min. Then, 1 mg of CNTs was added to 10 mL of the PEI solution (a concentration of 2 mg/mL) and sonicated for 4 h. The graphene oxide dispersion was diluted in ultrapure water and sonicated for 30 min, obtaining a stable GO sheet concentration with a concentration of 1 mg/mL. For the LbL film formation, PEI-CNTs and GO solutions were used as positive and negative polyelectrolytes, respectively. The pH of each polyelectrolyte and wash water was adjusted to 3.4 using 0.1 mol/L HCl. The immersion times in the LbL assembly were fixed at 10 min for each polyelectrolyte and 1 min for washing, thus producing (PEI-CNT/GO)_{n} LbL films, n is the number of deposited bilayers. All the solutions were prepared and diluted by ultrapure water (18 MΩ cm) acquired from a Sartorius Arium Comfort system.

(PEI-CNT/GO)_{n} LbL films were deposited onto gold IDEs containing 60 fingers having 150 nm height (~140 nm of Au onto a ~10 nm Cr adhesive layer), 3 mm length, and 40 μm width, with a finger separation distance of 40 μm each other, patterned onto glass slides by standard photolithography at the Brazilian Nanotechnology National Laboratory (LNNano).

#### 4.2. Characterization Techniques

A UV–vis Biochro Libra S60 spectrophotometer was used to record absorption spectra from 190 to 800 nm. The chemical states of the constituent elements of CNTs, PEI-CNTs, and Pb(II) acetate were investigated by X-ray photoelectron spectroscopy (XPS) using a Thermo Alpha 110 hemispherical analyzer. The XPS measurement was performed using an Al cathode (hv = 1486.6 eV) as the X-ray source in the constant pass mode (CPM) using 20 eV pass energy. The XPS characterization of CNTs and lead (II) powder acetate was carried out on “as-received” materials, and the PEI-CNT composite was drop-cast on the Si substrate. The collected XPS spectra were fitted using Voigt line shapes and Shirley backgrounds, simulated by the QUASE software. The morphology of the LbL films was evaluated using a scanning electron microscope (Jeol JSM6490LV).

The electrical characterizations of the LbL film were performed at room temperature. I–V measurements were carried out with a PGSTAT 302N potentiostat/galvanostat (Autolab) between ±0.5 V using 50 mV/s. The impedance data were acquired using a Solarton 1260A impedance analyzer coupled to a 1296 dielectric interface with a sine-wave voltage signal amplitude of 25 mV, without a dc bias in the frequency range 1 Hz to 1 MHz. The electrical characterizations performed to detect Pb(II) acetate were carried out, keeping the solution under stirring. IS, chronoamperometry techniques, and PSA were performed with a PGSTAT 302N potentiostat/galvanostat (Autolab). IS and chronoamperometry measurements were performed using the two contact pads of the IDEs. However, for the PSA, an Ag/AgCl/KCl (0.1 M) reference electrode was used. For the (PEI-CNT/GO)_{25} LbL film operation as an impedimetric sensor, three cycles were carried out for each impedance measurement from 1 MHz to 1 Hz, applying a 25 mV_{RMS} AC voltage signal. Moreover, aqueous solutions of 0.1 mol/L KCl, 7.4 μmol/L Pb(II) acetate in 0.1 mol/L HCl solution, and ultrapure water were used to study the behavior of the electrical properties of the device and its ability to distinguish between different analytes. The error bar is the standard deviation of three repetitive measurements made at each concentration value.

### ASSOCIATED CONTENT

**Supporting Information**

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acsomega.1c02085.

Results of the linearization of the data obtained in the three different techniques used for the detection of lead (II) acetate (PDF)

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LABNANO, Centro Brasileiro de Pesquisas Físicas-RJ, Brazil, for the SEM measurements.

■ ABBREVIATIONS

GO, graphene oxide; CNTs, carbon nanotubes; PEI, polyethyleneimine; PEI-CNTs, polyethyleneimine-functionalyzed carbon nanotubes; LbL, layer-by-layer

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